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Electrochemical removal of arsenic from technical grade phosphoric acid

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Abstract

The electrolytic de-arsenication of technical grade phosphoric acid 85 wt % by cathodic deposition in order to produce chemically pure phosphoric acid was examined. Polarization curves using Cu, Pb, 316L stainless steel and graphite as cathodic rotating discs were determined. The best results were achieved for copper where the arsenic deposition takes place in a range of potentials without hydrogen evolution. Long term experiments in a laboratory batch reactor with a rotating cylinder cathode of copper showed that the electrodeposited arsenic was a non-conductor, poorly adherent and can be detached from the electrode by means of an ultrasonic cleaner. Experimental results with a pilot plant reactor with a three-dimensional cathode of copper nets showed a high degree of scatter. However, typical values of the figures of merit are: fractional conversion per pass 24%, specific energy consumption 250 kWh kg^{-1}As for a volumetric flow rate of 1.5 dm^3 min^{-1} at 60 A and 3.4 V of cell voltage.

List of symbols

a_e	specific surface area (m^{-1})
C	arsenic concentration (ppm)
C_{in}	inlet arsenic concentration (ppm)
E_s	specific energy consumption (kWh kg^{-1})
E_{SCE}	cathode potential referred to saturated calomel electrode (V)
i	current density (A m^{-2})
I	total current (A)
k	mass transfer coefficient (m s^{-1})
Q	volumetric flow rate (m^3 s^{-1})
t	time (min or h)
T	temperature (°C)
U	cell voltage (V)
V	volume of the three-dimensional electrode (m^3)
x	fractional conversion

Greek characters

β	current efficiency
$\Delta\eta$	admitted range of overpotential (V)
ρ_s	effective electrolyte resistivity (Ω m)
ω	rotation speed (rpm)

1. Introduction

Phosphoric acid is produced by two processes [1]: (i) a thermal process in which phosphorus is burned in an oven under controlled conditions followed by the hydration of the oxide, and (ii) a wet process where a mineral acid, usually sulfuric acid, reacts with phosphorus materials. Although the thermal process is preferred for the manufacture of phosphoric acid with higher purity, arsenic and also antimony are always present in small amounts. Thus a purification step is necessary for upgrading of phosphoric acid to specified levels of arsenic content: not more than 3 ppm for food grade quality [2], 3 ppm for pharmaceutical use [3] and lower than 1 ppm for ACS reagent grade.

The conventional method for arsenic removal [4] is precipitation, for example as arsenic sulphide, followed by filtration. This approach generates a filter cake, which must be retreated either to recover arsenic or to chemically stabilize it for disposal in landfill sites. Another strategy for removing arsenic from phosphoric acid is cathodic deposition. Thus, Slack [5] describes the use of fine-meshed copper nets as cathodes.

The removal of arsenic from groundwater is treated in the literature [6] but from the point of view of the application of electrochemical technology only an indirect procedure is offered [7], where iron(II) is generated at the anode, chemically oxidized to iron(III) and the arsenic is precipitated as ferric arsenate.

Arsenic deposition is scarcely treated in the literature. Stillwell and Audrieth [8] reported the deposition of arsenic as a black, lustrous, metallic plate from solutions of the chloride in glacial acetic acid but X-rays revealed an amorphous cathode product. Wranglén [9] studied deposition from solutions of $AsCl_3$ saturated in hydrochloric acid and from AsO_2^-. The feasibility of electrowinning or electrorefining of arsenic is problematic because the films are practically nonconductive. Csizi [10] describes the Siemens–Halske process, where arsenic is deposited from acid solutions from the electrorefining of copper at a mercury cathode. Recently, Maelgwyn Mineral Services Limited [11] reported the application of eV Cell Technology for arsenic removal from metallurgical treatment effluents at a copper plant in Chile. The production of high-purity arsenic and its compounds was summarized in [12] as an approach to destroy chemical warfare agents. Bejan and Bunce [13] reported the removal of As(III) and As(V) from acidic and basic solutions using a reticulated vitreous carbon cathode, giving arsine as the only product of the electrochemical reduction.

The electroplating of arsenic has very little practical application and arsenic is electrodeposited to produce a black or gray finish for antique effects [14]. For decorative purposes Machu [15] proposed arsenic deposition from alkaline arsenite solutions.

The main objective of this work was to study the feasibility of arsenic removal by electrodeposition from technical grade phosphoric acid and to perform a systematic analysis of the process variables.

