JOURNAL OF APPLIED ELECTROCHEMISTRY **26** (1996) 379–384

Selective electrodeposition of metals from simulated waste solutions

R. D. ARMSTRONG*, M. TODD

Chemistry Department, Bedson Building, Newcastle University, Newcastle upon Tyne, NE1 7RU, Great Britain

J. W. ATKINSON, K. SCOTT

Chemical & Process Engineering Department, Merz Court, Newcastle University,
Newcastle upon Tyne NE1 7RU, Great Britain

Received 27 June 1995; revised 13 September 1995

Most industrial waste streams contain a number of different heavy metals. The feasibility of selective electrodeposition of cadmium, cobalt and nickel as their pure metals (~99%) from binary mixtures has been investigated. Single cation linear sweep voltamograms and nucleation potential measurements have been made and used to predict the optimum potentials and conditions for selective electrodeposition from the mixed-cation solutions. The anions used in this work are SO_4^{2-}, Cl^- and BF_4^-. The optimum potential for removal by electrodeposition of Cd from a solution containing Cd(II) and Co(II) or Ni(II) without codepositing Co or Ni has been evaluated from a simple diagram constructed from nucleation potential measurements. It is shown that the [Cd(II)] remaining in the solution after exhaustive electrolysis at a fixed potential is determined by the Nernst equation, and not by the electrolysis time provided that a critical minimum time has been exceeded.

1. Introduction

Electrodeposition of metals, particularly from aqueous solutions, is an attractive method for the recovery and recycling of metal ions in many industries such as plating, metal finishing and electronics. Over thirty metals can be electrodeposited from aqueous solutions including many precious metals and heavy metals. Many of these metals pose environmental hazards and legislation generally imposes minimum discharge levels regarding quantity and concentration. A standard approach to satisfy these requirements is to precipitate the metal ions as oxide/hydroxide and process the subsequent sludge prior to disposal or further treatment. In many cases the solution to be treated will contain more than one metal ion, for example that produced in the dissolution of spent Ni/Cd batteries [1]. In this example there is a requirement to recover the individual metals separately to enable efficient economic recovery. It is, therefore, unattractive to adopt precipitation to recover the metal from solution, rather a method such as electrodeposition has attractions if selective deposition of individual metals can be achieved. The area of metal recovery by electrodeposition has been a subject of recent reviews [2]. There have been several studies of electrodeposition from mixed metal ion solutions, for example Cu/Ni [3], Pb/Cu [4] and Zn/Cu [3]. In many cases, especially those involving Cu, the difference in standard electrode potential indicates that selective electrodeposition is effective and research has demonstrated this to be true. In other cases, such as Ni/Co the closeness of the standard potentials indicates that selective electrodeposition will be more difficult.

In the work reported here the extent, both theoretically and experimentally, to which mixtures of metal cations in waste waters can be separated as metals using successive electrodeposition has been explored. For example, if we consider water containing Cd(II) and Ni(II) it is important to establish the concentration to which Cd(II) can be reduced in the solution by electrodeposition without depositing Ni and the purity of the electrodeposited Cd. Previous work of this sort has been carried out by Walsh and Gabe [5]. The theoretical basis of their work depended on the use of the Nernst equation for the metals involved. Although this approach is appropriate for the separation of for example Ag(II) and Cu(II) where the cations deposit close to their thermodynamic reversible potentials and where they are present in some solutions as uncomplexed species, a more realistic scheme has to take account of complexation of the cations and of the irreversible nature of the electrodeposition of cations such as Ni(II). The anions used in this work are SO_4^{2-}, Cl^- and BF_4^-. Appropriate conditions have been identified where selective electrodeposition is possible in the cases of Cd/Co and Cd/Ni mixtures.

