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The passivation of iron in ammoniacal solutions containing copper (II) ions

Anna D’Aloya and Aleksandar N. Nikoloski*

Parker Centre, Murdoch University, South Street, Murdoch, WA 6150, Perth, Australia

Abstract

In the present study it was found that the presence of millimolar amounts of copper (II) ions in ammoniacal solutions leads to the spontaneous formation of a stable passive layer on metallic iron and iron alloys with nickel and cobalt, under conditions in which they would otherwise remain in active dissolution. This finding may be of significance to industrial processes which employ ammoniacal solutions to leach metal values from materials rich in metallic iron, such as, for example, laterite ores which have undergone a reductive pre-treatment.

The spontaneous passivation is found to take place regardless of the presence or practical absence of dissolved oxygen, and occurs more readily the higher the copper concentration and the lower the ammonia-ammonium bicarbonate concentration, though it does not take place in ammonia-free aqueous solutions of similar copper (II) ion concentrations.

Electrochemical and scanning electron microscopy / energy dispersive X-ray spectroscopy (SEM/EDX) investigations conducted as part of this study showed that the observed passivation is promoted by the cementation of copper onto the actively dissolving iron surface, and subsequently by its re-dissolution. Such process is thought to create favourable conditions which promote the formation of a stable passive layer on the iron surface.

Keywords: Caron; process; iron; nickel; cobalt; passivation; ammonia; copper.

1. Introduction

Ammoniacal solutions are often employed in hydrometallurgical processes, such as the leaching stage of the Caron process, in which nickel and cobalt are recovered from laterite ores by means of a reductive roast which is followed by ammoniacal leaching. Due to the ferruginous nature of the ore, the pyrometallurgical pre-treatment step results in the material to be leached having a relatively high content of metallic iron, as well as iron-nickel and iron-cobalt alloys, from which the metal values are to be recovered. The leaching behaviour of nickel and cobalt is hence inevitably influenced by the behaviour of iron and its alloys in ammoniacal solutions. In fact, the passivation of iron has been identified as one of the possible factors limiting the efficiency of the Caron process in extracting nickel and cobalt from pre-reduced laterite ores (Kho et al., 1992; Kim et al., 1991; Lee et al., 1985; Nicol et al., 2004; Nikoloski and Nicol, 2006; Osseo-Asare et al., 1983).

Based on voltammetric measurements conducted on metallic iron and copper, Nikoloski predicted that the cementation of dissolved copper onto iron is likely to occur under Caron process conditions (Nikoloski and Nicol, 2006). In fact, copper cementation onto iron has been experimentally observed during the anodic dissolution of Cu-Co-Fe-Pb alloys in ammonia/ammonium chloride solutions (Burzynska et al., 2008). Senenayake and co-workers also suggested it takes place during dissolution of ferronickel alloys with small amounts of cobalt and copper in ammonia-ammonium carbonate solutions replicating the Caron process conditions (Senenayake et al., 2010). However, it has not been shown so-far that copper (II) ions play a catalytic role in the spontaneous passivation of iron under conditions in which it would otherwise continue to dissolve anodically.

Although the cementation of copper onto iron has been exploited for centuries and studied extensively in view of a wide variety of applications, the focus has mainly been on non-ammoniacal, usually acidic solutions (Agrawal and Kapoor, 1982; Biswas and Reid, 1972; Karavasteva, 2005; Rickard and Fuerstenau, 1968). On the other hand, the electrodeposition of copper from ammoniacal solutions onto substrates other than iron has been studied extensively. Based on thermodynamic and electrochemical studies, numerous authors agree that the electrodeposition of copper from ammoniacal solutions of different compositions occurs via the reduction of cupric tetrammine to cuprous diammine, which is then further reduced to metallic copper (Darchen et al., 1997; Giannopoulou et al., 2009; Giannopoulou et al., 2009; Giannopoulou et al., 2009).

* Corresponding author. Tel.: + 61 8 9360 2835; fax: + 61 8 9360 6343.