2. Fundamental studies with rotating disc electrodes

2.1. *Experimental details*

The working electrode was a rotating disc (5 mm dia.) embedded in a Teflon bell (27 mm base dia.). Copper, lead, 316L stainless steel and graphite were studied as cathodic materials. As counterelectrode three platinum wires (1 mm dia. and 90 mm long), placed symmetrically, were used. A saturated calomel electrode was used as reference and the potentials are referred to this electrode.

The surface of the working electrode was polished with emery paper 1000; it was washed with acetone in an ultrasonic cleaner. At the end of the experiment, the disc was washed with copious amounts of distilled water, but special attention was paid to the integrity of the arsenic deposit. The working electrode could be taken out of the Teflon bell and accepted by the stage plate of the electron microscope. Therefore, the composition could be determined by an energy dispersive X-ray microanalyser (EDAX) without removing the thin deposit from the disc. The electrolyte was technical grade phosphoric acid, 85 wt %. The arsenic concentration, measured using the standard silver diethyldithiocarbamate photometric method of ASTM E 533-91, was 40 ppm or 57 ppm. However, the latter was the concentration most frequently used. The oxidation state of the arsenic in the technical grade phosphoric acid was +3.

2.2. *Results and discussion*

Figure 1 shows typical polarization curves at different angular velocities obtained with a copper rotating disc electrode. These experiments were performed at 30 °C under a slow potentiodynamic sweep of 1 mV s^{-1}. For comparison, in Figure 1 the polarization curve at $\omega = 1000$ rpm for pro-analysis phosphoric acid (85 wt %, [As] = 1 ppm) is also reported.

Figure 2 shows polarization curves at different temperatures. These experiments were performed with a static copper electrode under a slow potentiodynamic sweep of 1 mV s^{-1}.

In Figures 1 and 2, the current densities in the potential range from +0.05 V to −0.35 V can be attributed to arsenic deposition. However, in this range of potentials a lack of reproducibility in the experimental results was observed, which can be attributed to the nonconducting nature of the electrodeposited arsenic. Thus, the electrolysis takes place mainly at the bottom of pores in the arsenic layer. Since the porosity must change between experiments, erratic results seem natural. Likewise, the curves of Figures 1 and 2 show that the current density increases for potentials lower than −0.35 V, which indicates the onset of a side reaction such as hydrogen evolution. It must be emphasized that on one hand hydrogen evolution as side cathodic reaction can be beneficial in order to dislodge the nonconducting layer of arsenic and to restore the electrode active surface. But on the other hand arsine can be cathodically produced [16]. These conflicting issues can be resolved by working with a closed reactor and processing its gaseous effluent.

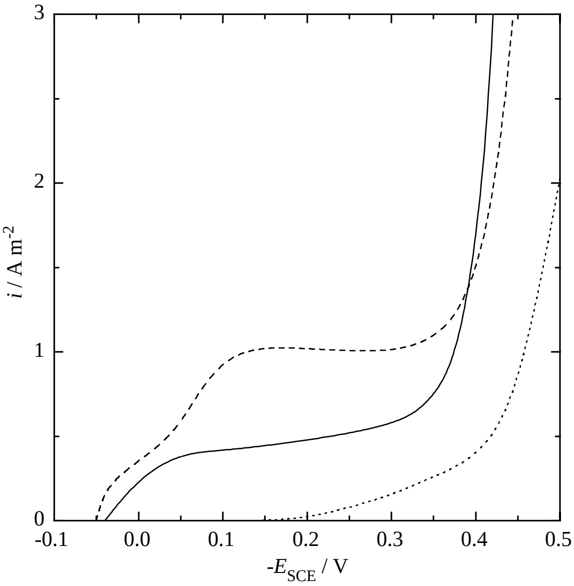

Fig. 1. Current density as a function of the electrode potential for different angular velocities for the arsenic deposition at a copper rotating disc electrode. Full line: technical grade phosphoric acid, $\omega = 0$ rpm. Dashed line: technical grade phosphoric acid, $\omega = 1500$ rpm. Dotted line: pro-analysis phosphoric acid, $\omega = 1000$ rpm. $T =$ 30 °C. $C = 40$ ppm. Potential sweep rate 1 mV s^{-1}.

