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# Separation of Nickel and Cobalt by Electrodialysis Using Ion-Exchange Membranes in the Presence of EDTA

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## Abstract

Electrodialytic separation of $Ni^{2+}$ and $Co^{2+}$ cations has been realized by using ion-exchange membranes in the presence of EDTA by preferentially complexing $Ni^{2+}$($Ni^{2+}$ concentration = EDTA concentration). The degree of complexation is calculated as a function of the pH and of the concentration by using data taken from the literature. Due to a systematic study of the influence of the different separation parameters (nature of the membranes, flow rate, electric current intensity, pH), the conditions of separation have been optimized on a computer, and then pure solutions of nickel and cobalt ions have been obtained experimentally. The decomplexation of $Ni^{2+}$ is accomplished in acidic medium by cooling.

Most nickel ores also contain cobalt (e.g., laterites from New Caledonia, Cuba, and New Guinea contain serpentine and garnet, and some sulfur ores contain segenite). Pure nickel can be prepared industrially by acid attack (*1*) followed by selective extraction. However, the use of ion exchangers (resins and membranes) should enable separations and preparative purifications to be made without using more tedious methods. At the present time hydrometallurgy is being widely developed; its aim is to extract the ions that can be found in residual water. The use of ion exchangers is a good application in this field because they simplify the experimental set-up. Selegny and Prigent (*2*) have separated some very close cations ($Li^+$ and $K^+$; $Rb^+$ and $Cs^+$) by electrodialysis with membranes and pseudomembranes (ion selective resins suspended in water between two permselective membranes). Ordinary cation exchangers (with sulfonic groups) are practically useless by themselves as far as the Ni(II)–Co(II) couple is concerned (*3*), but in certain cases the formation of complexes in solution can overcome this lack of selectivity. In this way nickel and cobalt can be separated analytically by forming anionic complexes through selective elution with concentrated hydrochloric acid.

Tremillon (*4*) has proposed a method of preparative separation by countercurrent flow elution with EDTA. Bril (*5*) has described a technique of separating the rare-earth metal ions by complexing some of them by electrodialysis in the presence of EDTA. Under the same conditions the separation of $Cs^+$ and $Sr^{2+}$ is discussed by Herschey (*6*). Fenyo et al. have calculated, experimented, and described a very efficient and currently used chromatographic separation of rare-earth metals by selective complexing during elution. They also took out patents on procedures of ion separation by electrodialysis (*7*, *8*).

We will present comparable results for the $Ni^{2+}$–$Co^{2+}$ mixture in the presence of EDTA. These results include the elaboration and evaluation of a possible process starting from laboratory experimental data.

## PRINCIPLE OF THE METHOD

Starting with a mixture of known composition of $Ni^{2+}$ and $Co^{2+}$, complexation between nickel and EDTA [$(NiY)^{2-}$] modifies the ionic charge of the former. The mixture is sent through an electrodialysis cell in which the nickel complex and the cobalt are subject to an electric field, and the nickel complex is recovered on the anode side whereas the cobalt migrates toward the cathode. To elaborate a practically applicable process, one must: (a) design the electrodialyzer, (b) fix the exact composition of the influent solution, and (c) investigate the influence of the different separation parameters (entering flow, intensity, transport numbers).

## COMPLEXATION BY EDTA

The efficiency of the process requires the complexing to be selective. The two complexing reactions are

$$Ni^{2+} + Y^{4-} \rightleftarrows NiY^{2-} \qquad K_{Ni} = 10^{-18.6} \qquad (1)$$

$$Co^{2+} + Y^{4-} \rightleftarrows CoY^{2-} \qquad K_{Co} = 10^{-16.2} \qquad (2)$$

The value of the pH determines the $Y^{4-}/Y$ total ratio and hence the degree of complexing. It is the nickel complex that is the more stable and, whatever the conditions, one can write

$$Ni^{2+} + CoY^{2-} \rightleftarrows NiY^{2-} + Co^{2+} \tag{3}$$

with

$$K_f = \frac{(NiY^{2-})(Co^{2+})}{(Ni^{2+})(CoY^{2-})} = 10^{2.4}$$

Thus, in a mixture containing EDTA, nickel, and cobalt, it is always the $NiY^{2-}$ complex that will be preferentially formed. If, then, a solution is chosen such that the EDTA concentration is the same as or lower than that of the $Ni^{2+}$ ions and a pH is used where that $Y^{4-}$ is sufficiently concentrated, then practically only the nickel ions will be complexed in the $NiY^{2-}$ form and the cobalt ions will remain in the $Co^{2+}$ form. Subject then to an electric field, $NiY^{2-}$ and $Co^{2+}$ will migrate in opposite directions.

Let us define the percentages of complexation by

$$T_1 = 100\frac{(NiY^{2-})}{C_{Ni}}$$

$$T_2 = 100\frac{(CoY^{2-})}{C_{Co}}$$

and

$$T = 100\frac{(NiY^{2-})}{(NiY^{2-}) + (CoY^{2-})}$$

in which $C_{Ni}$ and $C_{Co}$ represent the total quantities of nickel and cobalt.

