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Senanayake, G. and Zhang, X.M. (2012) Gold leaching by copper(II) in ammoniacal thiosulphate solutions in the presence of additives. Part II: Effect of residual Cu(II), pH and redox potentials on reactivity of colloidal gold. *Hydrometallurgy*, 115-116 . pp. 21-29.

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# Gold leaching by copper(II) in ammoniacal thiosulphate solutions in the presence of additives II. Effect of residual Cu(II), pH and redox potentials on reactivity of colloidal gold

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## Abstract

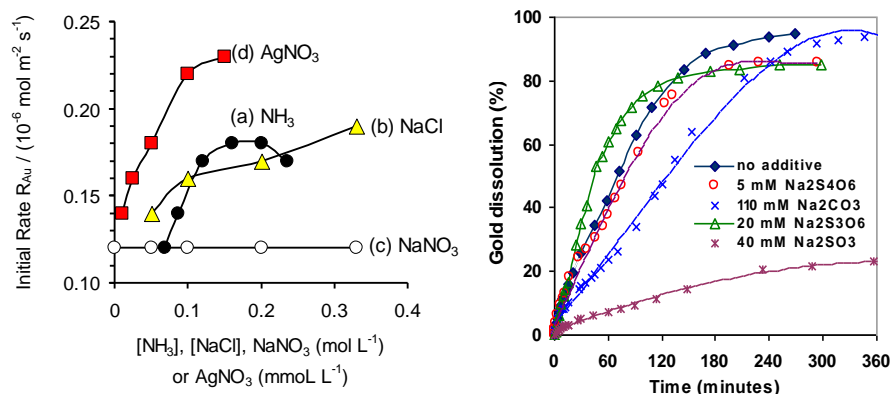
The effect of additives on the dissolution of gold colloids (20 nm) by copper(II) in ammoniacal thiosulphate media has been investigated by measuring the residual gold and Cu(II) concentrations in solution using UV-visible spectrophotometry, and the redox/mixed potentials ( $E_H$  or  $E_{mix}$ ) using platinum and gold electrodes immersed in solution. Results show a beneficial effect of increasing free  $NH_3$  on gold dissolution caused by an increase in pH from 8.9-11 which enhances residual Cu(II) and  $E_H$ . The beneficial effect of additives follow the descending order:  $AgNO_3 > NaCl > Na_2SO_4 > none \sim Na_2CO_3 > NaNO_3 > Pb(NO_3)_2 > Na_2S_4O_6 \sim Na_2S_3O_6 > Na_2SO_3$ . The two reagents  $AgNO_3$  and  $NaCl$  do not affect the residual Cu(II) concentration,  $E_H$  or  $E_{mix}$  but enhance gold dissolution (~100% in 1-2 h) due to the involvement of  $Ag(I)$  and  $Cl^-$  in the anodic reaction of gold. Both  $Na_2SO_4$  and  $Na_2CO_3$  have beneficial effects on residual Cu(II) which enhance  $E_H$  and retard the reaction with thiosulphate due to ion-association and stabilisation of  $Cu(NH_3)_x^{2+}$ . Thus, the gold dissolution is slow and steady with  $Na_2CO_3$  (95% in 5 h). Despite the faster initial gold dissolution in the presence of  $Na_2S_3O_6$  due to high  $E_H$  and  $E_{mix}$ , gold dissolution reaches a plateau (~85% after 2 h). The presence of  $Na_2S_4O_6$  causes lower  $E_H$  and  $E_{mix}$ , lower residual Cu(II); and gold dissolution reaches a plateau (~85% after 3 h), indicating surface blockage. Strong interaction between Cu(II) and  $Na_2SO_3$  is evident from very low residual Cu(II), low  $E_H$  and  $E_{mix}$ , causing low gold dissolution reaching a plateau (~20%) after 6 h.

Key words: Gold, colloids, thiosulphate, leaching, background salts, redox potentials, ion-properties

## Research Highlights

- UV-visible spectroscopy can measure the reaction extent of Cu(II) with 20 nm gold colloids and thiosulphate ions under nitrogen
- Increase in pH from 9 to 10 increases residual Cu(II) and free ammonia to enhance gold dissolution
- Ag(I) or chloride ions do not affect residual Cu(II) but enhance gold dissolution (100% in 1-2 h) by catalysing anodic reaction
- Carbonate ions enhance residual Cu(II) leading to slow but steady gold dissolution (95% in 5 h)
- Sulphite ions react with Cu(II) and cause low gold dissolution (20% in 6 h)
- Tetra/trithionate lower the residual Cu(II) and cease gold dissolution at 85% after 2-3 h indicating surface blockage
- Overall effect of additives follow the order:  $\text{AgNO}_3 > \text{NaCl} \sim \text{Na}_2\text{SO}_4 > \text{NaNO}_3 \sim \text{none} > \text{Pb}(\text{NO}_3)_2 > \text{Na}_2\text{S}_4\text{O}_6 \sim \text{Na}_2\text{S}_3\text{O}_6 > \text{Na}_2\text{SO}_3$

## Graphical Abstract



## 1. Introduction

Thiosulphate leaching of gold by Cu(II) in ammoniacal thiosulphate has attracted the interest of many researchers since the late seventies (Berezowsky and Sefton, 1979). The overall reaction  $\text{Au} + \text{Cu(II)} = \text{Au(I)} + \text{Cu(I)}$  involves the electrochemical half cell reactions:  $\text{Au} = \text{Au(I)} + \text{e}^-$  (anodic) and  $\text{Cu(II)} + \text{e}^- = \text{Cu(I)}$  (cathodic) and allows fundamental studies using electrochemical or chemical oxidation of rotating gold discs which can be compared with leaching studies using gold foil, powder or ores (Jeffrey, 2001; Feng and van Deventer, 2002; Zhang and Nicol, 2003, 2005). Results from such studies provide a wealth of information on (i) reaction orders with respect to key reagents such as Cu(II),  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{NH}_3$  and  $\text{OH}^-$ , (ii) reaction mechanisms, and (iii) reasons for beneficial or detrimental effects of various additives. The effect of additives on gold leaching is a result of their direct interaction with Cu(II) or gold surface, affecting the cathodic or anodic reactions, respectively; or formation/removal of passivating or surface blocking products on gold surface. Some of the published information on the effect of additives on thiosulphate leaching has been reviewed in part I of this series (Senanayake, 2011).