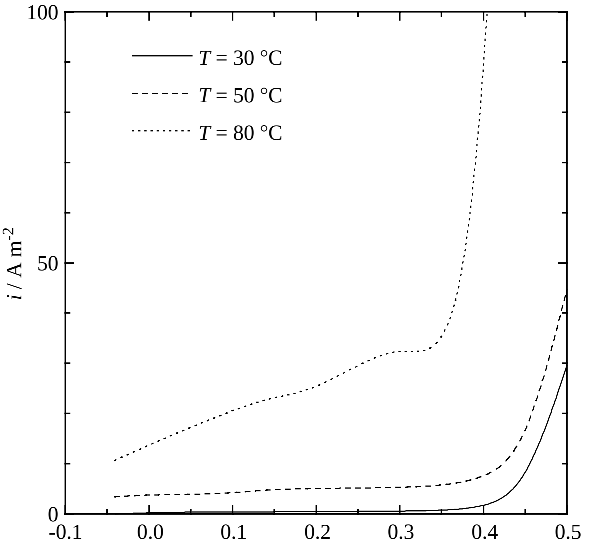

Fig. 2. Current density as a function of the electrode potential at different temperatures for the arsenic deposition from technical grade phosphoric acid at a copper disc electrode. $\omega = 0$ rpm. $C = 57$ ppm. Potential sweep rate 1 mV s^{-1}.

Additional experiments were performed by changing the preparation conditions of the electrodes as follows: (i) electrodes prepared following the above procedure; (ii) electrodes partially covered with arsenic from a previous experiment; and (iii) electrodes covered with arsenic from a conventional alkaline electroplating bath. Independently of the preparation method the same behaviour was observed: that is, a big increase in the current density for potentials more negative than -0.35 V and a lack of reproducibility of the results in the middle range of potentials.

Figure 3 shows polarization curves for different electrode materials obtained at a potential sweep rate of 1 mV s^{-1} from technical grade and pro-analysis phosphoric acid. The insets in each part of Figure 3 correspond to the kinetic behaviour at low current densities. There are significant differences in the polarization curves between copper and the other electrode materials. Thus, lead, 316L stainless steel and graphite show the same kinetic behaviour for both types of phosphoric acid at low current densities, but when the cathodic potential becomes more negative higher current densities are observed for the pro-analysis phosphoric acid because in technical grade phosphoric acid the codeposition of arsenic inhibits hydrogen evolution. For a copper cathode at a given potential the current density is always higher for the technical grade acid. Comparison of the polarization curves of Figure 3 indicates copper as the more promising cathodic material for arsenic deposition.

To obtain steady state values of current density for arsenic deposition, experiments at a constant cathodic

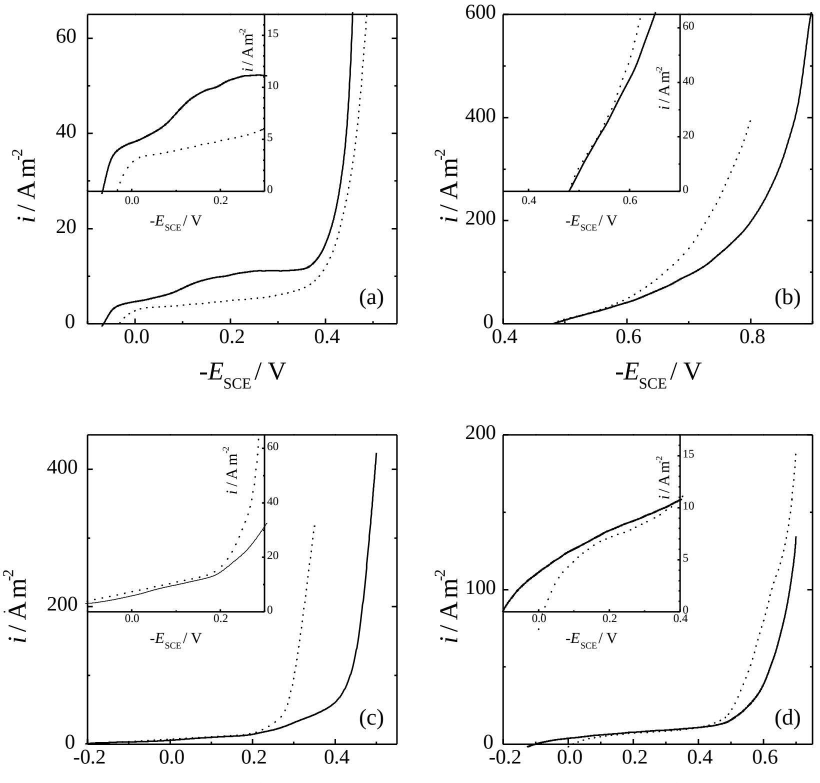

Fig. 3. Current density as a function of the electrode potential at different electrode materials for the arsenic deposition. (a) copper, (b) lead, (c) 316L stainless steel and (d) graphite. $\omega = 1000$ rpm. $T = 80$ °C. $C = 57$ ppm. Potential sweep rate 1 mV s^{-1}. Full line: technical grade phosphoric acid. Dotted line: pro-analysis phosphoric acid.