We have solved numerically (on an IBM 360–20), without any approximations, the equations describing the complexation system in which the variables are total EDTA concentration $C_E$, total concentrations of each of the metallic cations $C_{Ni}$ and $C_{Co}$, and the pH. This calculation is given in the Appendix. By writing the equations of conservation of species and of conservation of EDTA, the calculation results in a parametric equation of the third degree. The values of $T_1$ and $T_2$ for $C_{Ni} = C_{Co} = C_E = 0.05\ M$ are represented in Fig. 1 as functions of the pH. A series of results was obtained for nickel concentrations varying from $10^{-2}$ to $5 \times 10^{-2}\ M$ and for cobalt from $5 \times 10^{-3}$ to $5 \times 10^{-1}\ M$. It is noted that in very acidic medium (pH 0.8) cobalt is not complexed at all (0.4%) and nickel insufficiently (44%). At pH 2, however, when the degree of

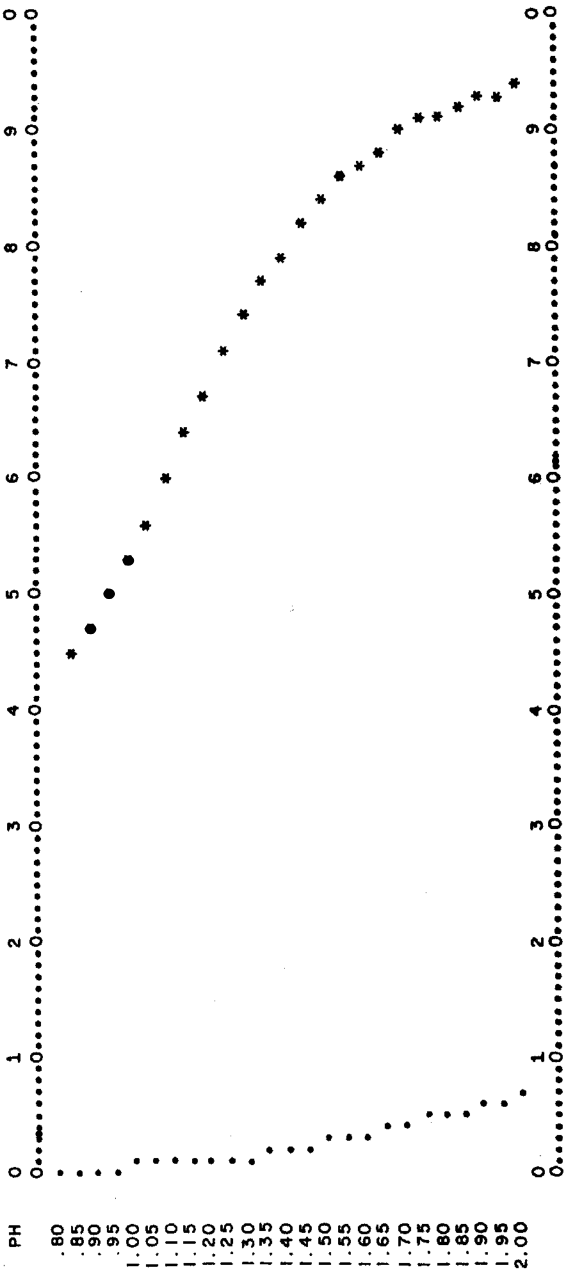

FIG. 1. Complexation ratio of $Ni^{2+}$ ($T_1$: *) and $Co^{2+}$ ($T_2$: ·) by EDTA vs pH. $C_{Ni} = C_{Co} = C_{EDTA} = 10^{-2}M$.

complexation of nickel is very high ($T_1 = 93.5\%$), that of cobalt is no longer negligible (6.5%). We thus came to a compromise and fixed the pH of the solution at 1.5. Under these conditions $T_1 = 83.7\%$ and $T_2 = 2.5\%$.

### Diagrammatic Design of the Electrodialyzer (Fig. 2)

The above mixture circulates in the central compartment of an electrodialyzer; the cell is limited on the one side by a cation exchange membrane and on the other by an anion exchange one. The cations ($Co^{2+}$, uncomplexed $Ni^{2+}$, and $H^+$) attain Compartment III while the anions $NiY^{2-}$, $CoY^{2-}$, and $NO_3^-$) are found in Compartment I: this diagrammatic representation is intentionally simplified for theoretical study. In practice, we had to add two safety compartments near the electrodes.

## THE SEPARATION PARAMETERS

These parameters are the nature of the membranes and the concentration and pH of the influent solution as well as its rate of flow and the current density.

