Electrowinning of nickel at the Bindura Smelting and Refining Company

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SYNOPSIS

After a brief discussion of theoretical considerations in the electrowinning of nickel, an account is given of the electrowinning process and plant used at the Bindura Smelting and Refining Company.

SAMEVATTING

Na 'n kort bespreking van die teoretiese oorwegings in verband met die elektrowinning van nikkel, word daar verslag gedoen oor die elektrowinningsproses en -aanleg wat deur die Bindura Smelting and Refining Company gebruik word.

Introduction

The refinery at the Bindura Smelting and Refining Company (B.S.R.), Rhodesia, treats the nickel–copper–sulphide alloy that is produced in its pyrometallurgical smelting plant. The design of the refinery circuit was formulated by Outokumpu Oy, and the nickel and copper products are electrowon from solution. The control of the refinery circuit is based on the rate at which nickel is plated out of solution. New nickel–copper alloy must be added to match that rate, and allowances must be made for the sulphide content, or 'non-leaching' fraction, in the calculation.

Copper is essential to the process, and care has to be taken with the addition rate of the alloy, as well as with the copper-plating rate, if the circuit is not to be denuded of copper.

This paper examines the theoretical aspects of the electrowinning of nickel, and describes the equipment used at B.S.R. and some of the problems that have been encountered.

Theoretical Considerations

The nickel is electrowon with insoluble anodes and nickel cathodes in a diaphragmed compartment from a purified nickel sulphate solution containing boric acid.

The cell potential can be considered to be made up of three potentials:

E_{cell}, the cell potential,
E_A, the anode electrode potential, and
E_C, the cathode electrode potential.
$E_{cell} = E_A - E_C + E_R$, where
E_R = potential across the electrolyte.

The anode and cathode electrode potentials, E_A and E_C, are made up of further potentials:

E.P. (electrode potential) = R.P. + C.P. + A.D.

E.P. is the driving force required for a reaction to occur at a given electrode–electrolyte interface. It is the voltage between the electrode and the adjacent electrolyte and depends on composition of electrode and electrolyte, temperature, and current density.

R.P. (reversible potential) is the voltage that can be theoretically measured across the interface when no current is flowing. It is independent of whether the

electrode is an anode or cathode. Standard reference reversible potentials are available.

C.P. (concentration polarization) is the voltage necessary to overcome the effects of gradients in the concentration of reacting ions. These gradients are produced in the electrolyte layer adjacent to the electrode by operating at practical current densities. The concentration polarization increases with current density.

A.O. (activation overvoltage) is necessitated by some slow step in the electrode reaction. The transfer of an electron in the initial ion discharge at the cathode and the incorporation of the nickel atom in the crystal lattice are slow steps and require an overvoltage. The activation overvoltage increases with current density.

In electrowinning, the electrons are discharged from the cathode and collected onto the anode. The electrode potential for the various reactions that take place at the anode or cathode are best represented by the electromotive series of Table I. The more negative the potential, the more readily the reaction takes place at the anode; and the more positive the potential, the more readily the reverse reaction takes place at the cathode.

TABLE I
STANDARD ELECTRODE POTENTIAL AT 25°C

Element	Anodic reaction	Reversible electrode potential, V
Zinc	$Zn = Zn^{2+} + 2e$	—0,76
Iron	$Fe = Fe^{2+} + 2e$	—0,44
Cobalt	$Co = Co^{2+} + 2e$	—0,28
Nickel	$Ni = Ni^{2+} + 2e$	—0,25
Lead	$Pb = Pb^{2+} + 2e$	—0,13
Hydrogen	$H_2 = 2H^+ + 2e$	0,00
Copper	$Cu = Cu^{2+} + 2e$	+0,34
Oxygen	$2H_2O = O_2 + 4H^+ + 4e$	+1,23

The Cathodic Reaction

Comparison of the reversible electrode potentials indicates that hydrogen would be evolved at the cathode, its potential being more positive than that of nickel. This does not occur because the hydrogen electrode potential is made substantially more negative than the nickel electrode potential by the following.

(1) The concentration of hydrogen ions in the cathode compartment is kept low by the use of a diaphragm bag, thus inducing a high concentration polarization.

(2) The deposition of hydrogen on nickel requires a high liberation overvoltage.

