

An electrochemical investigation of the dissolution of copper, nickel, and copper-nickel alloys in ammonium carbonate solutions

by M. J. NICOL*, Ph.D., B.Sc. (Hons.) (Wits.) (Visitor)

SYNOPSIS

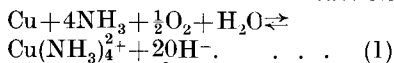
The dissolution of copper and nickel in ammonium carbonate solution was studied by techniques involving electrochemical anodic dissolution and ring-disc electrodes. The rate of oxidation of both copper and nickel by copper (II) was shown to be controlled mainly by diffusion to the surface. Variations in rate with changes in copper (II) concentration, agitation, pH, ammonia concentration, temperature, and copper (I) concentration were investigated and rationalized in terms of their effects on the electrochemical half-reactions involved. Evidence was found for the passivation of nickel and nickel-copper alloys of more than 50 per cent nickel.

SAMEVATTING

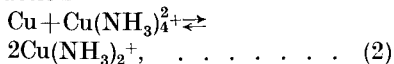
Die oplossing van koper en nikel in 'n ammoniumkarbonaatoplossing is bestudeer deur tegnieke waarby elektrochemiese anodiese oplossing en ringskyfelektrodes betrokke was. Daar is getoon dat die oksidasietempo van sowel koper en nikel deur koper (II) hoofsaaklik deur diffusie na die oppervlak beheer word. Tempovariasies in ooreenstemming met veranderinge in die koper (II) konsentrasie, agitatie, pH, ammoniakkonsentrasie, temperatuur en koper (I) konsentrasie is ondersoek en gerasionaliseer in terme van hul uitwerking op die elektrochemiese half-reaksies daarby betrokke. Daar is tekens van die passivering van nikel en nikkelpoelings met meer as 50 persent nikel gevind.

INTRODUCTION

In the presence of oxygen, copper dissolves readily in ammoniacal solution in accordance with the reaction



The $\text{Cu}(\text{NH}_3)_4^{2+}$ formed can also oxidize copper according to the reaction



the copper (I) produced being rapidly oxidized by oxygen to copper (II). Several studies of the overall process have been reported in the literature, the most important of which are critically reviewed below.

Lane and McDonald¹ studied the kinetics of the dissolution of rotating copper cylinders in oxygenated ammonia solutions at normal temperatures and pressures. The rate of production of copper (II) in solution was found to be zero-order at high ammonia concentrations, although an approximately twofold decrease in rate was noted at a well-defined point during the reaction. They found no evidence of autocatalysis by copper (II), the maximum concentration of which never exceeded $2 \times 10^{-2}\text{M}$ during the experiments. Both apparent zero-order regions were found to be affected by agitation, temperature, and ammonia

concentration in a similar way. The formation of basic films at the surface due to local increases in pH as a result of reaction (1) were invoked to account for the observed decreases in rate and dependence of the rate on ammonia concentration. However, no detailed mechanism of the reaction was suggested.

Lu and Graydon² studied the dissolution in both oxygenated and aerated ammonia solutions at atmospheric pressure with and without the addition of copper (II) before the start of the reaction. The maximum concentration of copper (II) during any run was 10^{-2}M . They found the reaction to be zero-order in oxygenated solutions, but apparently half-order in aerated solutions, although limited data at low concentrations of copper (II) showed a zero-order dependence on copper (II). The reactions were found to be controlled by mass transport under all conditions of the experiments. There are two main criticisms of their interpretation of the results.

(1) Autocatalytic behaviour will be observed only above a minimum ratio of copper (II) to oxygen, which can be deduced as follows. For diffusion-controlled reductions of oxygen and copper (II), the relative contribution of each to the reaction will be proportional to $nD^{2/3}C$ (see the Appendix), where n is the

number of electrons in the reduction of the oxidant, D is the diffusion coefficient, and C the concentration. Thus, the contributions will be equal at a concentration ratio

$$\begin{aligned} [\text{Cu}(\text{II})]/[\text{O}_2] &= 4D_{\text{O}_2}/D_{\text{Cu}(\text{II})} \\ &= 17 \text{ (for } D_{\text{O}_2} = 2.6 \times 10^{-5} \text{ cm}^2\text{s}^{-1} \\ &\text{ and } D_{\text{Cu}(\text{II})} = 6 \times 10^{-6} \text{ cm}^2\text{s}^{-1}\text{).} \end{aligned}$$

Thus, in oxygenated solutions at 25°C ($[\text{O}_2] = 1 \times 10^{-3}\text{M}$), autocatalysis will become appreciable only at concentrations of copper above $2 \times 10^{-2}\text{M}$. The corresponding figure for aerated solutions is $4 \times 10^{-3}\text{M}$. Thus, the absence of an autocatalytic effect in the case of Lu and Graydon's experiments in oxygenated solutions is readily explained. Furthermore, the half-order dependence in aerated solutions must be apparent only in that a continuously variable order from zero at low copper (II) to one at high copper (II) concentrations would be expected.

(2) Their attempt to rationalize this half-order dependence in terms of a mechanism is invalid for the following reasons. They assume that the slow step is the removal of copper (I) from the surface and that this copper (I) is produced via the assumed rapid equilibrium (2) at the surface.

*National Institute for Metallurgy, Johannesburg.

These assumptions result in a rate equation of the form

$$\text{Rate} = k[\text{Cu(II)}]_s^{\frac{1}{2}}$$

where $[\text{Cu(II)}]_s$ is the concentration of copper (II) at the surface. The final assumption required is that this concentration is the same as that in the bulk. This, however, is true only if the above equilibrium results in a small perturbation of the bulk concentration at the interface. Thermodynamic data (to be presented later) show that the equilibrium constant for reaction (2) under the conditions of their experiments is large (50M), so that the interfacial concentration must necessarily be much lower than that in the bulk. Halpern^{3, 4} and Habashi⁵ have erroneously subscribed to the same mechanism.

Halpern^{3, 4}, in a study of the reaction at various oxygen pressures from 1 to 8 atmospheres, found that the reaction could be described in terms of two distinct rate-

determining processes. At low oxygen pressures, the rate is limited by diffusion of oxygen to the surface, while at high pressures and, particularly, at low ammonia concentrations, the rate was found to be independent of oxygen pressure and agitation, but approximately first order in ammonia concentration. The slow step in this region was postulated in terms of the reaction of NH_3 and NH_4^+ with an oxide film on the surface. Habashi⁵ treated Halpern's^{3, 4} data in terms of an electrochemical mechanism, which, however, is qualitatively invalid in that it ignores the potential dependence of the half-reactions and requires continuously variable separate areas to be available for the anodic and cathodic processes.

A recent study of reaction (2) by Smith, Lower, and Hockings⁶ has, to some extent, confirmed Halpern's^{3, 4} results, i.e., a diffusion-controlled process at low concentra-

tions of copper (II) with decreased rates, and the formation of a visible oxide film at high concentrations. Their treatment of the data in the region of no film formation is similar to that of Lu and Graydon² in that it tacitly, but incorrectly, assumes a small equilibrium constant for reaction (2). They also postulate the formation of an oxide film (Cu_2O in particular), and the passivation is attributed, rightly, to the decrease in the concentration of free ammonia at the higher concentrations of copper (II).

A process for the ammoniacal leaching of nickel metal in reduced iron ore has been described by the staff of Inco⁷. They found that both nickel and iron tended to passivate in oxygenated ammonium carbonate solutions, and frequent reactivation by hydrogen reduction was necessary. Morioka and Shimakage⁸, in a study of the dissolution of nickel and copper powders in

