MATERIAL BALANCE AS THE BASIS FOR PROCESS CONTROL IN ELECTROWINNING AND ELECTROREFINING

W.W. HARVEY

EIC Corporation, 55 Chapel Street, Newton, Massachusetts 02158 (U.S.A.)

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ABSTRACT

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Electrowinning and electrorefining, like chemical processes generally, are amenable to comprehensive material balance analysis for purposes of process control. However, current efficiency in electrowinning is insufficient to provide the requisite agreement between current and electrolyte flows on the one hand and observed concentration changes on the other. The many factors contributing to volume change and metal loss in electrowinning determine a "volume efficiency", as previously defined, which can differ significantly from 100%. Use of volume efficiency in conjuction with current efficiency is illustrated by experimental data for the case of nickel electrowinning employing a porous separator. In electrorefining, anode current efficiency is a major factor in the material balance. The chemical compositions of anodes and cathodes and their respective current efficiencies contribute the source terms for soluble impurity buildup in the electrolyte. An analysis is developed which takes into account the principal mechanisms of extraneous weight loss of anodes, including dissolution of oxide inclusions, disintegration and chemical corrosion. The considerations involved are illustrated for nickel impurity in copper anodes.

INTRODUCTION

Since publication of a previous communication [1] on material balance in electrowinning, the author has received a number of inquiries relative to (a) the applicability of the formulism to the case of electrowinning cells with separators and (b) the feasibility of precisely treating material balance in electrorefining. The answer to both questions is affirmative. Of course, in the case of electrowinning in divided cells, there is a larger number of solution compositions and volumes to be taken into account. For example, in conventional nickel electrowinning from sulfate electrolyte, a minimum of four solutions must be included in the material inventory, viz., influent electrolyte, catholyte, anolyte, and cell effluent. In electrorefining, anode composition and current efficiency dominate the material balance considerations, and an approach and frame of reference that differ from those appropriate to electrowinning are warranted. Accordingly, electrorefining and divided-cell electrowinning are treated separately below.

ELECTROWINNING WITH DIAPHRAGM CELLS

As stated above, the same conceptual framework pertains for electro-winning in cells with internal separators, or diaphragms, as for the previously illustrated case of electrowinning in diaphragm-less cells. Thus, a "volume efficiency", V.E. (%), may be defined (eqn. (1)) in terms of the mass w of metal deposited, the volumes V' and V'' of influent and effluent electrolyte, and the respective concentrations c' and c'' of the metal being electrowon:

$$w = V'c' - V''c'' - \delta w \equiv V' \left(c' - \text{V.E.} c''/100 \right) \tag{1}$$

Note that most prior formulations of material balance in electrowinning (e.g., ref. [2]) take V' and V'' to be sensibly equal and also omit consideration of a weight decrement, δw, which includes the resultant of errors in the measurement of volume and concentration as well as metal value actually lost from the electrowinning circuit. The previous communication lists a number of factors that contribute to volume change and metal loss in electrowinning.

There are other and possibly more convenient ways of defining a volume efficiency in electrowinning, but this possibility has not been fully explored. As defined above, V.E. is given by

$$\text{V.E.} = 100 \left(\frac{V''}{V'} + \frac{\delta w}{V'c''} \right) \cong 100 \left(\frac{V''}{V'} + \frac{\delta w}{V''c''} \right) \tag{2}$$

i.e., by the ratio of effluent to influent electrolyte volumes plus the ratio of apparent metal loss (or gain) to metal contained in the effluent electrolyte (approximately). In electrowinning cells with separators, the estimation of δw requires a knowledge of any changes in volume as well as in concentration of the distinguishable cell solutions. A method of V.E., C.E. analysis will now be illustrated for the case of conventional nickel electrowinning from sulfate electrolyte, following approximately the Outokumpu conditions [3,4].

In a four-day nickel electrowinning campaign, analyzed cell feed was transferred daily to a holding tank, from which it was metered into the cathode compartment. The partially nickel-depleted electrolyte flowed out under a small hydrostatic head through a permeable separator (cathode bag) into the anode compartment and exited the cell via an overflow. The weight of nickel deposited was 17.46 kg, as obtained by quantitative analysis of the weighed deposits, i.e., this figure does not include the small amounts of co-deposited metals and oxide oxygen.