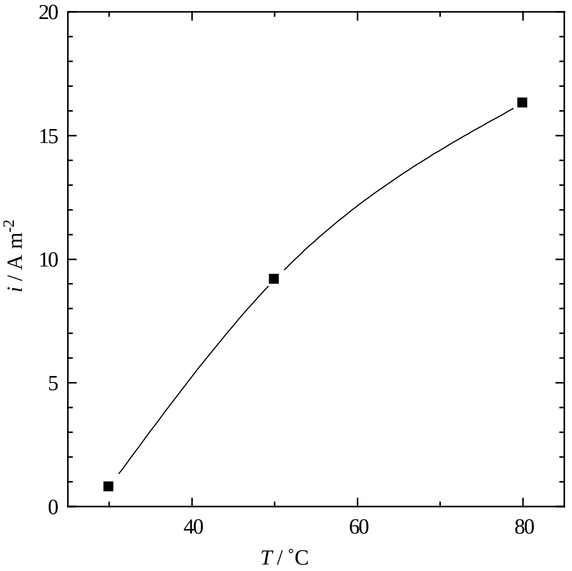

Fig. 4. Steady state values of the current density as a function of the temperature for the arsenic deposition from technical grade phosphoric acid at a copper rotating disc electrode. $E_{SCE} = -0.3$ V. $\omega = 1000$ rpm. $C(0) = 57$ ppm.

potential were performed and the current was plotted as a function of time. The necessary time to achieve the steady state was between 30 and 60 min. Figure 4 shows steady state values of the current density as a function of temperature for a cathodic potential of −0.3 V. An increase in current density occurs when the temperature increases. The best result is obtained at 80 °C, which is close to the temperature of the phosphoric acid at the outlet of the production process. All the following laboratory experiments were performed at 80 °C.

Figure 5 shows steady state values of current density as a function of applied potential at 0 and 1000 rpm for a copper disc electrode. A high scatter of the experimental results is observed, which can be explained taking into account the physical properties of the electrodeposited arsenic. In spite of the difficulty of reproducing the results, for potentials more negative than −0.075 V a limiting current density may be detected, which is close to 18 A m^{-2}. From the Levich equation and assuming 5.1×10^{-10} m^2 s^{-1} for the kinematic viscosity the arsenic(III) diffusion coefficient can be roughly estimated as 6.8×10^{-11} m^2 s^{-1}.

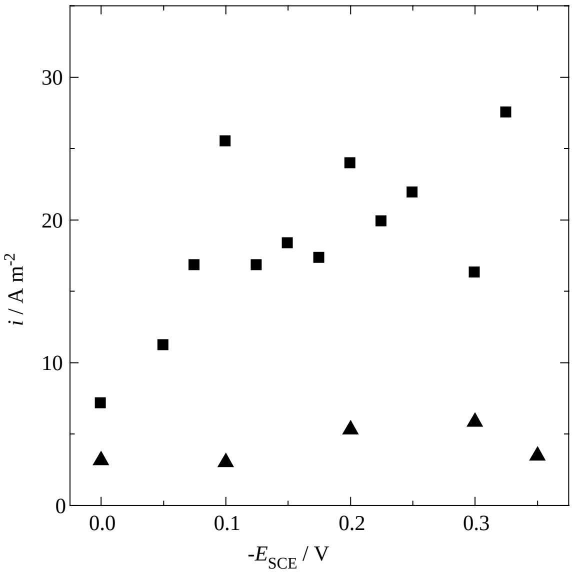

Fig. 5. Steady state values of the current density as a function of the electrode potential for the arsenic deposition from technical grade phosphoric acid at a copper rotating disc electrode. $T = 80$ °C. $C(0) = 57$ ppm. (▲) $\omega = 0$ rpm and (■) $\omega = 1000$ rpm.

The compositional analysis of the deposits was performed by EDAX at different points on the surface electrode. The spectra show arsenic as the only element deposited on the copper disc. The presence of phosphorus in the deposit was not detected in spite of the special attention paid to its determination. Several deposits produced under different working conditions were examined, but the same result was obtained.