TABLE I
THERMODYNAMIC DATA

Reaction	Temp. °C	Medium	$\log_{10}K$	E^0 V vs NHE
$\text{Cu}^+ + e \rightleftharpoons \text{Cu}$	25	0	—	0,518
$\text{Cu}^+ + \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)^+$	18	2M NH_4NO_3	5,93	—
$\text{Cu}(\text{NH}_3)^+ + \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_2^+$	18	2M NH_4NO_3	4,93	—
$\text{Cu}(\text{NH}_3)_2^+ + e \rightleftharpoons \text{Cu} + 2\text{NH}_3$		Derived from above	—	-0,134
$\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$	25	0	—	0,338
$\text{Cu}^{2+} + \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)^{2+}$	25	2M NH_4NO_3	4,27	—
$\text{Cu}(\text{NH}_3)^{2+} + \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_2^{2+}$	25	2M NH_4NO_3	3,59	—
$\text{Cu}(\text{NH}_3)_2^{2+} + \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_3^{2+}$	25	2M NH_4NO_3	3,00	—
$\text{Cu}(\text{NH}_3)_3^{2+} + \text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$	25	2M NH_4NO_3	2,19	—
$\text{Cu}(\text{NH}_3)_4^{2+} + 2e \rightleftharpoons \text{Cu} + 4\text{NH}_3$		Derived from above	—	-0,054
$\text{Cu}(\text{NH}_3)_4^{2+} + e \rightleftharpoons \text{Cu}(\text{NH}_3)_2^+ + 2\text{NH}_3$		Derived from above	—	0,026
$\text{Cu}(\text{NH}_3)_4^{2+} + \text{Cu} \rightleftharpoons 2\text{Cu}(\text{NH}_3)_2^+$		Derived from above	1,33	—
$\text{Ni}^{2+} + 2e \rightleftharpoons \text{Ni}$	25	0	—	-0,232
$\text{Ni}^{2+} + 6\text{NH}_3 \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}$	30	2M NH_4NO_3	8,74	—
$\text{Ni}(\text{NH}_3)_6^{2+} + 2e \rightleftharpoons \text{Ni} + 6\text{NH}_3$		Derived from above	—	-0,494
$\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$	25	2M NH_4NO_3	9,50	—

ammonia with oxygen pressures of up to 10 atmospheres, found that both the amount and rate of nickel dissolution were considerably lower than those for copper. Although they did not rationalize this behaviour in terms of passivation of the nickel, the results tend to support this view.

Since, as will be demonstrated, these processes are indeed electrochemical in nature, an electrochemical approach was considered to be the most useful in arriving at a complete description of the mechanisms of these reactions. This paper summarizes the results of such an investigation.

Table I lists published (Martell and Sillen⁹) and derived thermodynamic data relevant to the leaching of copper and nickel in ammoniacal solutions. These data illustrate several relevant points.

- (1) The greater stability of the copper (I) amines relative to the copper (II) amines (approximately an order of magnitude difference in the K values) results in a favourable shift in the $\text{Cu (II)} + \text{Cu} \rightleftharpoons 2\text{Cu (I)}$ equilibrium in ammoniacal solutions. However, since the actual value of this formal equilibrium constant will depend on the concentration of free ammonia, it was thought that actual measurement of K at various pH values would be of value in an assessment of any thermodynamic limitations to the copper-leaching reaction.
- (2) The relatively high stability of the copper amines means that they can compete with H^+ for the free NH_3 and will even persist at pH values as low as 8.
- (3) The difference in the E_o values of about 0,5 V between those for oxidation of nickel and reduction of copper (II) in ammonia solutions means that there are no thermodynamic restrictions to the leaching of nickel with copper (II) as the oxidant.

EXPERIMENTAL METHOD

Three types of measurements were involved: thermodynamic, electrochemical, and chemical-dissolution.

Thermodynamic Measurements

The formal reduction potentials of the $\text{Cu (II)} - \text{Cu (I)} - \text{Cu (O)}$ couples were obtained by direct measurement as follows. A solution of $4 \times 10^{-3}\text{M}$ CuSO_4 in 1M $(\text{NH}_4)_2\text{CO}_3$ was reduced cathodically in a thermostatted, well-stirred deoxygenated cell. A large platinum-gauze cathode and an isolated anode were used, and a constant current of 5,0 mA was passed for a period that was calculated as being equivalent to half-reduction of the copper (II) present. The potential of a platinum plate electrode was then measured against a saturated calomel electrode in the solution and taken as the formal reduction potential of the $\text{Cu (II)} - \text{Cu (I)}$ system at the particular pH value. The pH value of the solution was then recorded. Similar experiments were carried out at different pH values, either concentrated sulphuric acid or sodium hydroxide pellets being used for the adjustment of pH.

Complete reduction of the copper (II) solution resulted in a copper (I) solution, and the potential of a copper-plated platinum plate electrode versus a saturated calomel electrode was used in the calculation of the formal reduction potential of the $\text{Cu (I)} - \text{Cu (O)}$ couple. Complete reduction of the copper (II) solution was essential, and the following criteria were employed:

- (1) persistence of a visible copper plate on the cathode for at least half an hour,
- (2) a platinum potential of at least 200 mV more cathodic than that for half-reduction (this corresponds to a reduction in the ratio of copper (II) to copper (I) of about 10^4), and
- (3) a difference of less than 2 mV in stirred and unstirred solutions, which would confirm that any 'mixed potentials' due to the reaction $\text{Cu} + \text{Cu (II)} \rightleftharpoons 2\text{Cu (I)}$ are minimal.

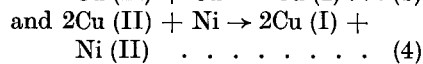
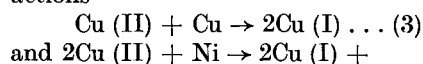
Electrochemical Measurements

Rotating discs of the metals (A.R. grade) set in PTFE holders were used in the study of the anodic dissolution of copper and nickel. The areas of the exposed faces were 0,32 and 0,39 cm^2 respectively.

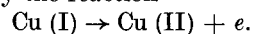
Discs of copper-nickel alloys supplied by Johnson, Matthey having an exposed area of 1,77 cm^2 were similarly employed. Steady-state potentiostatic and cyclic voltammetric measurements were made in a three-electrode system by the use of a potentiostat and triangular wave generator assembled from solid-state operational amplifiers. Unless stated otherwise, all measurements were made at $22 \pm 0,1^\circ\text{C}$, and all potentials are quoted with respect to a saturated calomel reference electrode (+0,245 V versus normal hydrogen electrode).

Chemical-dissolution Measurements

The rates of the dissolution reactions



were studied when they were allowed to occur on the copper-plated (or nickel-plated) platinum disc of a ring-disc electrode (dimensions $r_1=0,48$ cm, $r_2=0,51$ cm, and $r_3=0,56$ cm). The copper (I) produced by the reactions at the disc was monitored at the platinum ring by the reaction



The theoretical background for this use of a ring-disc electrode is outlined in the Appendix. The ring was connected in a conventional three-electrode potentiostatic circuit, and the disc to a variable-voltage power supply for plating of the disc. In general, the disc was plated from the same solution that was used for stripping, the amount of copper removed in a 5-minute plate being negligible. On completion of the plate, the disc was open-circuited, and the ring current at a suitable potential was monitored as a function of rotation speed. A study of the anodic oxidation of copper (I) showed that the process becomes diffusion-controlled at potentials anodic to 200 mV versus SCE. In all experiments, the ring potential was therefore set at 400 mV.

In experiments with nickel-plated discs, a solution of 0,1M NiSO_4 in 1M $(\text{NH}_4)_2\text{CO}_3$ at a pH value of 8 was used for plating. Owing to the low current efficiency, longer deposi-

tion times (up to 20 minutes) were necessary.

The collection efficiency of the ring was determined from copper anodic-dissolution experiments, care being taken to exclude oxygen from the system. A mean value of $33,2 \pm 0,3$ per cent for the efficiency was obtained in the range 50 to 1000 rev/min.

Unless stated otherwise, all experiments were carried out at $22 \pm 0,1^\circ\text{C}$ in a thermostatted Metrohm EA-880T cell fitted with reference (saturated calomel) and counter electrodes for both ring and disc, and with a gas-inlet tube for deoxygenation with high-purity nitrogen. Solutions were made up by the dissolution of A.R.-grade copper sulphate and A.R.-grade ammonium carbonate in triply distilled water.

RESULTS AND DISCUSSION

The three types of measurements are again treated separately.

Thermodynamic Measurements

Results of the equilibrium potential measurements are shown in Fig. 1 as plots of the formal potentials (versus SCE) for the Cu (I)—

Cu (O) and Cu (II)—Cu (I) couples as a function of pH. From the figure, it is apparent that K for the reaction $\text{Cu (II)} + \text{Cu} \rightleftharpoons 2\text{Cu (I)}$ increases with pH, and calculation shows that it reaches a limiting value of about 60 at pH values above 9,2. The slope of the linear portion (below a pH value of 9) of the Cu (I)—Cu (O) line of -120 mV per pH unit is consistent with the formation of a strong $\text{Cu(NH}_3)_2^+$ complex. A value of 10,3 for $\log K_1K_2$ is obtained from the extrapolated value of E°_f at a pH value of 8, on the assumption that $E_{\text{Cu(I)/Cu(O)}} = 0,518$ V (versus NHE). This is in good agreement with the value of 10,86 quoted in Table I.

Similarly, the slope of the Cu (II)—Cu (I) line of -68 mV per pH unit confirms the stability-constant data, which indicate increased stabilization of the copper (II) state relative to copper (I) at higher pH values in terms of increasing amounts of the triamines and tetramines. The value of -68 mV per pH unit suggests that the predominant copper (II) species in this range of pH is the triammine (predicted -60

mV) with small amounts of the tetramine (predicted -120 mV).

