Electrochemical antimony removal from accumulator acid: Results from removal trials in laboratory cells

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ABSTRACT

Regeneration of spent accumulator acid could be an alternative process for crystallization, neutralisation and disposal. Therefore, for the first time in a study of the possibilities of electrochemical removal of antimony and accumulator acid regeneration on a laboratory scale, two synthetic and several real systems containing sulfuric acid of concentrations ranging between 28% and 36%, and antimony species were tested. Discontinuous electrochemical reactors with anion exchange membranes were successfully used in these experiments, which were conducted at a temperature of 35 °C. Removal of antimony using cells that were not divided by a separator, however, was not possible. In selected experiments, by varying the electrode material, type of electrolyte, and cell current, the concentration of antimony could be reduced from the range of 5 ppm to 0.15 ppm. This resulted in current efficiencies between 0.00002% and 0.001%, and in specific electroenergy demands between 100 Wh L^{-1} and 2000 Wh L^{-1}. In other experiments on substances with antimony contents up to 3500 mg L^{-1}, the current efficiencies obtained were more than a thousandfold higher. In contrast to the formally high relative energy consumption parameters absolute demand parameters are relatively small and favour the electrochemical method in small scale application. Besides plate electrodes, 3D-cathodes were used. Copper- and graphite cathodes produced the best results.

1. Introduction

The US Environmental Protection Agency (USEPA) and the European Union (EU) view antimony (Sb) and its compounds as pollutants whose removal is a priority [1]. Antimony is ubiquitously present in the environment as a result of natural processes and activities of humans [1]. Elevated concentrations of antimony in soils and sediments are either related to the anthropogenic sources of antimony or associated with the high arsenic concentrations present in sulfudic ores. Also, of importance appears to be the subject of airbone pollution by antimony of aquatic and terrestrial systems [1,2]. Antimony is known to be a special element employed in the semiconductor industry and as an additive in anti-inflammatory agents. It has been used, in the past, for enhancing the hardness and mechanical stability of lead alloys [3]. Antimony is a constituent of highly concentrated acids, in used accumulator acids, and hydrometallurgical systems; it is usually encountered in small concentrations [4,5].

Antimony has been the focus of environmental studies for decades. However, the environmental behaviour and effects of this poorly studied metalloid have only recently evoked interest as a consequence of its elevated concentrations in the vicinity of smelters, chemical plants, and mining and mineralised areas [6]. But recent studies on antimony contamination have usually been confined to contaminated areas near smelters [7], and old mining areas [8].

Suggested methods for antimony removal were mostly ion exchange and extraction [9–11]. In electrochemistry, the application of polarography is known even for deposition of antimony [12–15]. Results of kinetic studies using different electrodes in electrochemical processes for antimony removal have been published by the authors earlier [16]. That its removal by this process is possible was clearly demonstrated. However, it was also found that the simulation of real systems in kinetic studies was difficult. As preliminary work showed [16] deposition of antimony by this process depends on the species present in the electrolyte, which may vary in their composition. The deposition process is a multi-step mechanism that involves adsorption effects, formation of intermediates,

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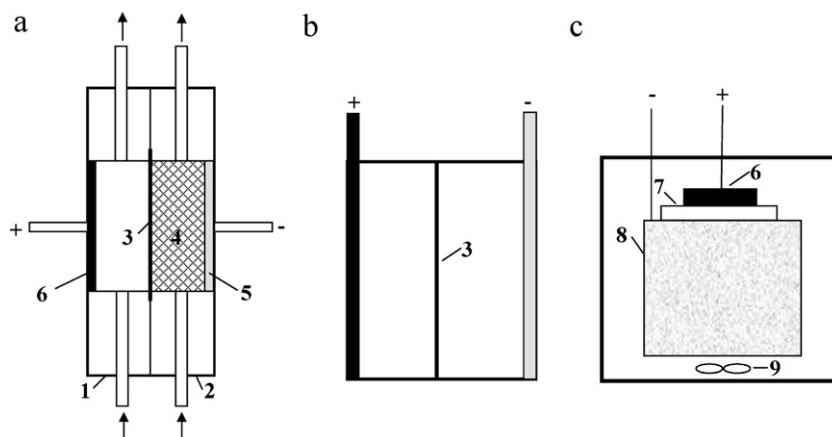[1] Tel.: +49 03496 67 2313; fax: +49 03496 67 2642.