3. Long term experiments with a rotating cylinder electrode

3.1. *Experimental details*

The long-term experiments were performed in an undivided batch reactor (95 mm int. dia. × 140 mm high). The reactor was thermostated by a heating jacket. The working electrode was a copper rotating cylinder (38.1 mm dia. × 85 mm long, 101.7 cm^2 electrode surface area). The upper end of the cylinder is attached to the motor shaft. As counterelectrode three platinum wires (1 mm dia. × 90 mm long) placed symmetrically were used. The working electrode and the counterelectrode were concentric, thereby assuring a uniform primary current distribution. The interelectrode gap was 12 mm. As reference a saturated calomel electrode was used.

The surface of the working electrode was carefully polished with emery paper 1000 and it was washed with acetone in an ultrasonic cleaner. At the end of the experiment, the electrode was carefully washed by immersion in distilled water and the arsenic deposit was detached from the electrode by means of an ultrasonic cleaner. All the experiments were performed at 1000 rpm and 80 °C. The electrolyte was technical grade phosphoric acid, 85 wt %. The initial arsenic concentration was 57 ppm. The electrolyte volume in each experiment was 0.5 dm^3 and at the end of the experiment a sample of the solution was taken from the reactor in order to determine the residual arsenic concentration by the standard ASTM E 533-91 test.

3.2. *Results and discussion*

Figure 6 shows a typical response of the current as a function of time. It can be observed that the current sharply increases during the initial stages of the experiment and decreases for longer times because in a batch

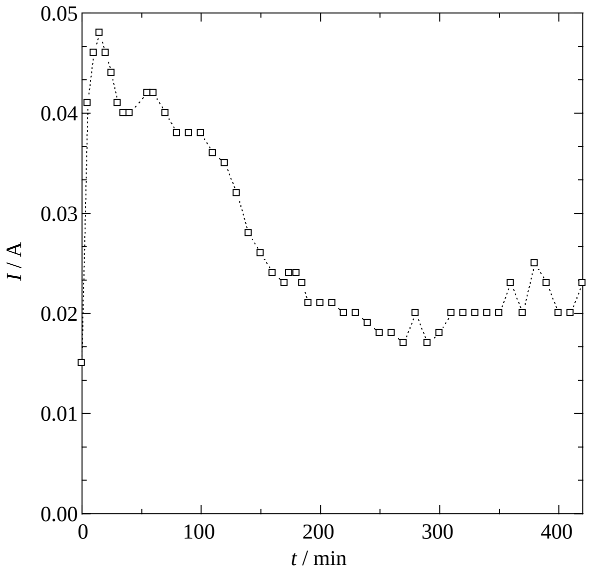

Fig. 6. Total current as a function of time for the arsenic deposition from technical grade phosphoric acid at a copper rotating cylinder electrode. $E_{SCE} = -0.2$ V. $T = 80$ °C. $C(0) = 57$ ppm. $\omega = 1000$ rpm.

reactor the arsenic concentration decreases with time and also the nonconducting deposit of arsenic masks the electrode surface. Likewise, at high times the current approaches a constant value, which indicates that side cathodic reactions take place simultaneously with arsenic deposition.

Table 1 summarizes the experimental results of the long-term experiments. The minimal value of residual arsenic concentration was 3 ppm after seven hours of electrolysis. Similar results were achieved in experiments at higher times. Taking into account column 6 of Table 1 it can be observed that the current efficiency for arsenic deposition is near 16%, which confirms the presence of side reactions at the cathode, and the current efficiency decreases at high electrolysis times.

The cell voltage was in the range 2.3–2.0 V, depending on the applied current. An additional experiment was performed with a 316L stainless steel rotating cylinder electrode at a cathodic potential of −0.4 V for one hour, but in spite of the long time of electrolysis only a very thin layer of arsenic was deposited.

Likewise, samples of the deposits obtained with the rotating cylinder electrode were examined by EDAX. The spectra were similar to those obtained at the rotating disc electrodes, the main difference is a peak of antimony, which has been previously identified as an impurity in technical grade phosphoric acid. Therefore, the deposits obtained in long-term experiments show that antimony codeposits simultaneously with arsenic.