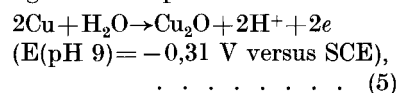
Studies of Anodic Dissolution

Copper

Linear sweep voltammetric curves for the anodic dissolution of a rotating copper disc in $1\text{M (NH}_4)_2\text{CO}_3$ solutions of various pH values at a sweep rate of $0,25$ V min^{-1} are shown in Fig. 2. The curves are not compensated for iR drops and can therefore be treated quantitatively only at low currents. The inflection at about -50 mV in the curves at the lower pH values is probably associated with the formation of copper (II).

A plot of the potential at constant current (1,0 mA) versus the pH value is linear, with a slope of 104 mV versus pH value, suggesting second-order dependence on OH^- (or free NH_3) concentration.

Partial passivation of the copper is observed at low concentrations of free ammonia as shown by the cyclic voltammograms in Fig. 3. The peak at about $-0,15$ V can be assigned to the process



and that at $+0,040$ V to the process

$$\text{Cu}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{Cu} + 2\text{H}^+ + 2e$$

(E(pH 9) = $-0,11$ V versus SCE).
 (6)

The voltammogram (c) obtained in the absence of ammonia also exhibits a shoulder at potentials anodic to $-0,2$ V and a cathodic peak at $-0,32$ V, which agrees well with that predicted for the reverse of reaction (5). In addition, a cathodic transient is evident in the region of $-0,10$ V during the cathodic sweep in voltammogram (b). The excellent agreement of this value with that predicted for the reverse of reaction (6) lends further support to the above assignments. The absence of cathodic peaks for reaction (5) in the presence of ammonia suggests that the Cu_2O formed dissolves relatively rapidly in the solution. A comparison of the peak heights for voltammograms (a) and (b) indicates that the rate of the oxide-dissolution reaction is approximately proportional to the square of the ammonia concentration.

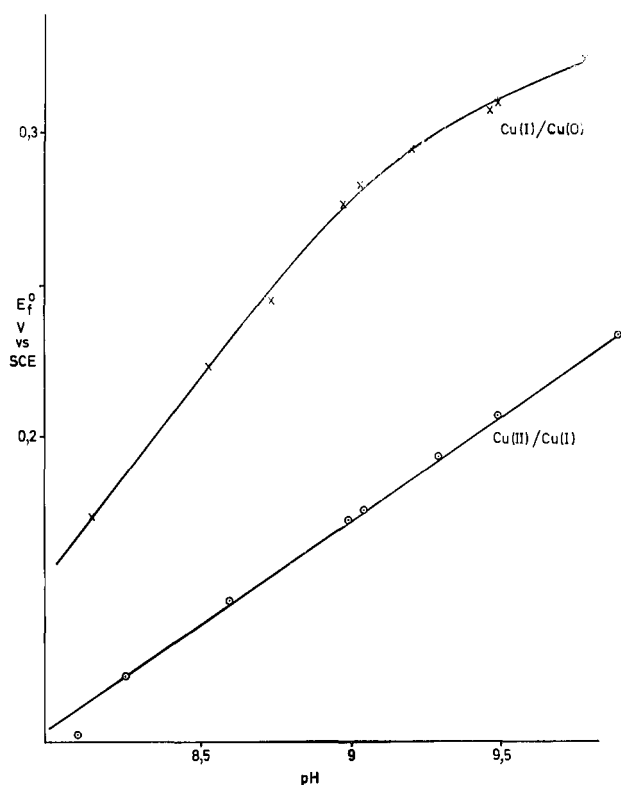


Fig. 1—Variation of the formal reduction potentials of the Cu (II)/Cu (I) and Cu (I)/Cu (O) couples with pH in $1\text{M (NH}_4)_2\text{CO}_3$

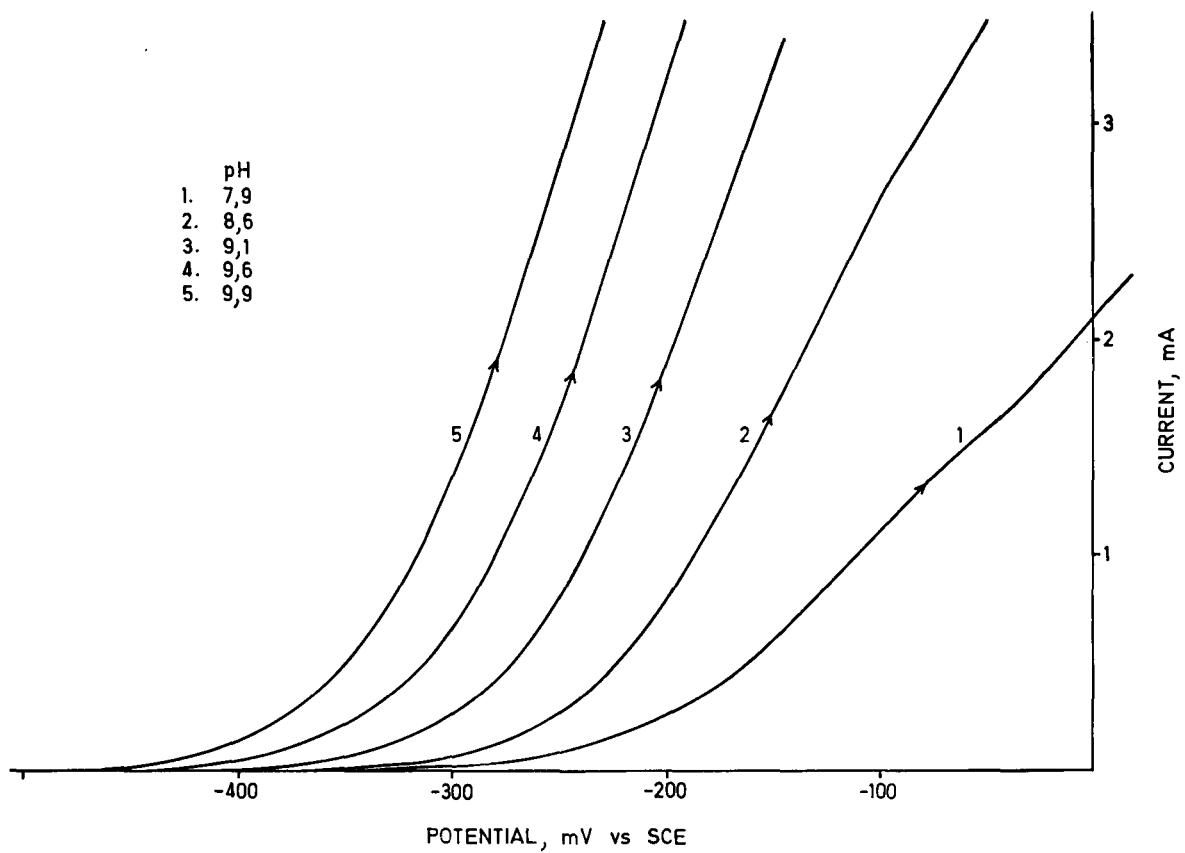


Fig. 2—Linear sweep voltammograms ($0,25 \text{ V min}^{-1}$) for the anodic dissolution of a rotating copper disc (250 rev/min) at various pH values in $1\text{M } (\text{NH}_4)_2\text{CO}_3$

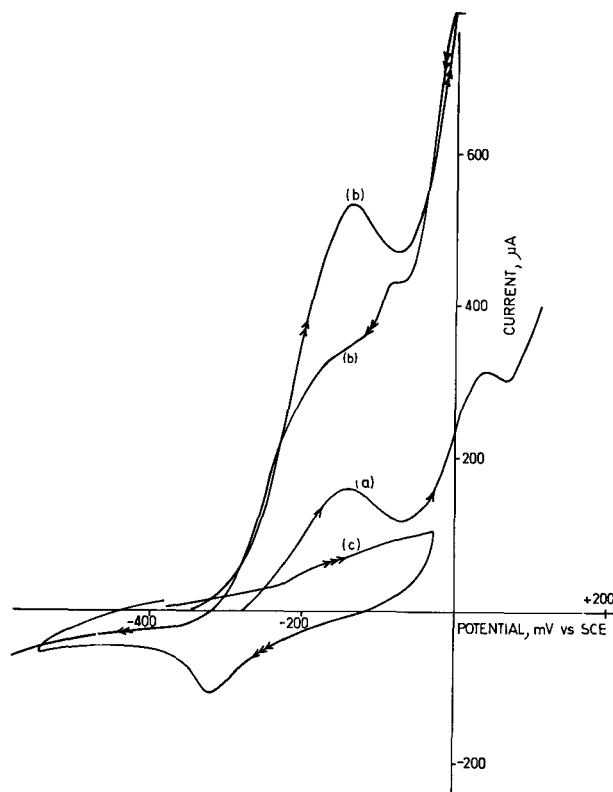


Fig. 3—Cyclic voltammograms for a rotating copper disc (1000 rev/min) in 1M NaClO_4 , containing (a) $0,01\text{M } (\text{NH}_4)_2\text{CO}_3$, (b) $0,02\text{M } (\text{NH}_4)_2\text{CO}_3$ at $0,3 \text{ V min}^{-1}$, and (c) $0 (\text{NH}_4)_2\text{CO}_3$ at 3 V min^{-1}