E-mail address: A.N.Nikoloski@murdoch.edu.au (A.N. Nikoloski).
Graham et al., 2002; Grujicic and Pesic, 2005; Nila and González, 1996a; Nila and González, 1996b; Ramos et al., 2001; Vazquez-Arenas et al., 2007a; Vazquez-Arenas et al., 2007b). The direct reduction of cupric tetrammine to metallic copper is also thought to take place at more negative applied potentials (Grujicic and Pesic, 2005). In addition, Grujicic states that the anodic dissolution of metallic copper in ammoniacal solution occurs as a two electron oxidation process to cupric tetrammine, which could be the case when the oxidant is dissolved oxygen and no cupric tetrammine is present in the solution. In the presence of cupric tetrammine however, the dissolution is generally believed to take place via the reproportionation of metallic copper and cupric tetrammine to form cuprous diammine (Darchen et al., 1997; Grujicic and Pesic, 2005; Nicol, 1975; Nikoloski and Nicol, 2006; Ramos et al., 2001). In the presence of oxygen, the cupric tetrammine is regenerated by oxidation of the cuprous diammine, the Cu(II)/Cu(I) couple therefore functioning as a redox mediator.

2. Methods and materials

The electrochemical experiments were carried out using a model 6310 EG&G Princeton Applied Research potentiostat and a jacketed three electrode cell connected to a thermostat-controlled water bath. The working electrode consisted of a 99.98% polycrystalline iron rotating disk electrode (RDE) cast in an insulating epoxy-resin holder. The counter-electrode used for potentiodynamic experiments consisted of a platinum wire. The reference electrode consisted of a saturated calomel electrode (SCE) placed in a salt bridge containing a saturated potassium chloride solution. This was connected to the cell via a Luggin capillary filled with the cell solution and positioned with its tip close to the working electrode in order to minimise the solution iR drop. All potentials reported were converted to the standard hydrogen electrode (SHE) scale. For all of the experiments, the thermostat-controlled water bath was set to a temperature of 45°C, the electrode rotation speed was 500 rpm and the iron surface was polished with 1200 grit silicon carbide paper wetted with ammonia-ammonium bicarbonate solution immediately prior to immersion.

The cell solutions were prepared from AR grade reagents and de-ionised water, and in order to simulate typical Caron plant conditions, the total ammonia-ammonium ion concentration (referred to as [NH$_3$$_2$]) was approximately 5 M and the total carbonate-bicarbonate concentration (referred to as [CO$_3$$_2$]) was approximately 1 M, giving a solution pH of around 10.5 at 45°C. All experiments were conducted at these concentrations unless otherwise stated in the text and figure captions. For the first set of experiments (Section 3.1) the solutions were prepared from ~28% ammonia solution and ammonium bicarbonate-ammonium carbamate double salt (NH$_4$HCO$_3$$\cdot$NH$_2$CO$_2$NH$_4$), which after dissolution and equilibration results in the same species as using ammonium carbonate. However, due to the instability of the double salt which only initially had a stoichiometry of 1:1, ammonium bicarbonate was used as reagent for all other experiments.

The small scale of the experiments and the high vapour pressure of ammonia made it difficult to accurately control the ammonia concentration in solution, in particular for experiments carried out under de-oxygenated conditions which required the solution to be sparged with nitrogen. In order to reduce the loss of ammonia, the nitrogen line was passed through a bubbler containing ammoniacal carbonate solution of approximately the same composition. A rotating paraffin oil seal was employed to prevent oxygen from entering the cell during the measurement, so that the nitrogen sparge could be stopped during the measurements and the loss of ammonia minimised. The results reported generally refer to experiments that were not conducted under de-oxygenated conditions, unless it is stated in the figure caption that the solutions were de-oxygenated.

