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TECHNICAL NOTE

On the anodic dissolution of a high Si-Cr iron alloy (Durichlor 51)

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High-silicon iron alloys have been widely used in various areas of cathodic protection where the alloy serves as a 'sacrificial' anode [1,2]. One specific alloy, Durichlor 51, has been employed in processes containing sulfuric acid, e.g. electroplating, anodizing and water treatment. In Table 1 some physical and chemical characteristics of the alloy are assembled. Table 2 contains selected data on its corrosion performance.

Although recent research on using conventional lead anodes in high-acid electrolytes [3] in the electrowinning of copper appears promising, current technological practice is still limited to moderate acidic media. Increasing the acid concentration in copper electrowinning is one technological incentive and the reportedly high corrosion resistance to sulfuric acid at low temperatures invites the question whether the alloy could replace the conventional 6% Sb-lead anode. The density ratio of nearly 2 between the lead anode and Durichlor 51 is an additional factor for such a consideration.

Table 1. Some physical and chemical characteristics of Durichlor 51 [1,2]

		Chemical composition, %	
Tensile strength ($\frac{1}{2}$ in diameter bar), MN m^{-2}	110·32	Si	14·50
Compressive strength, MN m^{-2}	689·48	Mn	0·75
Brinell hardness	520	C	0·95
Density, kg dm^{-3}	7·0	Cr	4·50
Thermal conductivity, J m^{-1} K^{-1} s^{-1}	52·3	Fe	79·30
Specific resistance $\mu\Omega$ cm(20° C)	72		

Table 2. Performance of Durichlor 51 in cathodic protection applications [1,2]

Application	*Consumption rate*	*Unit*
Synthetic sea water	0·426·	kg A^{-1} yr^{-1}
Sea water (ambient suspended anode) at current densities, A m^{-2}		
10·76	0·317	kg A^{-1} yr^{-1}
32·29	0·331	
53·82	0·476	

Resistance to sulfuric acid at temperatures below 38° C, less than 0·0127 cm yr^{-1}; H_2SO_4: 0–100%

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This note summarizes the results of our preliminary experiments in which a Durichlor 51 bar was used as anode in a small copper electrowinning cell. The cell characteristics are given in Table 3.

Table 3. Characteristics of the experimental copper electrowinning cell

Cathode:	Pure copper cylinder diameter 14 cm; height 14 cm
Anode	Durichlor 51 bar; diameter 5 cm; height 14 cm
Electrolyte:	$CuSO_4$ (29 g dm^{-3}) and H_2SO_4 (160 to 345 g dm^{-3})
Temperature of electrolysis:	25°C
Effective anode area:	219·91 cm^2
Effective cathode area:	615·75 cm^2
Anode weight:	1·92 kg
Effective cell volume:	1·878 dm^3
Electrode configuration:	Anode inside - cathode outside, placed concentrically.

In the sequence of experiments the acid concentration, time-span of electrolysis and the imposed voltage drop were varied from run to run. After each run the cathode and anode were weighed and the electrolyte concentration analyzed; the electrolyte concentration was then set and the next experiment was started. The results are summarized in Table 4. Table 4 also contains the results of two reference runs, performed with a conventional Sb/Pb anode of essentially the same effective area. The apparent anode loss in Experiments 5 and 6 is the difference in the weight between the starting anode and the clean, dried anode; due to re-oxidation of the surface after an experiment, the true weight loss of the lead anode is larger than that shown in Table 4. A loose residue has invariably accumulated at the bottom of the cell regardless of the anode used. During electrolysis, the surface of the Durichlor 51 anode acquired a loose powdery deposit which was easily removed from the otherwise uniform surface. On the other hand, the lead anode had to be thoroughly cleaned from a slime-like deposit; upon its removal, a strong durable surface was re-established.

