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# Electroseparation of cobalt and nickel from a simulated wastewater

R. D. ARMSTRONG*, M. TODD*, J. W. ATKINSON‡, K. SCOTT‡

*Departments of Chemistry* and Chemical and Process Engineering‡, Newcastle University, Newcastle upon Tyne NE1 7RU, Great Britain*

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A study of the electrodeposition at sheet electrodes was carried out under potentiostatic control for solutions containing either 0.1 M Co(II) or 0.1 M Ni(II) and a 1:1 mixture of both 0.1 M Co(II) and 0.1 M Ni(II). From the linear sweep voltammetry of solutions containing only either Co(II) or Ni(II), a potential region in which cobalt would be expected to be electrodeposited without the simultaneous electrodeposition of nickel was identified and a theoretical deposit composition against potential plot was constructed. Deposition from a 1:1 Ni(II): Co(II) mixture at the optimum potential for separation produced a 90% cobalt /10% Ni alloy. Long term, potentio-selective extraction from a 1:1 Ni(II): Co(II) mixture showed that when the stainless steel cathode was predeposited with pure cobalt, the cobalt level in the solution could be reduced to less than 5% of its original value whilst leaving the Ni(II) at 85% of its original value.

## 1. Introduction

Electrodeposition has been widely used for the removal of metal cations from industrial wastes where there is only one metal cation present [1, 2] and a number of studies using wastes containing two or more metal cations have recently been reviewed [3, 4]. Some of the reports found that the selective separation of the metals will depend on the relative deposition potentials and if the deposition potentials are quite different then it may be possible to separate the metals. Such a separation can be seen in an earlier paper from this laboratory [5] where it was shown that cadmium, of purity greater than 95%, can be electrodeposited from a mixed solution of Ni(II) and Cd(II) even when the cadmium concentration is very much lower than the nickel concentration, and that the optimum separation conditions can be predicted from a simple diagram. The level to which Cd(II) can be reduced in the solution without depositing Ni can also be predicted from the diagram. The scheme described [5] is appropriate for a mixture of a reversible metal (e.g. Cd) and an irreversible metal (e.g. Ni) but cannot be used for a mixture of irreversible metals (e.g. Ni(II) and Co(II)). Nickel and cobalt exhibit very similar electrochemical behaviour; it is, therefore, one of the most difficult metal separations to achieve by electrodeposition. Ni(II)/Co(II) separation using electrochemical methods described in the literature include the use of chemicals such as sodium hydroxide and ammonia [6]. Morris [7] has described such a method using mercury-coated rotating discs. Although good separations are obtained, use of these methods may cause further environmental damage.

In this paper we report on electrodeposition from solutions containing only 0.1 M Ni(II) or 0.1 M Co(II), using a number of different substrate materials and configurations. The data from the single cation deposition experiments are used to predict the extent of separation possible from solutions containing both 0.1 M Ni(II) and 0.1 M Co(II) and these predictions are compared with experiment. The method used for the Ni/Co separation is a more environmentally exceptable alternative since no additions are made to the solution.

## 2. Experimental details

Linear potential sweeps were measured using a computer-controlled potentiostat consisting of a 386SX computer connected to an EG&G Versastat system through an IEEE-488 GPIB card. Linear sweep voltammograms (LSV) were carried out on the solutions at a sweep rate of 10.0 mV $s^{-1}$. Both the computer-controlled system and an analogue system (based on an analogue potentiostat, a coulometer and chart recorder) were used to obtain electrodeposition from the nickel–cobalt solutions. A three-electrode cell was used which had the counter electrode separated by a Nafion® 117 cationic membrane. The working electrode compartment was surrounded by a thermostatically controlled water jacket and the mixtures were stirred with a stream of nitrogen gas. The working electrode comprised: 4.0 $cm^2$ 318 stainless steel sheet or 4.0 $cm^2$ 99.9% nickel sheet. The electrodes are cleaned with acetone and distilled water then dilute nitric acid with further washing with deionized water but no other surface preparation was carried out. After each LSV was obtained for the single cation solution, the freshly plated electrode was carefully washed and then a LSV was carried out in the base electrolyte. The LSV using the base electro-

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lyte was subtracted from the LSV using the single cation solution, to eliminate other reactions such as the hydrogen evolution reaction, thereby producing a LSV which was only for metal deposition. This procedure was applied to all the LSVs in this paper.