3. Results

3.1. Open circuit behaviour and SEM/EDX surface analysis

The open circuit potential (OCP) of an iron RDE was measured over 3 hours in an aqueous solution of ammonia and ammonium bicarbonate – ammonium carbamate double salt, at the concentrations stated above, and 0.2 mM copper sulfate. The potential was found to increase slowly from just above -0.7 V, reaching -0.6 V after 3 hours (Figure 1). The electrode was then taken out of solution, rinsed immediately with de-ionised water and gently dried with air. The surface was analysed by scanning electron microscopy / energy dispersive X-ray spectroscopy (SEM/EDX), which revealed the presence of a dendritic copper deposit (Figure 2a). The experiment was then repeated at a higher copper (II) concentration of 12 mM. In this case, the OCP was found to initially increase slowly at potentials around -0.5 V, followed by a sharp increase after about 5 minutes. Following a brief pause at around -0.25 V, which lasted a
few minutes, the OCP increased to a high potential region of 0.1 - 0.2 V, where it remained for the rest of the 3 hour measurement (Figure 1). Analysis for the electrode surface by SEM/EDX indicated only the presence of iron. The processes occurring on the iron surface during the OCP transition from the lower to the higher potential region were further studied by conducting SEM/EDX analyses on the electrode taken out at different immersion times. The results, summarised in Figure 1, revealed the presence of an adherent, thick but porous, copper deposit during the initial phase of increase in the potential (insert A) which appeared thinner at the OCP shoulder at around -0.25 V (insert B) and was no longer detectible at potentials above 0 V (insert C).

![Figure 1](image_url)

Figure 1. The OCP of the iron RDE in ammonia - ammonium bicarbonate/carbamate solutions containing 12 mM Cu(II) ions (solid line) and 0.2 mM Cu(II) ions (dotted line), and the corresponding surface changes during the transition from -0.6 V to above 0.1 V.

The OCP behaviour of the iron RDE in solutions containing varying concentrations of copper ions displayed relative consistency in terms of the transition from active to passive with a shoulder at around -0.25 V. This appeared to be the case irrespective of whether oxygen was present in the solution or not and whether the solution was prepared using ammonia and ammonium bicarbonate or ammonia and ammonium bicarbonate-carbamate double salt.
However, the morphology of the copper deposit was found to change from dendritic (Figure 2a) to botroydal (Figures 2b and 2c) when the solution was prepared using ammonium bicarbonate instead of the double salt. It is well known that the morphology of this kind of deposit is sensitive to the conditions under which it was formed, in particular to variables such as temperature, rotation speed, pH, concentration of depositing ion and anions present (Power and Ritchie, 1975). In the ammonia-carbonate solutions employed in this study, a number of species such as $\text{NH}_3$, $\text{NH}_4^+$, $\text{CO}_3^{2-}$, $\text{HCO}_3^-$ and $\text{NH}_2\text{CO}_2^-$ exist in a complex equilibrium with each other (Mani et al., 2006; Wen and Brooker, 1995). The metal complex speciation may also be rather complicated. The observed change in copper deposit morphology is likely to have been caused by a variation in the ratios of the species present, which may have affected the nucleation mechanism and crystal growth.

Figure 2. SEM image of the iron RDE following a) 3 hours in 0.2 mM Cu(II) solution prepared using ammonia and ammonium bicarbonate/carbamate; b) 3 hours in 0.2 mM Cu(II) solution prepared using ammonia and ammonium bicarbonate, and c) a few minutes in 12 mM Cu(II) solution prepared using ammonia and ammonium bicarbonate, under de-oxygenated conditions.

3.2. Rotating disk cyclic voltammetry

Potentiodynamic studies were conducted in ammonia – ammonium bicarbonate solutions containing 6 mM copper (II) ions. Following a 2 minute immersion of the iron RDE under open circuit conditions, the potential was scanned in the anodic direction at a rate of 10 mV/s from the OCP to +0.24 V, and then back in the cathodic direction to -0.56 V. The resulting current density response is shown in Figure 3. The first anodic peak (A) observed close to -0.43 V during the positive sweep is assigned to the anodic dissolution of metallic iron, followed by a second anodic peak (B) around -0.13 V, assigned to the re-dissolution of cemented copper. During the cathodic scan, a small negative current becomes visible at potentials below 0 V, with the anodic dissolution of iron resuming just above -0.4 V and peaking at -0.47 V ($A'$).