Gold colloids, due to their smaller particle size, dissolve much faster than massive gold. Moreover, the concentration of residual colloidal gold can be measured using UV-visible spectrophotometry. Thus, the use of gold colloids provides a convenient and rapid method to monitor cyanide concentration during gold cyanidation and to test the effect of additives and other variables on gold leaching kinetics in cyanide or thiosulphate solutions (McCarthy et al., 1998, Nicol and Hindmarsh, 2001; Zhang et al., 2004, 2008). The failure to identify passivation layers using surface analysis techniques is one of the limitations in studies with gold colloids, compared to the electrochemical or leaching studies with massive gold. Nevertheless, some of the published results show comparable rates of dissolution per unit surface area of gold powder and colloids (Zhang et al., 2008).

In addition, the use of a test cell without gold colloids can be used to monitor the decrease in concentration of residual copper(II) using UV-visible spectrophotometry. The decrease in Cu(II) concentration is a result of the background reaction with thiosulphate. The redox potential of the solution ( $E_{Pt}$ ,  $E_{Cu(II)/Cu(I)}$  or  $E_H$ ) and the mixed potential of gold ( $E_{Au}$  or  $E_{mix}$ ) can also be determined in the same cell by measuring the potentials of platinum and gold electrodes with respect to a reference Ag/AgCl/KCl electrode immersed in the solution with a suitable salt bridge (Zhang et al., 2004, 2008).

The present study considers the rate data and the extent of dissolution of gold colloids by copper(II) in ammoniacal thiosulphate solutions under nitrogen over a period of 3-6 h and examines the relative effects of various salts NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaCl, Na<sub>2</sub>CO<sub>3</sub>, AgNO<sub>3</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub>, Na<sub>2</sub>S<sub>3</sub>O<sub>6</sub> on the residual copper(II) concentration and extent of gold dissolution. Some of the observed trends are used for the rationalisation of thiosulphate leaching of gold on the basis of interactions between metal ion and background reagents, and the measured potentials of platinum and gold electrodes.

## 2. Experimental

All reagents were of analytical grade and Millipore water was used throughout the experiments. The gold colloids were prepared using standard methods (Pal and Ganguly, 1987; McCarthy et al., 1998) and stored in brown bottles in a cool room at a temperature of 3°C-5°C. Unstabilised gold colloids prepared according to the procedure described by Turkevich et al. (1951) can flocculate in high concentrations of background salts or if left in storage for a long time. This was avoided by using stabilised gold colloids prepared in the presence of gelatine. Colloid particle size (20 nm) was determined using a transmission electron microscope (Philips CM 100 Biotwin). The initial concentration of colloids was maintained at 0.1 mM in most experiments. The temperature was maintained at 25±0.5°C using a water bath and the ionic strength (I) was adjusted to 0.5 using

$\text{Na}_2\text{SO}_4$  according to Eq. 1, where  $c$  and  $z$  represent the concentration and valency of ions respectively.

$$I = 0.5 \sum \{ (c_{\text{Na}^+} \cdot z_{\text{Na}^+}) + (c_{\text{SO}_4^{2-}} \cdot z_{\text{SO}_4^{2-}}) \} \quad (1)$$

The oxidation of gold colloids in the presence of copper(II) and the reduction of copper(II) by thiosulphate were carried out in two 100 ml glass vessels with water jackets. The variation of gold colloid concentration with time was monitored in the first vessel whilst the residual concentration of copper(II) in the absence of gold colloids was monitored in the second vessel (blank cell). The solutions were magnetically stirred. All experiments were carried out under anaerobic conditions under a nitrogen atmosphere. The absorbance due to residual concentration of gold colloids at 530 nm and copper(II) at 610 nm, respectively, was measured using a MultiSpec-1500 (SHIMADZU) UV-visible spectrophotometer. In the case of colloids, the measured values were corrected for background absorbance of copper(II) at the same wavelength. The method of measuring pH and electrode potentials ( $E_{\text{Pt}}$  and  $E_{\text{Au}}$ ) has been described previously (Zhang et al., 2004).

### 3. Results and discussion

#### 3.1 Initial rates

Table 1 lists the conditions and variables tested in this study. For the purpose of comparison with results for massive gold from the literature, the initial rates of dissolution of gold colloids were calculated using Eq.2, where  $c$  = colloid concentration (mM),  $r$  = initial particle size of colloids (m),  $\rho$  = density of gold ( $1.98 \times 10^7 \text{ g m}^{-3}$ ),  $M$  = molar mass of gold ( $197 \text{ g mol}^{-1}$ ) (Zhang et al., 2008). Table 1 summarises the values of  $R_{\text{Au}}$ .

$$R_{\text{Au}} (\text{mol m}^{-2} \text{ s}^{-1}) = R_{\text{Au}} (\text{mM min}^{-1}) / \{ 3cM/r\rho \} \quad (2)$$