2. Experimental details

2.1. *Electrodeposition from single cation solutions*

The electrodepositions of Cd, Co and Ni from aqueous sulphate solutions were investigated using stainless steel and Cd rotating disc electrodes (RDE) of area 0.16 cm^2, shrouded in Teflon. The rotation rate was 500 r.p.m. throughout. The RDE surfaces were prepared by polishing with 0.05 μm alumina and washed with 1 mol dm^{-3} ($\equiv$1 M) sulphuric acid followed by deionized water. The Cd RDE was pretreated by Cd electrodeposition using a cathodic linear sweep from the solutions rest potential (E_r) for 100 mV at 0.5 mV s^{-1}. Cd(II) solutions were made up from $3CdSO_4.8H_2O$ (Fluka, >99%) or $CdCl_2.2H_2O$ (Fluka, >96%) or $Cd(BF_4)_2$ (Strem, 50% aqueous solution). Co(II) solutions were made up using $CoSO_4.7H_2O$ (Fluka, >99%). Ni(II) solutions were made up using $NiSO_4.6H_2O$ (Fluka, >99%). A base electrolyte was added in each case: for sulphate solutions, Na_2SO_4 (Fluka, >99%), for chloride solutions, NaCl (Aldrich, >99%), and for fluoroborate solutions, $NaBF_4$ (Fluka, >98%). Boric acid was present in some solutions (Fluka, >99.5%). The pH of the solutions was adjusted in some cases by the addition of: for sulphate solutions, H_2SO_4 (Aldrich, 99.999%), for chloride solutions, HCl (Fluka, >99%), and for fluoroborate solutions, HBF_4 (Strem, 48% aqueous solution).

Measurements were made in a 3 electrode glass cell of volume 200 cm^3 surrounded by a water jacket. A saturated calomel electrode (SCE) was connected to the cell via a potassium nitrate salt bridge and a Luggin capillary. All potential measurements listed are recorded against the SCE. The counter electrode was a platinum spade (1.9 cm^2). The solution was purged with nitrogen for 5 min prior to runs in order to deaerate the system. The potential of the electrode was controlled using an EG&G Versastat system controlled by a Vtech 486SX25 computer via an IEEE-488 GPIB card. Current–potential measurements were made by linear sweep from anodic to cathodic potentials at 1 mV s^{-1}.

2.2. *Electrodeposition from mixed cation solutions*

A three electrode glass cell was used which had two compartments each of 100 cm^3 volume, separated by a Nafion® cation exchange membrane. The working electrode compartment was surrounded by a water jacket. The solution in this compartment was deaerated and stirred by a stream of water saturated nitrogen. The working electrode was a stainless steel plate of area 4 cm^2 blanked off on one side using a stopping off lacquer (Lacomit, Canning). The working electrode was held at a constant potential using a potentiostatic coulometer and the current being passed was measured using a BBC SE120 chart recorder. All experiments were carried out at 20 °C. The pH of the solutions were controlled by the addition of H_3BO_3 (Fluka, >99.5%). The counter electrode, present in the other compartment, was a 2.0 cm^2 platinum spade electrode.

The electrodeposited metals were analysed using EDAX measurements. The solution concentration of Cd(II), Co(II) and Ni(II), after electrolysis, was determined by polarography.

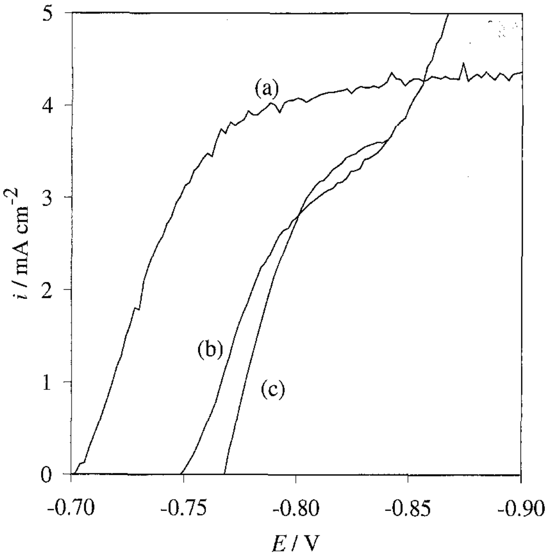

Fig. 1. Steady state i/E relationship for Cd deposition onto a Cd RDE (500 r.p.m.) at 20 °C from (a) 0.01 M $Cd(BF_4)_2$ + 1 M $NaBF_4$, (b) 0.01 M $CdSO_4$ + 1 M Na_2SO_4, (c) 0.01 M $CdCl_2$ + 1 M NaCl.