Figure 3. Cyclic voltammogram of the iron RDE in ammonia – ammonium bicarbonate solution containing 6 mM Cu(II).
In order to confirm that the spontaneous transition of the iron OCP to the higher potential region is due to the formation of a stable passive layer, potentiodynamic experiments were conducted following the OCP increase to above 0 V. The applied potential was scanned from the final OCP to +0.24 V and then back in the cathodic direction to -0.56 V. The measurements were conducted in ammonia – ammonium bicarbonate solutions containing 6 mM copper (II) ions, both under normal and de-oxygenated conditions. As can be seen in Figure 4, no significant anodic current was observed in either direction until the applied potential became negative enough to re-activate the anodic dissolution of iron, resulting in peak $A^1$. Prior to reaching this point, the cathodic scan again resulted in a negative current, visible between 0.1 V and -0.4 V. No anodic peak attributable to the dissolution of copper was observed, which is consistent with the fact that once the OCP of the iron RDE has reached the passive potential region all the cemented copper has re-dissolved.

Figure 4. Cyclic voltammogram of the iron RDE in de-oxygenated ammonia – ammonium bicarbonate solution containing 6 mM Cu(II), following its transition to the passive state.

3.3. The effect of copper concentration on the passivation time

A study of the effect of the copper (II) concentration in ammonia – ammonium bicarbonate solutions, on the immersion time required for passivation of the iron RDE, was conducted at copper concentrations ranging from 1 mM to 12 mM. The results indicated a trend by which the passivation time increased with decreasing copper (II) concentration, as shown for some of the concentrations studied in the presence of oxygen in Figure 5, and in de-oxygenated solutions in Figure 6. Such trend can be clearly seen for all of the copper (II) concentrations studied in Figure 7, which shows the dependence on copper (II) concentration of the time between immersion and the first and second increase in potential, above $E_1 = -0.4$ V and $E_2 = -0.2$ V respectively.
Figure 5. The variation over time of the OCP of the iron RDE in ammonia – ammonium bicarbonate solutions at [Cu(II)] = a) 1 mM; b) 2 mM; c) 3 mM; d) 6 mM; e) 10 mM.

Figure 6. The variation over time of the OCP of the iron RDE in de-oxygenated ammonia – ammonium bicarbonate solutions at [Cu(II)] = a) 1 mM; b) 3 mM; c) 4 mM; d) 5 mM; e) 6 mM.

Figure 7. The dependence on Cu(II) concentration of the time delay between immersion of the iron RDE and the increase in potential above \( E_1 = -0.4 \text{ V} \) and \( E_2 = -0.2 \text{ V} \), in the presence of dissolved oxygen (solid symbols) or its practical absence (outline symbols).

3.4. The effect of \([\text{NH}_3]_T\) and \([\text{CO}_2]_T\) on the passivation time

The effect of varying the ammonia concentration on the time required for passivation was studied without de-oxygenating the solutions, in order to better control the ammonia concentration. Due to the complex equilibria and the unstable nature of ammonia and ammonium bicarbonate solutions at 45°C, investigating the effect of \([\text{NH}_3]_T\) and \([\text{CO}_2]_T\) as independent variables resulted in poorly reproducible results. Nevertheless, the passivation time was found to be less sensitive to changes in the ammonia concentration at a constant \([\text{CO}_2]_T\), than it was to changes in ammonium bicarbonate concentration at a constant \([\text{NH}_3]_T\). The passivation time was found to increase with increasing ammonium bicarbonate concentration, as shown in Figure 8.
Figure 8. The variation over time of the OCP of the iron RDE in ammonia – ammonium bicarbonate solutions at [Cu(II)] = 2 mM; [NH$_3$]$_T$ = 5 M and [CO$_2$]$_T$ = a) 0.5 M; b) 1.5 M; c) 2 M.

This is consistent with the ammonium bicarbonate playing an important role in preventing or delaying the passivation of iron. It should also be noted that in the complete absence of ammonium bicarbonate, iron was found to be passive immediately upon immersion irrespective of the ammonia concentration, even at copper concentrations as low as 0.2 mM, as shown in Figure 9.

Figure 9. The variation over time of the OCP of the iron RDE in ammonia solutions at 0.2 mM Cu(II) (dotted lines) and [NH$_3$] = a) 0.1 M; b) 1 M; c) 5 M; at 1 mM Cu (II) and [NH$_3$]= d) 1 M; e) 5 M.