Nickel

Voltammograms for the anodic dissolution of a rotating nickel electrode in 1M $(\text{NH}_4)_2\text{CO}_3$ solution at a pH value of 9,65 are shown in Fig. 4. The curves exhibit a typical passivation peak at about -300 mV. A comparison between these curves and that obtained in the absence of ammonium ions, i.e., in 1M NaClO_4 solution having a pH value of 10, is shown in Fig. 5. It is apparent that the formation of oxide or chemisorbed oxygen at $-0,50$ V in NaClO_4 (E_f^0 for Ni-NiO at a pH value of 10 is $-0,70$ V) is suppressed in the presence of ammonium carbonate. This is presumably due to adsorption of NH_4^+ (or NH_3) at the negative potentials involved or to dissolution of the oxide film in the ammonia solution. However, the actual passivating species is possibly similar because of the presence of a cathodic peak in the region of -800 to -900 mV in both cases.

As shown in Fig. 4, the passive layer can be slowly removed if the

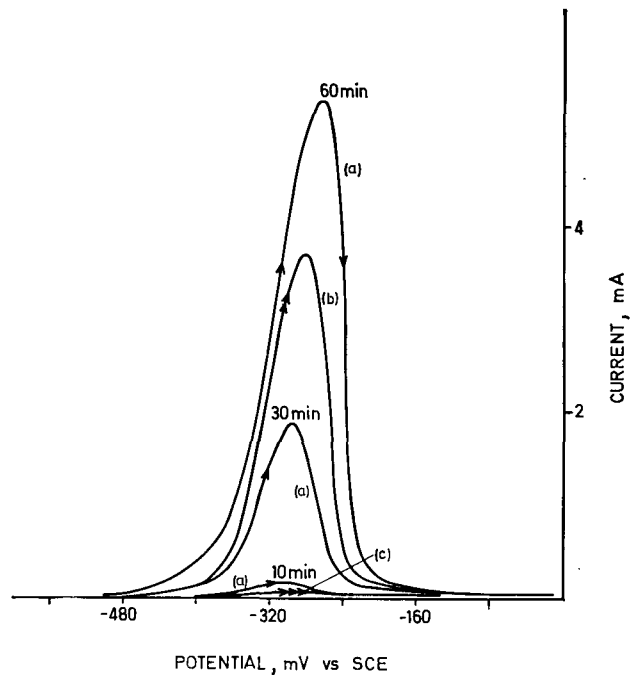


Fig. 4—Linear sweep voltammograms ($0,25 \text{ V min}^{-1}$) for the anodic dissolution of a rotating nickel disc (1000 rev/min) in $1\text{M } (\text{NH}_4)_2\text{CO}_3$.
 (a) Held open-circuit for various times before sweep
 (b) Held at -1030 mV for 30 s before sweep
 (c) Held at -700 mV for 30 s before sweep

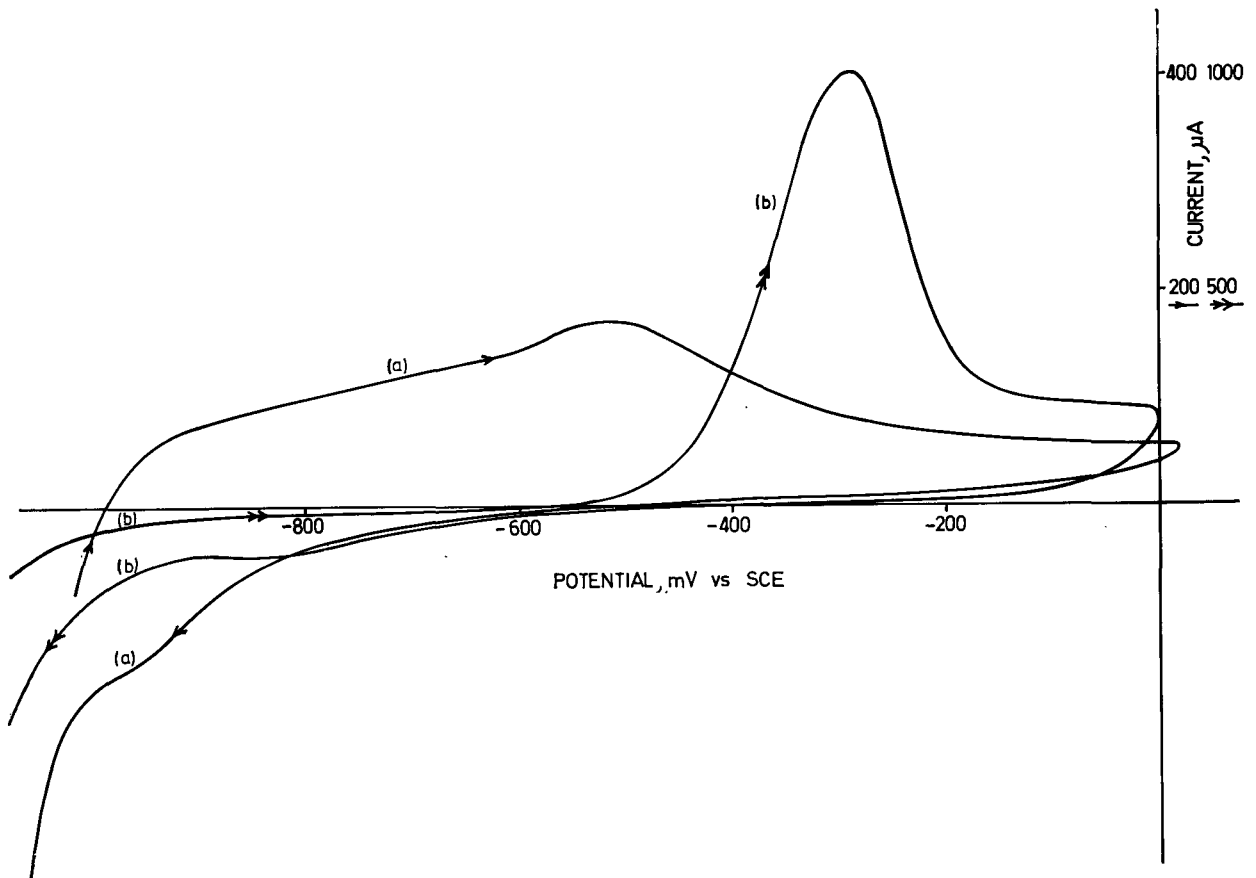


Fig. 5—Cyclic voltammograms (6 V min^{-1}) for a rotating nickel disc (1000 rev/min) in (a) $1\text{M } \text{NaClO}_4$, pH 10 and (b) $1\text{M } (\text{NH}_4)_2\text{CO}_3$

disc is simply left to stand in deoxygenated $(\text{NH}_4)_2\text{CO}_3$ solutions, increasing amounts being removed in 10, 30, and 60 minutes. Reduction of the passive layer is also possible as shown by the curve in which the cathodic limit was increased to -1030 mV, i.e., into the region of hydrogen evolution. These observations are in accord with the observations made by Inco⁷ in the leaching of nickel that activation in ammoniacal solutions in the absence of air was necessary prior to dissolution.

Copper-Nickel Alloys

Steady-state potentiostatic current-potential curves for the anodic dissolution of various copper-nickel alloys in 1M $(\text{NH}_4)_2\text{CO}_3$ solution are shown in Fig. 6. It is apparent from the curves that passivation is observed only at low potentials for the alloys having a copper content of 50 per cent or less, the 70 per cent alloy giving rise to a curve similar to that for pure copper. Analysis of the products of dissolution shows that no preferential solution of one of the components occurs. Similar results were obtained by Uhlig¹⁰ for the anodic dissolution of copper-nickel alloys in sulphuric acid solutions. Passive properties were found to begin at a critical copper content of between 60 and 65 per cent, which coincided with an unfilled *d*-band of electronic-energy levels as measured by magnetic saturation moment or electronic specific heat. Uhlig proposed the theory that the passive film on copper-nickel alloys is made up largely of chemisorbed oxygen, the formation of which is favoured by surface *d*-electronic vacancies. When such vacancies (0,6 per atom for nickel) are filled by valence electrons of the alloyed atom (1 unpaired electron per atom for copper), passive properties are no longer observed, presumably because oxygen is no longer chemisorbed.