3. Results

3.1. *Electrodeposition from single cation solutions*

Figure 1 shows the steady state i/E relationship for Cd deposition onto a Cd RDE. The shapes of the initial region of the sweeps are consistent with the quasi-reversible deposition of Cd since deposition starts immediately negative to the measured reversible potential for the Cd(II)/Cd couple and plots of E against log $[i_d/(i_d - i)]$ give slopes between 0.040 and 0.050 V decade^{-1} which is close to the theoretical value of 0.030 V decade^{-1} (Fig. 2). As the potential becomes more negative a diffusion limited current becomes evident. The current density increases further due to powder formation. Due to complexation the

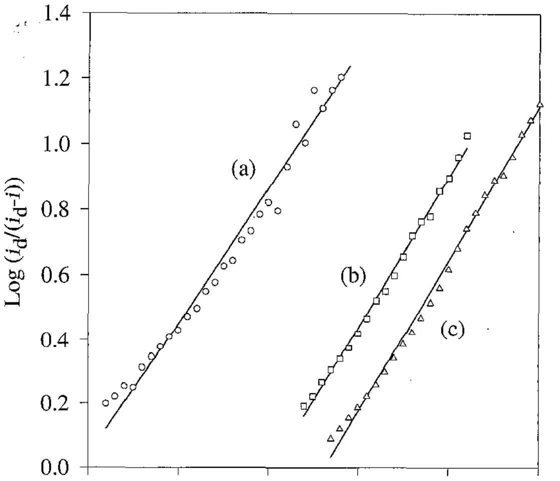

Fig. 2. Plots of log$(i_d/i_d - i)$ against E for steady state Cd deposition onto a Cd RDE (500 r.p.m.) at 20 °C from (a) 0.01 M $Cd(BF_4)_2$ + 1 M $NaBF_4$, (b) 0.01 M $CdSO_4$ + 1 M Na_2SO_4, (c) 0.01 M $CdCl_2$ + 1 M NaCl.

Table 1. Comparison of experimental and theoretical E_r values for 0.01 M *Cd(*II*) + 2* M *Na(*I*) for different anions using a Cd RDE (500 r.p.m.) at 20 °C*

Anion	*Experimental, E_r /V*	*Theoretical, E_r /V*	*Majority Cd(*II*) species*	*% Cd(*II*) as Cd^{2+} (aq)*
BF_4^-	−0.701	−0.704	Cd^{2+} (aq)	100
SO_4^{2-}	−0.748	−0.732	$CdSO_4$ (aq)	24
Cl^-	−0.767	−0.777	$CdCl_2$ (aq)	2

different anions cause differences in the activity and concentration of the Cd^{2+} species and this leads to different values for the reversible potentials (E_r) for the Cd/Cd(II) couple (Table 1). The limiting current densities are also different because the majority Cd(II) species is different in each case due to complexation. Powder formation occurs at a more negative potential from fluoroborate solutions than from sulphate or chloride solutions.

Increasing the temperature increases the current density at all potentials by decreasing the kinematic viscosity of the solution and increasing the diffusion coefficient of the electroactive species thus enhancing the mass transport rates of the system. E_r becomes less negative as the temperature increases as the activity of the Cd^{2+} increases. The limiting current density increases due to a decrease in the solution viscosity and the resultant increase in the diffusion coefficient. The pH of the solution has no effect on the i/E curves over the range of 2 to 5.5.

Figure 3 shows the steady state i/E relationship for Cd, Co and Ni deposition onto a stainless steel RDE from sulphate solutions. The $E_{1/2}$ values for the different solutions differ by about 100 mV from each other. Cd is deposited at the least negative potential followed by Co and then Ni. Distinct limiting currents are observed followed by the evolution of hydrogen negative to −1.2 V in the case of Co and negative to −1.3 V in the case of Cd. For Ni, no distinct limiting current is observed before hydrogen evolution. The i/E curves for Co and Ni are consistent with irreversible deposition since deposition starts well negative to the calculated reversible potentials for the metal/metal ion couples. Powder formation is only observed in the case of cadmium deposition.