Fig. 1. Crossections of cells used: (a) flow-through cell with anion exchange membrane, (b) box cell with anion exchange membrane without convection, and (c) glass beaker cell with ceramic diaphragm. (1) Anode half cell, (2) cathode half cell, (3) anion exchange membrane, (4) 3D cathode, (5) cathodic feeder or cathode in studies without 3D electrode, (6) plate IrO_2 anode in (a), graphite rod anode in (c), (7) ceramic beaker, (8) carbon felt cathode and (9) magnetic stirrer.

and electron transfer. If additives are present, complexation of antimony is possible. Therefore, further detailed studies are necessary to clarify mechanisms. For simplicity, and calculation of energy consumption in the deposition process may be calculated from Eq. (1) using 3 electrons for Sb(III) reduction:

$$Sb(III) + 3e^- \leftrightarrow Sb \qquad (1)$$

The complicated chemistry of antimony and the usage of a large number of electrolytes lead to the possibility of using various removal mechanisms. However, only comprehensive and integrated experimental methods can give more insights.

There are a few studies considering acid regeneration by several methods mostly not focusing on metal species removal. Ion exchange and electrodialysis are used to obtain 10% H_2SO_4 in battery recycling [17]. Recycling industry prefers neutralisation technologies at first stages of recycling. Patent literature also describes thermal decomposition and synthesis processes (US Patents (US Patent 5628976 and 5730950)).

The work presented here was carried out against following background: recycling enterprises accumulate spent sulfuric acid from accumulators. Both neutralisation/disposal and replacement are probable more expensive than a selective regeneration, i.e. antimony removal from the system. In addition, a potential user wished to combine a practicable technology with solar energy supply. Therefore, experiments were planned with the aim

- to check an electrochemical technology for antimony removal in cathodic processes
- to evaluate energy demands focusing on small-scale treatment units, which would be able to treat in m^3 per week range.

As results, in this study, results obtained from depletion experiments on laboratory scale are presented. Two synthetic electrolyte systems were tested together with other technical systems (spent lead/lead dioxide accumulator acid). Different electrode materials and types of reactors were employed according to their specific requirements to check the feasibility of efficient removal. As mentioned above the study also includes assessment of the energy consumption required for antimony removal in small scale.

2. Experimental

Besides preliminary trials with glass beakers and cells using platinum plate electrodes (20 mm × 20 mm) and platinum mesh cathodes, discontinuous experiments were first carried out using a

flow-through cell composed of two cylindrical half cells (Fig. 1a). The chambers for the anolyte and catholyte were cylindrical in form and each had an inner diameter of 30 mm and a depth of 25 mm. Circular plates of nearly same diameter and of 2 mm thickness served as anode (IrO_2 mixed oxide electrode from *Heraeus*) as well as cathode or cathodic current feeder (electrolytic grade copper). In certain experiments, 3D cathodes made of titanium mesh (*Heraeus*), copper wire wool (wire diameter 0.2 mm), carbon felt (*Sigri*), and electrode graphite particles with a grain size of 3 mm were used. (Prior to experiments, copper wool was washed in hot 5% Na_2CO_3 solution, washed with deionized water, activated by 10% sulfuric acid and washed thrice with deionized water.) The cell was divided into two halves using an anion exchange membrane (*SEPRON MA-3475*). The electrolyte, stored in glass beakers (0.25–0.5 L), was pumped through the electrode chambers with the help of centrifugal pumps. Due to energy dissipation, the working temperature quickly rose to and stabilized around 35 °C. Regulation of temperature was not resorted to because it remained nearly unchanged over time. Samples were analysed at different intervals. A second laboratory cell using the same separator was designed as an open box (Fig. 1b) having a volume of 75 mL per electrolyte chamber. A third was a stirred divided laboratory cell. An aqueous solution of 100 mL of 36% H_2SO_4 containing trivalent antimony with concentrations of 1500 and 3500 mg L^{-1} was used. In this cylindrical cell, a carbon felt electrode (*Sigri*) and graphite rod electrode passed through the centre of a ceramic diaphragm (thickness 2 mm) were used (Fig. 1c). The projection of the cathode area was 55 cm^2. The cell which was of diameter 60 mm had a cathodic volume of 200 mL. Anode compartment was filled with Agar. The Agar was prepared by adding 2.5 g Agar powder to 50 mL boiled water. By the addition of Na_2SO_4, its concentration was adjusted to 4 M. Ceramic porous diagram was filled with this gel. Rod electrode was placed in the centre as the anode. Thus electrode bridge was formed by the conductive gel. Gel obtained allows for the electron transfer whilst avoiding the solution in the cathode compartment to pass through the anode compartment. This system is more cost effective than the anode cathode separation by membrane. It has an ease of preparation. When desired it can be removed and replaced after reactor maintenance [18]. The concentration range of H_2SO_4 used in the experiments corresponded well with that found in typical Pb/PbO$_2$ accumulators.

