An Investigation of Fluidized Bed Electrowinning of Cobalt Using 50 and 1000 Amp Cells

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50 Amp and 1000 Amp cells equipped with fluidized bed cathodes were used to investigate the electrowinning of cobalt from sulfate solutions. The catholytes employed ranged in cobalt concentration from 100 to 4.8 grams per liter of cobalt and from acid (pH = 1) to near neutral (pH = 6). Superficial current densities up to 1.09 A cm\(^{-2}\) were used. The cells were equipped with a nearly impermeable diaphragm, permitting the use of an anolyte of composition different from that of the catholyte. The current efficiency for cobalt deposition (as conveniently determined by measuring the rate of hydrogen evolution), electrical energy consumption, and appearance of the deposit were studied as a function of catholyte composition. Reasonable current efficiencies were observed. The electrical energy consumptions were much higher than that of conventional electrowinning, but this was shown to be due to the anode chamber and diaphragm resistance losses rather than the fluidized cathode.

I. INTRODUCTION AND PREVIOUS INVESTIGATIONS

Over the past decade, the use of fluidized bed electrodes to electrowin metals from aqueous solutions has been the subject of several investigations. In such applications, the fluidized bed electrode appears to offer advantages in terms of capital cost and automation of equipment when compared to conventional electrowinning. The present paper reports on one of a continuing series of investigations concerned with fluidized bed electrowinning of metals at the University of California, Berkeley. A recent paper in this journal, concerning with copper electrowinning, provides a fuller introduction to fluidized bed electrodes and an account of previous investigations of such electrodes.

Conventional electrowinning of cobalt has been reviewed by Löwe et al., who have reported that comparatively low current densities (0.02 to 0.03 A cm\(^{-2}\)) are used; current efficiencies fall in the range 65 to 88 pct and energy consumptions in the range 3.2 to 6.4 kwh/kg cobalt. Low current densities are necessary to avoid excessive hydrogen evolution at the cathodes and to prevent formation of metal hydroxides at the cathode by depletion of hydrogen ions from solution.

II. THEORY

The electrodeposition of cobalt from aqueous solutions is frequently accompanied by simultaneous evolution of hydrogen. This occurrence is due to the combined effect of negative equilibrium potentials for metal ion deposition (compared to the standard hydrogen electrode) and relatively low overpotentials for hydrogen evolution. The reactions to be considered and their electrode potentials at 25 °C are:

I) \(\text{Co}^{++} + 2e^- = \text{Co}\quad E_0 = -0.27\)
II) \(2\text{H}^+ + 2e^- = \text{H}_2\quad E_0 = 0\)
III) \(2\text{H}_2\text{O} + 2e^- = \text{H}_2 + 2\text{OH}^-\quad E = -0.414\) @ pH = 7

The water decomposition reaction is included due to the evidence that whenever the electrode polarizes with respect to reactions I and II (i.e., the electrode potential is substantially below the equilibrium potential), reaction III will naturally take place at the surface of the electrode. Furthermore, under these conditions the occlusion of cobalt hydroxide into the cobalt deposit with consequent deterioration in its quality has been reported by Nakahara and Mahajan.

Kinetic parameters for the electrodeposition of cobalt (e.g., parameters in a Butler-Volmer equation) are not available in the literature; in this investigation approximate values were estimated from published data. The overvoltage for the deposition of cobalt from solutions containing 50 grams per liter of cobalt as sulfate, in the range 0.02 to 0.1 A cm\(^{-2}\), can be estimated from the paper of Löwe et al. to be 0.1 to 0.12 volts. Overvoltages for hydrogen evolution at different current densities appear in Table I from the work of Pecherskaya and Stender. This suggests that in acidic solutions, high current densities are beneficial for cobalt electrolysis. Under these conditions, cobalt current efficiencies will be determined by the relative kinetics of reactions I and II modified by any mass transfer effects. However, at low cobalt concentrations and higher pH's, high current densities imply an electrode which is polarized with respect to reactions I and II resulting in the onset of reaction III and followed by a further increase of solution pH at the vicinity of the particulate electrode with consequent deterioration of cathode quality.

