A preliminary investigation of the electrodeposition of iron from partially neutralized simulated spent pickle liquor

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1. Introduction

Schemes for the electrodeposition of iron from spent sulphuric acid pickle liquors have been fairly frequently reported in the literature over the last 25 years. A review of work up to the early 1970s was made by Kuhn [1] and an update based on more recent patent literature [2–4] has been presented by Howes [5]. The main problem common to all schemes is due to the quite high residual concentration of sulphuric acid (~ 5%) which causes the hydrogen evolution reaction to be more kinetically favoured than iron deposition. Often the spent liquor is neutralized before electrolysis.

This note reports some preliminary data obtained using a small continuous flow cell and a feed of partially neutralized (pH 2), simulated spent pickle liquor. Feed flows first to the cathode compartment and thence through the diaphragm to the anode compartment from which it leaves the cell. The flow through the diaphragm opposes migration and diffusion of hydrogen ions formed by anodic reaction. The use of partial neutralization and cathode-to-anode flow is successfully exploited in the electrowinning of manganese and, of course, the same idea with anode-to-cathode flow is used in chlorine–caustic soda diaphragm cells.

2. Experimental details

A full account of all experimental procedures has been given by Howes [5]. The cell body was made of perspex with two lead plate electrodes and a diaphragm located in a vertical plane parallel configuration. The electrodes slotted into the cell body and the diaphragm (No. 1 Thermovyl woven PVC cloth supplied by P. & S. Filtration Ltd) was held in a rectangular frame which slotted into the cell dividing it into the two compartments each of volume 70 cm^3. The exposed area of each electrode was 52 cm^2 and the diaphragm area 48 cm^2.

Electrolyte was supplied to the cell from a headtank and the flow regulated by a fine control valve. The anolyte flowed out of the bottom of the cell and through a glass tube leg that functioned as a level control. Because of the very small flowrates employed they were measured by observing the volume of anolyte collected over various time intervals. The feed was approximately 7.5% w/v $FeSO_4$ and 5% w/v H_2SO_4 which was then adjusted to pH 2 with 2M NaOH solution, all chemicals being SLR grade. Iron in solution was determined spectrophotometrically making use of the complexes formed by both iron (II) and iron (III) with 1,10-phenanthroline. Both complexes have identical absorption at 396 nm, the amount being additive.

A conventional electrical circuit was employed with power supplied by a Coutant LB1000.2 unit operated on constant current mode. Measurements of current and voltage were made using Advance DMM2 and Fluke 8010A digital multimeters.

The experimental procedure consisted of establishing a steady flow in the absence of current and taking initial catholyte and anolyte samples with a 2.5 ml pipette. The power supply was then set at the required conditions and samples of both catholyte and anolyte withdrawn at regular time intervals. The duration of each run was about 90 min which was approximately twice the time required for the cell to reach a steady state.

3. Analysis of data

A very simple CSTR model can be used to analyse the experimental data. The only reactions considered are the cathodic reaction $Fe^{2+} + 2e^- \rightarrow Fe$

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and the anodic reaction $Fe^{2+} \rightarrow Fe^{3+} + e^-$. It is also assumed that the volumetric flow rates of feed and anolyte are equal. This assumption was found to be good.

Let C_{1f} and C_{1a} represent the molar concentrations of ferrous ions in the feed and anolyte respectively and similarly let C_{2f} and C_{2a} represent the corresponding ferric ion concentrations. Q is the volumetric flow rate of the solution and I the total current.

Since iron is removed from solution only by electrodeposition, an overall material balance gives

$$QC_{1f} + QC_{2f} = QC_{1a} + QC_{2a} + \frac{I\epsilon_1}{2F} \qquad (1)$$

where ϵ_1 is the fractional current efficiency for the reaction $Fe^{2+} + 2e^- \rightarrow Fe$ and F is the Faraday number.

A ferric ion balance gives

$$QC_{2f} + \frac{I\epsilon_2}{F} = QC_{2a} \qquad (2)$$

ϵ_2 being the current efficiency for the anodic reaction $Fe^{2+} \rightarrow Fe^{3+} + e^-$. Strictly, ϵ_2 represents the net current efficiency for the formation of Fe^{3+} since the reverse reaction $Fe^{3+} + e^- \rightarrow Fe^{2+}$ takes place at the cathode. However, the extent is likely to be small with near equilibrium concentrations of Fe^{3+}

4. Results and discussion

Fig. 1 presents the anolyte composition as a function of time for one run and it can be seen that an acceptable steady state was attained. The total iron concentration is seen to become nearly constant after about 45 min although minor fluctuations in ferric ion concentration are visible. Some nonuniformity in solution composition is probable despite the stirring produced by anodic oxygen evolution. Observed and derived data are given in Table 1 and current efficiencies plotted in Figs. 2 and 3. The data are for a few runs in which the cell current was held constant and the flow rate varied and others where the flow rate was kept approximately constant and the current varied.