Precision current supplies from *Steiber Mechanic* or from *Statron* were used to provide a constant flow of electric current. This current is given for all experiments. In addition, data for current density were calculated using front area of plate cathode. For
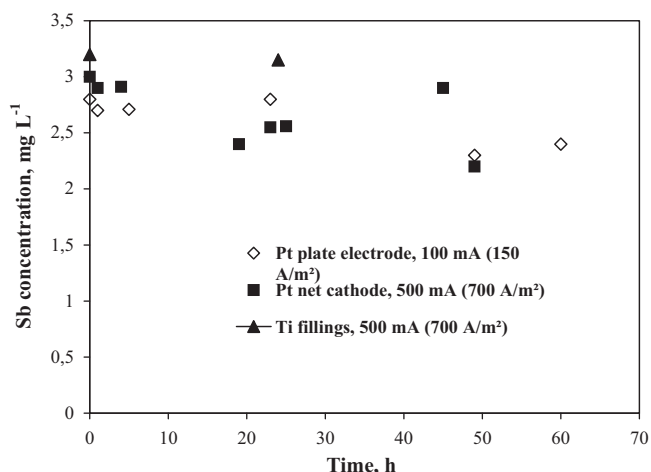
Fig. 2. Decrease in antimony concentration in discontinuous experiments using electrolysis cell according to Fig. 1a and varying current, and varied electrode material ($V = 200$ mL). Current density for 3D cathode was calculated with respect to separator area.

experiments using 3D electrode material current density was calculated for comparison with respect to separator area as usual. Commercial accumulator acid (36%) served as the electrolyte, which could be diluted with deionized water when needed. Due to the fact that synthetic antimony solutions cannot completely represent real systems [16] real spent acid was used in many experiments as received by the supplier. In selected experiments, various antimony concentrations were prepared by dissolving Sb_2O_3 (Clech/Poland) in hot sulfuric acid. Tartaric acid and King's water (5 mL nitric acid in 500 mL 36% sulfuric acid) were used to prepare the electrolytes. Addition of tartaric acid stabilizes antimony species by avoiding precipitation. At a first step of preparation, Sb_2O_3 was dissolved in 70 °C hot King's water. Then, sulfuric acid and tartaric acid were added. The second synthetic system was prepared by adding Sb standard (Baker 6968-04) to 36% H_2SO_4. A *Nanocolor 100D* instrument was used for spectrophotometrical analysis of the antimony [19]. Polarographical analysis was carried out using a *Metrohm* polarograph, model 646 [19]. Atomic absorption spectroscopy (AAS) was used in the experiments with high antimony concentration (*Varian AA+250*). The samples used were diluted for this analysis. Experiments were duplicated.

3. Results and discussion

3.1. Experiments in non-divided cells

In preliminary experiments, electrochemical deposition was tried in cells with no separator placed between the anode and cathode. This cell type is mostly the cheapest variant and preferred in electrochemical metal winning processes. Fig. 2 shows some chosen results using Pt and Ti as the electrode material. Both materials were chosen because the electrolyte conditions are highly corrosive. Current densities when given are calculated with respect to the cathode area or to the projected separator area (Section 3.2). For comparison, maximum specific charge consumed per liter at 60 h was between 30 and 150 Ah L^{-1}. Electrolyte losses were compensated by periodic additions of acid. That even platinum is applicable for antimony deposition was demonstrated in an earlier paper [16]. But, the results show that with both cathode materials only a negligible depletion of antimony occurred. (Furthermore, hydrogen evolution starts at much lower cathode potential compared with other materials.) The reason for this could be the partial oxidation at the anode of Sb(III) to Sb(V),

which does not deposit at the cathode. This is in congruence to electroanalytical conditions [20]. It was concluded that experiments had to continue using undivided (separated) electrochemical cells.