This discussion has been concerned with an electrode at an equipotential with respect to the solution. The variation in potential within a working fluidized bed electrode is well known. The potential distribution within the bed is a function of the relative effective conductivities of electrolyte and bed (the latter being dependent on bed expansion and particle size), the current passed through the electrode, the kinetics of the electrochemical reactions, as well as mass transfer. The mathematical model for a fluidized bed electrode developed at Berkeley was modified to a rectangular...
geometry and to incorporate the kinetic parameters germane to this investigation. The model is for a multicomponent electrolyte and employs a set of differential equations: Ohm's law for the current flow within the particulate electrode, equations for migration, convection and diffusion of each type of ion in solution, conservation equations for each ion, for current in the particulate electrode as well as in the electrolyte, and the Butler-Volmer equation describing the kinetics of the different electrochemical reactions. The last equation was modified to account for the influence of mass transfer on the kinetics of each reaction. It has been assumed that concentration gradients within the bed are negligible and that electroneutrality of electrolyte is obeyed. The kinetic parameters for cobalt deposition were those reported by Tanaka et al. for cobalt deposition from chloride solutions, while those for hydrogen evolution were estimated from the work of Pecherskaya and Stender. Reactions. The last equation was modified to account for the influence of mass transfer on the kinetics of each reaction. The model is for a multicomponent electrolyte and employs a set of differential equations: Ohm's law for the current flow within the particulate electrode, equations for migration, convection and diffusion of each type of ion in solution, conservation equations for each ion, for current in the particulate electrode as well as in the electrolyte, and the Butler-Volmer equation describing the kinetics of the different electrochemical reactions. The last equation was modified to account for the influence of mass transfer on the kinetics of each reaction.

The model predicts increased rates of cobalt deposition at the higher current density, and a higher current efficiency is therefore predicted for higher current densities.

Figure 3 depicts the predicted effects of electrolyte pH on current efficiency for cobalt deposition. Three regimes are to be distinguished according to the pH of the catholyte:

1. At catholyte pH 3.15 to 5.17 the hydrogen reaction is mass transfer limited and consequently cobalt current efficiencies are high;
2. An intermediate regime in the pH range of 2.00 where cobalt current efficiency is determined by relative kinetics of reactions I and II as well as by mass transfer effects for the hydrogen evolution reaction. Partial diffusion limitation for hydrogen evolution is most obvious at the diaphragm and near the current feeder zone.
3. Higher acidities (pH 1.42) where the current efficiency is determined mostly by the relative kinetics of the competing reactions.

The low current efficiency under more acidic conditions clearly emphasizes the importance of keeping reaction II under mass transfer control for efficient cobalt electrowinning. A similar result has been demonstrated experimentally by Goodridge et al. in the case of zinc.

<table>
<thead>
<tr>
<th>I (A cm⁻²)</th>
<th>1.10⁻³</th>
<th>5.10⁻³</th>
<th>1.10⁻²</th>
<th>2.10⁻²</th>
<th>4.10⁻²</th>
<th>1.10⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>η H₂ (V)</td>
<td>0.32</td>
<td>0.39</td>
<td>0.42</td>
<td>0.45</td>
<td>0.48</td>
<td>0.52</td>
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Table I. Hydrogen Evolution Overvoltage at Different Current Densities as Related to Hydrogen Evolution on Cobalt Metal in 2N H₂SO₄ at 25 °C

I(A cm⁻²) 1.10⁻³ 5.10⁻³ 1.10⁻² 2.10⁻² 4.10⁻² 1.10⁻¹
η H₂ (V) 0.32 0.39 0.42 0.45 0.48 0.52

Fig. 1 — Variation of electrolyte and particulate potentials with position in bed as computed with multi-component model using the following parameters: ρo = 2Ω cm; ρe = 4.4Ω cm; i₀ cobalt = 1.10⁻⁶ A cm⁻²; i₀ hydrogen = 1.10⁻⁷ A cm⁻²; a = 50 cm⁻¹; kₓ = 0.05 cm s⁻¹; cobalt ion concentration = 88 g/l.

Fig. 2 — Predicted variation of reaction rate distribution in bed at particulate surface for different current densities. Parameters as in Fig. 1, pH = 3.15.