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The anodic dissolution of iron in ammoniacal–carbonate–thiosulfate–copper solutions with formation of Cu_2S and dendritic copper

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ABSTRACT

The presence of thiosulfate ions in ammoniacal–carbonate solutions containing copper(II) ions was found to prevent the passivation of iron, even though iron passivation is observed in solutions with no thiosulfate at very low copper(II) concentrations. The prolonged anodic dissolution of iron resulted in the formation of a partly crystalline sulfide layer on its surface, which based on Grazing Incidence X-Ray Diffraction (GI-XRD) analysis is thought to consist mainly of Cu_2S. The effect of the sulfide layer was investigated using rotating disk cyclic voltammetry. Unlike the formation of an amorphous CoS_x layer, which took place in similar solutions containing cobalt ions, the cuprous sulfide layer was not found to promote passivation of the iron. A significant amount of solid precipitate also became detached from the iron surface, remaining undissolved in the solution. This was analysed by X-Ray Diffraction (XRD) and scanning electron microscopy (SEM)–energy dispersive X-ray spectroscopy (EDX). Dendritic copper was observed both in the solid separated from the solution and in the precipitate still attached to the iron surface. The absence of iron passivation is thought to be due to both to the non-adherent nature of the cuprous sulfide layer, and to a disrupting effect caused by the cementation of copper.

1. Introduction

Ammoniacal solutions are often employed in hydrometallurgical processes due to their high selectivity towards the metal values. In the Caron process, nickeliferous laterites are roasted under reducing conditions in order to reduce the nickel and cobalt to the metallic state, and then leached in ammoniacal–carbonate solutions in order to dissolve the metal values as ammine complexes. During the reduction step, a significant amount of iron is also reduced to the metallic state, and forms alloys with the metal values. Therefore, the dissolution behaviour of these alloys, and hence the recovery of the metal values, is strongly influenced by the behaviour of iron. For this reason, numerous investigations have been conducted on the anodic behaviour of iron in ammoniacal solutions, with a particular focus on its active–passive behaviour both during polarisation experiments and under open circuit conditions (Jandova and Pedlik, 1991; Kho et al., 1992; Kim et al., 1991; Lee et al., 1985; Nicol et al., 2004; Nikoloski and Nicol, 2006; Nikoloski et al., 2003; Osseo-Asare et al., 1983).

Depending on the ore feed, the solutions involved in the Caron process contain variable amounts of dissolved metals, including at times copper, as well as metastable thiosulfate ions. These originate from the dissolution of sulfides formed during the reductive roast as a result of sulfur being present in the fuel. A previous study has shown that the dissolution of iron is significantly suppressed, with a tendency to passivate, in solutions containing both dissolved cobalt and thiosulfate ions (D'Aloya and Nikoloski, 2013; Nikoloski et al., 2003). This behaviour was attributed to the progressive coverage of the iron surface by a cobalt sulfide or polysulfide layer, which appears to play a key role in the passivation mechanism. The study was particularly relevant to the QNi Caron plant in Yabulu, Australia, where cobalt and thiosulfate ions appear to be the main species influencing the anodic behaviour of iron. It is also relevant because cobalt losses into such layers may further affect the process efficiency. On the other hand, the typical dissolved copper concentrations found in the leach liquor at the Yabulu plant are quite low.

More significant amounts of copper may be encountered in ammoniacal–carbonate solutions employed in the processing of ores richer in copper, such as at the Votorantim Metais plant in Brazil. A previous study has found that iron readily passivates in the presence of millimolar amounts of dissolved copper (D'Aloya and Nikoloski, 2012). However studies conducted in ammoniacal–carbonate solutions containing both copper (II) and thiosulfate ions are complicated by the possibility of a homogeneous redox reaction between these two species (Rábai and Epstein, 1992). The oxidation of thiosulfate by copper (II) in the presence of ammonia has been studied extensively due to its relevance to the ammoniacal leaching of metal sulfides and to the thiosulfate leaching of gold, which is enhanced by the addition of copper (II) and

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ammonia (Breuer and Jeffrey, 2003; Byerley et al., 1973a,b, 1975). The reaction is known to produce tetrathionate, which then undergoes further oxidative degradation resulting mainly in sulfate and trithionate, and cuprous thiosulfate, ammine or mixed complexes, depending on the relative concentrations of ammonia and thiosulfate. In the presence of oxygen, the copper (I) species are re-oxidised to copper (II) ammines, which therefore function as redox mediators, resulting in much higher rates of thiosulfate degradation. The reaction rate is known to be significantly lower at higher ammonia concentrations, such as those employed in the Caron process.

The present study focuses on the interaction between metallic iron and both copper and thiosulfate ions under conditions similar to those encountered in the Caron process. Based on the results obtained, it was possible to identify some of the main reactions involved.

2. Experimental details

The electrochemical measurements were recorded using a three electrode jacketed cell connected to a 6310 EG&G Princeton Applied Research potentiostat. The working electrode was a rotating disk electrode (RDE) made of 99.98% polycrystalline iron, rotating at a speed of 500 rpm. The counter electrode was a platinum wire and the reference electrode was a saturated calomel electrode (SCE). This was placed in a Luggin capillary filled with the cell solution and placed with its tip a few millimetres away from the working electrode, in order to minimise the effect of solution resistance. All of the potentials reported in this study were converted to the standard hydrogen electrode (SHE) scale. The jacketed cell was connected to a thermostat-controlled water bath set to 45 °C in order to simulate the Caron process temperature. All of the solutions used in this study were prepared using deionised water and AR grade aqueous ammonia, ammonium bicarbonate, copper sulfate and sodium thiosulfate. Concentrations reported in the text as $[NH_3]_T$ and $[CO_2]_T$ refer to the total concentration of ammonia and carbonate species respectively, which resulted in a solution pH of around 10.5. The copper and thiosulfate species concentrations are referred to as [Cu(II)] and $[S_2O_3^{2-}]$ for simplicity, although they are expected to undergo various redox transformations once in solution. Since the presence of dissolved oxygen was not found to have a significant effect on the observed behaviour, the solutions employed for the experiments reported were not sparged with nitrogen, in order to maintain a more accurate control of the ammonia concentration.