The solutions used contained 1 M of $Na_2SO_4$ as a base electrolyte, 0.1 M $NiSO_4$ or 0.1 M $CoSO_4$ or, 0.1 M $NiSO_4$ and 0.1M $CoSO_4$ (1:1 Ni:Co). In what follows the term single cation solutions refers to solutions containing either Co(II) and no Ni(II) or Ni(II) and no Co(II). For all of the experiments, boric acid, at a concentration of 0.25 M, was used to maintain the pH constant in the vicinity of the electrode.

The predeposited cobalt electrodes were prepared in 0.1 M $CoSO_4$ + 1 M $Na_2SO_4$ + 0.25 M $B(OH)_3$ at a potential of –1.00 V until about 20 C had passed.

The solution was analysed by either polarography or ICP (inductively coupled plasma absorption spectroscopy). The composition of the deposit was obtained by either dissolving the deposit in nitric acid then carrying out polarography or ICP on the resulting solution or by EDAX measurements.

All glass equipment was cleaned with water followed by concentrated nitric acid then thoroughly rinsed with deionized water. All the solutions were deaerated with white spot water-saturated nitrogen for at least 5 min and then agitated using the same gas. Measurements were carried out at 25 °C unless otherwise indicated and all potential measurements listed are as recorded against the SCE.

## 3. Results and discussion

### 3.1. *Linear sweep voltammograms of single cation containing solutions*

Current–potential measurements were obtained by linear potential sweep using single cation solutions and 4 cm$^2$ stainless steel sheet electrodes. A limiting current was observed for Co(II) but a limiting current could not be observed for Ni(II). To see a limiting current for Ni(II), the base electrolyte LSV, using the freshly deposited nickel electrode, had to be subtracted from the Ni(II) LSV (Fig. 1) using the procedures reported in Section 2. Sherwood *et al.* [8] and Ettel [9] also reported that no limiting current could be observed for the discharge of nickel which is possibly due to the hydrogen evolution reaction masking the Ni(II) deposition wave. The limiting currents values ($i_d$) were approximately proportional to the cation concentrations and increased with the gas bubbling rate. For the cobalt predeposited substrate, the limiting current value for cobalt ($i_{dCo}$) is similar to that for nickel ($i_{dNi}$).

For deposition on a virgin stainless steel substrate, there is no difference between the deposition potential of cobalt and nickel (Fig. 2). When the electrode in the Co(II)-only solution is subjected to a potential sweep again, the Co(II) deposits at a more positive potential (Fig. 3). There is a small difference between the nickel deposition potential onto stainless steel or freshly deposited cobalt. Thus, the predeposition of cobalt onto the steel sheet increases the separation window for nickel and cobalt to almost 200 mV which suggests that cobalt could be completely separated from nickel using a cobalt predeposited electrode. A similar pattern is observed for a nickel substrate (Fig. 4).

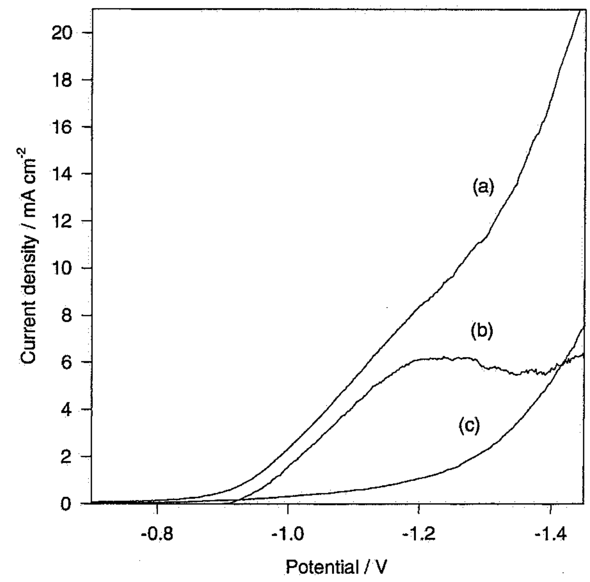

Fig. 1. 0.1 M $NiSO_4$ sweeps on stainless steel sheet.(a) Ni(II), (b) subtraction and (c) Ni-deposited stainless steel sheet in base electrolyte. Sweep rate: 10 mV s$^{-1}$. Base electrolyte: 1 M $Na_2SO_4$ and 0.25 M $B(OH)_3$.