3.2. Experiments in separated cells at relatively low antimony concentration

Prediction of deposition behaviour is difficult. Usual factors such as electrode material, surface state, type and concentration of species inside electrolyte, mass transfer conditions and electrode potential (or potential distribution in electrodes of 3D character) have significant influence on deposition quality and efficiency. As it will be explained later the term efficiency can be used in systems, which are poor in reactants, only as a relative characterizing parameter. Parameters used for example in metal winning industry (current efficiency, specific energy demand) must be completed by absolute characteristics considering process and wastewater treatment. This work intended in receiving feasibility information varying and screening promising electrode materials and working conditions as used in plating processes.

To prevent the oxidation of the Sb(III) species at the anode, a separator made of *SEPRON* anion exchange membrane was tested. In control experiments no antimony (detection limit 0.03 mg L^{-1}) could be detected in the anolytes. In further experiments, spent accumulator acid (32%) at the same concentration but without the additional antimony dosing was used. Because it is known in electrochemical engineering that 3D electrodes may show better metal removal properties, materials with extended specific surface were used in addition. Fig. 3a shows with one exception some satisfying curves obtained using three-dimensional cathodes. The highest specific charged consumed in these experiments was about 220 Ah L^{-1}. All cathode materials had again relatively high corrosion resistance against sulfuric acid. The curve relating to spent acid experiments does not, in principle, differ from the one for dissolved Sb_2O_3 without admixtures. With the exception of the carbon felt electrode, the other cathodes (of graphite and of copper wool) showed good potential for deposition of antimony. The obviously insufficient current distribution inside the carbon felt was responsible for the reduced activity of the material where a surface block caused by a gas bubble may possibly have occurred [21]. In general, the depositing ability of 3D cathodes depends on additional factors such as electrolyte and bed conductivity, electrochemical kinetics, contact to the feeding plate and hydrodynamics. This variety of conditions makes prediction impossible. However, this material showed better results, when antimony concentration was chosen much higher (see later in Fig. 7).

At small antimony concentrations, the removal curves decrease more gradually as was expected. It is also obvious that the removal rate was proportionally higher. This is because the products of antimony covered the cathode, at least in the initial period of experiment, at sufficiently high hydrogen overvoltage [16].