Pertinent items of electrolyte inventory are presented in Tables 1 and 2. The net volume change was 847.4-862.5 l = -15.1 l, or -1.8%. The volume of catholyte displaced by the nickel deposit, namely, 17.46 kg ÷ 8.90 kg/l = 1.96 l is a correction to the apparent decrease of combined catholyte + anolyte volumes: 195.8 l (end)-204.5 l (start) + 1.96 l (displaced) = -6.8 l.

TABLE 1

Nickel electrowinning, material balance: inputs to system*

Electrolyte	Weight (kg)	Density (kg/l)	Volume (l)	Ni (g/l)	Ni (kg)	H_2SO_4 (g/l)	H_2SO_4 (kg)
Initial holding tank contents			73.7	73.78	5.43_8	pH 2.86	—
Initial catholyte	43.1_8	.1.2303	35.1_0	50.22	1.76_3	pH 3.48	—
Initial anolyte	209.4_7	1.2365	169.4_1	50.76	8.59_9	38.15	6.46_3
1st day cell feed	204.3_9	1.2780	159.9_3	76.00	12.15_5	pH 3.00	—
2nd day cell feed	186.5_2	1.2879	144.8_2	79.89	11.57_0	pH 2.63	—
3rd day cell feed	177.3_1	1.2862	137.8_6	78.77	10.85_9	pH 2.80	—
4th day cell feed	182.1_2	1.2851	141.7_2	78.40	11.11_1	pH 2.71	—
Totals			862.5_3		61.49_3		6.46_3

* Numbers shown as subscript are not significant; precision of liquid weight measurements ca. 0.05 kg, repeatability of nickel analyses ca. 0.1 g/l.

TABLE 2

Nickel electrowinning, material balance: outputs from system*

Electrolyte	Weight (kg)	Density (kg/l)	Volume (l)	Ni (g/l)	Ni (kg)	H_2SO_4 (g/l)	H_2SO_4 (kg)
1st day cell effluent	207.9_3	1.2373	168.0_5	50.69	8.51_9	45.04	7.56_9
2nd day cell effluent	175.8_1	1.2388	141.9_3	51.09	7.25_1	47.69	6.76_8
3rd day cell effluent	166.0_6	1.2388	134.0_5	50.75	6.80_3	50.06	6.71_0
4th day cell effluent	199.7_6	1.2394	161.1_7	50.08	8.07_2	51.79	8.34_7
Final anolyte	154.0_0	1.2410	124.0_9	50.01	6.20_6	48.60	6.03_1
Final catholyte	88.6_3	1.2365	71.6_8	51.35	3.68_1	pH 2.54	—
Final holding tank contents			46.4	78.35	3.63_3	pH 2.88	—
Totals			847.3_7		44.16_6		35.42_6

* Numbers shown as subscripts are not significant; precision of liquid weight measurements ca. 0.05 kg, repeatability of nickel analyses ca. 0.1 g/l.

Part of this measured decrease in volume of cell liquids is ascribable to inability to effect quantitative withdrawal of anolyte and catholyte from the cell, and part may be due to changes in electrolyte levels. For prolonged electrowinning campaigns, these factors would exert diminished influence on overall solution inventory. However, there would still remain those contributions to a change in electrolyte volume such as evaporation, misting, etc., as enumerated in the previous paper [1].

Nickel recovery was nearly quantitative: 17.46 kg (deposited) + 44.17 kg (effluent)−61.49 kg (feed) = + 0.14 kg. The measured apparent gain in the quantity of nickel illustrates the point that the weight decrement (in this case, δw = −0.14 kg) includes errors in the determination of volumes and concentrations. It is, therefore, an operationally significant quantity. An average effective volume efficiency can now be calculated according to eqn. (2):

$$\text{V.E.} = \frac{100}{862.5 \, \text{l}} \left(847.4 \, \text{l} - \frac{-140 \, \text{g}}{50 \, \text{g/l (approx.)}} \right) = 98.6\%$$

It is interesting and significant that, for lack of prior knowledge of V.E., the electrowinning of this example was conducted on the basis of an apparent volume efficiency of 100%. In order finally to arrive at the target nickel concentration of 50 g/l in the cell effluent (Table 2) by daily adjustment of the cell current, assumed values of cathode current efficiency were assigned as follows (successive days): C.E. (assumed) = 97.5, 97.5, 94.5, 93%. By comparison, the actual overall current efficiency of nickel deposition was 96.1%. Clearly, without accounting for $V'' \neq V'$ and $\delta w \neq 0$, an exact correlation will not generally be obtained between C.E. and $-\Delta c$.