*Membranes.* The ordinary characteristics (degree of swelling, capacity, transport numbers, conductibility, mechanical strength) were determined for two types of cation exchange membranes, Zerolit C 20 and Asahi

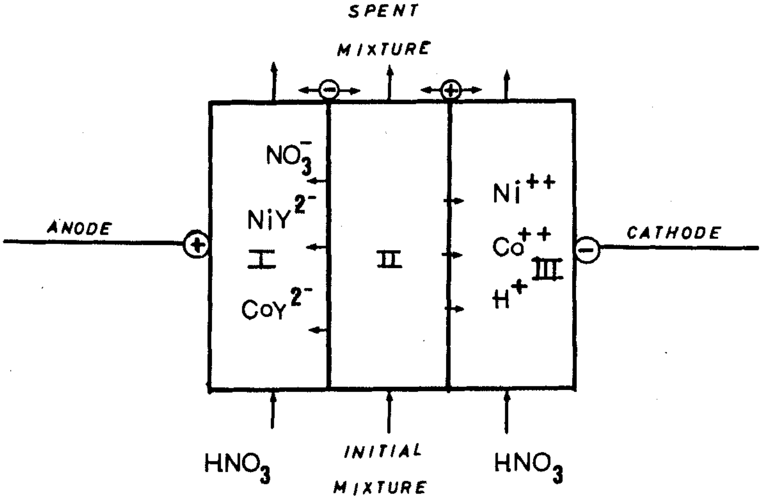

FIG. 2. Diagrammatic design of the electrodializer.

Selemion CMV 10. We chose the latter because of its low degree of swelling due to a high degree of cross-linking which assures good mechanical strength, because its electrical resistance is low, and also because the high capacity and the cation transport number ($\bar{t}_{Na^+} = 0.96$) show its good permselectivity. We used also a Zerolit C 20 anion exchange membrane.

*Rate of Flow.* For simplicity's sake, we fixed the following conditions for the influent solution in II: $C_{Ni} = C_{Co} = C_{EDTA} = 3 \times 10^{-2}$ *M*, pH = 1.5, *I* = 400 mA; $10^{-2}$ *N* $HNO_3$ circulates in Compartments I and III.

We will now describe the phenomena that occur between Compartments II and III. Circulation is maintained by a multichannel peristaltic pump. In this way the flow rate is the same in all the cells and the out-going concentrations can be compared directly with each other. The cation exchange membrane had been previously conditioned by $Co^{2+}$. It was established that the quasi-stationary state is attained under these conditions after 30 min. We doubled this time before taking the samples. The results are given in Table 1 and in Figs. 3 and 4.

TABLE 1

Influence of Flow Rate[a]

| | | | Cobalt | | | |
|---|---|---|---|---|---|---|
| Flow Rate, cm³/hr | 59 | 89 | 120 | 154 | 167 | 180 |
| Output of II, *M* | $1.76 \times 10^{-2}$ | $2.16 \times 10^{-2}$ | $2.08 \times 10^{-2}$ | $2.54 \times 10^{-2}$ | $2.54 \times 10^{-2}$ | $2.50 \times 10^{-2}$ |
| Output of III, *M* | $1.08 \times 10^{-2}$ | $0.94 \times 10^{-2}$ | $0.73 \times 10^{-2}$ | $0.59 \times 10^{-2}$ | $0.62 \times 10^{-2}$ | $0.65 \times 10^{-2}$ |
| % in III (+) | 36.1 | 31.4 | 24.9 | 18.7 | 20.4 | 20.5 |
| $t_{Co}$ | 0.086 | 0.112 | 0.118 | 0.120 | 0.139 | 0.157 |
| $R = \frac{(Co)}{(Ni)}$ in III | 2.73 | 4.09 | 5.98 | 6.21 | 6.77 | 7.52 |
| | | | Nickel | | | |
| Output of II, *M* | $2.78 \times 10^{-2}$ | $2.88 \times 10^{-2}$ | $2.95 \times 10^{-2}$ | $3.01 \times 10^{-2}$ | $3.03 \times 10^{-2}$ | $3.06 \times 10^{-2}$ |
| Output of III, *M* | $4.25 \times 10^{-3}$ | $2.20 \times 10^{-3}$ | $1.25 \times 10^{-3}$ | $0.94 \times 10^{-3}$ | $0.90 \times 10^{-3}$ | $0.85 \times 10^{-3}$ |
| % in III (+) | 12.9 | 7.3 | 4.0 | 3.0 | 2.9 | 2.7 |
| $t_{Ni}$ | 0.034 | 0.026 | 0.020 | 0.0197 | 0.021 | 0.021 |
| $t_{(Ni+Co)}$ | 0.12 | 0.14 | 0.139 | 0.139 | 0.160 | 0.178 |

[a] $C_{Ni} = C_{Co} = C_{EDTA} = 3 \times 10^{-2}$ *M*. *I* = 400 mA. pH = 1.5. (+): percentage of the input solution in II.