Fig. 3b is related with the same experimental settings for two electrode materials varying current load and initial concentration. The influence of current is marginal because an electrochemical process in lower ppm range of reacting species is usually mass transfer controlled. Additionally, larger amount of gas may hinder deposition inside 3D structures. Both Fig. 3a and b are characterized by high depletion rates in the time period shortly after starting the experiments when deposition occurs still on the initial cathode material. Later, the cathode is coated by the deposition having worse antimony reduction ability. From this behaviour an important conclusion can be drawn: enlarged removal efficiencies could be reached if cathodes with renewing surface are used. There are not so much cells in the field. Famous representatives are the so-called cells of Chemelec type [22] and the VMPB (vertically
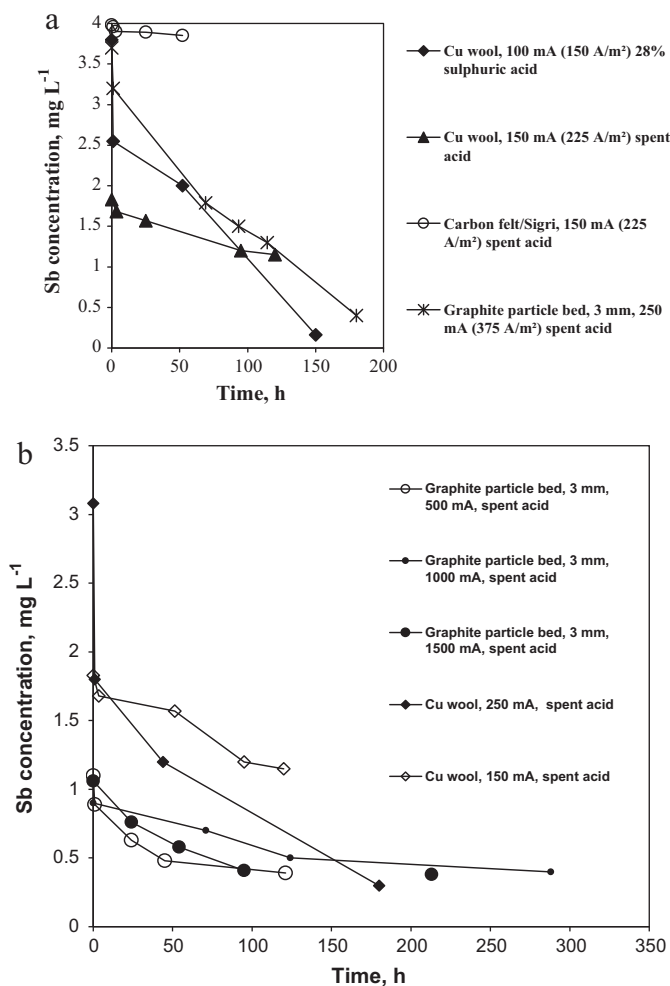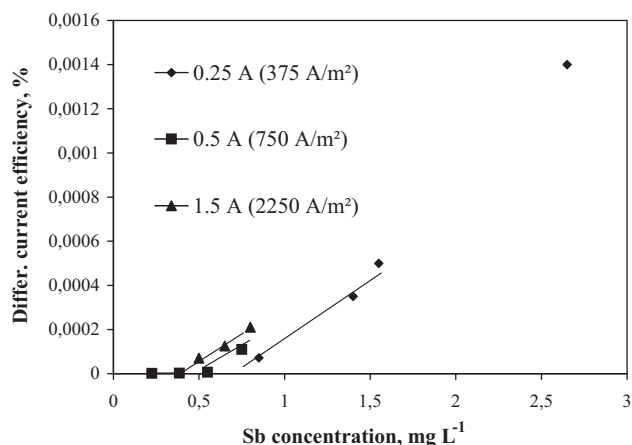
Fig. 4. Calculated differential current efficiency versus antimony concentration with varying current density for discontinuous experiments in laboratory cells divided by anion exchange membrane and using graphite cathode (grain size 3 mm, lead dioxide anode, spent 28% accumulator acid, $V = 200$ mL, conditions of experiments shown in Fig. 3).

Fig. 3. Decrease in antimony concentration in discontinuous experiments in a laboratory cell separated by anion exchange membrane (Fig. 1a) varying mainly cathode material (a) and cell current (b) (spent acid, for comparison in one experiment dissolved Sb_2O_3 was used as electrolyte, $V = 200$ mL). Current density was calculated with respect to separator area.

moving particle bed) reactor [23,24]. These constructions can keep cathode surface clean. Negative effects are reactions of re-dissolution and particle formation making filtration necessary. Additional work could be done but this was not in the scope of this paper.

Fig. 4 shows the calculated differential current efficiency for experiments using the graphite cathode and with varying current density and initial antimony concentration. Calculations were carried out using Eq. (2):

$$\varphi_{\text{diff}} = \frac{\Delta C_{Sb} \cdot 3 \cdot F \cdot V}{I \cdot \Delta t \cdot M_{Sb} \cdot 1000} \tag{2}$$

where ΔC_{Sb} is the decrease of antimony concentration (mg L^{-1}) in an incremental time Δt (h), I is the current (A), M_{Sb} is the molar weight of antimony (g mol^{-1}), and F is the Faraday constant (Ah mol^{-1}), V is the electrolyte volume (L). The parameter φ_{diff} is calculated for comparing different experiments. In general, it is expected that for electrolytes with reacting species at mg L^{-1} level is extremely low. This is the reason that in electrochemical engineering φ_{diff} cannot be used as the only characterizing parameter as well as the specific energy demand (Eqs. (3) and (4)) that results in very high amounts for small φ_{diff}.

Removal seems to be effective at very small concentrations (1–5 ppm) under the concrete experimental conditions used. The

extremely low current efficiency leads to relatively high specific energy consumption which was, however, not a criterion in this study as it is in many applications of environmental technology where only small quantities of metal are removed from solutions.