Unlike  $\text{NaNO}_3$  which does not show a significant effect on  $R_{\text{Au}}$  (Set A), the increasing concentration of  $\text{NaCl}$  (Set B),  $\text{AgNO}_3$  (Set C) or increasing pH (Set D) have significant beneficial effects on  $R_{\text{Au}}$  (Table 1). The latter is largely a result of the increase in free  $\text{NH}_3$  concentration with increasing pH according to Eqs. 3 and 4, where  $pK_a$  ( $\sim 9.3$  at 298 K) depends on the ionic strength and temperature. The concentration of free  $\text{NH}_3$  calculated using Eq. 5 is also listed in Table 1. Thus, the effect of increasing pH can be treated as an effect of increasing free  $\text{NH}_3$ , which in turn can be compared with the effect of other additives.



$$pH = pK + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \quad (4)$$

$$[\text{NH}_3] = 10^{(pH - pK_a)} \cdot \frac{[\text{NH}_3 + \text{NH}_4^+]}{(1 + 10^{(pH - pK_a)})} \quad (5)$$

A further comparison of the effect of  $\text{NaNO}_3$ ,  $\text{NaCl}$ ,  $\text{AgNO}_3$  and free  $\text{NH}_3$  is made in Fig. 1. The figure shows that the beneficial effect of low levels of  $\text{Ag(I)}$  (0.14-0.23 mM) is much larger than that of more concentrated  $\text{NaCl}$  (0.05-0.33 M) or free  $\text{NH}_3$  (0.07-0.24 M). The beneficial effect of  $\text{NaCl}$  and free  $\text{NH}_3$  is consistent with published results based on rotating discs reviewed in part I of this series (Senanayake, 2011). Although the increase in pH from 8.9 to 9.6 has a dramatic beneficial effect on  $R_{\text{Au}}$  due to the increase in free  $\text{NH}_3$ , a further increase in pH from 9.6 to 11 causes  $R_{\text{Au}}$  to plateau with a slight decrease in  $R_{\text{Au}}$  at pH 11, as shown in Fig. 1 and Table 1. Other additives, especially polythionates, have a detrimental effect on initial rates (Set E in Table 1). These effects can be related to the changes in  $\text{Cu(II)-NH}_3\text{-S}_2\text{O}_3\text{-OH}$  speciation and detailed reaction mechanisms as described previously (Senanayake, 2004; 2011).

Equilibrium constants for the formation of mixed  $\text{Cu(II)-NH}_3\text{-S}_2\text{O}_3\text{-OH}$  complex species are listed in Table 2. Fig. 2 shows the effect of pH on the composition of various

Cu(II) species in solution. As pH increases from 9 to 10 the concentration of  $\text{Cu}(\text{NH}_3)_4^{2+}$  increases, but that of  $\text{Cu}(\text{NH}_3)_2(\text{S}_2\text{O}_3)_2^{2-}$  decreases whilst  $\text{Cu}(\text{NH}_3)\text{S}_2\text{O}_3^0$  remains relatively unaffected. A high concentration of  $\text{Cu}(\text{NH}_3)_2(\text{S}_2\text{O}_3)_2^{2-}$  at a low pH of 9 facilitates the reduction of Cu(II) to Cu(I) by thiosulphate and the production of polythionates as described previously (Senanayake, 2011). Thus, the increase in rate with increasing pH in the range 8.9-9.6 is largely a result of the enhanced concentration of free  $\text{NH}_3$  and stabilisation of Cu(II). A further discussion of these effects on the basis of residual Cu(II),  $E_{\text{Pt}}$  and  $E_{\text{Au}}$  is presented next.

### 3.2 Residual Cu(II) and extent of gold dissolution

#### 3.2.1 Effect of pH and redox potentials

Figs. 3a-b summarise the effect of pH on residual copper(II) concentration and gold dissolution (%) as a function of time. The large and rapid decrease in residual Cu(II) concentration at a low pH of ~8.9 in Fig. 3a is a result of the higher % of mixed Cu(II)- $\text{NH}_3$ - $\text{S}_2\text{O}_3$  complexes predicted in Fig. 2 facilitating the reaction between Cu(II) and  $\text{S}_2\text{O}_3^{2-}$ . This also causes a rapid decrease in  $E_{\text{Pt}}$  (Fig. 3c), as  $E_{\text{Pt}}$  measures the activity ratio of  $\text{Cu}^{2+}/\text{Cu}^+$  ions according to the Nernst equation expressed by Eq. 6, where  $E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} = 0.15 \text{ V}$  at 298 K. The decrease in  $E_{\text{Pt}}$  can also be interpreted according to Eq.7 by considering the molar ratio of actual Cu(II) and Cu(I) species and the values of  $E^\circ_{\text{Cu(II)/Cu(I)}}$  listed in Table 3 calculated using Eq.8. Likewise, the measured values of  $E_{\text{Au}}$  can be interpreted on the basis of Eqs. 9-11 reported previously (Zhang et al., 2004, 2008).

Platinum electrode potentials

$$E_{\text{Pt}} = E_{\text{Cu(II)/Cu(I)}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} + \frac{RT}{F} \ln \left( \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}^+}} \right) \quad (6)$$



$$E_{Pt} = E_{Cu(II)/Cu(I)} = E^o_{Cu(II)/Cu(I)} + \frac{RT}{F} \ln \left( \frac{[Cu(II)]}{[Cu(I)]} \right) \quad (7)$$

$$E^o_{Cu(II)/Cu(I)} = E^o_{Cu^{2+}/Cu^+} - \frac{RT}{F} \ln \left( \frac{\beta_n Cu(II)_{complex}}{\beta_n Cu(I)_{complex}} \right) \quad (8)$$

Gold electrode potentials

$$E_{Au} = E_{Au(I)/Au(0)} = E^o_{Au^+/Au(0)} + \frac{RT}{F} \ln \left( \frac{a_{Au^+}}{a_{Au}} \right) \quad (9)$$

$$E_{Au} = E_{Au(I)/Au(0)} = E^o_{Au(I)/Au(0)} + \frac{RT}{F} \ln[Au(I)] \quad (10)$$

$$E^o_{Au(I)/Au(0)} = E^o_{Au^+/Au^0} - \frac{RT}{F} \ln(\beta_n Au(I)_{complex}) \quad (11)$$