It may be of interest to consider briefly the efficiency of the simultaneous anodic generation of acid, since erroneous interpretations are sometimes given to a measured deviation of $-\Delta c(\text{acid})/\Delta c(\text{metal})$ from the stoichiometric value. In the example cited, the values of $[H_2SO_4/[Ni^{2+}]$ on successive days were (Tables 1 and 2): 1.780, 1.656, 1.787, 1.829, as compared with the stoichiometric ratio 1.670. These results suggest that, on average, the current efficiency of anodic acid generation was appreciably greater than the current efficiency of cathodic nickel deposition, i.e., greater than 96.1%.

In actual fact, anodic current efficiency was slightly less. Thus, total H_2SO_4 generation was 35.43−6.46 = 28.96 kg, yielding a real anodic current efficiency of 95.4%. As described in the previous paper [1], the same considerations relative to inclusion of volume changes and extraneous losses apply to the principal anodic reaction as to the principal cathodic reaction.

ELECTROREFINING (SOLUBLE ANODES)

The considerations presented in this section were developed largely in conjunction with a previously reported [5] experimental study of copper

electrorefining. The formulism is sufficiently general, however, that it doubtless has applicability to the electrorefining of impure metallic anodes rather broadly. The approach is to evaluate the resultant of the processes occurring at the anode and the cathode, the ratio of anode to cathode weight changes being a particularly significant characteristic.

Ratio of anode to cathode weight changes

It is assumed by reference to Fig.1 that the effect of cathode-anode shorting and stray current is to decrease the real electrorefining current, fI, where I is the total current, without affecting the ratio of anode weight loss to cathode weight gain. If the "chemical" corrosion rate of the cathodes is denoted as r_c (in compatible units), then,

$$\text{cathodic current efficiency (fractional), c.e.} = (fI-r_c)/I \qquad (3)$$

An appreciable magnitude for r_c is usually the result of dissolved oxidants in the electrolyte. However, depending upon whether c.e. is evaluated on the basis of weight gain only or weight plus assay, the concept for r_c may require modification to reflect the actual assay value.

The principal mechanisms of extraneous, i.e., superequivalent, weight loss of anodes are taken to be oxide dissolution, disintegration with the formation of finely divided elemental metal and insoluble compounds, and "chemical" corrosion. It is assumed that the sum of the first two effects is a simple function of the current and that the rate of weight loss due to chemical corrosion
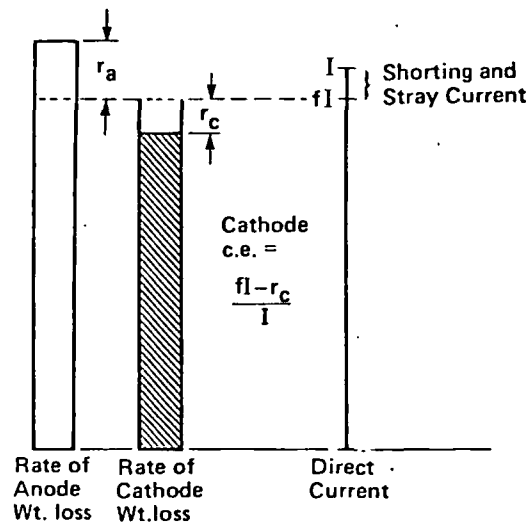

Fig.1. Graphic illustration of rates of cathode and anode weight losses in electrorefining.

of the anodes is proportional to the corresponding rate for the cathodes. The net rate of extraneous anode weight loss r_a is, then (see Fig. 2),
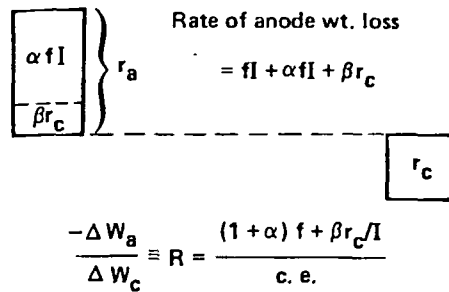
$$r_a = \alpha f I + \beta r_c \qquad (4)$$

Fig. 2., Detail of Fig. 1, illustrating the components of r_a, the rate of extraneous weight loss of electrorefining anodes.