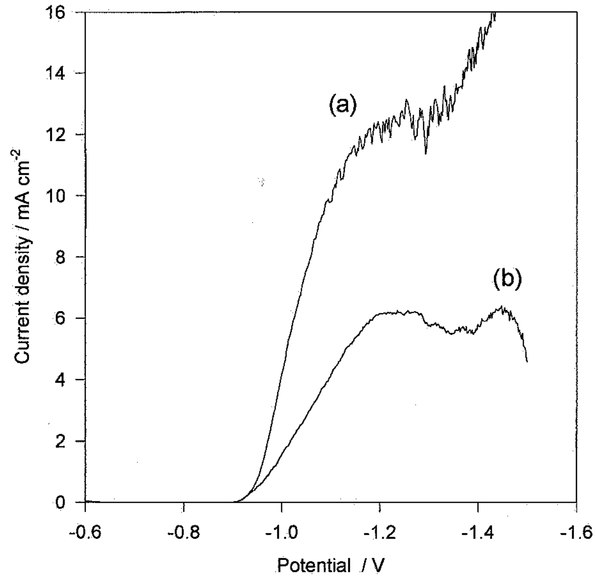

Fig. 2. Sweeps on stainless steel after subtraction. (a) Cobalt deposited onto steel (1st sweep) from 0.1 M Co(II). (b) Nickel deposited onto steel (1st sweep) from 0.1 M Ni(II). Sweep rate: 10 mV s$^{-1}$ Base electrolyte:1 M $Na_2SO_4$ and 0.25 M $B(OH)_3$.

The deposition of Co(II) and Ni(II) were irreversible and the Tafel slope for Co(II) onto the stainless steel substrate is 110 mV decade$^{-1}$ with an exchange current of $6.9 \times 10^{-13}$ A cm$^{-2}$ and for nickel the slope is 135 mV cm$^{-2}$ with an exchange current of $2.0 \times 10^{-13}$ A cm$^{-2}$ which is close to the literature values [10]. There is little change in the values for both the Tafel slope and the exchange current for the cobalt predeposited electrode systems.

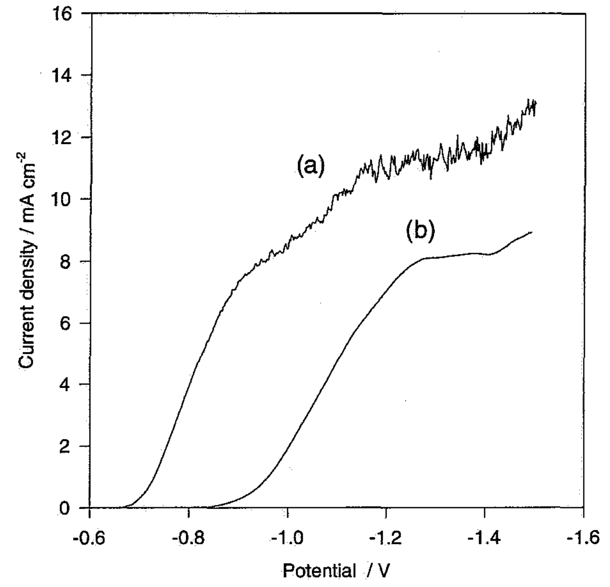

Fig. 3. Sweeps for stainless steel freshly deposited with cobalt. (a) 0.1 M Co(II) and (b) 0.1 M Ni(II). Sweep rate: 10 mV s$^{-1}$ Base electrolyte: 1 M $Na_2SO_4$ and 0.25 M $B(OH)_3$.