For example, the measured values of  $E_{Pt}$  and  $E_{Au}$  for Au(colloid)-Cu(II)-NH<sub>3</sub>-S<sub>2</sub>O<sub>3</sub><sup>2-</sup> system at pH 8.9 (Fig. 4a) and pH 9.3 (Fig. 4b), respectively, are compared with the calculated values based on the Nernst equation. After the initial decrease in measured  $E_{Pt}$  due to the reaction between copper(II) and thiosulphate, a constant value was reached over a period of 40-60 minutes. The measured values of  $E_{Pt}$  were close to the calculated values of the couple(s) Cu(NH<sub>3</sub>)<sub>3</sub><sup>2+</sup>/Cu(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub><sup>3-</sup> or Cu(NH<sub>3</sub>)<sub>3</sub><sup>2+</sup>/Cu(S<sub>2</sub>O<sub>3</sub>)<sub>3</sub><sup>5-</sup> at equilibrium (Figure 4a), based on Eq.7. In Eq.7 [Cu(II)] represents the measured residual concentration of copper(II) in the blank cell and [Cu(I)] represents the difference between the concentrations of initial and residual copper(II). In contrast, the measured initial values of  $E_{Au}$  are much larger than the calculated values using Eqs. 10-11, where [Au(I)] represents the difference between the concentrations of initial and residual colloidal gold. Moreover, the initial values of  $E_{Au}$  in Fig.4b are closer to the initial values of  $E_{Pt}$  in Fig. 4a. This is an indication that the measured initial  $E_{Au}$  is a mixed potential  $E_{mix}$  where  $E_{Au(I)/Au(0)} < E_{mix} \leq E_{Cu(II)/Cu(I)}$ . The electrochemical theory in relation to the mixed potential model for redox leaching has been reviewed by Nicol and Lazaro (2002)

and Breuer and Jeffrey (2002). Thus, the low gold dissolution of ~60% after 150 min at pH 8.9 in Fig. 3b is consistent with the dramatic decrease in copper(II) concentration in Fig.3a, causing a low value of  $E_{\text{Cu(II)/Cu(I)}}$  and  $E_{\text{mix}}$ , leading to slow and low dissolution of gold. The measured values of  $E_{\text{Au}}$  shown in Fig. 4d follow a similar trend to those of  $E_{\text{Pt}}$  shown in Fig. 4a at higher pH.

The increase in pH from 9.3 to 11 at 298 K has a larger beneficial effect on residual copper(II). This is a result of the decrease in concentration of mixed complexes at higher pH evident from Fig. 2, which retards the reduction of Cu(II) to Cu(I) by thiosulphate ions. The large increase in residual Cu(II) with increasing pH in Fig. 3a is consistent with the increase in free  $\text{NH}_3$  in Table 1 and % of  $\text{Cu}(\text{NH}_3)_4^{2+}$  in Fig. 2. This increases  $E_{\text{Cu(II)/Cu(I)}}$  and facilitates gold dissolution, as revealed by the general ascending order of  $E_{\text{Pt}}$  (Fig.3c) and  $E_{\text{Au}}$  (Fig. 3d) with increasing pH and 90% gold dissolution at pH 11 after 150 min (Fig.3b). Similar effects have been observed on the rate of dissolution of massive gold by 25 mM Cu(II) in more concentrated 0.4 M  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  with the increase in  $\text{NH}_3$  from 0.2 to 0.4 M (Jeffrey, 2001). Likewise, the increase in pH from 8.5 to 10.5 increased the % gold leached from a pressure leach residue of a refractory gold ore after 1 h using 50 mM  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  and 0.5-2 mM  $\text{CuSO}_4$ , from 7% to 70% (Jeffrey et al., 2008).

### 3.2.2 Effect of $\text{Na}_2\text{SO}_4$ and $\text{NaNO}_3$

The increase in concentration of  $\text{Na}_2\text{SO}_4$  and hence the ionic strength (Eq. 1) from 0.2 to 1.0, enhanced the residual Cu(II) (Fig. 5a) and consequently the dissolution of gold colloids (Fig. 5b). The measured values of  $E_{\text{Pt}}$  and  $E_{\text{Au}}$  during this period shown in Figs. 5c and 5d follow the same trend as the concentration of residual Cu(II). However, under the experimental conditions described in Fig. 5 gold dissolution only reached 60-80% after 6 h (Fig.5b). This is largely caused by the lower reagent concentrations: 1.5 mM Cu(II), 10 mM  $\text{Na}_2\text{S}_2\text{O}_3$  and 60 mM  $\text{NH}_3+\text{NH}_4^+$  used in this experiment conducted at a different ionic strength. The increase in concentration of Cu(II),  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{NH}_3+\text{NH}_4^+$

to 2 mM, 20 mM and 240 mM, respectively at pH 9.6 caused an increase in gold dissolution to over 90% after 3 h (Fig. 6b).

The curves for the variation of residual Cu(II) concentration or gold dissolution shown in Fig.6a-b were relatively unaffected by the increase in concentration of NaNO<sub>3</sub> in the range 0-0.33 M, but all led to over 95% gold dissolution after 4 h. The incomplete dissolution of gold colloids in Fig. 5b can be related to the slow kinetics caused by low concentrations of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and NH<sub>3</sub> compared to those in Fig. 6b. Nevertheless, a significant increase in residual copper(II) concentration was observed with the increase in concentration of Na<sub>2</sub>SO<sub>4</sub> (Fig.5a), which also improved gold dissolution (Fig.5b). The gold leaching results from an oxide ore over 24 h also show a beneficial effect of adding Na<sub>2</sub>SO<sub>4</sub> by lowering thiosulphate consumption and increasing gold extraction (Xia et al., 2003).