Studies of Chemical Dissolution

Copper

Preliminary experiments suggested that the rate of dissolution of copper from the disc of the ring-disc electrode as a result of reaction (5) is controlled by mass transport,

i.e., the rate (as measured in terms of a ring current, i_R) is proportional to the copper (II) concentration and dependent on the rotation speed. Application to a rotating disc of the Levich equation¹¹ for convective diffusion results in a relation between the ring current and the

product $[\text{Cu(II)}]\omega^{\frac{1}{2}}$, where ω is the disc rotation speed as derived in the Appendix. A log-log plot of this relation for data in the range $3 \times 10^{-3}\text{M}$ to $8 \times 10^{-2}\text{M}$ copper (II) is shown in Fig. 7. The results over a more-extensive range ($2 \times 10^{-2}\text{M}$ to 0,6M) are summarized in Fig. 8.

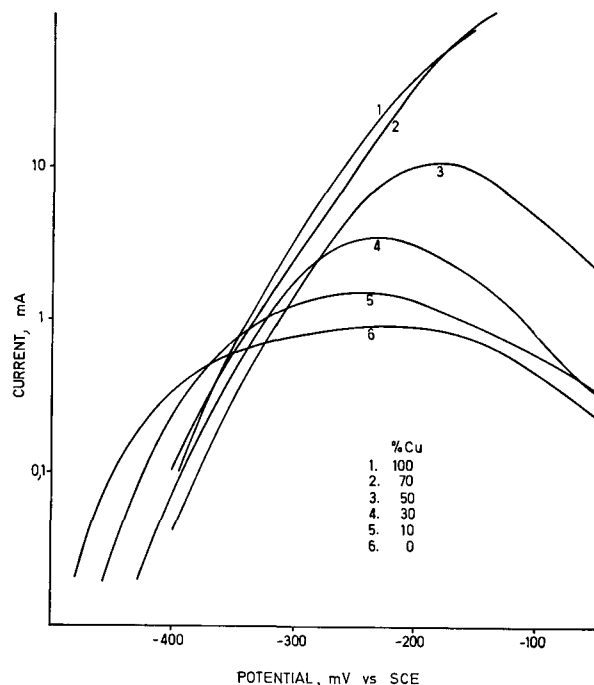


Fig. 6—Steady-state current-potential curves for the anodic dissolution of rotating copper-nickel alloy discs (1000 rev/min) in 1M $(\text{NH}_4)_2\text{CO}_3$

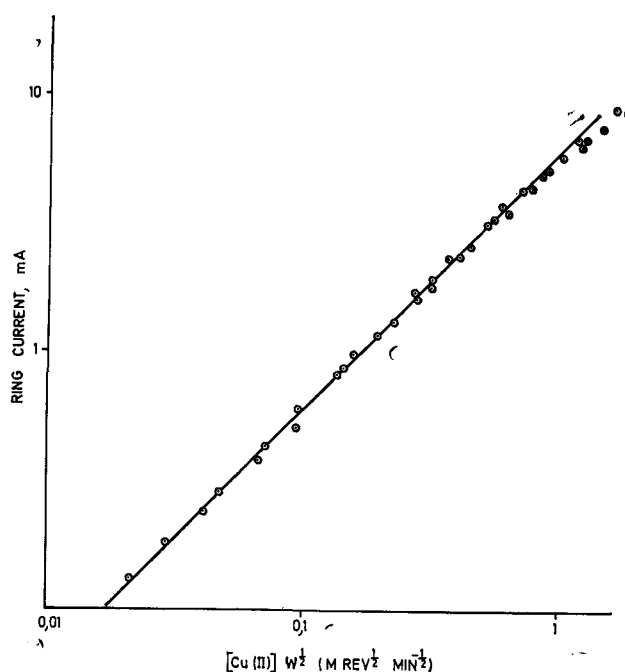


Fig. 7—Variation of the ring current due to copper dissolution with disc rotation speed and copper (II) concentration in 1M $(\text{NH}_4)_2\text{CO}_3$

The deviations from linearity at high copper (II) concentrations are more apparent in this case. As outlined in the Appendix, the slope of the lines in Figs. 7 and 8 should be given by $19,5D_2^{2/3}$, where D_2 is the diffusion coefficient of copper (II). — calculation yields D_2 values of $5,7 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ and $5,0 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ respectively. An analysis of the diffusion-limited current for the reduction of copper (II) to copper (I) at the rotating disc measured from the curves in Fig. 13, yields a value of $6,9 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ for D_2 , which is in reasonable agreement with the above values.

The effect of pH on the dissolution rate in 1M $(\text{NH}_4)_2\text{CO}_3$ containing 0,02M copper (II) is shown in Fig. 9. The pH value was adjusted by the addition of sulphuric acid or sodium hydroxide. Below a pH value of 9,3, pH has little effect on the rate, which decreases with increasing pH above 9,3. A similar decrease was noted in a 0,2M copper (II) solution, and, in addition, the rate decreased at pH values below about 9,3. The addition of 1M $(\text{NH}_4)_2\text{SO}_4$ to the solution had the effect of increasing the rate at low pH values (below 8,5) and decreasing it above 8,5. The effects on the rate of variations in the ammonium carbonate concentration, as demonstrated by the curves in Fig. 10, parallel those observed as a result of variations in pH, which are therefore simply a reflection of variations in free NH_3 concentration. Plots of ring current versus rotation speed for several pH values in 0,20M copper (II) are shown in Fig. 11. The difference between the measured rates of dissolution and that for a process controlled by mass transport (broken line) are seen to be greatest at the low pH values.

Reasons for the above effects become apparent when the potential of the copper disc is measured during dissolution. The effect of the copper (II) concentration on this potential is shown in Fig. 12 as a plot of $\log [\text{Cu} (\text{II})]$ versus potential. The resulting curve parallels that for the anodic dissolution (also shown), thus confirming that the chemical dissolution is first order in copper (II) over the range 10^{-4}M to 10^{-3}M . Dissolution rates in 10^{-3}M

and $5 \times 10^{-3}\text{M}$ solutions, as measured by the ring current, are shown in Fig. 12. These points fall close to the anodic current-potential curve, thus confirming the electrochemical nature of the process. Also shown are the potentials observed in oxygenated-saturated and air-

saturated solutions. It is apparent that the rate in oxygenated solution (10^{-3}M O_2) is equivalent to that in $5 \times 10^{-3}\text{M}$ copper (II) solution. Since the ratio of D_{O_2} to $D_{\text{Cu}(\text{II})}$ is about 2,6, this implies that there are only two electrons involved in the reduc-

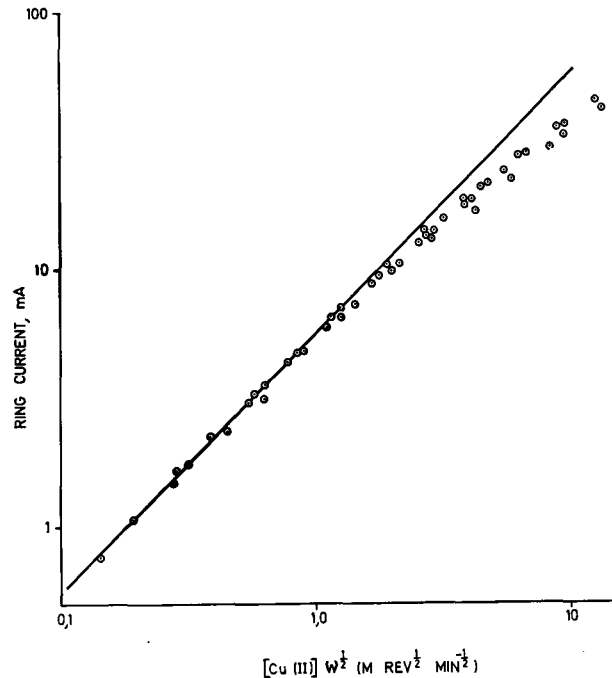


Fig. 8—Variation of the ring current due to copper dissolution with disc rotation speed and copper (II) concentration over a wider range in 1M $(\text{NH}_4)_2\text{CO}_3$