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It can be mentioned here that certain organic chemicals, e.g., amines from boiler-water chemicals and lubricating oils, are considered to lower the overvoltage to such an extent that hydrogen is evolved at the cathode in place of nickel deposition. Thus, at the cathode the reaction can be taken as

$$Ni^{2+}+2e=Ni. \qquad \qquad (1)$$

At 225 A/m² and 65°C, an electrode potential of −0,56 V would be made up of the following voltages, which are estimates from rough measurement to serve only as a guide:

Reversible potential	−0,25 V
Deposition overvoltage	−0,15 V
Concentration overvoltage	−0,16 V.

Some hydrogen is evolved, but this is probably due to the reaction

$$2H_2O+2e=H_2+2OH^-. \qquad \qquad (2)$$

The hydroxyl ion could raise the catholyte pH and cause the nickel to precipitate. To prevent this, boric acid is introduced as a buffer. Boric acid, which is a weak acid, normally forms complexes with nickel ions, preventing the precipitation of the nickel hydroxide.

Because of the high electrode potential, it is necessary to purify the catholyte of metal ions such as copper, cobalt, lead, iron, and zinc that would otherwise plate with the nickel.

The Anodic Reaction

Because insoluble anodes are used, the reaction must involve either the decomposition of water or the oxidation of the anion if current is to pass. The electrode potential for the oxidation of the sulphate anion is greater than that for the decomposition of water, and oxidation therefore becomes the principle anodic reaction:

$$2H_2O=O_2+4H^++4e. \qquad \qquad (3)$$

At 225 A/m² and 65°C, an electrode potential of +1,99 V was made up of

Reversible potential	+1,23 V
Oxygen overvoltage	+0,76 V.

The potential is high enough for hydroxyl ions to be oxidized at the anode but, because their concentration in acid solution is low, they consume very little anode current.

The Overall Cell Reaction

Reactions (1) and (3) combine to give the overall cell reaction

$$2Ni^{2+}+2H_2O=2Ni+4H^++O_2 \qquad (4)$$

or

$$2NiSO_4+2H_2O=2Ni+2H_2SO_4+O_2. \qquad (5)$$
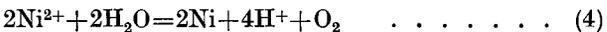
The combined potentials are

$E_A=+1,99$ V
$E_C=-0,56$ V
$E_R=+1,05$ V.
$E_{cell}=E_A-E_C+E_R$
$\qquad =1,99-(-0,56)+1,05$
$\qquad =3,60$ V.

It should be noted that E_R includes a voltage drop across the diaphragm bag of 0,25 V.

The Plant

Cells

The cells are constructed in pairs, and are of reinforced concrete with an acid-resistant lining.

Cell measurements
6,6 by 1,15 by 1,2 m internal

Cell linings
Original : 4% antimonial lead. Testing : pure lead, fibreglass, Telcovin (thermoplastic), neoprene. (It has been necessary to replace antimonial lead linings every 2 to 3 years.)

Cathodes
39 trimmed nickel starting sheets or stainless-steel blanks.

Anodes
40 6 mm pure-lead plates (originally 4% antimonial lead).

Spacing
160 mm anode to anode.

Cathode compartment
Fibreglass cathode bag frame with terylene diaphragm bag. Catholyte distributed to each compartment.

Unscreened plating surface
Starting sheets: 1000 mm by 855 mm. Cathodes: 990 mm by 805 mm.

Fume
Anodes are bagged and the cloth effectively filters the gases.

Power Source

The d.c. power to the cells is obtained from silicon rectifiers connected to a 24 phase 4800 kV.A transformer arrangement. On load tap-changing and transductors are used to provide constant current output up to a maximum of 15 000 A. The voltage range is 40 to 280 V.

The Process

Nickel is first plated at a current density of 210 A/m² onto stainless-steel blanks to form three-day starting sheets, which are trimmed and have nickel loops welded to them. Thinner sheets may be used but would require rigidizing. The stainless-steel blanks are sanded with a 270 grit emery cloth, and need only a thin coating of shellac.