The results shown in Figure 9 are included only for comparison, since ammoniacal leaching systems operate at a lower pH due to the addition of an ammonium salt, which is necessary for the active dissolution of the metals. A more relevant study was conducted on the dependence of the passivation time on both [NH$_3$]$_T$ and [CO$_2$]$_T$ varied at a constant molar ratio of 5 to 1. This had the additional advantage of maintaining the pH close to 10.5 for all of the measurements, therefore removing such additional variable which may separately affect the passivation time. In this set of measurements, more clear trends were obtained, as shown for a copper (II) concentration of 2 mM in Figures 10 and 11.
As it can be seen in Figures 10 and 11, the higher the concentration of ammonia and ammonium carbonate, the longer the immersion time required for passivation to occur. At 1 M [NH₃]ₜ the OCP appears to be dominated by the effect of ammonia and is consistent with the behaviour shown in Figure 9. This suggests that below a certain concentration, the ammonium bicarbonate becomes ineffective at preventing the passivation of iron. On the other hand, at high enough [NH₃]ₜ, passivation does not occur at all, and copper continues to cement onto the dissolving iron for longer than 16 hours. These results are also consistent with ammonium bicarbonate playing a significant role in preventing the passivation of iron.

3.5. Iron-nickel and iron-cobalt alloys

OCP measurements carried out on an 80% iron – 20% nickel alloy and a 99% iron – 1% cobalt alloy showed results very similar to those observed on iron under the same conditions (Figure 12). This confirms that the findings
regarding the behaviour of iron apply to the alloys of iron with nickel and cobalt, which appear to undergo passivation via a similar mechanism.

Figure 12. The variation over time of the OCP of an 80% iron – 20% nickel alloy RDE (solid line) and a 99% iron – 1% cobalt alloy RDE (dotted line) in 4 mM Cu(II), [NH$_3$]$_T$ = 5 M and [CO$_2$]$_T$ = 1 M.

4. Discussion

The anodic dissolution of iron in ammoniacal solutions is generally thought to involve the formation of ferrous ammine complexes. It has been suggested that in the ammoniacal – carbonate leaching system the dominant species formed are ferrous tetrammine (Kim et al., 1991; Lee et al., 1985; Nikoloski and Nicol, 2006; Senanayake et al., 2010), and ferrous pentammine (Asselin, 2008). Published thermodynamic data (Isaev et al., 1990) suggests the most stable ferrous ammine complex is the tetrammine. It is therefore reasonable to assume that the anodic dissolution of iron takes place via the following half-reaction:

$$\text{Fe} + 4\text{NH}_3 \rightarrow [\text{Fe(NH}_3)_4]^{2+} + 2\text{e}^-$$

The standard reduction potential for this half-reaction was calculated from published Gibbs free energy ($\Delta G_f$) data (Asselin, 2008) to be -0.5 V. More negative values have also been published, namely -0.57 V (Senanayake et al., 2010), -0.58 V (Nikoloski and Nicol, 2006), -0.586 V (Kim et al., 1991) and -0.548 V (Lee et al., 1985). It should be noted that calculations carried out directly from the iron ammine stability constants (Isaev et al., 1990) also result in a more negative value for the standard reduction potential. This varies depending on the value chosen for the $\Delta G_f$ of aqueous ferrous ion, for which different values are available in the literature. In order to ensure that the following argument holds valid in all cases, all calculations are based on the more positive standard reduction potential calculated from the most recently published data (Asselin, 2008), since the same line of reasoning will also apply for more negative values, but would no longer hold for a more positive value.

The dependence of the equilibrium potential of ferrous tetrammine / iron half-reaction on the ferrous tetrammine and ammonia activities at 45°C was calculated by applying the Nernst equation (2), as shown in Figure 13.

$$E = E^\circ - 0.137 \ln \left( \frac{a_{\text{NH}_3}^4}{a_{[\text{Fe(NH}_3)_4]^{2+}}} \right)$$

(2)
Figure 13. The dependence of the equilibrium potential of the iron / ferrous tetrammine half-reaction on iron tetrammine and ammonia activities at 45°C.