In the experimental range of acid concentration (15 to 29 wt. %) and anodic current densities (270 to 680 A m^{-2}), the anodic corrosion rate of Durichlor 51 is somewhat larger than that of the Pb–Sb anode. In view of the relatively large cell voltage drops imposed for the purpose of attaining high current flow across the cell, a number of anode reactions can occur, as shown in Table 5. Inasmuch as the thermodynamic e.m.f. of the copper/oxygen cell (with reaction $2Cu^{2+} + 2H_2O \rightarrow 2Cu + O_2 + 4H^+$) is about $-0{\cdot}9$ V for the given electrolyte range, the Durichlor 51 anode was sufficiently polarized to permit the occurrence of all listed reactions. In addition, the formation of HSO_5 species [4] and the disproportionation reaction $Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$ could also be envisaged. From the point of view of anode dissolution, inspection of the Pourbaix diagram for iron [5] indicates that only Reactions 1 and 2 are of importance in the given acid strength range. Indeed, if it is assumed that the anode loss is completely accounted for by Fe^{3+} ions which, upon migration to the cathode are fully reduced to Fe^{2+} ions, the accordingly computed cathode current efficiencies agree reasonably well with the corresponding quantities in Table 4. The mechanism of the anode dissolution process is not yet understood, however, a rough comparison of the results of Donahue and Nobe [6–8] with our observations suggest that the relatively low corrosion rate of Durichlor 51 is most likely linked to the formation of a protective (SiO_2?) layer on its surface.

It appears, therefore, that high-silicon iron alloys such as Durichlor 51 may serve as adequate anode material in relatively high-strength sulfuric acid solutions and at relatively high current densities. Further experiments will be necessary to ascertain whether corrosion rates diminish or increase in prolonged electrolysis under such conditions. Our preliminary results suggest that such anodes might offer a serious technological alternative to lead anodes in the copper electrowinning process.

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Table 4. Comparison of the experiments using Durichlor 51 and a Pb–Sb alloy as anode in the electrowinning of copper

Experiment	*1*	*2*	*3*	*4*	*5**	*6**
Cu^{2+}, g dm^{-3}	29	29	29	29	29	19·2
H_2SO_4, g dm^{-3}	161	161	330	330	330	345
ΔCu^{2+}, g dm^{-3}	–	–19	–19	–9·6	–9·8	–
ΔH_2SO_4, g dm^{-3}	–	31	38	15	15	–
Anode loss, g	None	5·0	7·5	6·0	1·0	1·0
Cathode gain, g	24	137	133	67	69	64
Time-span of electrolysis, h	1·4	7·7	10·5	9·5	9·62	8·42
Average cell voltage drop, V	3·12	3·12	2·86	2·56	2·27	–
Average IR drop, V	2·70	2·70	2·10	0·93	0·93	–
Average cell current, A	15·0	15·0	13·8	6·0	6·0	–
Average cathode current density, A m^{-2}	243·6	243·6	224·1	97·4	97·4	–
Average anode current density, A m^{-2}	682·1	682·1	627·5	272·8	267·8	–
Apparent anode loss rate, g h^{-1}	None	0·649	0·714	0·631	0·104	–
kg A^{-1} yr^{-1}	None	0·380	0·453	0·923	0·152	–
Apparent cathode current efficiency, %†	96·4	95·0	100	99·1	100	–
Apparent penetration rate, μm h^{-1}	–	4·21	4·64	4·10	–	–

*Anode: 6% Sb-lead plate, size 14 × 8 cm, placed in cylinder axis. Effective anode area: 224 cm^2.

†Computed via Faraday's law and experimental values of cathode gain.

Table 5. Summary of the electrochemical reactions at the anode

Reaction Number	*Reaction scheme*	*Standard potential,* V
1	$Fe \rightarrow Fe^{2+} + 2e^-$	0·440
2	$Fe^{2+} \rightarrow Fe^{3+} + e^-$	–0·771
3	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	–1·228
4	$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$	–1·776
5	$2SO_4{}^{2+} \rightarrow S_2O_8{}^{2+} + 2e^-$	–2·010

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[8] *Ibid,* Report 67–45, August 1967.