### 3.2.3 Effect of NaCl, AgNO<sub>3</sub> and Pb(NO<sub>3</sub>)<sub>2</sub>

Although NaCl has no significant effect on residual Cu(II) concentration in Fig. 7a the increase in NaCl concentration shows a dramatic beneficial effect on gold dissolution in Fig. 7b. This is consistent with the enhanced initial rates in the presence of NaCl shown in Fig. 1. The gold extraction from an oxide ore in ammonium thiosulphate was also enhanced from 39% to 84% with the addition of NaCl (Li and Kuang, 1998). This also suggests the possible involvement of chloride ions in the anodic reaction which leads to a catalytic effect on the overall reaction and warrants further studies.

Like NaNO<sub>3</sub> (Fig.6a), the increase in AgNO<sub>3</sub> concentration from 0.01 to 0.1 mM has no significant effect on residual copper(II), as shown in Fig. 8a. However, it causes a dramatic increase in gold dissolution as shown in Fig. 8b. This is consistent with the faster thiosulphate leaching of gold-silver alloys by ammoniacal Cu(II) (Jeffrey, 2001) and dissolved oxygen (Webster, 1986), and warrants further studies to examine the possibility of cementation of silver on gold surface predicted from thermodynamics

(Zhang et al., 2008). The effect of 0.01 mM  $\text{AgNO}_3$  and  $\text{Pb}(\text{NO}_3)_2$  are compared in Figs. 9a-b. Although both salts do not show a significant effect on residual  $\text{Cu}(\text{II})$  concentration in Figs. 8a and 9a,  $\text{Ag}(\text{I})$  (beneficial) and  $\text{Pb}(\text{II})$  (detrimental) show opposite effects on gold dissolution in Fig. 9b. An attempt to examine the effect of variation in concentration of  $\text{Pb}(\text{II})$  failed in this study due to low solubility of  $\text{Pb}(\text{II})$ .

#### 3.2.4 Effect of $\text{Na}_2\text{S}_4\text{O}_6$ , $\text{Na}_2\text{S}_3\text{O}_6$ , $\text{Na}_2\text{SO}_3$ and $\text{Na}_2\text{CO}_3$

Fig. 10a-b compares and contrasts the effect of  $\text{Na}_2\text{S}_4\text{O}_6$ ,  $\text{Na}_2\text{S}_3\text{O}_6$ ,  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{CO}_3$  on residual copper(II) concentration and gold dissolution. The rapid decrease in residual copper(II) concentration in the presence of  $\text{Na}_2\text{SO}_3$  is a result of the reaction between  $\text{Cu}(\text{II})$  and  $\text{SO}_3^{2-}$  described in part I (Senanayake, 2011), which in turn leads to lower gold dissolution. Although the residual  $\text{Cu}(\text{II})$  concentration remains high in the presence of  $\text{Na}_2\text{CO}_3$ , the initial rate is relatively unaffected (Table 1), while initial gold dissolution remains low (Fig. 10b). However, in comparison to the situation in the absence of additives, the residual  $\text{Cu}(\text{II})$  in solution remains high over a long period of time in the presence of  $\text{Na}_2\text{CO}_3$  (Fig. 10a). This is responsible for the continued but slow reaction, leading to over 90% gold dissolution after 5 h (Fig. 10b).

The addition of  $\text{Na}_2\text{S}_4\text{O}_6$  lowers the residual  $\text{Cu}(\text{II})$ , compared to the reference with no additives (Fig. 10a), and causes lower gold dissolution (Fig. 10b). Although the addition of  $\text{Na}_2\text{S}_3\text{O}_6$  also decreases the residual  $\text{Cu}(\text{II})$ , the initial gold dissolution is faster. Gold dissolution in the presence of  $\text{Na}_2\text{S}_4\text{O}_6$  or  $\text{Na}_2\text{S}_3\text{O}_6$  reaches about 85% and remains unchanged after about 2 to 3 h. This situation for the dissolution of gold colloids under nitrogen is consistent with the beneficial/detrimental effects of polythionates on the dissolution and passivation of massive gold caused by the formation of products such as  $\text{HS}^-$ , described in part I (Senanayake, 2011). The plateau in the % dissolution of colloidal gold by  $\text{Cu}(\text{II})$  around 60% or 80% has also been observed in the presence of excess oxygen with 0.5 mM dissolved  $\text{O}_2$  or air respectively (Zhang et al., 2004). This is a result

of the Cu(II) catalysed oxidation of thiosulphate by oxygen which produces high concentrations of polythionates. Faster dissolution in the presence of  $\text{Na}_2\text{S}_3\text{O}_6$  suggests the beneficial effect of  $\text{HS}^-$  formed, as was found with massive gold (Feng and van Deventer, 2007). Incomplete gold dissolution of 85% with both  $\text{Na}_2\text{S}_3\text{O}_6$  and  $\text{Na}_2\text{S}_4\text{O}_6$  also indicates the continued interaction between Cu(II) and polythionates which may lead to other products causing surface blockage/passivation, which warrants further studies.