Deposition of metals at very small concentrations under limited current conditions is generally effective when specialised cathode surfaces are used such as 3D electrodes. If, however, very strong gas evolution effects are observed and the surface is blocked, 3D electrodes can lose their advantage and then both types of electrodes (2D and 3D) become comparable. Table 1 shows as an example of comparisons of electrolysis using cathodes made of plates, copper wool, as well as graphite particles (3 mm grain size) with a volume of 0.2 L.

The specific electroenergy demand was calculated by Eq. (3):

$$W_{Sb} = \frac{U \cdot n \cdot F}{M_{Sb} \cdot \varphi_{\text{final}}} \tag{3}$$

where W_{Sb} is the specific electroenergy consumption (Wh g^{-1}), U is the cell voltage (V), F is the Faraday constant (Ah mol^{-1}), n is the number of the transferred electrons, φ_{final} is the integral current efficiency taking into account cycle time of electrolysis necessary for reaching the final antimony concentration as indicated in Table 1.

When W_{Sb} was calculated in Wh L^{-1}, Eq. (4) was applied for a given depletion ΔC over Δt, where V is the solution volume (L):

$$W_{Sb} = \frac{U \cdot I \cdot \Delta t}{V} \tag{4}$$

Specific energy demand appears extremely high, but as the amounts of antimony removed are small, the total electricity consumption is expected to be relatively low. Parameters such as current efficiency and specific energy consumption are here given because common in considering deposition processes. But as explained above in electrochemical process water treatment in ppm range of concentration, both parameters may be irritating because of associating high total energy demand. Energy demand or economical efforts per cubic meter of treated solutions are parameters of better choice. A first estimation may explain this: the assumption of 0.150 kWh per treated liter results in electricity costs for electrolysis of 18.75 € m^{-3} at specific electricity costs of 0.125 € kWh^{-1}. This is relatively low compared, for example, with 370 € m^{-3} as only chemical costs in sulfuric bath neutralisation (ISTC Fact Sheet [25]) and demonstrates the economical potential of electrochemical methods even at very low concentrations.

Table 1
Comparison of experimental parameters and results from discontinuous experiments using 2D- and 3D cathodes and technical- and synthetic accumulator acid in a cell as shown in Fig. 1b.

	Fixed bed reactor	Fixed bed reactor	Plate reactor
Current, A	0.25	0.25	0.5
Cathode material	Cu	Graphite	Cu on Pt
Initial Sb concentration, mg L^{-1}	3.08 (technical spent accumulator acid)	3.7 (technical spent accumulator acid)	3.5 (36%-sulfuric acid)
Final Sb concentration, mg L^{-1}	0.3	0.4	0.3
Electrolysis time, h	180	180	72.5
Integral current efficiency, %	0.00081	0.00097	0.00044
Specific electroenergy consumption			
Wh g^{-1}	81,566	33,375	453,103
Wh L^{-1}	225	110	1450

The experiment using Cu and Pt (where Cu was electrochemically deposited prior to commencement of the experiment) is shown for comparison with experiments using 3D electrodes. The concentration decay is comparable but it was reached in quicker time (72.5 h), three times faster at the higher current and without convection. This necessarily affected the energy parameters, which are ten times higher. The experiment shows an extreme case of possible treatment of the electrolyte, applying suitable cathode potential.

More results are shown for experiments when 36% sulfuric acid was spiked with antimony standard (Fig. 5). In the separated cells, no antimony was deposited on copper, titanium, and platinum, especially at small current densities. Colouring of the electrolyte was observed at the final stage of experiments indicating anode and/or steel cathode corrosion. Better results were obtained when a copper cathode was used at high current densities. In fact, high current density had a very positive effect on antimony depletion. At the same time, however, the cell potential and the specific electroenergy consumption showed an increase.

3.3. Experiments in separated cells at relatively low antimony concentration

For theoretically possible technologies using pre-concentration of antimony one has to expect higher process efficiency in electrochemical deposition due to better mass transfer and current efficiency. To demonstrate this, experiments were carried out at higher antimony concentration. The concentration factor was about 1000. This means that per liter about 2000 kJ would be needed what results in energy demand of approximately 0.5 kWh per liter initial solution.

Higher concentration significantly improves energetic parameters of electrochemical deposition. For example, differential current efficiency is dependent on antimony concentration as may be seen from the two experiments shown in Fig. 6. Towards the end of the experiment, the integral current efficiency amounted to 0.000293%, and the specific current consumption to 676773 Wh g^{-1} or 2300 Wh L^{-1}. Because both values are relatively high, smaller concentration range or relatively higher final concentrations should be arranged in practical treatment.