If the anodic current efficiency is defined in the usual way, it may be written

$$\text{anodic ``current efficiency'' (fractional)} = \frac{fI + r_a}{I} \approx \frac{fI + \alpha f I + \beta r_c}{I} \qquad (5)$$

The ratio, R, of the total anode weight loss to total deposit weight is substantially the same as the ratio of current efficiencies given by eqns. (3) and (5), namely,

$$\frac{-\Delta W_a}{\Delta W_c} \equiv R \approx \frac{fI + r_a}{fI - r_c} = \frac{(1 + \alpha)f + \beta r_c / I}{\text{c.e.}} \qquad (6)$$

Consider, for example, the laboratory data plotted in Fig. 3. If f is taken to be unity (i.e., no shorting and negligible stray current) and if the current I is taken to be numerically equal to the current density (i.e., calculated on the basis of 1 ft^2 of cathode area) and if $\beta r_c = r_c$ (i.e., equal chemical corrosion rates of anodes and cathodes), Table 3 is then constructed based on $r_c = 2$ ASF and two assumed values of a.

The $\alpha = 0.01$ column of calculated values of R was used to plot the heavier curve of Fig. 3. Better agreement with the experimental data is thereby obtained than by use of $\alpha = 0.02$ (lighter curve). However, an equally good fit could presumably be obtained using other sets of reasonable, assumed values of α and β; furthermore, these quantities probably vary to some degree with current density. The purpose of this illustration is mainly to systematize consideration of electrode weight changes.
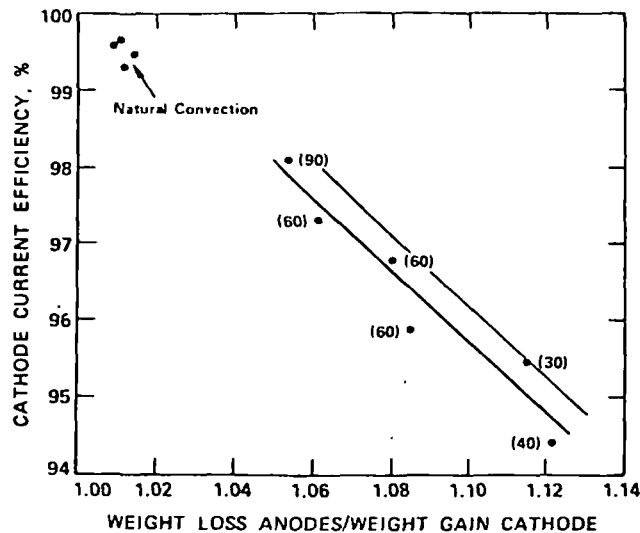
Fig.3. Anode and cathode efficiencies for air-agitation electrorefining in a small laboratory cell.

TABLE 3

Numerical example of material balance in copper electrorefining under air agitation

I (ASF)	C.E. (%)	R (kg/kg)	
		$\alpha = 0.02$	$\alpha = 0.01$
30	93.3	1.164	1.154
40	95.0	1.126	1.116
50	96.0	1.104	1.094
60	96.7	1.090	1.079
70	97.1	1.079	1.069
80	97.5	1.072	1.062
90	97.8	1.066	1.055

Assumptions: $f = \beta = 1$, $r_c = 2$ ASF.

As a hypothetical example of commercial copper electrorefining at 20 ASF, take $\alpha = 0.01$, as before, and $f = 0.90$ (i.e., 10% of the current shunted through shorts or stray paths), $r_c = 0.1$ ASF (i.e., 1/20th the cathode corrosion rate assumed above for air-agitation electrorefining), $\beta = 0.1$ (i.e., reduced chemical corrosion rate of anodes due to protective coating of anode slimes), then C.E. = 89.5% and $R = 1.016$, both being reasonable values [6].