The results in Fig. 10a-b can be further examined on the basis of measured values of  $E_{\text{Pt}}$  and  $E_{\text{Au}}$  during the dissolution of colloidal gold as shown in Figs. 10c and 10d respectively. The values of  $E_{\text{Pt}}$  in Fig. 10c follow the same trend as the residual Cu(II) concentration with different additives:  $\text{CO}_3^{2-} > \text{none} > \text{S}_4\text{O}_6^{2-} > \text{S}_3\text{O}_6^{2-} \gg \text{SO}_3^{2-}$ , again, as expected from Eqs. 6-7. However, the measured gold potentials represent the mixed potential which seem to follow a slightly different order:  $\text{S}_3\text{O}_6^{2-} > \text{none} > \text{S}_4\text{O}_6^{2-} > \text{CO}_3^{2-} \gg \text{SO}_3^{2-}$  over the initial 120 min. This is the result of a combination of several effects described in part I of this series (Senanayake, 2011) summarised below:

- (i) Ions such as  $\text{SO}_3^{2-}$  reduce Cu(II) to Cu(I) and thus decrease residual Cu(II), increase the molar ratio  $[\text{Cu(I)}]/[\text{Cu(II)}]$  and lower the value of  $E_{\text{Pt}}$ . This in turn decreases  $E_{\text{Au}}$  in the presence of  $\text{Na}_2\text{SO}_3$  compared to that without additives (Fig. 10d). Gold dissolution continues to remain low (<20%) and eventually ceases after 240 min (Fig. 10b).
- (ii) The change in the Cu(II) complex from  $\text{Cu(II)(NH}_3)_x\text{S}_2\text{O}_3$  to the more stable  $\text{Cu(II)(NH}_3)_x\text{X}$  (with species such as  $\text{X} = \text{PO}_4^{3-}, \text{CO}_3^{2-}, \text{EDTA}$ ) lowers  $E^\circ$  but enhances residual Cu(II) due to retardation of the oxidation of  $\text{S}_2\text{O}_3^{2-}$  by Cu(II). Although this causes an initial decrease in  $E_{\text{Au}}$  with  $\text{Na}_2\text{CO}_3$ , largely due to the lower  $E^\circ$ , it remains constant over a longer period of time (Fig. 10d) due to the high and unchanged residual Cu(II) concentration (Fig.10a). Thus, % gold dissolution shows a linear increase as shown in Fig. 10b with  $\text{Na}_2\text{CO}_3$ , leading to a higher gold dissolution of 95% after 6 h.

(iii) Residual Cu(II),  $E_{Pt}$  and  $E_{Au}$  follow the same general trend in Figs. 10a, 10c and 10d, respectively, in the presence of  $Na_2S_4O_6$ , and continue to decrease with time. As a result both  $E_{Au}$  and gold dissolution in the presence of  $Na_2S_4O_6$  remains lower than that without additives. In contrast, higher values of  $E_{Au}$  in the presence of  $Na_2S_3O_6$  lead to a higher initial rate of gold dissolution, compared to that without additives.

#### 4. Summary and conclusions

The beneficial effect of increasing pH on colloidal gold dissolution in the present study is a result of the increase in concentration of free  $NH_3$  which stabilises Cu(II). Unlike the increase in pH (or free  $NH_3$ ), the addition of  $NaNO_3$  or  $NaCl$  has no significant effect on residual copper(II), yet  $NaCl$  has a large beneficial effect on colloidal gold dissolution, while  $NaNO_3$  has no effect. In contrast, the increase in ionic strength from 0.2 to 1.0 by increasing the concentration of  $Na_2SO_4$  causes a slight increase in residual Cu(II),  $E_{Pt}$ ,  $E_{Au}$  and gold dissolution (10%). This indicates the stabilisation of Cu(II) by  $SO_4^{2-}$  ions due to ion-association as described in part I of this series (Senanayake, 2011). Neither  $AgNO_3$  nor  $Pb(NO_3)_2$  have a significant effect on residual Cu(II), but the beneficial effect of  $AgNO_3$  on gold dissolution increases at higher concentrations, compared to the slightly detrimental effect caused by  $Pb(NO_3)_2$ . Residual Cu(II) and  $E_{Pt}$  in the presence of various anions follow the descending order:  $Na_2CO_3 \gg$  None  $> Na_2S_4O_6 \sim Na_2S_3O_6 \gg Na_2SO_3$ . Despite this the rate of gold dissolution in the first 2 h follows the order of mixed potential ( $E_{Au}$ ):  $Na_2S_3O_6 > None > Na_2S_4O_6 > Na_2CO_3 \gg Na_2SO_3$ . However, gold dissolution continues with  $Na_2CO_3$ , reaching ~95%, compared to only 20% with  $Na_2SO_3$  after 5 h. This difference is due to the rapid reaction of Cu(II) with  $SO_3^{2-}$ , compared to the stabilisation of Cu(II) by complexation with  $CO_3^{2-}$ . In comparison, gold dissolution in the presence of  $Na_2S_4O_6$  and  $Na_2S_3O_6$  reaches a plateau at ~85% after 2-3 h indicating surface blockage. The overall effect of various

additives follows the order  $\text{AgNO}_3 > \text{NaCl} \sim \text{Na}_2\text{SO}_4 > \text{NaNO}_3 \sim \text{none} > \text{Pb}(\text{NO}_3)_2 > \text{Na}_2\text{S}_4\text{O}_6 \sim \text{Na}_2\text{S}_3\text{O}_6 > \text{Na}_2\text{SO}_3$ .

### Acknowledgement

Financial assistance and support from the Parker CRC for Integrated Hydrometallurgy Solutions and Murdoch University are gratefully acknowledged.

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## Figures

Fig. 1

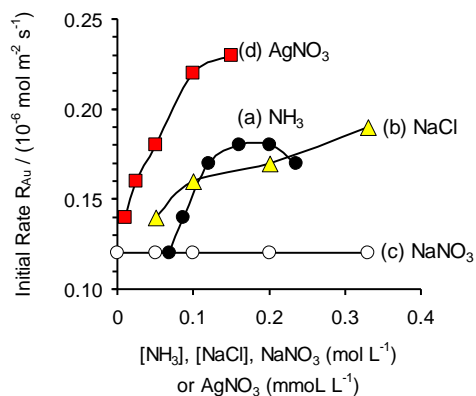


Fig. 1. Effect of NaNO<sub>3</sub>, NaCl, AgNO<sub>3</sub> or free NH<sub>3</sub> on initial dissolution rate of colloidal gold at 25°C and particle size 20 nm: (a) pH change from 8.9-11.0, [NH<sub>3</sub>+NH<sub>4</sub><sup>+</sup>] = 0.24 M, [Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>] = 40 mM, [Cu(II)] = 2; (b,c,d). pH 9.5, [NH<sub>3</sub>+NH<sub>4</sub><sup>+</sup>] = 0.12 M; [Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>] = 20 mM, [Cu(II)] = 1.5 mM.