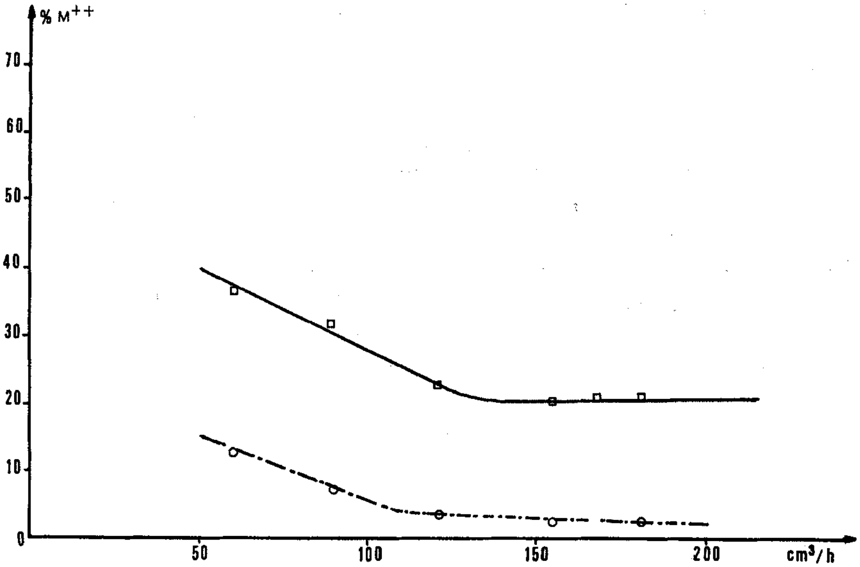

FIG. 3. Percentage of Co (□) and Ni (○) collected in Compartment III vs flow rate. Composition of the input in Compartment II: $C_{Ni} = C_{Co} = C_{EDTA} = 3 \times 10^{-2}$ *M*. pH = 1.5, *I* = 400 mA.

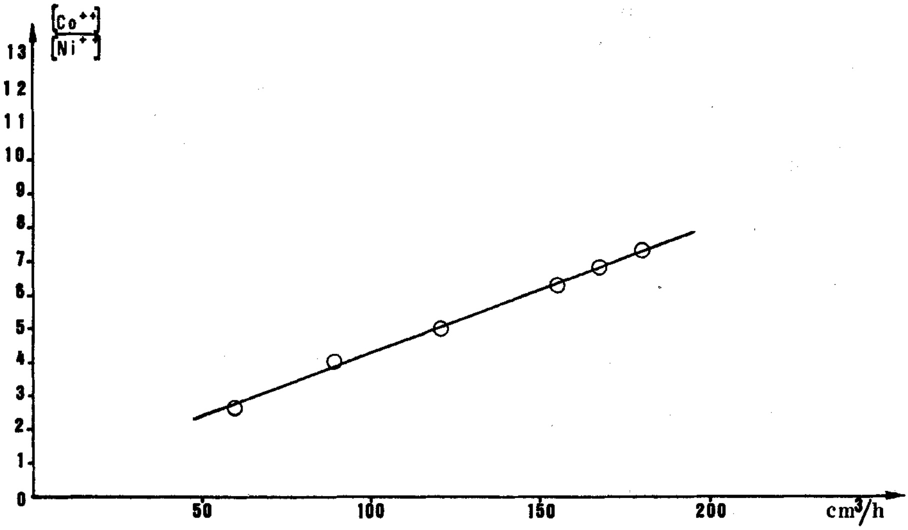

FIG. 4. Ratio Co/Ni in Compartment III vs flow rate. Same initial conditions as in Fig. 3.

At a rate of 150 cm$^3$/hr, saturation conditions are already attained, i.e., the Co concentration in Compartment III becomes constant. Also, the higher the flow rate, the less the amount of ions arriving in III. But since the Co/Ni ratio becomes more favorable, we adopted a rate of 200 cm$^3$/hr for the following investigations.

*Current Intensity.* In Fig. 5 the transport numbers of Co and Ni are represented as functions of the current intensity for different initial concentrations. Between 200 and 500 mA the transport numbers depend only on the concentrations. There is a critical limiting current, however, around 500 mA (*9*). As was expected, the nickel concentration in III is lower than that of the cobalt because of preferential complexation by EDTA.

In the following investigations, $I = 400$ mA was retained.

*Initial Solution Concentration.* It can be noted from Fig. 6 that the amount of ions in III increases with the concentration of influent solution in II. Thus, for identical rates and intensities, the yield of the separation