Impurity build-up and electrolyte inventory

Whereas the rate of removal of major metal from solution by the cathodic reaction is equal to the rate of deposition, $fI - r_c$, the rate of addition of

major metal to the solution is, of course, less than the corrosion rate, $fI + r_a$, of the impure anodes. Specifically, if $y < 1$ is the "soluble" major metal assay of the anodes (Fig. 4), the net rate of addition of major metal to the solution, in units of weight per unit time, is

$$y(fI + r_a) - (fI - r_c) \approx -(1 - y)fI + (r_a + r_c) \qquad (7)$$

to first-order terms. The case of anode-derived impurities that precipitate out of the electrolyte has been treated recently [7]. The electrochemistry of conventional copper anodes is such that $y(1 + \alpha) \geqslant 1$, so that even for negligible chemical corrosion, there is a net addition of copper to the electrolyte.

A comparison of the rates of build-up of soluble impurities with that of the major metal is of particular interest. Let the assay of a specific "soluble" impurity (i.e., that portion thereof not reporting to the anode slimes or incorporated in the cathodes) in the anodes be z (Fig. 4). Then the rate of addition of that impurity to the electrolyte is $z(fI + r_a)$. It is recognized that individual anodes may be grossly nonuniform with respect to the distribution and, even, mineral form of the contained impurities. It is clear, therefore, that the assay value z is the average for the entire batch of anodes to be refined in the electrolyte being monitored.

Material balance gives the manner in which the ratios of matrix metal to impurities in the electrolyte change with time. Taking as example the electrorefining of copper anodes, with no bleed-off, the total amounts of copper and nickel in the electrolyte are·

$$V[\text{Cu}] = V_o[\text{Cu}]_o + [y(fI + r_a) - (fI - r_c)]t \qquad (8)$$

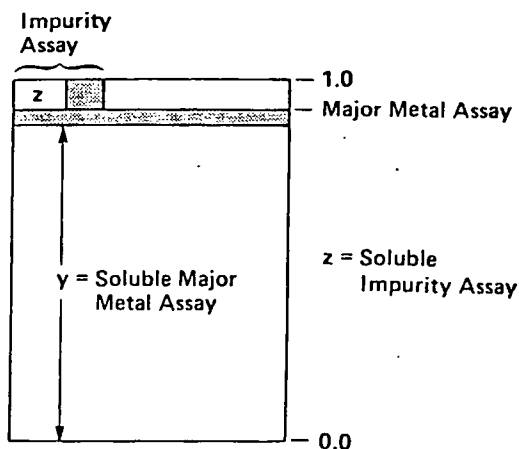$$V[\text{Ni}] = V_o[\text{Ni}]_o + z(fI + r_a)t \qquad (9)$$

Fig.4. Anode composition showing weight fractions of the major metal and one of several impurities.

where V_o, $[Cu]_o$ and $[Ni]_o$ are the volume and concentrations at some initial time, $t = 0$. The ratio $[Cu]/[Ni]$ will increase or decrease, respectively, depending upon whether

$$\frac{yR - 1}{zR} > \text{ or } < \frac{[Cu]_o}{[Ni]_o} \qquad (10)$$

That is, if no other factors are operating, the ratio of major metal concentration to soluble impurity concentration tends toward the value $(yR-1)/zR$.

In the previously-reported electrorefining pilot plant operation [5], $[Cu]_o/[Ni]_o$ was about 20 at the start, but the superequivalent solubilization of copper caused the ratio of copper to nickel to increase with time. By way of illustration, if the soluble copper and nickel assays were 98% ($y = 0.98$) and 0.1% ($z = 0.001$) and the ratio of anode weight loss to cathode weight gain were 1.06, $[Cu]/[Ni]$ would tend toward the limiting value 30.8. Electrolyte bleed-off would then not be regulated by nickel build-up but by copper build-up. On the other hand, if for the same anodes in normal practice, y and R were 0.985 and 1.02, the ratio of copper to nickel in the electrolyte would tend toward the much lower limit, 4.65, and nickel would become a major component of the electrolyte. Some measure of indirect control of electrolyte composition in electrorefining is inherent in these considerations.

ACKNOWLEDGEMENT

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