Fig. 2

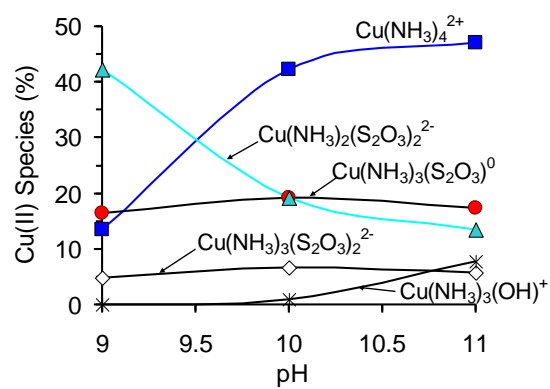


Fig. 2. Effect of pH on Cu(II) speciation at 25°C (1 M ammonia, 0.1 M  $\text{Na}_2\text{S}_2\text{O}_3$ , 0.01 mM Cu(II), Senanayake, 2004)

Fig. 3

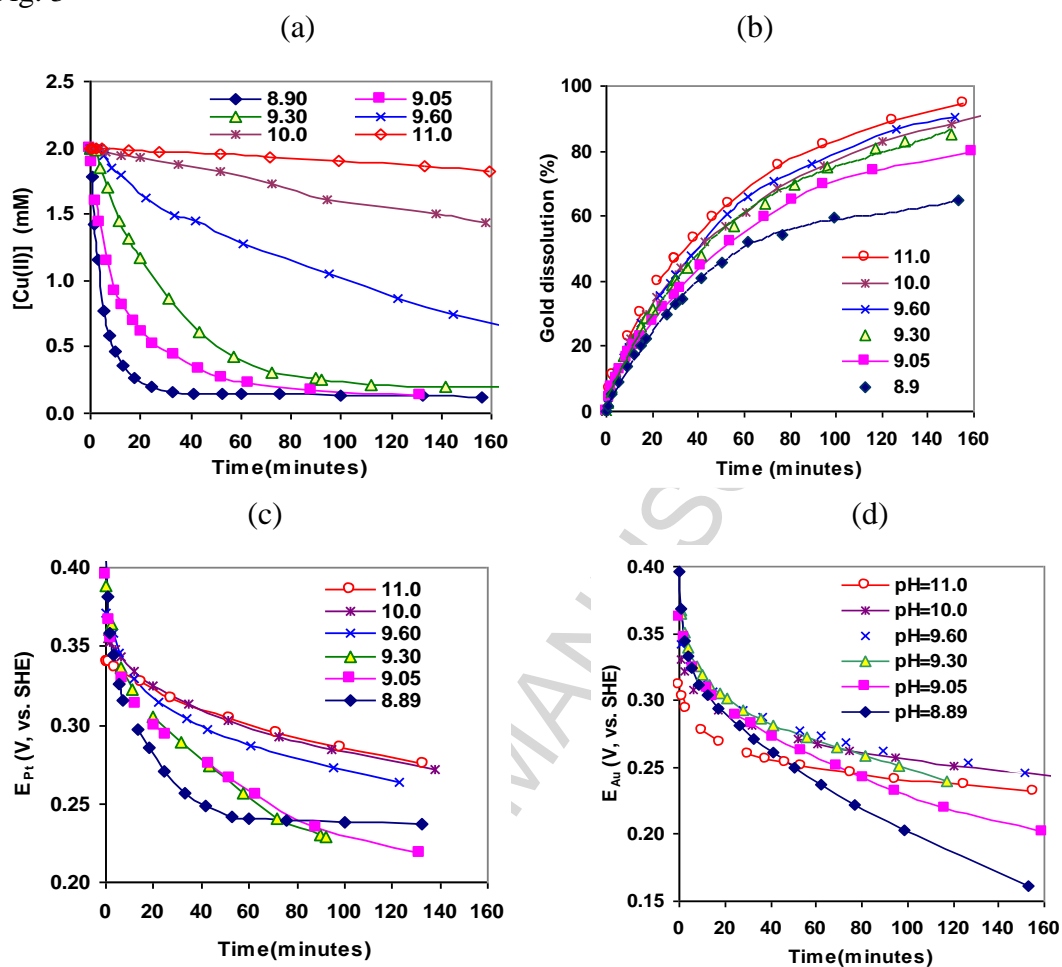
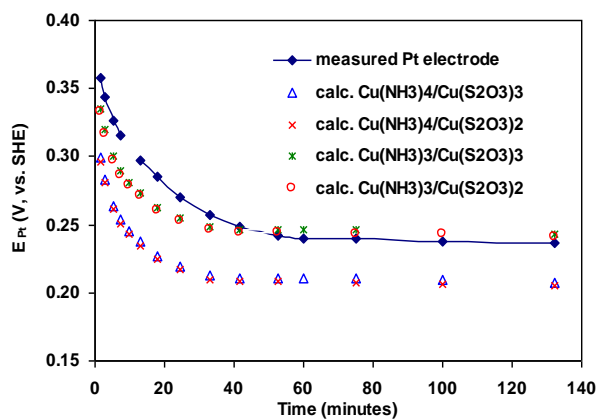