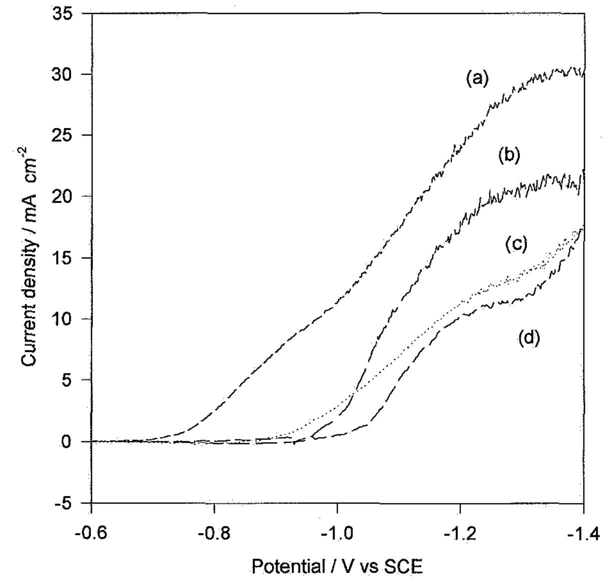

Fig. 4. Deposition onto nickel sheet. (a) Cobalt depositing onto freshly deposited cobalt; (b) Co(II) depositing onto nickel; (c). nickel depositing onto freshly deposited nickel; and (d) Ni(II) depositing onto nickel. Sweep rate: 10 mV s$^{-1}$. Base electrolyte: 1 M $Na_2SO_4$ and 0.25 M $B(OH)_3$.

### 3.2. *Electrodeposition from 1:1Co(II)/Ni(II) mixtures*

Figure 5 shows the composition of the deposit produced from a 1:1 Co(II):Ni(II) sulfate solution for a nickel substrate at a range of different potentials. The corresponding theoretical prediction based on partial currents for the percentage of cobalt in the deposit at potential $E$ is given by

$$(\%\mathrm{Co})_E = \frac{i_{\mathrm{Co}}/i_{\mathrm{dCo}}}{i_{\mathrm{Co}}i_{\mathrm{dCo}} + i_{\mathrm{Ni}}/i_{\mathrm{dNi}}} \times 100 \qquad (1)$$

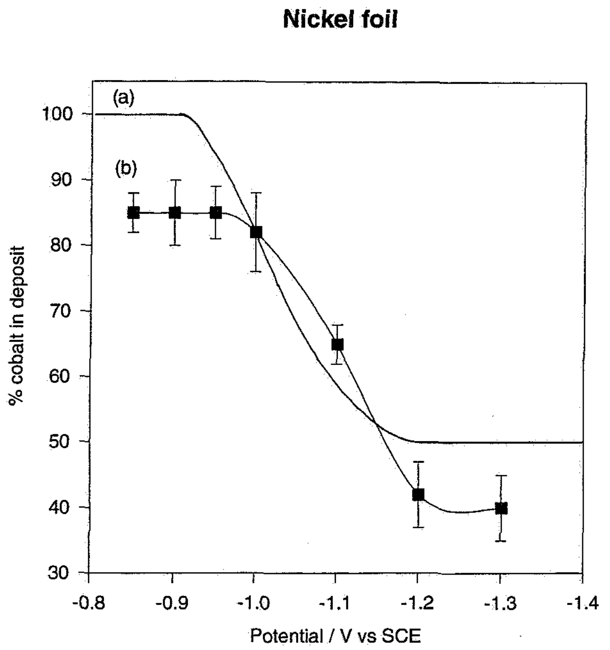

Fig. 5. Percentage of Co in the deposit produced on nickel sheet. (a) Curve predicted from 0.1 M single cation data, and (b) actual deposit from 0.1 M Co(II) and 0.1 M Ni(II). Base electrolyte: 1 M $Na_2SO_4$ and 0.25 M $B(OH)_3$.

where $i_{\mathrm{dCo}}$ and $i_{\mathrm{dNi}}$ are the limiting currents for the discharge of Co(II) and Ni(II), respectively, and $i_{\mathrm{Co}}$ and $i_{\mathrm{Ni}}$ are currents for the discharge of Co(II) and Ni(II), respectively, at a potential $E$. Equation 1 assumes that the electrodeposition currents for the different metals are unchanged in the presence of a mixture. It can be seen that the experimental deposit composition curve follows the theoretical curve reasonably well although the predicted 100% cobalt deposit, which should be produced in the region –0.80 V to –0.9 V, is never observed for the 1:1 mixture. In this study only 10% of the cobalt available in solution was electrodeposited. It is widely reported [11] that it is not possible to deduce the alloy composition from single cation current–potential curves although in many of these studies the hydrogen evolution reaction has not been subtracted, no limiting currents has been seen for nickel and only a small difference in the Ni(II) and Co(II) current–potential curve has been reported. In this study the hydrogen evolution reaction has been subtracted and a large difference in the deposition potential is observed for cobalt and nickel which is consistent with that produced of a cobalt rich alloy from a 1:1 Co(II):Ni(II) electrolyte although the predicted 100% cobalt deposit is never found. For the stainless steel substrate, the deposition is independent of the potential when a small amount of charge is passed. This has been observed for the Fe–Co system by Bertazzoli *et al.* [12] who found that the composition of the alloy is mainly determined by the ratio of [Fe(II)]/[Co(II)] in solution with a very slight dependence on temperature or potential/current density. When a greater charge is passed (90% of the available cobalt was electrodeposited), the experimental data follows the theoretical curve (Fig. 6) more closely.