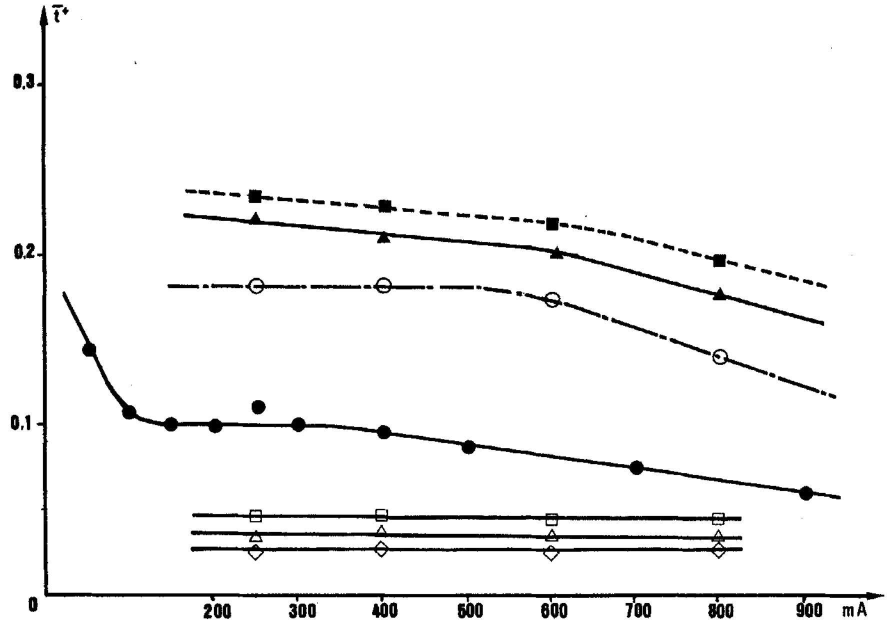

FIG. 5. Transport number across the (+) membrane (between Compartments II and III). Co at the input of Compartment II: (■) 5 × $10^{-2}$ *M*; (▲) 4 × $10^{-2}$ *M*; (○) 3 × $10^{-2}$ *M*; (●) 1 × $10^{-2}$ *M*. Ni at the input of Compartment II: (□) 5 × $10^{-2}$ *M*; (△) 4 × $10^{-2}$ *M*; (◇) 3 × $10^{-2}$ *M*.

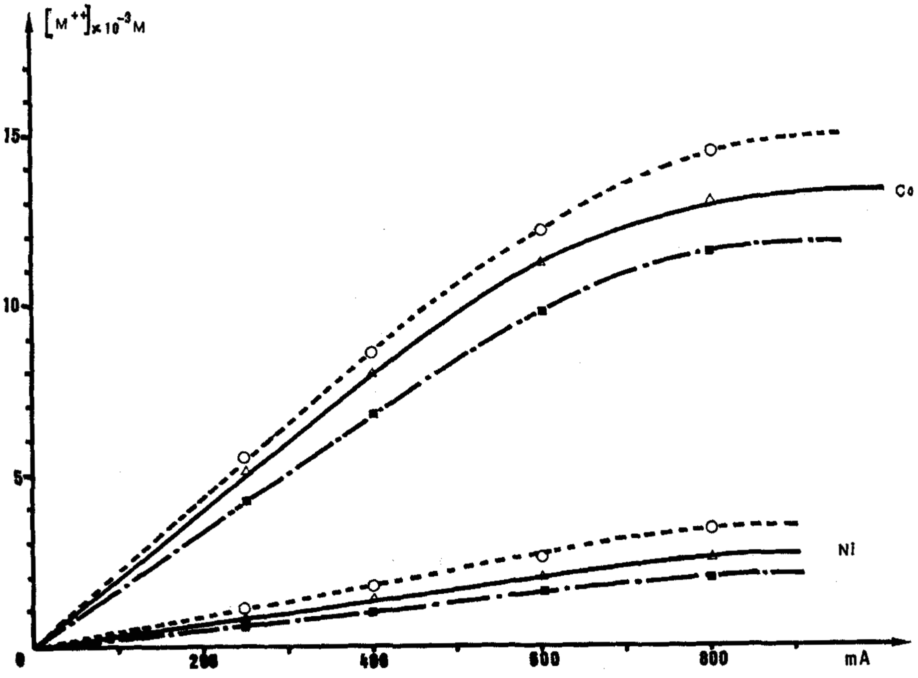

FIG. 6. Concentration in $M^{2+}$ at the output of Compartment III vs intensity. $M^{2+}$ at the input of Compartment II: (○) $5 \times 10^{-2}$ *M*; (△) $4 \times 10^{-2}$ *M*; (■) $3 \times 10^{-2}$ *M*.

is favored by high concentrations. It is limited, however, by the solubility of the $NiY^{2-}$ complex (about 0.05 *M* at room temperature).

*Influence of pH.* We have been unable to note any significant influence of pH even when it was varied from 1.5 to 5.4 by adding ammoniac to the influent solution. It is difficult to discuss this quantitatively, since the $NH_4^+$ ions can complex the $M^{2+}$ ones and form mixed M-EDTA-$NH_4$ complexes. It can be concluded, however, that the amount of electricity carried by the $H^+$ ions alone remains almost the same as that carried by $NH_4^+$–$H^+$ mixtures for different pH values. To vary the pH, alien cations which do not improve the separation should be introduced.