The grazing incidence X-ray diffraction (GIXRD) pattern was recorded using a Panalytical Empyrean diffractometer, while the normal incidence XRD was obtained using a GBC EMMA diffractometer. The microscope images and elemental analyses were obtained using a Philips XL20 scanning electron microscope (SEM) combined with an Oxford Link ISIS 5175 energy dispersive X-ray spectroscopy (EDX) detector. The UV–Visible spectra were obtained using a HP 8453 spectrophotometer with 1 and 0.1 cm path length quartz cells for the lower and higher [Cu(II)] respectively. The experiments carried out in order to obtain samples for the XRD and UV–Visible characterisation studies were conducted at room temperature in a closed glass vessel, in which the solution was stirred by a magnetic stirrer. A 99% iron disk was attached to the lid of the vessel, in such manner that no air was present above the solution during the experiment. All of the iron surfaces were polished immediately prior to immersion using 1200 grit silicon carbide paper wetted with ammonia–ammonium bicarbonate solution.

3. Results

3.1. OCP Measurements

The OCP of an iron rotating disk electrode was found to remain in the active dissolution region of iron in ammoniacal–carbonate solutions, throughout a number of 3 hour measurements conducted using various copper (II) concentrations between 1 mM and 12 mM, and thiosulfate concentrations between 4 mM and 24 mM. This behaviour can be seen for example in Fig. 1 (curve a). By comparison, the OCP behaviour with the same copper (II) concentration but with no thiosulfate (curve (b)) shows a distinct transition due to the passivation of iron.

During dissolution, the formation of a black solid on the iron surface was also observed. This was found to be non-adherent and to continuously fall off the iron surface, remaining suspended in the agitated solution. Sharp drops in the OCP of up to 50 mV were observed each time a piece of the black solid layer became detached from the iron surface. The precipitation of significant amounts of finely divided iron (III) hydroxides was also observed.

In solutions containing cobalt and thiosulfate ions, the presence of copper ions, even at very low concentrations, was found to significantly delay the onset of passivation. For example, a copper concentration as low as 0.1 mM in an ammoniacal–carbonate solution containing 12 mM [Co(II)] and 24 mM $[S_2O_3^{2-}]$ resulted in the passivation taking place after 2 h of immersion, as opposed to the 30–40 min it took when no copper ions were added (Fig. 2).

In a final experiment, an iron RDE which had been allowed to passivate in an ammoniacal–carbonate solution containing copper(II) but no thiosulfate was then immersed in ammoniacal–carbonate solutions containing both copper(II) and thiosulfate ions. In this case, the OCP measurements on the iron RDE showed that it remained passive.

3.2. XRD and SEM/EDX Analyses

As the OCP behaviour did not exhibit significant differences across the concentration ranges of copper and thiosulfate, XRD and SEM/EDX analyses were only carried out for one representative combination. The iron RDE immersed for 3 h in an ammoniacal–carbonate solution containing 12 mM Cu(II) and 24 mM thiosulfate ions was analysed. SEM–EDX analysis of its surface revealed the presence of a predominantly dendritic deposit, with an elemental analysis of approximately 30% Cu and 20% S. An iron RDE immersed for 4 h under the same conditions was analysed by GIXRD, which revealed the presence of metallic copper and Cu_2S (Fig. 3).

The solid precipitate which formed following immersion of the iron RDE in the absence of air above the solution was also analysed. SEM images of the filtered solid revealed a mixture of phases with different morphologies (Fig. 4) and the EDX elemental analysis resulted in major variations in the relative amounts of copper and sulfur in different parts of the precipitate. XRD analysis of the solid indicated the presence of metallic copper, Cu_2O, Cu_2S, possibly $CuFe_4S_7$ and FeS (Fig. 5).

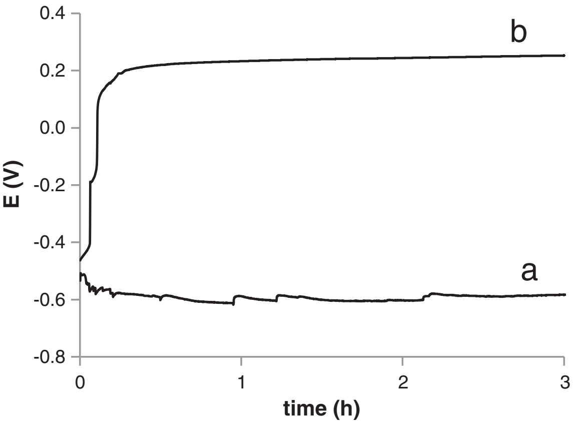

Fig. 1. OCP of Fe in 5 M $[NH_3]_T$, 1 M $[CO_2]_T$ and a) 12 mM [Cu (II)], 22 mM $[S_2O_3^{2-}]$; b) 12 mM [Cu (II)].