Aspects of the Development of a New Copper Electrowinning Cell based on Reactive Electrodialysis

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Several authors have discussed the limitations of conventional copper electrowinning (EW) cells (e.g. Kammel, 1982; Gupta & Mukherjee, 1990): a) low mass transfer rates due to low electrolyte flowrates, which have limited the cell current density to values below 360 A/m^2; b) low specific cathode surface area (m^2/kg), which also limits the copper deposition rate; c) high energy requirements (about 2kWh per kg of deposited copper) caused by an anodic reaction ($2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e$) which exhibits both a high equilibrium potential and a high anodic overpotential, resulting in a 2 V cell voltage; d) an anodic reaction which produces acid mist, causing environmental problems.

In order to overcome these limitations, various proposals have been made: a) new cell designs to allow for electrolyte agitation; b) particulate cathodes to increase the specific cathode surface area; c) alternative anodic reactions, with less positive equilibrium potentials and which do not produce acid mist; d) alternative anodic materials to decrease the anodic overpotential. As a result of these proposals, a number of attempts have been made to develop new cells. Kammel, 1982, has considered 12 alternative cell designs and pointed out that the most promising ones are the particulate bed cell and the fluidized bed cell. In spite of all the work that has been carried out, there is at present only one industrial operation implementing a particulate bed cell for the processing of dilute electrolytes, which points to the need for further work in this area.

The sustitution of an alternative anodic reaction has been studied (e.g. Das, 1996). The one which has shown more promise is the ferrous to ferric ion oxidation ($Fe^{2+} \rightarrow Fe^{3+} + e$) whose standard electrode potential is about 0.46 V less than the water decomposition potential.

One way of using the ferrous/ferric anodic reaction while avoiding a decrease in cathode current efficiency due to ferric ion reduction, is to separate the anolyte from the catolyte. The separation and concentration of charged species in solution by using membranes in an electric field is called electrodialysis (ED) (Strathmann, 1995). When the separation is carried out in order to obtain a product at an electrode, the technique is called reactive electrodialysis (RED, also known as 'electro-electrodialysis', Audinos, 1992).

This work aims to contribute to the development of a copper EW cell which overcomes the main limitations of conventional technology. The electrochemical kinetics of the ferrous/ferric reaction was characterized on various anodic materials: lead sheet, platinum sheet, graphite rod, Pt (as a surface layer on Ti mesh), RuO_2 (on Ti) and IrO_2 (on Ti) by means of potentiodynamic sweeps. Results for the limiting c.d. of the anodic reaction and the starting potential for O_2 evolution are presented in Table 1.

The ferrous/ferric reaction on Pb exhibits a very low exchange current density even at high overpotentials, therefore, Pb is not a suitable anodic material for this reaction. In the RED cell which uses the ferrous/ferric reaction and catalytic anodes, the graphite anode affords a degree of electrocatalysis which is similar to that of more expensive materials.

The cell voltage for the Fe^{2+}/Fe^{3+} reaction was measured for various anode materials at constant cell current density. Results are in Table 2 and show that the cell voltage is lower by 30-60% than those obtained in conventional copper EW cells. The anodic materials, in decreasing order of performance, are: Pt > Pt/Ti > $RuO_2/Ti \cong IrO_2/Ti \cong$ graphite.

The separation of Fe and Cu species in the RED cell is achieved by means of anion membranes. Cu ions are retained in the catholyte, where they are electrodeposited on copper sheet or copper mesh cathodes. Results for cell voltage depending on membrane type ('low' and 'high' selectivity) and number are shown in Table 3, where A = anolyte and C = catholyte. It is clear that both the number of membranes used and their selectivity influence the cell voltage and also the cation separation efficiency.

References

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Tables

Table 1 Kinetics of the Fe^{2+}/Fe^{3+} reaction

Material	i_L, A/m^2	E_{start}, V
Pt	290	1.8
RuO_2/Ti	260	1.7
IrO_2/Ti	330	1.7
Graphite	290	1.5
Lead	<10	1.7

Table 2 Cell voltages, RED cell (V)

i_{cell}, A/m^2	200	250	400
Material			
Pt	0.97	1.23	1.72
Pt/Ti	1.07	1.29	1.88
RuO_2/Ti	1.17	1.35	1.92
IrO_2/Ti	1.18	1.38	2.02
Graphite	1.19	1.40	2.04

Table 3 Anion membrane performance

System	Vcell, V	Cu (A), %	Fe (C), %
1 low sel.	0.93	0.30	0.45
2 low sel.	1.04	0.12	0.23
1 high sel.	0.91	0.08	0.12
2 high. sel.	0.99	0.02	0.03