## BALANCE OF THE FIRST STAGE OF SEPARATION

Here follow results which were obtained after optimizing the different parameters (Table 2): influent rate, 200 cm³/hr; intensity, 400 mA;

TABLE 2

Evaluation of a First Stage of Separation[a]

| | | Cell | | | | |
|---|---|---|---|---|---|---|
| | | I | | II | III | |
| $Ni^{2+}$ | Input | 0 | | 0.009 | 0 | |
| | Output | 0 | | $0.007_2$ | $0.001_7$ | (3.6%) |
| $NiY^{2-}$ | Input | 0 | | 0.041 | 0 | |
| | Output | $0.002_8$ | (5.6%) | 0.038 | 0 | |
| $Co^{2+}$ | Input | 0 | | $0.048_9$ | 0 | |
| | Output | 0 | | $0.042_5$ | $0.008_5$ | (17%) |
| $CoY^{2-}$ | Input | 0 | | $0.001_1$ | 0 | |
| | Output | $10^{-5}$ | | $0.0010_8$ | 0 | |
| Ratio Co/Ni | Input | — | | 1 | — | |
| | Output | $< 10^{-2}$ | | 0.96 | 5 | |

[a] Input flow rate: 200 cm³/hr. $I = 400$ mA. Input concentrations in II: $C_{Ni} = C_{Co} = C_{EDTA} = 5 \times 10^{-2}$ *M* pH = 1.5. ($HNO_3$) in I and III: $10^{-2}$ *M*. All concentrations are expressed in molarities

concentrations $C_{Ni} = C_{Co} = C_{EDTA} = 5 \times 10^{-2}$ *M*; pH, 1.5; $HNO_3$ concentrations in the receptor compartments, $10^{-2}$ *M*.

Thus 9% of the nickel ions have migrated either into Compartment I (5.6%) or Compartment III (3.6%). Thus the nickel enrichment factor in the effluent of II is 1.04. The cobalt concentration in I is negligible (purity in nickel is higher than 99.7%). The effluent solution from III contains 3.6% nickel and the influent solution contains 17% cobalt (ratio Co/Ni = 5).

The conclusions that can be drawn after this first stage are: (a) About 5% of $NiY^{2-}$ are found on the out-going side of I; these ions contain only traces of cobalt and no longer need purification before decomplexation. (b) The effluent composition of II is close to its influent one. Recycling is possible. (c) A mixture rich in cobalt is found on the out-going side of III ($R = 5$).

From these results a second stage of separation can be envisaged which involves treating the effluent solutions from II and III. The details of this procedure are given in Fig. 7.

The solution from Compartment III is recycled after addition of Ni, Co, and EDTA to bring it back to its initial composition and concentration.

The effluent of Compartment IV could be concentrated and EDTA added until its molarity equals that of nickel and this solution treated

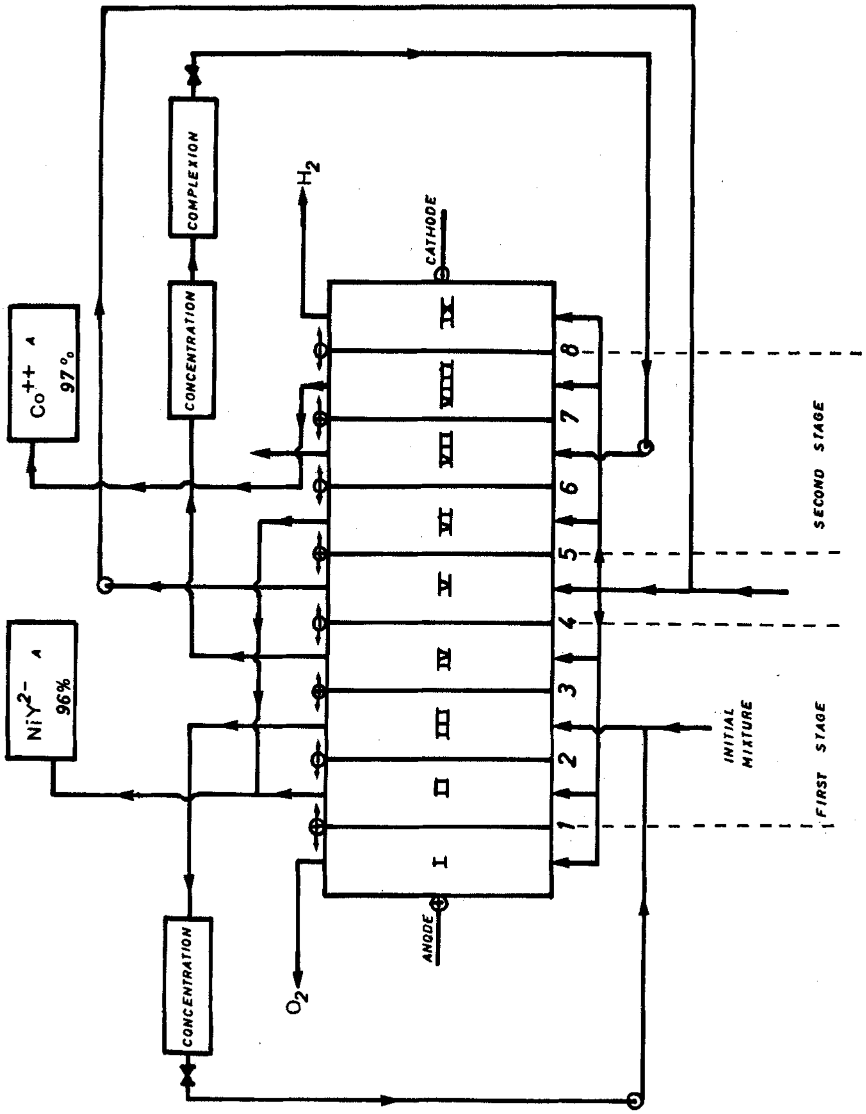

FIG. 7. Design of a two-stages electrodializer for the separation of $Ni^{2+}$–$Co^{2+}$ cations.

again in a second step of the electrodialysis. $NiY^{2-}$, collected in Compartment VI, would be mixed with the effluent of Compartment II. The outflowing composition in Compartment VIII is now enriched in $Co^{2+}$ by another factor of 5 and its purity attains 96%, sufficient for most uses.