Figure 4 shows the steady state i/E relationship for Cd, Co and Ni deposition onto a Cd RDE. Cd deposits at a potential which is 0.040 V more negative and Co deposits at a potential which is 0.120 V more negative onto a stainless steel RDE compared with deposition onto a predeposited Cd RDE. Ni deposits at a similar potential onto both RDEs. Distinct limiting currents are observed followed by the evolution of hydrogen at potentials negative to −1.2 V in all three cases. Powder formation is only observed in the case of cadmium deposition.

To establish the minimum electrode potential at which electrodeposition of Co and Ni could be achieved onto a stainless steel plate linear sweep measurements were carried out at relatively low sweep rate of 0.05 mV s^{-1}. Typical results for Co are shown in Fig. 5. The minimum electrodeposition potentials were calculated by extrapolation of the rising curve to the base line.

3.2. *Electrodeposition from Co/Cd solutions*

It can be seen from Fig. 3 that for a 0.01 M : 0.01 M Co/

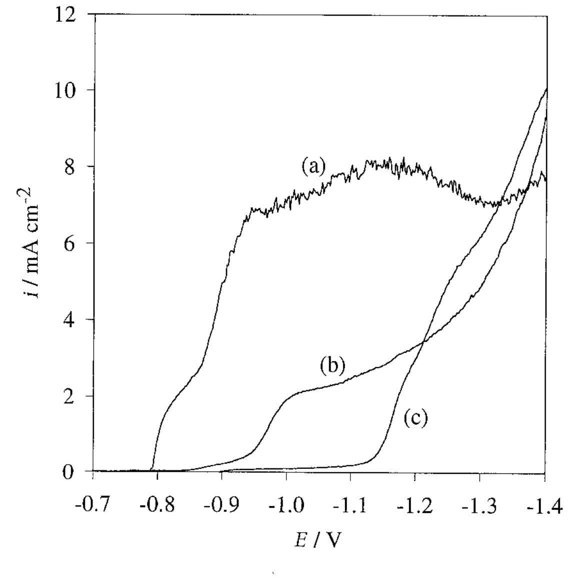

Fig. 3. Steady-state i/E relationship for deposition onto a stainless steel RDE (500 r.p.m.) at 20 °C from (a) 0.01 M $CdSO_4$ + 0.04 M H_3BO_3 + 1 M Na_2SO_4, (b) 0.01 M $CoSO_4$ + 0.04 M H_3BO_3 + 1 M Na_2SO_4, (c) 0.01 M $NiSO_4$ + 0.04 M H_3BO_3 + 1 M Na_2SO_4.

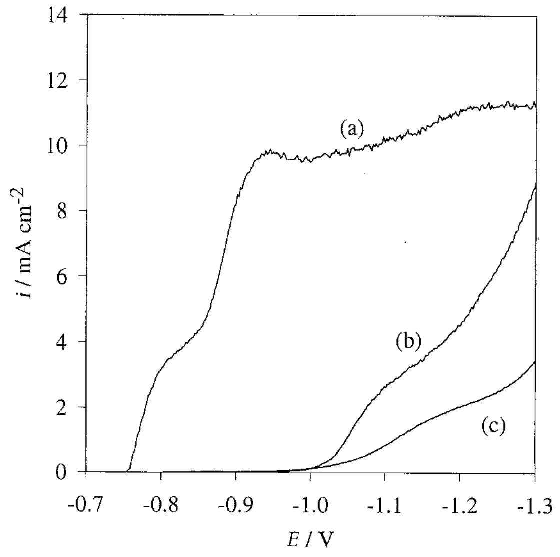

Fig. 4. Steady state i/E relationship for deposition onto a Cd RDE (500 r.p.m.) at 20 °C from (a) 0.01 M $CdSO_4$ + 0.04 M H_3BO_3 + 1 M Na_2SO_4, (b) 0.01 M $CoSO_4$ + 0.04 M H_3BO_3 + 1 M Na_2SO_4, (c) 0.01 M $NiSO_4$ + 0.04 M H_3BO_3 + 1 M Na_2SO_4.