For runs at a current of 3A the current efficiency for iron deposition increases slightly with increased flow rate and, apart from one very high value, is in the range 86–89%. In all these runs the anolyte attained a pH of 1.6–1.7 and the catholyte 2.3–2.4 so that the flow through the diaphragm was effective in suppressing hydrogen ion transfer from the anode compartment. The very slight change in iron deposition rate with flow rate suggests that this is taking place under conditions of activation control which is to be expected from previous work under similar experimental conditions [6]. At the anode the current efficiency for ferrous

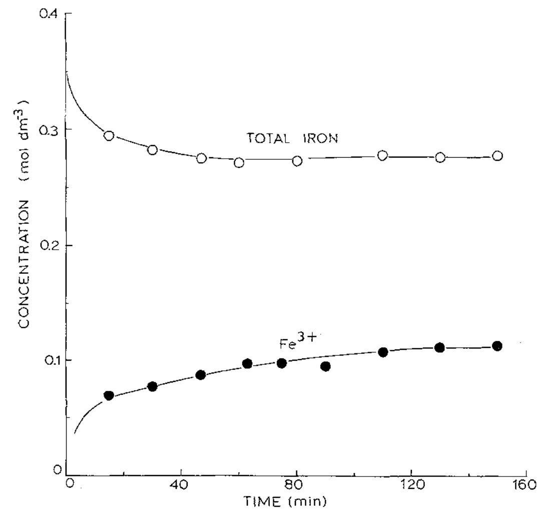

Fig. 1. Typical anolyte composition as a function of time.

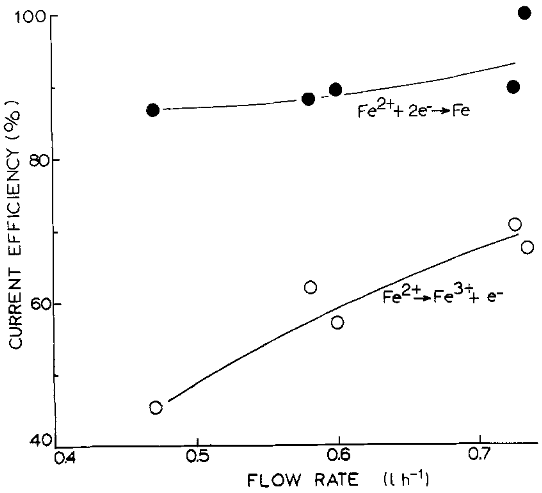

Fig. 2. Current efficiencies vs flow rate at a total current of 3A.

Table 1. Measured and derived data

Flow rate ($ml\,h^{-1}$)	*Current* (*A*)	*Cell voltage* (*v*)	*Concentrations* ($mol\,dm^{-3}$)				*Current efficiency*	
			C_{1f}	C_{2f}	C_{1a}	C_{2a}	ϵ_1	ϵ_2
470	3.00	6.4	0.3327	0.0056	0.1219	0.1133	0.869	0.454
584	3.00		0.3304	0.0097	0.1270	0.1286	0.881	0.620
600	3.00	6.5	0.3420	0.0061	0.1522	0.1125	0.894	0.570
725	3.00	6.6	0.3411	0.0029	0.1638	0.1113	0.894	0.705
735	3.00		0.3572	0.0048	0.1789	0.1070	0.999	0.671
727	4.00	7.6	0.3408	0.0060	0.1424	0.1150	0.870	0.530
731	2.00	5.5	0.3386	0.0018	0.2170	0.0846	0.760	0.829
737	5.00	8.0	0.3456	0.0027	0.1071	0.1287	0.889	0.498

oxidation increases more rapidly with increasing flow rate which suggests that this reaction is taking place under conditions of appreciable mass transfer control which is consistent with known information [7].

The above observations are supported by the runs at constant flow rate and variable current and the current efficiency vs current plot of Fig. 3. Here again only small changes in iron deposition efficiency are seen so that both hydrogen and iron production are activation controlled over the entire current (and cathode potential) range. The ferrous oxidation is now seen more clearly to be influenced by mass transfer. The overall cell voltage increase (7.6 to 8.0 V) between the 4 and 5A runs is attended by a fairly modest increase (2.12 to 2.49A) in the Fe^{2+}/Fe^{3+} partial current. The ratio of these partial currents 2.12:2.49 differs little from the ratio of the corresponding anolyte ferric ion concentrations, which is 0.1150:0.1287, so that the anodic oxidation of Fe^{2+} at 5A total current must be taking place at near limiting current conditions. The limiting current with this process would progressively rise at increased anode potentials due to the stirring produced by increased oxygen evolution.

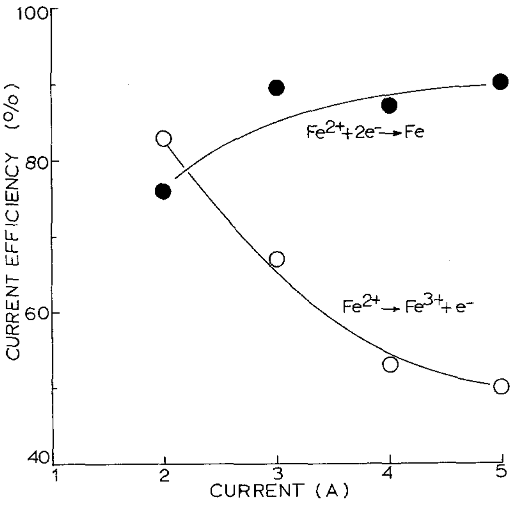

Fig. 3. Variation of current efficiencies with total current at flow rates around 730 $ml\,h^{-1}$.

5. Concluding remarks

Iron can be electrodeposited with between 85 and 90% current efficiency from a partially neutralized spent pickle liquor using a continuous cell with internal flow from the cathode compartment to the anode compartment. Further experimental work and the development of a more complete model are progressing.

References

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