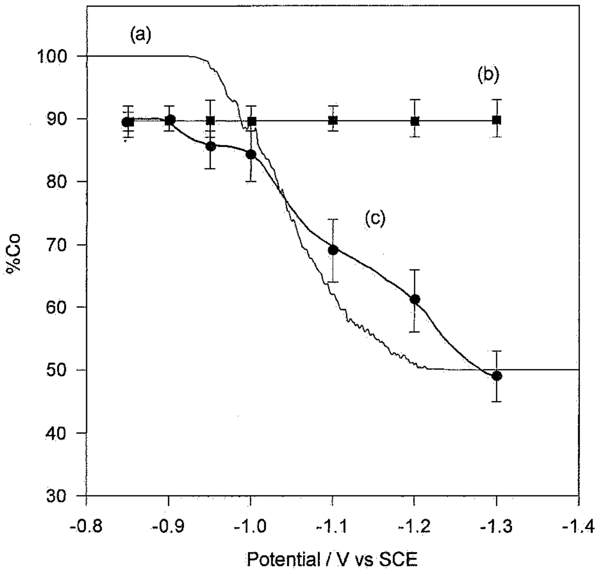

Fig. 6. Percentage of Co in the deposit produced on stainless steel sheet. (a) Curve predicted from 0.1 M single cation data; (b) actual deposit when a low amount of charge was passed (10% of the charge required to deposit all of the Co(II)) and (c) actual deposit when higher charge was passed (90% of charge required to deposit all of the Co(II)). 0.1 M Ni(II), 0.1 M Co(II), 1 M $Na_2SO_4$ and 0.25 M $B(OH)_3$.

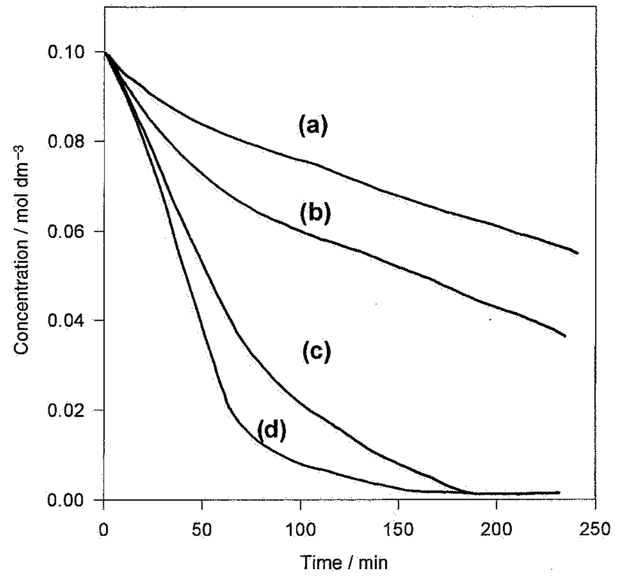

Fig. 8. Continuous runs at –1.10 V and –1.30 V on virgin stainless steel. (a) Ni(II) concentration (potential –1.10 V); (b) Co(II) concentration (potential –1.10 V); (c) Ni(II) concentration (potential –1.30 V); and (d) Co(II) concentration (potential –1.30 V). 0.1 M $CoSO_4$, 0.1 M $NiSO_4$, 1 M $Na_2SO_4$ and 0.25 M $B(OH)_3$.