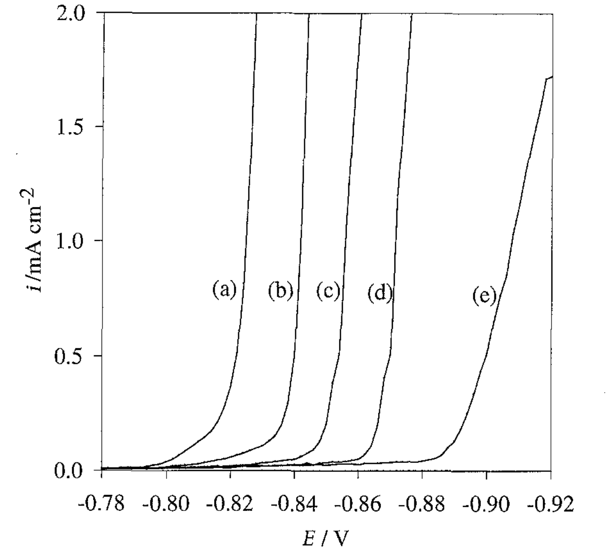

Fig. 5. i/E relationship for Co deposition onto a stainless steel sheet at 20 °C from 0.04 M H_3BO_3 + 1 M Na_2SO_4 + (a) 0.5 M, (b) 0.1 M, (c) 0.05 M, (d) 0.025 M, (e) 0.01 M $CoSO_4$. Stirring by water saturated nitrogen.

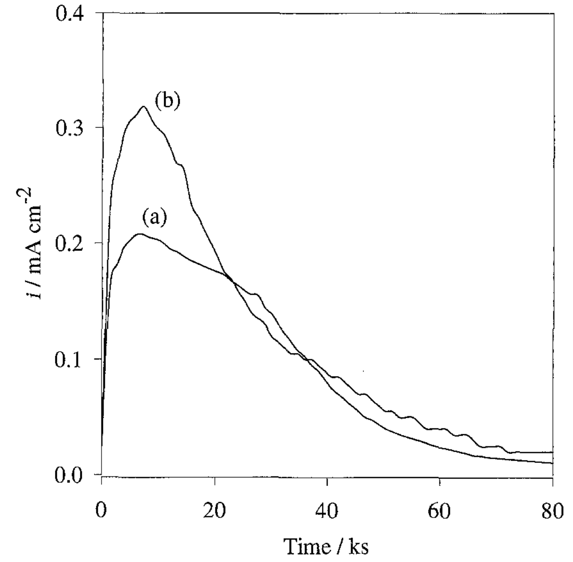

Fig. 6. Current–time for the electrolysis of 0.002 M $CdSO_4$ + 0.2 M $CoSO_4$ + 0.04 M H_3BO_3 + 1 M Na_2SO_4 at (a) −0.79 V and (b) −0.80 V onto a stainless steel plate at 20 °C. Stirring by water saturated nitrogen.

Cd mixed solution there is a region of potential of 60 mV where the electrodeposited metal would be expected to be predominantly Cd. In the electrolysis of 1 M Na_2SO_4 + 0.2 M $CoSO_4$ + 0.002 M $CdSO_4$ + 0.04 M H_3BO_3 the Co : Cd ratio in the solution is 100 : 1 and the potential range in which Cd is expected to be deposited without the codeposition of Co is decreased. Electrodeposition was carried out on this solution at a variety of potentials. Fig. 6 shows the i against t transients for the electrolysis of this solution at two of these potentials. The current sharply rises over the initial period as the Co nucleates onto the RDE, becomes diffusion controlled at longer times and then slowly decreases as the Cd(II) species is removed from the solution. Electrolysis was stopped when either the current dropped below 0.01 mA cm^{-2} or 40 C (the charge available from complete removal of Cd(II) from the working electrode compartment) had been passed. Table 2 summarizes these electrodeposition experiments. The current efficiency was close to 100% at −0.79 V. At more cathodic potentials it fell due to simultaneous hydrogen evolution. At −0.78 V the fall is due to the longer time available for stray reactions to occur. The basis for the theoretical values is described in Section 4. The electrodeposited metal produced at potentials between −0.78 and −0.81 V was 95 ± 3% Cd. The concentration of Cd(II) remaining in the solution fell systematically as the potential was made more cathodic. At a potential of −0.82 V Co nucleation occurs before the predicted $[Cd(II)]_{min}$ is reached.