The observed OCP of iron in each of the solutions used in this study is always more positive than the equilibrium potential of the iron / ferrous tetrammine half-reaction at 45°C, in the likely ferrous ion activity and ammonia activity ranges encountered in each experiment. Therefore, the experimental values are thermodynamically consistent with the iron oxidation being coupled with a higher redox potential oxidant such as oxygen or copper ions. According to the mixed potential theory (Wagner and Traud, 1938), the OCP of the electrode, on which the anodic and cathodic sites are short circuited, is a complex function of the forward and reverse rate constant for each half-cell, as well as reactant and product concentrations and the cathodic/anodic area ratio (Miller, 1979). Thus, based on the observed OCP alone, it is not possible to draw any conclusion as to which reduction half-reaction is coupled with the anodic dissolution of iron.

The standard potentials of some copper-reduction half-reactions which may be coupled with the iron oxidation half-reaction were calculated using HSC 7 (Roine, 2009) software and are given below.

\[
\begin{align*}
[Cu(NH_3)_4]^{2+} + e^- &\rightarrow Cu + 4NH_3 \\
E^o &= -0.124 \text{ V} \\
\end{align*}
\]

\[
\begin{align*}
[Cu(NH_3)_4]^{2+} + 2e^- &\rightarrow Cu + 4NH_3 \\
E^o &= -0.023 \text{ V} \\
\end{align*}
\]

\[
\begin{align*}
[Cu(NH_3)_4]^{2+} + e^- &\rightarrow [Cu(NH_3)_2]^+ + 2NH_3 \\
E^o &= 0.078 \text{ V} \\
\end{align*}
\]

The dependence of the equilibrium potentials of half-reactions 3 and 4 (equations 6 and 7 respectively) on the copper ammine and ammonia ammonia activities at 45°C is shown in Figure 14.

\[
E = E^o - 0.0274 \ln \left[ \frac{a_{NH_3}^2}{a_{[Cu(NH_3)_2]^+}} \right] \\
\]
Figure 14. The dependence of the potentials of the copper / copper ammine half-reactions on copper ammine and ammonia activities at 45°C.

The observed cementation of copper onto iron confirms that the overall reduction of copper (II) to metallic copper, possibly via the formation of a cuprous ammine, takes place at the iron surface during its anodic dissolution. By comparison of Figure 14 with Figure 13 it can be seen that the oxidation of iron by ether cupric tetrammine or cuprous diammine is thermodynamically feasible under the Caron process conditions. In the latter case, the oxidant would form via the initial coupling of half-reaction 5, of even higher standard reduction potential, with half-reaction 1.

After the iron dissolution ceases, the cemented copper is no longer cathodically protected and there is a sharp rise in OCP to around -0.25 V, which indicates a change in behaviour of the metallic copper from cathodic to anodic, as it is above the equilibrium potential for the cuprous diammine/copper reaction. The same may not be said for the cupric tetrammine/copper reaction, which occurs at potentials higher than the measured OCP. This suggests that the cemented copper re-dissolves anodically by initially forming cuprous diammine. This can be brought about by the cupric tetrammine acting as an oxidant as it is reduced to cuprous diammine, resulting in the following re-proportionation reaction:

\[
Cu + [\text{Cu(NH}_3\text{)}_4]^{2+} \rightarrow 2[\text{Cu(NH}_3\text{)}_2]^{+} \quad (7)
\]

From the OCP measurements at different copper (II) concentrations it can be observed that in the presence of oxygen, the time delay from immersion to the first rapid increase in potential is longer than the delay between the first and the second potential increase. In de-oxygenated solutions, this difference is much less pronounced. This may suggest that the deposition of metallic copper takes longer, and its re-dissolution is faster, in the presence of dissolved oxygen, which is consistent with oxygen participating in the process either by directly oxidising metallic copper or by regenerating the cupric ammine oxidant.
During the observed cementation of copper onto the iron surface, the anodic sites at which iron is actively dissolving progressively decrease in area, while the cathodic sites at which metallic copper is being deposited increase. Due to the porous morphology of the deposit, which allows the dissolution of iron to continue, the cathodic area increases to increase leading to a very small anodic to cathodic area ratio. As a result, the oxidative current densities experienced by the anodic sites may oxidise the iron at the solution interface to a non-reactive oxide such as, for example, magnetite. A possible half-reaction which may describe this process is as follows:

$$3\text{Fe} + 4\text{OH}^- + 4\text{NH}_3 \rightarrow \text{Fe}_3\text{O}_4 + 4\text{NH}_4^+ + 8\text{e}^- \quad (8)$$