## DECOMPLEXATION OF $NiY^{2-}$

We tried to obtain both the metallic cation and the EDTA in their free state. Addition of a very concentrated base gives only low precipitation of the hydroxide.

We then attempted the decomplexation in an acidic medium, but at room temperature the conditions are unfavorable. This led us to compare the effects obtained by addition of different acids to 100 cm³ of 0.05 *M* $NiY^{2-}$ at −30°C.

HCl and $H_2SO_4$ are inefficient. In the presence of $HNO_3$, however, $H_4Y$ precipitates and the solution becomes green in color ($Ni^{2+}$ ions). We therefore made a more quantitative study of the decomplexation as a function of the volume of added $HNO_3$. The results given in Table 3 are those obtained after 10 days. It is noted that the reaction becomes stationary for 30 cm³ of commercial acid and 100 cm³ of solution ($HNO_3$, 3.2 *M*).

TABLE 3

Decomplexation of $NiY^{2-}$ by Adding Concentrated $HNO_3$ at 100 cm³ to a Solution of $NiY^{2-}$ after 10 days (−30°C)

| Added $HNO_3$ | $HNO_3$ (*N*) | % of free nickel | % of EDTA removed (filtration) | Remaining % of complexated nickel |
|---|---|---|---|---|
| 10 cm³ | 1.2 | 67.1 | 64.5 | 32.8 |
| | 1.2 | 72.6 | 66.6 | 27.3 |
| 20 cm³ | 2.3 | 78.1 | 72.2 | 21.8 |
| | 2.3 | 81.1 | 79.1 | 18.8 |
| 30 cm³ | 3.2 | 86.1 | 83.5 | 13.9 |
| | 3.2 | 82.6 | 81.1 | 17.4 |
| 40 cm³ | 4.04 | 86.6 | 80.6 | 13.4 |
| | 4.04 | 83.0 | 81.3 | 17.0 |
| 50 cm³ | 4.6 | 81.1 | 80.7 | 18.8 |
| | 4.6 | 84.6 | 83.1 | 15.3 |
| 100 cm³ | 7 | 82.5 | 81.2 | 17.5 |
| | 7 | 84.5 | 83.0 | 15.5 |

Fifteen to 18% of $NiY^{2-}$ remains in solution. After a second filtration under the same conditions, another 8% of $H_4Y$ was obtained.

Kinetic studies spaced over a month with 30 $cm^3$ of $HNO_3$ added showed us that after a day and a half the amount of decomplexed nickel is constant and equals 83% of the original.

## CONCLUSIONS

Cobalt and nickel can be separated following the process described above. However, the electric yield is low and much of the current is transported by other ions ($NO_3^-$ and $H^+$). It seems difficult to improve the first stage of separation because this method is limited by the very low transport number of $NiY^{2-}$. The use of a less charged and sterically less hindered complexing agent could give better results.

A full process could use a battery of cells similar to the first one.

### Experimental

*Determination of the Membrane Characteristics.* We have applied the usual methods cited in the literature e.g., by Hellferich (*10*), Prigent (*2*), and DGRST contract report no. 69.0.050 (*11*).

*Concentrations of Nickel and Cobalt.* These titrations were spectrophotometric ones using a Hilger and Watts Atomspek spectrophotometer.

*Apparatus.* The electrodialyzer was made of altuglass cells (inside volume, 18.8 $cm^3$; efficient area, 12.6 $cm^2$) mounted on an aluminum stand. A Bühler multichannel pump giving identical flow rates in each cell was used for the circulation of the fluids. The two platinum disk electrodes were supplied by a Tacussel amperostat.

*Chemicals.* All chemicals, $Ni(NO_3)_2$, $CO(NO_3)_2$, and EDTA (in acid form), were RP Prolabo.

## APPENDIX

Here are the calculations of complexation by which $T_1$, $T_2$, and $T$ are obtained. We impose $C_{EDTA} = C_{Ni}$. In fact, since Ni(II) is complexed preferentially to Co(II), an excess of EDTA would also lead to the complexation of the latter, but this is not what we are looking for. This calculation aims at determining the values of the variables $|NiY^{2-}|$, $|Ni^{2+}|$, $|Y^{4-}|$, $|CoY^{2-}|$, $|Co^{2+}|$ as functions of nickel, cobalt, and EDTA (here $C_{Ni} = C_{EDTA}$) and of the pH.