3.3. *Electrodeposition from Ni/Cd solutions*

It can be seen from Fig. 3 that for a 0.01 : 0.01 Ni/Cd mixed solution there is a region of potential of 160 mV where the electrodeposited metal would be expected to be predominantly Cd. In the electrolysis of 1 M Na_2SO_4 + 0.2 M $NiSO_4$ + 0.002 M $CdSO_4$ + 0.04 M H_3BO_3 the Ni : Cd ratio in the solution is 100 : 1 and the potential range in which Cd is expected to be deposited without the codeposition of Ni is decreased. Electrodeposition was carried out on this solution at a variety of potentials. Figure 7 shows the i against t transients for the electrolysis of this solution at two potentials in this potential region. Electrolysis was stopped when either the current dropped below 0.01 mA cm^{-2} or 40 C had been passed. Table 3 summarizes these electrodeposition experiments. The current efficiency was close to 100% at −0.80 V. At more

Table 2. Results of selective electrodeposition of Cd onto a stainless steel plate at 20 °C from a Cd/Co mixture with 0.002 M $CdSO_4$ + 0.2 M $CoSO_4$ + 0.04 M H_3BO_3 + 1 M Na_2SO_4

Stirring by water saturated nitrogen.

Potential /V	*Charge passed* /C	*Predicted* $[Cd(II)]_{min}$ /p.p.m.	*Final* $[Cd(II)]$ /p.p.m.	*Current efficiency* /%
−0.770	1.1	190	220	–
−0.780	24.0	89	100	89
−0.790	30.7	41	48	99
−0.800	38.5	19	27	88
−0.810	39.8	8.9	19	89
−0.820	39.9	4.1	65	67

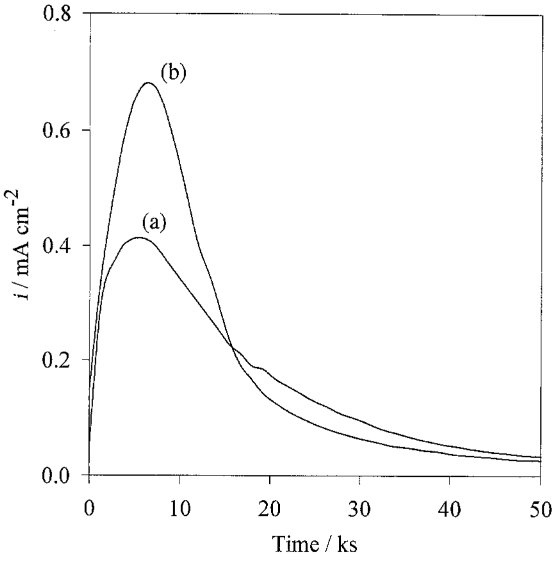

Fig. 7. Current–time for the electrolysis of 0.002 M $CdSO_4$ + 0.2 M $NiSO_4$ + 0.04 M H_3BO_3 + 1 M Na_2SO_4 at (a) −0.81 V and (b) −0.82 V onto a stainless steel plate at 20 °C. Stirring by water saturated nitrogen.

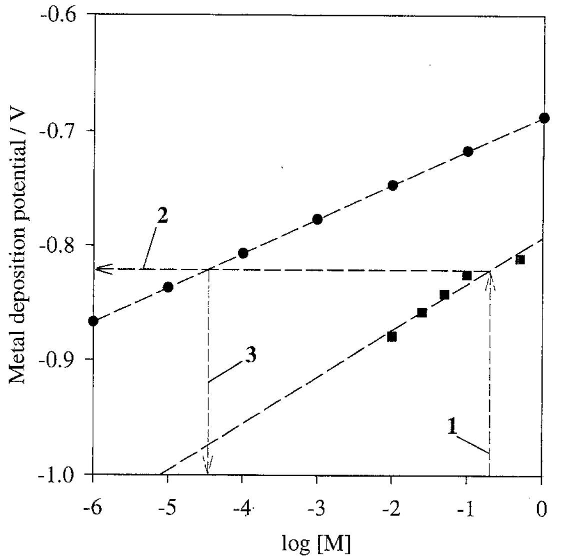

Fig. 8. Variation of metal deposition potential with different concentrations of $CdSO_4$ and $CoSO_4$ with 0.04 M H_3BO_3 + 1 M Na_2SO_4 onto a stainless steel plate at 20 °C. Stirring by water saturated nitrogen. Key: (●) Cd and (■) Co.