Table 1. Summary of the experimental results using a batch reactor with a rotating cylinder electrode

$C_{initial}$ /ppm	C_{final} /ppm	t /h	$-E_{SCE}$ /V	Charge /C	β /%
57	19	3	−0.3	452.25	16.23
57	40	2	−0.1	209.40	15.68
57	40	2	−0.2	194.40	16.89
57	5	13	−0.2	960.98	10.45
57	3	7	−0.2	675.18	15.45
57	5	10	−0.2	693.98	14.47

4. Experiments with a pilot plant electrochemical reactor

4.1. *Experimental details*

The experiments were performed in a pilot plant electrochemical reactor of flow-by configuration with a three-dimensional cathode. The working electrode (200 mm wide × 300 mm high) was a stack of copper nets of 50 mesh (0.15 mm wire dia. and 0.36 mm distance between wires) which were bolted at several points to a copper feeder plate in order to achieve mechanical stability and to ensure isopotentiality of the metal phase. The geometric specific surface area was approximately 8.58×10^3 m^{-1} with a void fraction of 0.68. The thickness of the three-dimensional electrode was 15 mm, which is the optimum bed depth according to Kreysa [17]. For the calculation of the optimum bed depth it was assumed that $\Delta\eta = 0.2$ V, $\rho_s = 0.069$ Ω m. The limiting current density was calculated for 57 ppm arsenic concentration with a mass transfer coefficient according to a previous correlation [18]. A platinum foil was used as anode. Both electrodes were isolated by means of a plastic net, whose geometric characteristics were similar to the copper nets in order to avoid by-pass of the electrolyte through the separator. The reactor was made part of a flow circuit system consisting of a pump, a flow meter, facilities for gas separation and absorption of arsine.

4.2. *Results and discussion*

Figure 7 shows the inlet arsenic concentration, cell voltage, fractional conversion, current efficiency and specific energy consumption as a function of time for a long term experiment of five days with a volumetric flow rate of 1.5 dm^3 min^{-1} at a current of 60 A and a temperature of 70 ± 4 °C. The inlet arsenic concentration was in the range 22 ppm to 89 ppm depending on the batch of phosphorus used in the production process. The cell voltage shows an initial decay and approaches a value of 3.4 V. The fractional conversion shows a high scatter with a mean value of 24%. The current efficiency is low, about 1.5% when the inlet concentration was 25 ppm, but β increases to 5% or higher values when arsenic concentration increases. As expected the specific energy consumption follows the inverse tendency of the current efficiency. At the end of the experiment the cathode was examined and it was detected that arsenic was deposited at all points of the three-dimensional electrode.

The surface morphology of the electrodeposited arsenic was examined by scanning electron microscopy

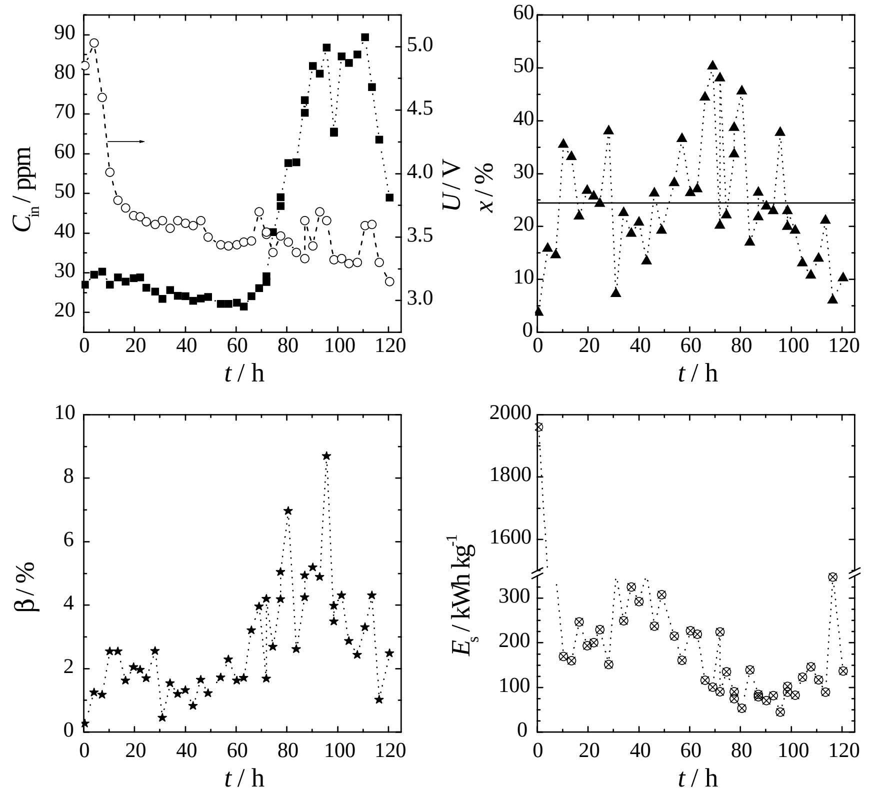

Fig. 7. Performance parameters of the pilot plant electrochemical reactor with a three-dimensional cathode as a function of the operation time. $I = 60$ A. $Q = 1.5$ dm^3 min^{-1}. $T = 70 \pm 4$ °C.