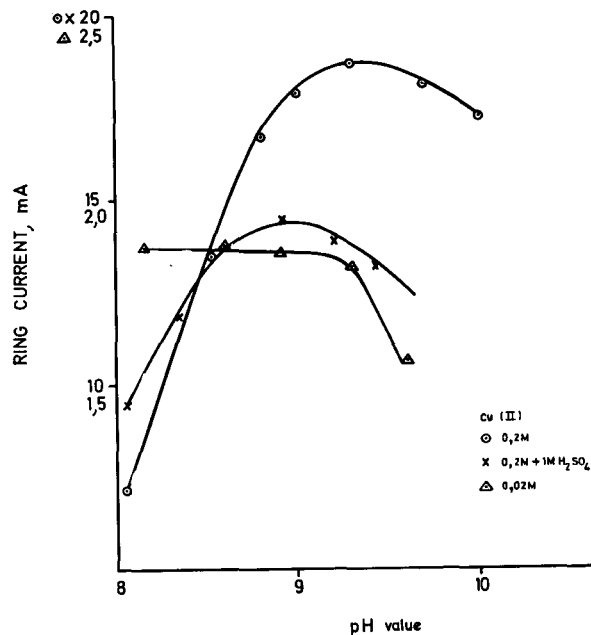


Fig. 9—Variation of ring current due to copper dissolution with pH at 250 rev/min in 1M $(\text{NH}_4)_2\text{CO}_3$

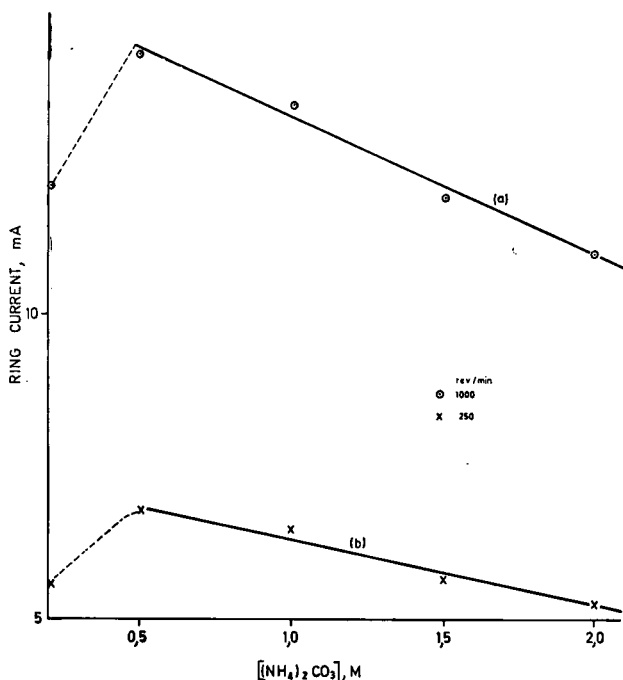


Fig. 10—Variation of the ring current due to copper dissolution with $(\text{NH}_4)_2\text{CO}_3$ concentration at a pH value of 9

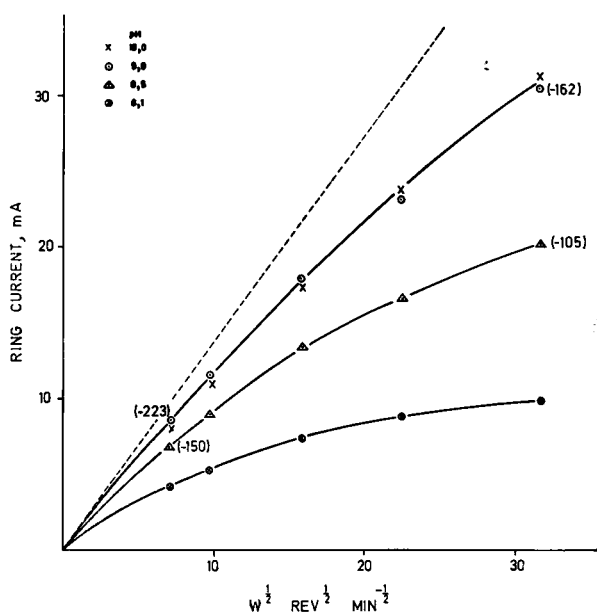


Fig. 11—Variation of the ring current due to copper dissolution with disc rotation speed in $1\text{M } (\text{NH}_4)_2\text{CO}_3$ containing $0.2\text{M } \text{Cu(II)}$. Values in parentheses are the potentials of the copper disc measured during dissolution

tion of each O_2 molecule (i.e., peroxide, and not water, is the initial product).

For the chemical-dissolution reaction to be mass-transport controlled, these potentials must fall in the diffusion-controlled region for the reduction of copper (II) to copper (I). Fig. 13 shows linear sweep voltammograms for this reduc-

tion on a platinum disc at various pH values. The second wave at about -0.5 V corresponds to reduction to the metal. Several selected values of the potentials measured during dissolution are indicated on the curves. These potentials were obtained during the experiments, the results of which are given in Fig. 11, in which the corresponding points

have been indicated. It is apparent that both decreasing pH and increasing agitation result in mixed potentials that are below (less cathodic than) those required for the diffusion-controlled reduction of copper (II), and hence a dissolution controlled by mass transport. It must be pointed out that no quantitative estimates of these effects can be made on the basis of the available data, which were obtained on a platinum electrode at copper (II) concentrations considerably lower than that used for the measurements of mixed potentials. However, the general conclusion is probably valid, i.e., that the difference in the formal reduction potentials of the two couples involved (100 mV at pH values greater than 9 and 50 mV at a pH value of 8) is not sufficient to ensure that the mixed potential will always fall in the potential region where the reduction of copper (II) is diffusion controlled.

The effect of temperature in the range 20 to 50°C on the rate of dissolution in 0.08M copper (II) was investigated. Activation energies of 24.7 kJ mol^{-1} at 1000 rev/min , 19.3 kJ mol^{-1} at 250 rev/min , and 17.2 kJ mol^{-1} at 50 rev/min were obtained. The increase with increasing agitation is in accord with the increasing departure of the rate from mass-transport control with increasing rotation speed.

The effect of added copper (I) on the dissolution rate was determined from the addition of known amounts of cuprous chloride to the leaching solution. The concentration of copper (I) was determined *in situ* at the end of the run by amperometric titration with standard dichromate solution, zero ring current being used to indicate the end-point. A plot of $[\text{Cu(II)}]\omega^{1/2}$ versus i_R for a series of experiments at approximately 0.04M copper (II) with the addition of increasing amounts of copper (I) is shown in Fig. 14. It can be seen that, except for small decreases in i_R at the highest concentration of copper (I) — a ratio of copper (I) to copper (II) of 7 to 5 — there is a negligible effect on the dissolution rate under these conditions.