cathodic potentials it fell due to simultaneous hydrogen evolution. At −0.79 V the fall to 60% is due to the longer time available for stray reactions to occur. The basis for the predicted values is described in the discussion section. The final [Cd(II)] is significantly higher than that predicted using the Nernst equation. This may be because there is a significantly higher concentration of sulphate ions in the solution containing Cd(II) and Ni(II) than in that with Cd(II) alone leading to a greater extent of Cd(II) complexation. The electrodeposited metal produced at potentials between −0.79 and −0.83 V was 95 ± 3% purity. The concentration of Cd(II) remaining in the solution fell systematically as the potential was made more cathodic. At a potential of −0.84 V Ni nucleation occurs before the predicted $[Cd(II)]_{min}$ is reached.

4. Discussion

The above results show that it is possible using electrodeposition to remove cadmium from solutions containing mixtures of Cd/Co and Cd/Ni. The lowest level of Cd remaining in the solution is determined by the potential which is used for the Cd electrodeposition. The optimum potential for the removal of Cd(II) from solution without the simultaneous

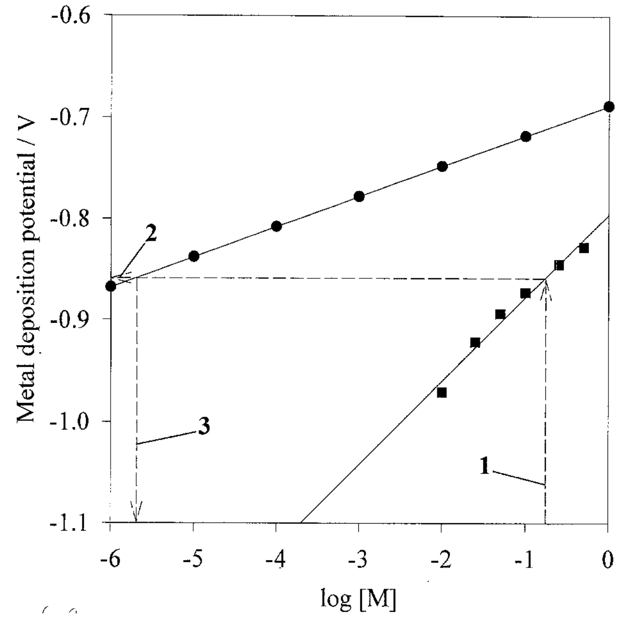

Fig. 9. Variation of metal deposition potential with different concentrations of $CdSO_4$ and $NiSO_4$ with 0.04 M H_3BO_3 + 1 M Na_2SO_4 onto a stainless steel plate at 20 °C. Stirring by water saturated nitrogen. Key: (●) Cd and (■) Ni.

Table 3. Results of selective electrodeposition of Cd onto a stainless steel plate at 20 °C from a Cd/Ni mixture with 0.002 M $CdSO_4$ + 0.2 M $NiSO_4$ + 0.04 M H_3BO_3 + 1 M Na_2SO_4

Stirring by water saturated nitrogen.

Potential /V	*Charge passed* /C	*Predicted* $[Cd(II)]_{min}$ /p.p.m.	*Final [Cd(II)]* /p.p.m.	*Current efficiency* /%
−0.790	26.8	41	131	60
−0.800	31.6	19	39	101
−0.810	36.5	8.9	27	93
−0.820	39.6	4.1	17	90
−0.830	39.8	1.9	6	94
−0.840	39.8	0.9	35	82

Table 4. The metal deposition potentials (E_m) for Cd, Co and Ni over a range of concentrations onto a stainless steel plate at 20 °C

Stirring by water saturated nitrogen.