(SEM) and the results are shown in Figure 8. Micrograph (a) shows a portion of the three-dimensional cathode coated with arsenic after the long term experiment and micrograph (b) shows a powdery structure with platelets. After the experiment the arsenic retained in the three-dimensional cathode was removed as a slurry in distilled water by means of an ultrasonic cleaner; the clean electrode surface is shown in micrograph (c).

The slurry was profusely washed with distilled water. The powder was separated by centrifugation, dried in a vacuum oven at 40 °C and the composition was determined by EDAX. Figure 9 shows a typical spectrum. The composition of the powder was As = 50%, Cu = 46%, Sb = 4% and Si < 1%. The presence of copper in the powder can be attributed to the corrosion of the cathode during the shut down time, which may cause detachment of some grains from the copper meshes. Further experiments are now in progress in order to purify the cathodic deposit.

4.3. *Comparison with theoretical predictions*

An electrochemical reactor with a three-dimensional cathode can be represented by the plug flow model. Thus, the fractional conversion is given by [19]

$$x = 1 - \exp\left(-\frac{ka_e V}{Q}\right) \qquad (1)$$

Taking into account for the calculation the mean value of fractional conversion results $ka_e = 7.62 \times 10^{-3}$ s^{-1} and evaluating the mass-transfer coefficient with the Cano and Böhm correlation [18] yields $a_e = 1021$ m^{-1}, which represents only 12% of the geometric specific surface area. The observation that the surface area is not fully used in a three-dimensional electrode was previously reported [20, 21] and was explained by taking into account the shielding effect between wires in the nets and also by the fact that the different regions of a wire do not offer the same contribution to the total current. In the present study the nonconducting nature of the electrodeposited arsenic can be identified as an additional and fundamental factor in decreasing the active electrode surface and for the necessity of frequent deposit removal.

5. Conclusions

The following can now be stated:

(a) Copper was identified as a promising electrode material for the removal of arsenic from technical grade phosphoric acid. (b) It was possible to reduce the arsenic concentration in phosphoric acid to 3 ppm using a rotating copper cylinder electrode. This concentration satisfies the requirements for food grade quality and NF grade. (c) Long term experiments with a pilot plant electrochemical reactor with a three-dimensional cathode showed the feasibility of arsenic removal with fractional conversion per pass 24%, from technical

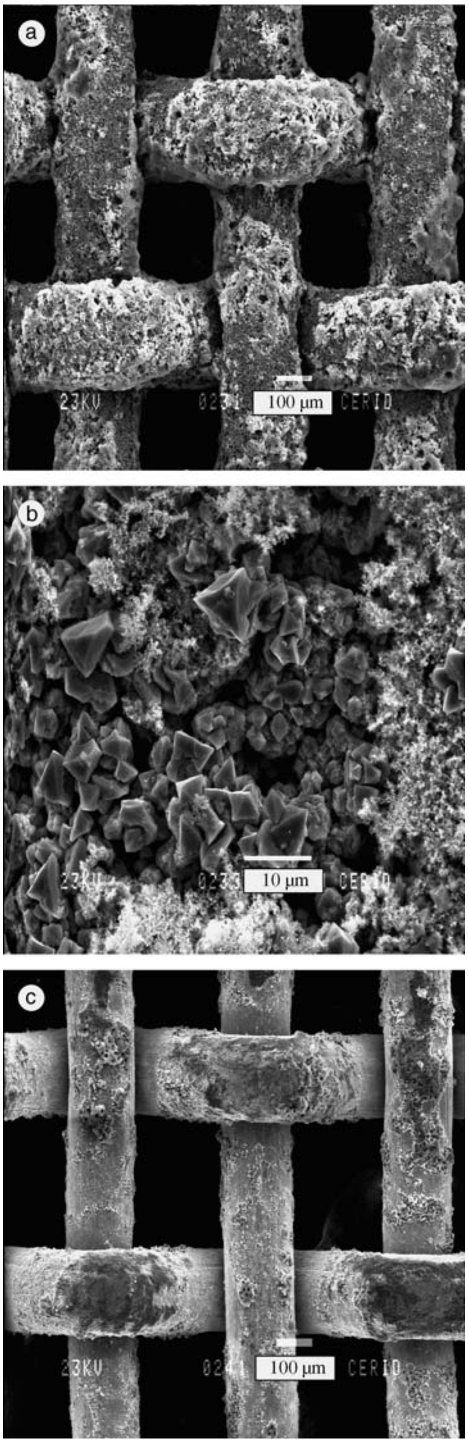

Fig. 8. Three-dimensional cathode after 120 h electrolysis. (a) Scanning electron micrograph of the net with electrodeposited arsenic, magnification ×100. (b) idem as (a), magnification ×2000. Micrograph (c) three-dimensional cathode after removal of arsenic with the ultrasonic cleaner, magnification ×100.