As shown in the Appendix, the

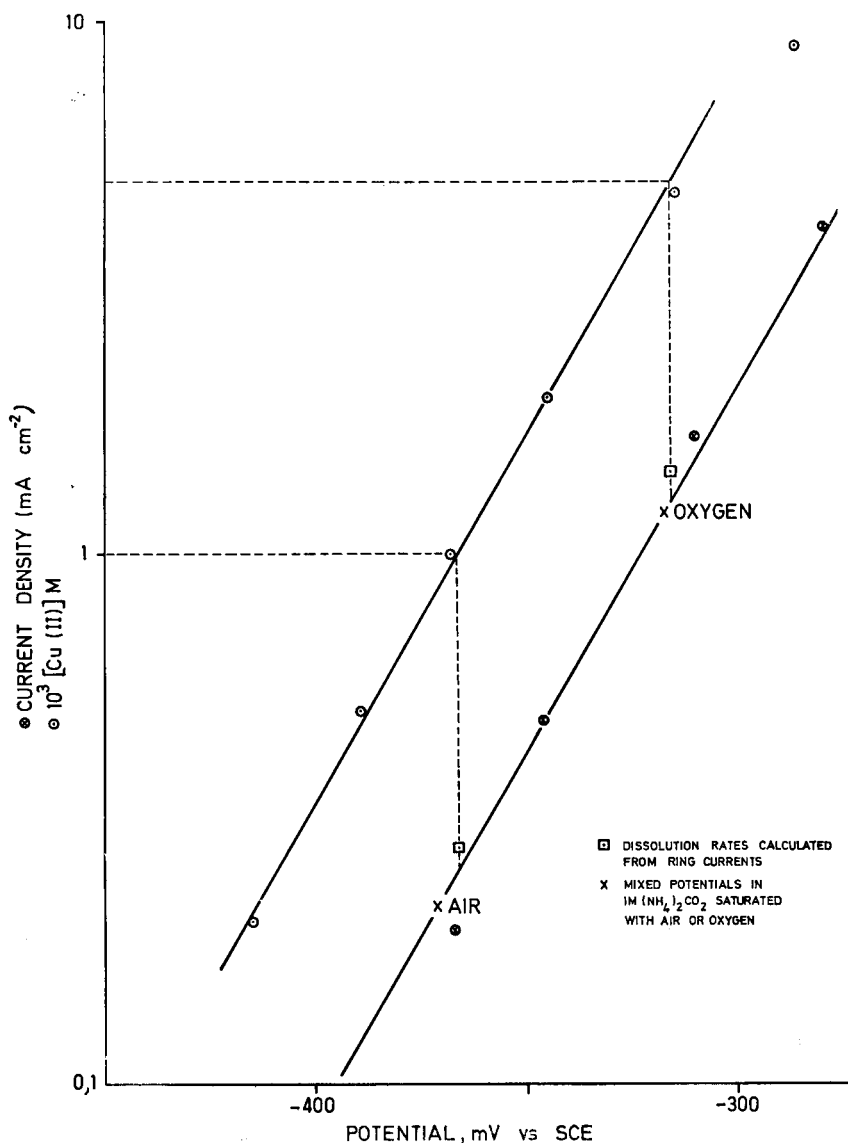


Fig. 12—Lower: Steady-state current-potential curve for the anodic dissolution of a rotating copper disc (500 rev/min) in 1M $(\text{NH}_4)_2\text{CO}_3$. Upper: Variation of the mixed potential of the disc with Cu (II) concentration in 1M $(\text{NH}_4)_2\text{CO}_3$.

dissolution rate (measured by i_R) is proportional to the copper (II) concentration if K is large, but is proportional to the square root of the concentration if K is small. Data obtained in 1M $(\text{NH}_4)_2\text{SO}_4$ having a pH value of 6.6 where K is certainly less than 1, are shown in Fig. 15, in which the better fit to a root dependence is confirmation of the theory. These results reinforce the remarks made in the introduction about the source of the apparent square-root dependence of the rate on the copper (II) concentration as observed by some workers, i.e., such a dependence

can be obtained only under conditions in which K is small.

Nickel

Preliminary experiments showed that the nickel passivated at relatively low copper (II) concentrations, as would be predicted from the anodic-dissolution characteristics outlined previously. Plots of $[\text{Cu (II)}]_{\omega}^{1/2}$ versus i_R are shown in Fig. 16 for the pre-passive region. The excellent linearity and slope, which yield an estimate of $5.5 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ for the diffusion coefficient of copper (II) in reasonable agreement with the values determined from the copper leaching

results, confirm the diffusion-controlled nature of the reaction. It was noted that passivation occurred at a copper (II) concentration of $6.0 \times 10^{-3} \text{M}$ in a 1M $(\text{NH}_4)_2\text{CO}_3$ solution adjusted to a pH value of 10 with sodium hydroxide, and at a concentration of $1.6 \times 10^{-3} \text{M}$ in a 1M $(\text{NH}_4)_2\text{CO}_3$ solution at a pH value of 9. In the pre-passive region, however, all three solutions gave the same dissolution rates. It was found that a passivated disc could be re-activated if left to stand in a deoxygenated $(\text{NH}_4)_2\text{CO}_3$ solution for approximately an hour, after which it exhibited dissolution behaviour similar to its pre-passive characteristics. On passivation, the potential of the nickel disc increased from about -400 mV to approximately -200 mV , i.e., into the passive region as found in the anodic dissolution studies (Fig. 4).

CONCLUSIONS

This study has conclusively demonstrated that the dissolution of both copper and nickel in ammoniacal solution containing copper (II) occurs electrochemically as reactions in which the anodic dissolution of the metal is coupled to cathodic reduction of copper (II). In the regions of active dissolution, the rate of dissolution has been shown to be determined mainly by mass transport of copper (II) to the metal surface, although deviation from such behaviour under conditions of high copper (II) concentrations, low pH, and increased agitation in the case of copper have been observed. Similar observations have been made by other investigators and, as demonstrated in this work, are to be expected as a result of the small difference in the equilibrium potentials of the half-reactions under these conditions. No such limitation is expected in the case of nickel dissolution, although a practical demonstration of this cannot be made because passivation of the nickel surface occurs at relatively low copper (II) concentrations. This passivation in the case of nickel, and also nickel-copper alloys of more than about 50 per cent nickel, is an obvious disadvantage in an ammoniacal leaching procedure for nickel, unless, as was done by

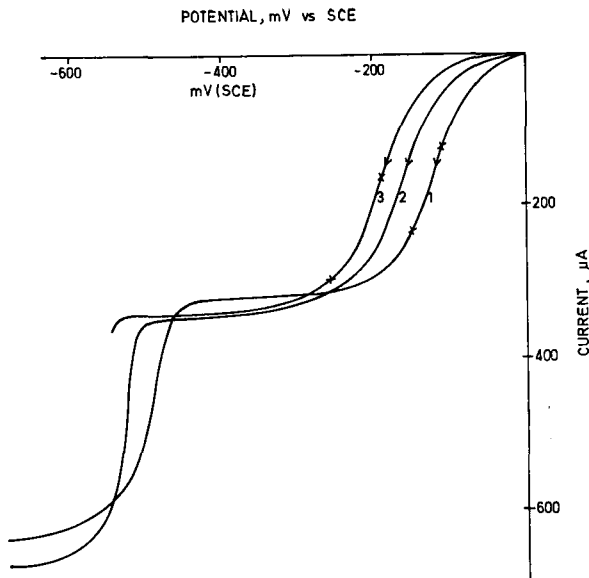


Fig. 13—Linear sweep voltammograms ($0,25 \text{ V min}^{-1}$) for the reduction of Cu (II) on a rotating platinum disc (250 rev/min) in $1\text{M } (\text{NH}_4)_2\text{CO}_3$ containing (1) $1,82 \times 10^{-3} \text{ M Cu (II)}$ at pH 8,6 (2) $1,88 \times 10^{-3} \text{ M Cu (II)}$ at pH 8,8 (3) $1,92 \times 10^{-3} \text{ M Cu (II)}$ at pH 9,2. Points (X) correspond to those indicated in Fig. 11

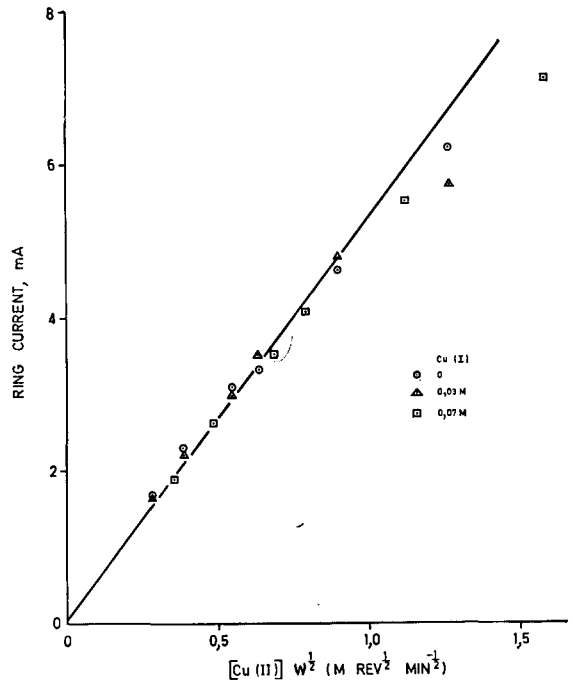


Fig. 14—Variation of the ring current due to copper dissolution with disc rotation speed and Cu (II) concentrations in $1\text{M } (\text{NH}_4)_2\text{CO}_3$

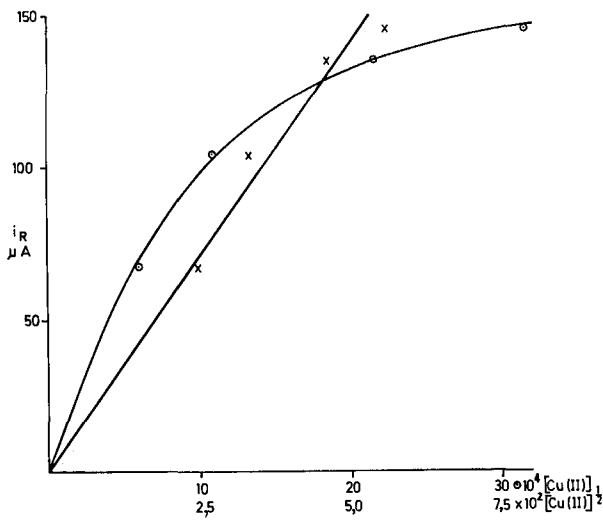


Fig. 15—Variation of the ring current due to copper dissolution with Cu (II) concentration in $1\text{M } (\text{NH}_4)_2\text{SO}_4$ pH 6,6 at 1000 rev/min