The trimmed and looped starting sheets are placed in an etching tank of 20 g/l sulphuric acid, and the current is reversed for about 30 minutes. The etched sheets are removed and, without being dried, are placed in a 10 to 15 g/l boric acid solution in a holding cell to await transfer to the commercial cells. In this manner, passivation of the etched starting sheets is avoided, and a clear *wettable* sheet is made available for plating, thus reducing the tendency for split or pitted cathodes.

Plating at a current density of 225 A/m² continues in the commercial cells for a further six days to provide cathodes within a specified thickness. The tankhouse is currently operating at 14,5 kA, with current efficiency in the region of 95 per cent.

The cathodes are pulled, washed, sheared into squares, packed, and despatched. Some whole cathodes are sold.

Process Control

Current density, catholyte flow, nickel concentration, pH, purity, and temperature are the most important control parameters.

Depletion of nickel ions in the liquid film adjacent to the cathode increases the concentration polarization, and thus the electrode potential. If this is taken to the extreme, excessive evolution of hydrogen may occur. Replenishment of the nickel ions in this liquid film depends on electromigration and diffusion. The rate of diffusion is controlled by the concentration of nickel in the bulk of the electrolyte, which in turn is dependent on the concentration in the catholyte, the catholyte flow, and the plating rate (current density).

It is evident therefore that the current density, the nickel concentration in the catholyte, and the drop in nickel concentration (on which the flow is based) are interdependent. It is current practice at B.S.R. to operate with a drop in nickel concentration of 28 g/l (from 96 g/l in the catholyte) at a current density of 225 A/m².

Liberation of hydrogen at the cathode is inhibited by the high concentration overvoltage. However, if the pH is allowed to drop by the back diffusion of hydrogen ions, excessive liberation of hydrogen may occur. To prevent this, a suitable diaphragm membrane is required so that a hydraulic head, preferably 25 mm, is maintained in the cathode compartment. On the other hand, if the pH is too high, nickel can precipitate at the cathode surface, affecting the quality of the deposit.

The pH of the catholyte is controlled to 3,5 by the addition of acid, and boric acid is added to prevent nickel precipitation. An indication of the pH of the electrolyte can be gained by inspection of the froth layer on the solution surface. Suspect bags are checked and changed as necessary.

As most metal ions will be deposited at the cathode at the high potentials employed, cathode purity is directly related to the efficiency of catholyte purification. The following are typical analyses.

	Catholyte p.p.m.	Cathodes p.p.m.
Cu	1	10
Co	1–2	40
Pb	1	10
Fe	1	5
Zn	1	2

Owing to the lack of sensitivity of catholyte analyses, no correlations have been possible between catholyte and cathode impurity at this level.

The temperature of the solution affects the stresses in the cathode deposit, the stresses being relieved once the temperature is above about 55 °C. As PVC piping in the circuit limits the upper temperature to 65 °C, the catholyte temperature is normally controlled at 62 °C. After long shutdowns, it is essential that the temperature should be raised before plating commences if the cathodes are not to split.

The plating current can be interrupted for several hours without adverse effect to the cathodes. It is not the practice at B.S.R. to hold with a trickle current. After a long shutdown, the current is reversed for a short period before normal plating is commenced, but it is uncertain whether this achieves anything other than heating of the electrolyte. However, cells that are shorted out and left loaded become passive, and current reversal is essential prior to normal plating.

Problems

Pitting of the Cathode

Sodium lauryl sulphate is added to the catholyte to prevent pitting of the cathode surface. This additive may act as a wetting agent; or it may increase the hydrogen overvoltage, or form complexes with organic material, particularly oil, present in the catholyte.

Nodules on the Cathode

Particulate matter adhering to the cathode forms nodules. For this reason, the catholyte is clarified in Stellar filters, and a turbidimeter has been installed to cause the filtrate to recycle if breakthrough occurs. Because precipitation of nickel at the cathode can also result in the growth of nodules, the pH of the catholyte is reduced.

Current Distribution

Uneven distribution of current between the cathodes can result in wide variation of current density and cathode quality. Cells are regularly steam-cleaned, and a close watch is kept on the busbar contacts.

Catholyte Distribution

The flow of catholyte to each bag is adjusted by the action of a screw clamp on flexible PVC pipe, and is measured by rotameter. The system is far from ideal, and there are large variations between the flows. This naturally affects the drop in nickel concentration, and thus the quality of the nickel cathode. An improved method of flow distribution is being sought.