grade phosphoric acid and the recovery of the element as a powder.

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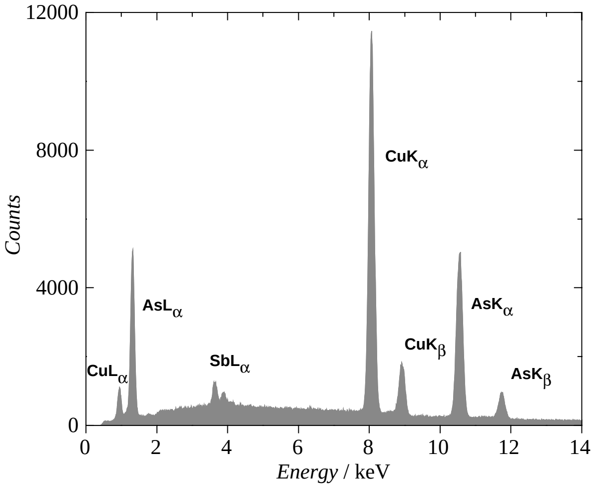

Fig. 9. EDAX spectrum of the powder detached from the three-dimensional cathode by means of an ultrasonic cleaner.

References

1. K. Schrödter, *in* ‘Ullmanńs Encyclopedia of Industrial Chemistry’, Vol. A19 (VCH Weinheim, 1991), p. 465.
2. ‘Food Chemicals Codex’ (National Academic Press, Washington DC, 3rd edn, 1981), p. 225.
3. ‘National Formulary’ (United States Pharmacopeial Convention, Rockville, 1994), p. 2278.
4. V.M. Norwood III and J.J. Kohler, *Fert. Res.* **26** (1990) 113.
5. A.V. Slack, ‘Phosphoric Acid’, Vol. 1, Part 1 (Marcel Dekker, New York, 1968), chapter 12, p. 971.
6. J.D. Chwirka, B.M. Thompson and J.M. Stomp III, *J. AWWA* **92** (2000) 79.
7. K. Rajeshwar and J. Ibanez, ‘Environmental Electrochemistry’ (Academic Press, San Diego, 1997), chapter 8, p. 704.
8. C.W. Stillwell and L.F. Audrieth, *J. Am. Chem. Soc.* **54** (1932) 472.
9. G. Wranglén, *J. Electrochem. Soc.* **108**(11) (1961) 1069.
10. G. Csizi, *Chemie-Ing.-Techn.* **36** (1964) 686.
11. Maelgwyn Mineral Services Limited, *Mining J.* **333** (1999), no. 8562.
12. A.V. Smetanin, M.K. Smirnov, I.N. Chernykh, V.V. Turygin, A.V. Khudenko, V.A. Fedorov and A.P. Tomilov, *Inorg. Mater.* **31** (2003) 27.
13. D. Bejan and N.J. Bunce, *J. Appl. Electrochem.* **33** (2003) 483.
14. M.L. Holt, *in* F. Lowenheim (Ed.), ‘Modern Electroplating’ (John Wiley & Sons, New York, 1974), chapter 17, p. 471.
15. W. Machu, ‘Galvanotecnia Moderna’ (Aguilar, Madrid, 1959), chapter XVIII, p. 502.
16. H.W. Salzberg and B. Goldschmidt, *J. Electrochem. Soc.* **107** (1960) 348.
17. G. Kreysa, *DECHEMA Monographs* **94** (1983) 123.
18. J. Cano and U. Böhm, *Chem. Eng. Sci.* **32** (1977) 213.
19. F.C. Walsh, ‘A First Course in Electrochemical Engineering’ (Alresford Press, Alresford, 1993), chapter 6, p. 180.
20. R. Alkire and B. Gracon, *J. Electrochem. Soc.* **122** (1975) 1594.
21. J.M. Bisang, *J. Appl. Electrochem.* **26** (1996) 135.