### 3.3. *Long term electrolysis of 1:1 mixtures on sheet electrodes*

The results for continuous runs can be seen in Fig. 7 for a potential of –0.90 V, for both a cobalt predeposited steel sheet ((a) and (d)) and a stainless steel sheet ((b) and (c)). From Fig. 7, it can be seen that cobalt is preferentially deposited from the 1:1 mixture, for both of the substrates. For the virginal stainless steel system, the concentration of Co(II) is reduced to about 30% of the original level while the nickel level is about 80% of its original concentration, after a charge is passed which is large enough to deposit all of the metals. The current efficiency for cobalt deposition based on the final concentration of cobalt is 40% and the current efficiency based on all metal deposition is ~60%. At the optimum potential for separation, the deposit contained 90% cobalt and 10% nickel. If a more negative potential is used, the nickel content of the deposit increases (Fig. 8) and the rate of metal extraction is increased.

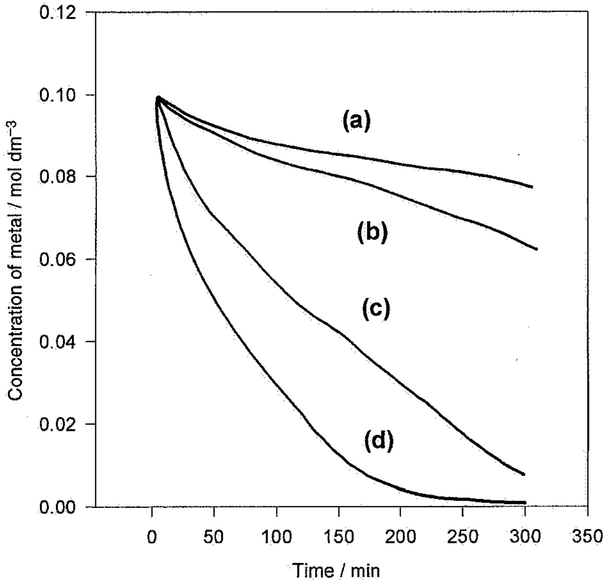

Fig. 7. Continuous run at –0.90 V from a solution of 0.1 M $CoSO_4$, 0.1 M $NiSO_4$, 1 M $Na_2SO_4$ and 0.25 M $B(OH)_3$. (a) Ni(II) level with Co predeposited on cathode; (b) Ni(II) level with stainless steel cathode; (c). Co(II) level with stainless steel cathode; and (d) Co(II) level with Co predeposited on cathode.

When a stainless steel sheet electrode which has been predeposited with cobalt is used for extraction of cobalt from a 1:1 mixture, almost all of the cobalt is removed from the solution and 85% of the nickel remains in solution after a charge is passed which is great enough to deposit all of the Co(II) (Fig. 7, curves (a) and (d)). The current efficiency for metal deposition is about 80% and the final surface of the deposit contains >90% cobalt. The composition of the final deposit cannot be accurately reported due to the incorporation of the initial 100% cobalt predeposit into the final deposit. It seems that predepositing a cobalt phase onto the stainless steel electrode surface, greatly facilitates the deposition of additional cobalt and may inhibit nickel deposition which results in more Co(II) being extracted. Nickel deposition inhibition by cobalt has been observed by Andricacos [13] who found that for a 1:1 Co(II): Ni(II) mixture with 0.4 M $B(OH)_3$, the Ni(II) deposition current was reduced by a factor of 10 by the presence of cobalt.

When the sheet electrodes are changed at regular intervals, the rate of cobalt removal is slower than for the continuous runs and more nickel is co-deposited with the cobalt.

## 4. Conclusions

(i) Linear sweep volatammetry (LSV) of single cobalt and nickel cations can be used to *approximate* the composition of metal deposited from a binary mixture when factors such as the hydrogen evolution reaction have been subtracted from the LSV. It can also be used to indicate best potential range to be used in order to produce the highest percentage of the more noble metal (cobalt).

(ii) From a 1:1 mixture of Co(II) and Ni(II) it is not possible to produce a 100% cobalt deposit using potentio-selective electrodeposition although cobalt rich alloys can be produced. These alloys could be electrorefined to produce pure cobalt metal.

(iii) Predeposition of cobalt onto the stainless steel electrode surface is found to facilitate additional cobalt deposition and produces a more complete separation of cobalt from nickel. Another advantage of using a predeposited system is that a less negative potential could be used for the extraction of cobalt from the mixture which could make the process more cost efficient. The extraction process based on a predeposited substrate also involved no additions to the waste solution and therefore should have little further environmental impact.

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