Under conditions of higher initial Sb concentration, materials such as carbon felt, which showed insufficient behaviour lower ppm range of concentration, were applicable (Fig. 7). Antimony concentration chosen was 3500 mg L^{-1}. Calculated current efficiency values were more than a thousandfold higher compared with experiments shown in Table 1. Also, energy consumption was a thousandfold lower (Fig. 7). Cheaper ceramic diaphragm could replace the more expensive ion exchange membrane. It can be seen from Fig. 7, that antimony can be removed efficiently. More details are given in [26] but one example is given here to estimate the total costs. If assumed from the studies that both pre-concentration and deposition results in 600 kWh/m^3 (Fig. 7), 75 € electricity costs under German industrial conditions can be calculated. From this point of view the method may compete with neutralisation technology. (Investment costs are not considered
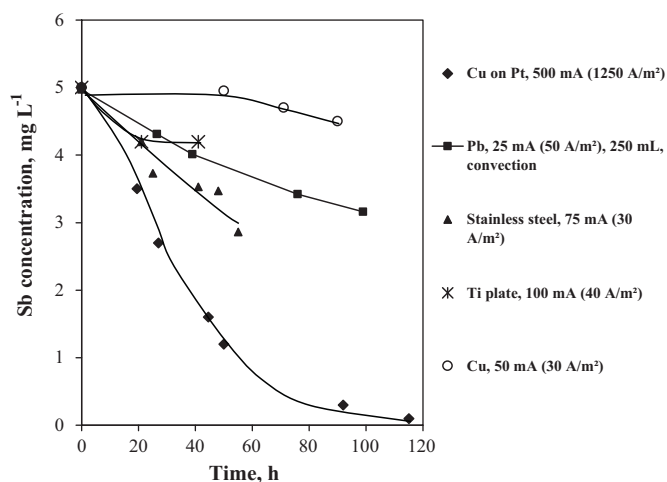

Fig. 5. Antimony concentration decay in discontinuous experiments using different plate electrode materials (cell according to Fig. 1b with 75 mL of electrolyte prepared by Sb standard addition to 36% sulfuric acid, no convection). An experiment using lead cathode with convection is shown for comparison with an electrolyte volume of 250 mL at 34–36 °C. Current density was calculated with respect to cathode area.
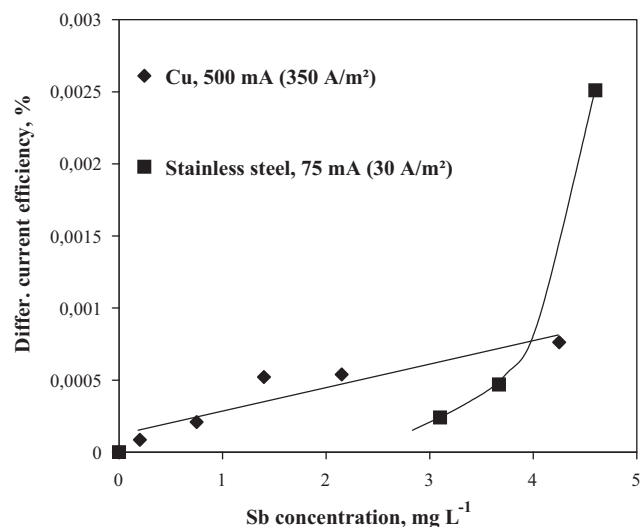