[M]/M	*Log [M]*	*Cd* E_m /V	*Co* E_m /V	*Ni* E_m /V
1×10^{-6}	−6	−0.868	–	–
1×10^{-5}	−5	−0.838	–	–
1×10^{-4}	−4	−0.808	–	–
1×10^{-3}	−3	−0.778	–	–
1×10^{-2}	−2	−0.748	−0.879	−0.971
2.5×10^{-2}	−1.6	–	−0.858	−0.922
5×10^{-2}	−1.3	–	−0.842	−0.894
1×10^{-1}	−1	−0.718	−0.825	−0.873
2.5×10^{-1}	−0.6	–	–	−0.845
5×10^{-1}	−0.3	–	−0.811	−0.828
1	0	−0.688	–	–

deposition of either Co or Ni is the potential which is just anodic to the potential (E_m(Co) or E_m(Ni)) at which electrodeposition of Co or Ni commences. In the case of Cd, $E_m(\text{Cd}) = E_r(\text{Cd})$ for any given [Cd(II)] since it exhibits a quasi-reversible wave. These values are summarized in Table 4 together with the related values for Co and Ni obtained by slow linear sweep as described earlier.

These values make it possible to predict the extent to which Cd(II) can be removed from any solution containing Co and Ni. The optimum potential for the removal of Cd(II) can be predicted from Figs 8 and 9. In order to evaluate this potential in the particular case of Cd(II) from Co(II) the following procedure is used:

(i) Select the value of log [Co(II)] on the x-axis and draw a line perpendicular from this point until the Ni line is reached.
(ii) Draw a line from the point on the Co line perpendicular to the y-axis. This point is the nucleation point for the Co when it is at this particular concentration.
(iii) Draw a line from the point where line 2 crosses the Cd line down to the x-axis. The value reached on the x-axis gives us the minimum concentration which we can take the Cd down to at this concentration of Co if there is to be no codeposition of the Co.

In the case of the electrolysis of a (a) Cd/Co and (b) Cd/Ni mixture:

(a) (i) $[\text{Co(II)}] = 0.200\,\text{M} \Rightarrow \log[\text{Co(II)}] = -0.699\,\text{V}$
(ii) $E_{\text{dep}} = -0.831\,\text{V}$
(iii) minimum $[\text{Cd(II)}] = 3.68 \times 10^{-5}\,\text{M}$
$= 4.14\,\text{p.p.m.}$

(b) (i) $[\text{Ni(II)}] = 0.200\,\text{M} \Rightarrow \log[\text{Ni(II)}] = -0.599\,\text{V}$
(ii) $E_{\text{dep}} = -0.853\,\text{V}$
(iii) minimum $[\text{Cd(II)}] = 3.16 \times 10^{-6}\,\text{M}$
$= 0.36\,\text{p.p.m.}$

These compare with experimental values of (a) 19 p.p.m. at −0.810 V and (b) 6.3 p.p.m. at −0.830 V.

5. Conclusions

(i) Cd(II) can be electrodeposited from a solution containing Cd(II) and Co(II) or Ni(II) without codepositing Co or Ni.
(ii) The [Cd(II)] remaining in the solution after exhaustive electrolysis at a fixed potential is determined by the Nernst equation, and not by the electrolysis time provided that a critical minimum time has been exceeded.
(iii) The optimum potential for removal by electrodeposition of Cd from a solution containing Cd(II) and Co(II) or Ni(II) without codepositing Co or Ni can be evaluated from a simple diagram.

References

[1] Z. Xue, Z. Hua and N. Yao, *Separation Sci. & Technol.* **27** (1992) 213.

[2] Ed. C. A. C. Sequeira, 'Environmental Oriented Electrochemistry', Elsevier, Amsterdam (1994) p. 657.

[3] C. M. S. Raats, H. F. Boon and G. van der Heiden, *Chem. and Ind.* July (1978) 465.

[4] A. M. Polcaro and S. Palmas, 'Electrochemical Engineering and the Environment', *IChem Symposium Series* no. 127 (1992) 85.

[5] F. C. Walsh and D. R. Grabe, *Surf. Technol.* **12** (1981) 25.