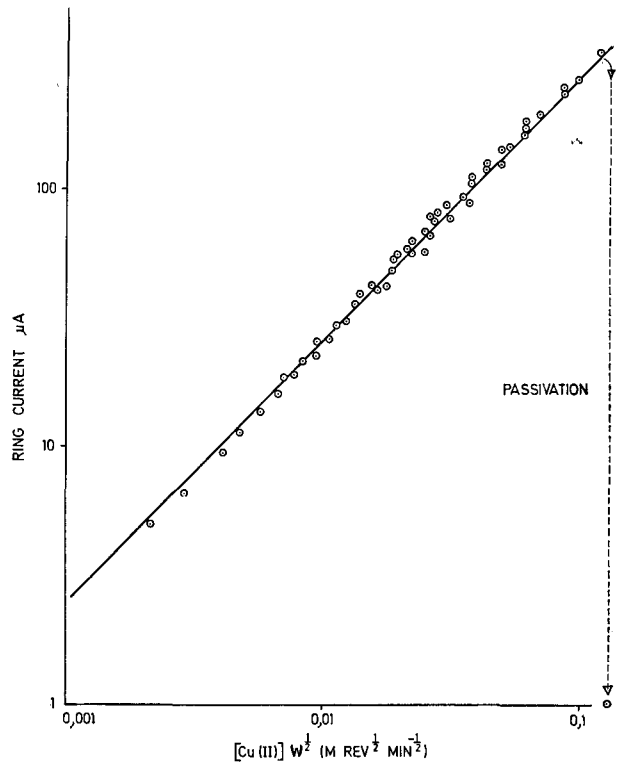


Fig. 16—Variation of the ring current due to nickel dissolution with disc rotation speed and Cu (II) concentration in $1\text{M } (\text{NH}_4)_2\text{CO}_3$

Inco⁷ and confirmed in this work, provision is made for frequent activation.

Passivation of copper was not observed during chemical dissolution under the conditions employed during this investigation. However, as Smith *et al.*⁶ and Halpern^{3,4} have shown, passivation can occur if the ratio of copper (II) to ammonia is high. Anodic dissolution experiments under such conditions have revealed the existence of two passivating oxides that have been electrochemically identified as Cu₂O and CuO. The latter, however, cannot be formed if copper (II) is the oxidant. The existence of an optimum pH value in the region of 9 to 9.5 for the rate of copper dissolution and the decreased rates with high ammonia concentrations have been interpreted in terms of their effects on the rates of the half-reactions involved.

The absence of any appreciable effect of copper (I) on the rate has an important bearing on the extent to which the copper (II) level can be lowered during leaching. This observation agrees with that made by Smith *et al.*⁶, who found a small (about 20 per cent) decrease in rate when copper (I) was added in amounts equivalent to the copper (II).

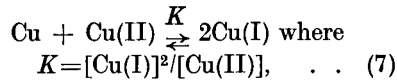
Finally, several of the discrepancies in the literature regarding the mechanism of the dissolution reaction have been clarified. In particular, conditions under which the dependence of the rate on the copper (II) concentration will become one-half order have been predicted and confirmed experimentally in ammonium sulphate solutions at low pH values.

APPENDIX

RING - DISC THEORY FOR CHEMICAL STRIPPING REACTIONS

Consider the chemical stripping of copper at a rotating disc by a

solution of copper (II).



and assume that this equilibrium is maintained on the surface of the disc, i.e., that the process is transport limited.

$$\text{At the disc surface,} \\ \text{flux of Cu (II) to surface} \\ = -\frac{1}{2} \text{flux of Cu (I) from} \\ \text{surface.} \quad \dots \dots \dots (8)$$

The Levich¹¹ equation for a rotating disc can be written as

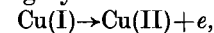
$$\text{flux} = 0,62D^{2/3}\nu^{-1/6}\omega^{1/2} \\ \{ \text{concentration in bulk} - \\ \text{concentration at} \\ \text{surface} \}, \quad \dots \dots \dots (9)$$

where D is the diffusion coefficient, ν the kinematic viscosity of the solution, and ω the rotation speed in rad s⁻¹.

$$\text{Substitution of (9) in (8) yields} \\ D_2^{2/3} \{ [\text{Cu(II)}]_o - [\text{Cu(II)}]_s \} \\ = \frac{1}{2} D_1^{2/3} [\text{Cu(I)}]_s = 0, \quad \dots \dots (10)$$

where subscripts s and o denote surface and bulk quantities respectively, and subscripts 1 and 2 refer to Cu (I) and Cu (II) respectively, and $[\text{Cu (I)}]_o = 0$.

Now if Cu (I) is detected at the ring by the reaction



then one can write for the collection efficiency, N , $N = i_R / FA$ (flux of Cu (I) produced at the disc), where i_R is the ring current and A is the disc area;

$$\text{i.e., } N = i_R / \{ (FA) \\ 0,62D_1^{2/3}\nu^{-1/6}\omega^{1/2} \\ [\text{Cu(I)}]_s \},$$

$$\text{or } \text{Cu(I)}_s = \delta i_R / \omega^{1/2}, \\ \text{where } \delta = 1 / (0,62FAD_1^{2/3}\nu^{-1/6}N).$$

Substitution in (10) yields, on rearrangement,

$$\text{Cu(II)}_s = \text{Cu(II)}_o \\ - D_1^{2/3} \delta i_R / 2\omega^{1/2} D_2^{2/3},$$

and substitution in (7) yields

$$\frac{\omega^{1/2} [\text{Cu(II)}]_o}{i_R} = \frac{D_1^{2/3} \delta}{2D_2^{2/3}} + \frac{\delta i_R}{K\omega^{1/2}}.$$

This equation has two limiting conditions.

(i) K very large, in which instance

$$i_R = \frac{2D_2^{2/3}\omega^{1/2} [\text{Cu(II)}]_o}{D_1^{2/3}\delta},$$

i.e., in this case, $[\text{Cu(II)}]_s = 0$ and i_R will be proportional to the product $\omega^{1/2} [\text{Cu(II)}]_o$.

(ii) K very small, in which instance

$$i_R = \frac{K^{1/2}\omega^{1/2} [\text{Cu(II)}]_o^{1/2}}{\delta^{1/2}}$$

i.e., in this case, $[\text{Cu(II)}]_s = [\text{Cu(II)}]_o$ and i_R is proportional to the product $\omega^{1/2} [\text{Cu(II)}]_o^{1/2}$.

ACKNOWLEDGEMENT

This paper is published by permission of the Director General, National Institute for Metallurgy.

REFERENCES

1. LANE, R. W., and McDONALD, H. J. Kinetics of the reaction between copper and aqueous ammonia. *J. Am. Chem. Soc.*, vol. 68. 1946. pp. 1699-1704.
2. LU, B. C. Y., and GRAYDON, W. F. Rates of copper dissolution in aqueous ammonium hydroxide solutions. *J. Am. Chem. Soc.*, vol. 77. 1955. pp. 6136-6139.
3. HALPERN, J. The kinetics of the dissolution of copper in aqueous ammonia. *J. Electrochem. Soc.*, vol. 100. 1953. pp. 421-428.
4. HALPERN, J. Some aspects of the physical chemistry of hydrometallurgy. *J. Metals*, 1957. pp. 280-289.
5. HABASHI, F. Kinetics and mechanism of copper dissolution in aqueous ammonia. *Ber. Bunsengesellschaft*, vol. 67. 1963. pp. 402-406.
6. SMITH, K. A., LOWER, G. W., and HOCKINGS, W. A. Kinetics of leaching metallic copper in aqueous cupric ammonium carbonate solutions. *PROC. INT. SYMP. ON HYDROMETALLURGY*, Chicago, 1973. pp. 265-292.
7. INCO. Development of the Inco iron ore recovery process. *Can. Min. Metall. Bull.*, vol. 59. 1956. pp. 337-343.
8. MORIOKA, S., and SHIMAKAGE, K. Studies on the ammonia pressure leaching of metallic nickel and copper powders. *Trans. Japan Inst. Metals*, vol. 12. 1971. pp. 197-205.
9. MARTELL, A. E., and SILLEN, L. G. Stability constants. London, Chemical Society, *Special Publication no.* 17. 1964.
10. URLIG, H. H. Effect of electron configuration on the passive properties of Cu-Ni alloys. *Electrochim. Acta*, vol. 16. 1971. pp. 1939-1947.
11. LEVICH, V. G. Physicochemical hydrodynamics. Engelwood Cliffs (New Jersey), Prentice-Hall, 1962.