Fig. 6. Differential current efficiency versus antimony concentration for two discontinuous experiments in a cell according to Fig. 1b without convection (antimony from dissolved Sb$_2$O$_3$ in 36% sulfuric acid, V = 200 mL). Current density was calculated with respect to cathode area.
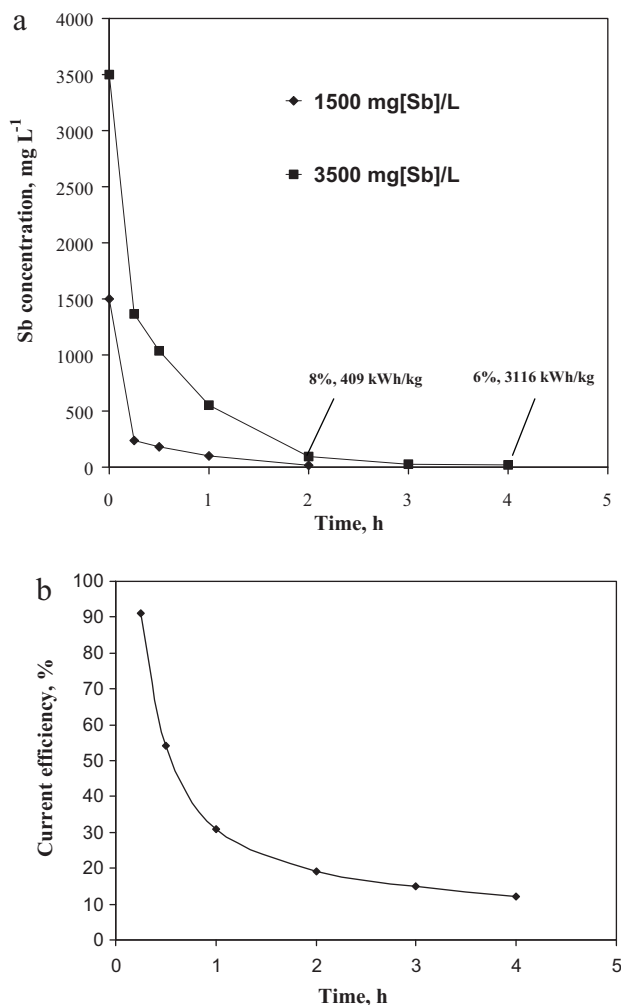
Fig. 7. Result of experiments conducted at enhanced antimony concentration. (a) Decrease in antimony concentration in a stirred divided cell (Fig. 1c, 50 A m^{-2}). (b) Current efficiency (initial antimony concentration 3500 mg L^{-1}, 50 A m^{-2}, V = 200 mL, App. Pot. 3 V).

here because they would have been considered for each treatment technology. Furthermore, in small scale, investment costs are often similar for different technologies.) 20–30 m^2 of photovoltaic panels are enough to cover the electricity demand if one week is considered for the whole process.
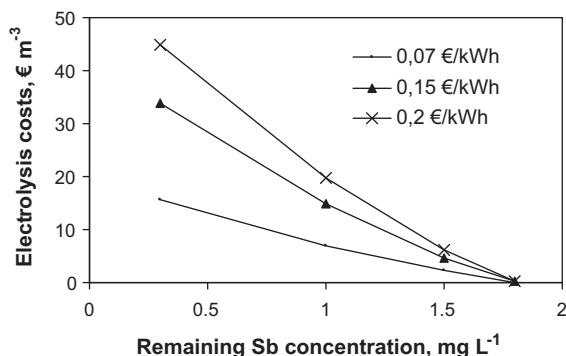

Fig. 8. Specific electrolysis cost in dependence on remaining antimony concentration varying specific electricity costs. (Conditions according to one experiment shown in Fig. 3b: starting concentration 3.08 mg L^{-1}, V = 200 mL, current 0.25 A, voltage 1 V, Cu wool cathode.)

For comparison and better illustration, electrolysis costs were calculated from a curve in Fig. 3b starting at 3.08 mg L^{-1} antimony in the initial solution. Fig. 8 summarizes specific costs for electrolysis by varying the remaining concentration and electricity costs per kWh between 0.07 and 0.20 € kWh^{-1}. All results show that treatment costs are still in a reasonable range and that electrolysis can compete with other recuperation or disposal methods.

4. Conclusions

- Removal of antimony by the electrochemical deposition process using separated cells was successfully achieved.
- In cells not divided into two halves, antimony was not deposited at the cathode due to the partial oxidation of Sb(III) to Sb(V) at the anode. It can, therefore, be concluded that electrochemical removal of antimony has to be performed in divided cells.
- Copper and graphite electrodes were found to be the most suitable electrode materials for deposition of antimony.
- Because electrode covering by Sb species lowers deposition efficiency with time periodical replacement or automatic renewing of cathode material is recommended.
- Although the calculated specific electroenergy consumption values were relatively high, absolute energy consumption was low because the quantities of antimony removed were small.
- Based on the results obtained by laboratory studies a technical anion exchange membrane-divided cell was constructed having a volume of 40 L. This cell is subject of further studies.

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