The passivation process is likely to involve the initial formation of ferrous hydroxide following the oxidative adsorption of hydroxyl ions, favoured by an increase in localised pH which may result from the de-coordination of ammonia ligands by the cathodic reactions (3-5). In this case, the passive layer may form on the iron surface according to the following reaction:

$$3\text{Fe(OH)}_2 + 2[\text{Cu(NH}_3)_4]^{2+} \rightarrow \text{Fe}_3\text{O}_4 + 2[\text{Cu(NH}_3)_2]^{+} + 2\text{NH}_3 + 2\text{NH}_4^+ + 2\text{H}_2\text{O} \quad (9)$$

As the thin oxide layer prevents further dissolution of metallic iron, the deposited copper is no longer cathodically protected and begins to re-dissolve anodically, exposing small fractions of the iron surface at a time, which passivate immediately upon contact with the solution. Once all the copper is re-dissolved, the iron surface is completely covered by the thin oxide layer, which is consistent with the observed increase in the OCP and the drop in current observed in the potentiodynamic measurements.

The presence of copper (II) ions in solution is therefore responsible for the passivation of iron under conditions in which it would otherwise continue to dissolve anodically. The presented results show that the higher the copper (II) concentration in solution, the sooner the passivation takes place. On the other hand, varying [NH$_3$]$_T$ and [CO$_2$]$_T$ at a constant molar ratio has the opposite effect, whereby lower concentrations appear to promote the passivation of iron, even though it does not take place in their complete absence. This trend is probably related to the effect of [NH$_3$]$_T$ on the stability of the metal complexes formed and on the rate of the metal displacement reaction which leads to the passivation. However, the passivation reaction itself is likely to be favoured by an increase in ammonia concentration if the ammonium bicarbonate concentration is maintained constant, due to the resulting increase in hydroxyl ion concentration. This may be a contributing factor to the lack of a clear trend when the ammonia concentration is varied at a constant [CO$_2$]$_T$. It is also consistent with the observed effect of the ammonium bicarbonate concentration varied at constant [NH$_3$]$_T$, which appears to reflect the effect of pH on the passivation reaction. Varying the ammonia and the ammonium carbonate at a constant molar ratio removes the pH as an additional variable, and the increase in the time required for passivation as [NH$_3$]$_T$ and [CO$_2$]$_T$ increase is attributed mainly to the increased stability of the copper complexes and the reduced rate of metal displacement. It follows that the ammonia and ammonium bicarbonate concentrations determine the critical copper (II) concentration at which iron will passivate immediately upon immersion and, as demonstrated by this work, at very low [NH$_3$]$_T$ the critical copper concentration can be very low also, as can be seen for example in Figure 10.

5. Conclusions

The presence of copper ions in ammoniacal solutions promotes the passivation of iron, which occurs more readily the higher the copper ion concentration and the lower the total ammonia-ammonium bicarbonate concentration.

The mechanism of passivation initially involves the cementation of copper onto the actively dissolving iron surface, which subjects the anodic sites to increasingly higher anodic current densities and relatively higher hydroxyl ion concentrations, due to the progressively smaller anodic to cathodic area ratio. This eventually leads to critical conditions under which the preferred product of the iron oxidation reaction is no longer a soluble complex ion, but an insoluble oxide compound. The iron passivation process then continues, small fractions at a time, during the re-dissolution of the cemented copper, which takes place once the copper is no longer cathodically protected by metallic iron, resulting in a thin passive oxide layer which covers the entire iron surface.

An analogous process is likely to take place on iron-nickel and iron-cobalt alloys, both of which display a similar OCP behaviour to that of iron. It is possible that under certain conditions, this mechanism of passivation may
adversely affect industrial processes in which ammoniacal solutions are employed to dissolve nickel and cobalt from alloys formed with iron.

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**References**