## General Calculation

The dissociation equilibria of EDTA are

$$\mathrm{YH_4} \rightleftarrows \mathrm{YH_3}^- + \mathrm{H}^+ \qquad (4) \qquad K_1 = \frac{|\mathrm{YH_3}^-||\mathrm{H}^+|}{|\mathrm{YH_4}|} = 10^{-2}$$

$$\mathrm{YH_3}^- \rightleftarrows \mathrm{YH_2}^{2-} + \mathrm{H}^+ \qquad (5) \qquad K_2 = \frac{|\mathrm{YH_2}^{2-}||\mathrm{H}^+|}{|\mathrm{YH_3}^-|} = 10^{-2.7}$$

$$\mathrm{YH_2}^{2-} \rightleftarrows \mathrm{YH}^{3-} + \mathrm{H}^+ \qquad (6) \qquad K_3 = \frac{|\mathrm{YH}^{3-}||\mathrm{H}^+|}{|\mathrm{YH_2}^{2-}|} = 10^{-6.3}$$

$$\mathrm{YH}^{3-} \rightleftarrows \mathrm{Y}^{4-} + \mathrm{H}^+ \qquad (7) \qquad K_4 = \frac{|\mathrm{Y}^{4-}||\mathrm{H}^+|}{|\mathrm{YH}^{3-}|} = 10^{-10.2}$$

Let

$C_{\mathrm{EDTA}} = C_{\mathrm{E}}$ = total EDTA concentration (complexed and uncomplexed form)

$C\mathrm{M}_1$ = total nickel concentration

$C_{\mathrm{E}} = \mathrm{CM}_1$

$C\mathrm{M}_2$ = total cobalt concentration

$|\mathrm{M_1}^{2+}|$ = concentration in uncomplexed nickel

$|\mathrm{M_1Y}^{2-}|$ = concentration in complexed nickel = $x$

$|\mathrm{M_2}^{2+}|$ = concentration in uncomplexed cobalt

$|\mathrm{M_2Y}^{2-}|$ = concentration in complexed cobalt = $y$

$A = A_0 + |\mathrm{H}^+|K_1K_2K_3 + |\mathrm{H}^+|^2K_1K_2 + |\mathrm{H}^+|^3K_1 + |\mathrm{H}^+|^4$

$A_0 = K_1K_2K_3K_4 = 10^{-21.2}$

The equation of the conservation of EDTA is

$$C_{\mathrm{E}} = |\mathrm{Y}^{4-}| + |\mathrm{YH}^{3-}| + |\mathrm{YH_2}^{2-}| + |\mathrm{YH_3}^-| + |\mathrm{YH_4}| + |\mathrm{M_1Y}^{2-}| + |\mathrm{M_2Y}^{2-}|$$

By taking into account Equilibria (4)–(7), as well as those of the complexes of nickel and cobalt with EDTA, the values of $x$ (concentration in complexed nickel) and $y$ (concentration in complexed cobalt) can be obtained from the previous equation.

The equilibrium constants of nickel and cobalt complexation with EDTA are, respectively,

$$Z\mathrm{M}_1 = \frac{|\mathrm{M_1}^{2+}||\mathrm{Y}^{4-}|}{|\mathrm{M_1Y}^{2-}|} \qquad Z\mathrm{M}_2 = \frac{|\mathrm{M_2}^{2+}||\mathrm{Y}^{4-}|}{|\mathrm{M_2Y}^{2-}|}$$

In this way the value of

$$y = C_E - x - \frac{ZM_1x}{(CM_1 - x)}\frac{A}{A_0}$$

is obtained.

The value of $x$ can be calculated from

$$Z = \frac{C_E - x - \dfrac{ZM_1xA}{(CM_1 - x)A_0}}{x} \; \frac{(CM_1 - x)}{CM_2 - C_E + x + \dfrac{ZM_1x}{(CM_1 - x)}\dfrac{A}{A_0}}$$

Resolution of this relation leads to the equation of the third degree in the coefficients:

$B_0x^3$, where $B_0 = A_0(1 - Z)$

$B_1x^2$, where $B_1 = Z|A_0(2C_E - CM_2)| + ZM_1A - A_0(3C_E + AZM_1)$

$B_2x$, where $B_2 = ZA_0C_E(CM_2 - C_E) + 3A_0C_E{}^2 + AC_EZM_1$

and the constant term

$$B_3 = -A_0C_E{}^3$$

We have solved this equation by Cardans's formula. The calculations of $R$ on a computer (IBM 360–20) were made for $C_E$ and $CM_2$ concentrations from 0.0005 to 0.05 *M* and for values of the pH between 0 and 5. We restricted the pH zone after the preliminary calculations because these showed that above pH 6 hydroxy complexes can be formed. ($R$ was positive in all cases; thus the existence of one real root is in agreement with the physical meaning.)

## Remarks

The coefficients of the third-order equation are simplified in respect to those of the general equation because of the imposed condition $C_E = CM_1$.

The program, relations, and calculations are general for couples of bivalent cations complexed by EDTA. Only the constants need to be changed.

The values of the dissociation constants of EDTA vary slightly according to different authors; we chose those given by Charlot (*13*).

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