Fig.3. Effect of pH on residual Cu(II) concentration and dissolution of colloidal gold.  $[Au(\text{colloid})] = 0.1 \text{ mM}$ ,  $[CuSO_4] = 2.0 \text{ mM}$ ,  $[Na_2S_2O_3] = 40 \text{ mM}$ ,  $[NH_3 + NH_4^+] = 240 \text{ mM}$

Fig. 4

(a)



(b)

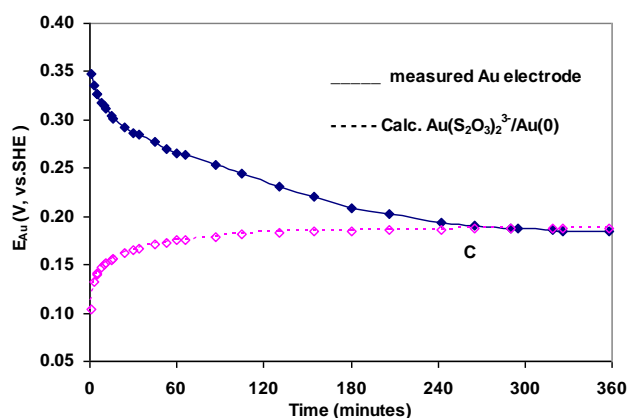


Figure 4. Measured and calculated potentials of platinum electrode and gold electrode during the reaction of copper(II) with thiosulfate and gold colloid: (a) 40 mM  $\text{S}_2\text{O}_3^{2-}$ , 240 mM  $\text{NH}_3+\text{NH}_4^+$ , 2.0 mM Cu(II), pH = 8.9; (b) 50 mM  $\text{Na}_2\text{S}_2\text{O}_3$ , 240 mM  $\text{NH}_3+\text{NH}_4^+$ , 1.5 mM Cu(II), pH = 9.3, equilibrium reached at point C (Zhang et al., 2008).

Fig. 5.

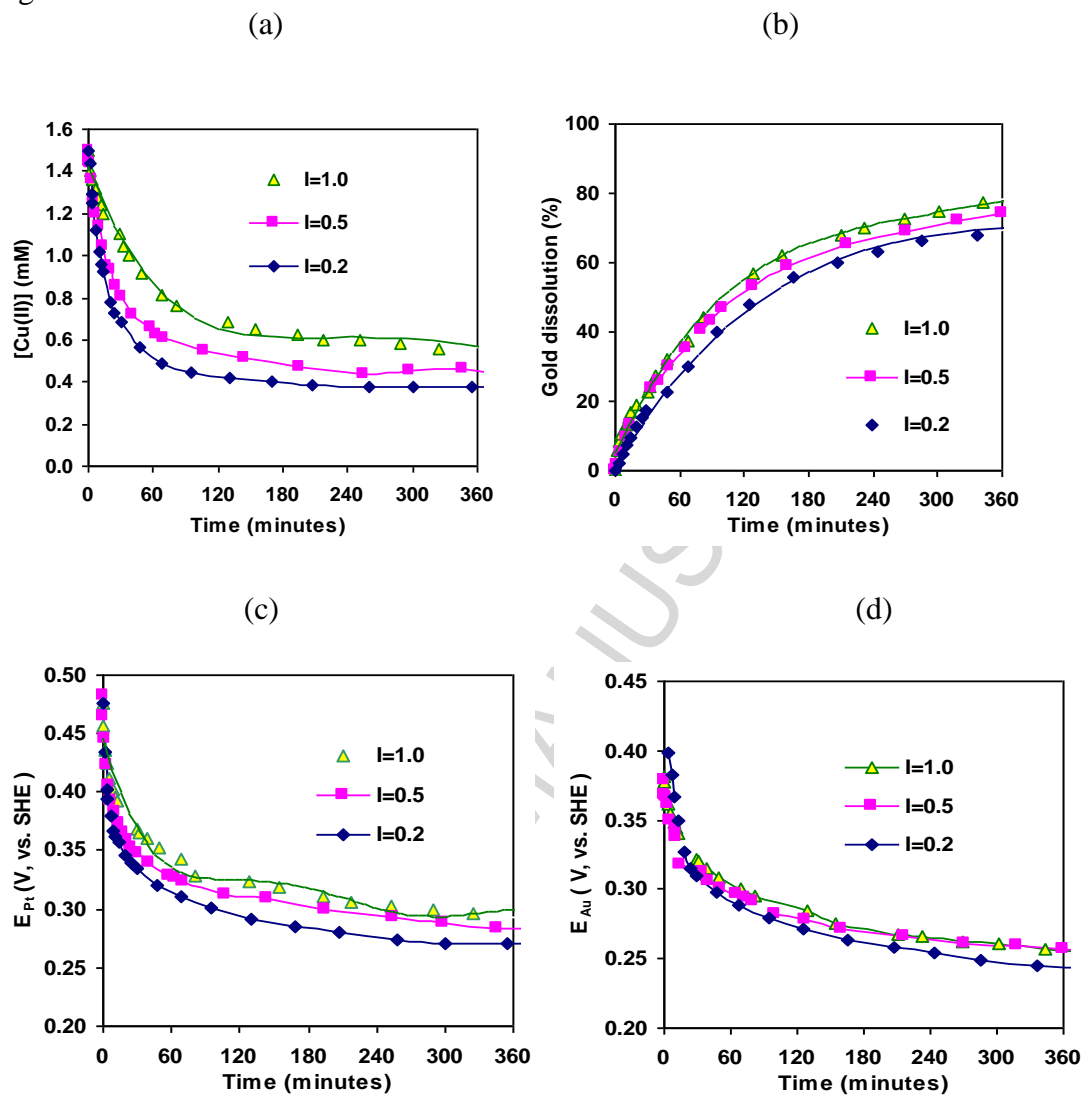


Fig.5. Effect of  $\text{Na}_2\text{SO}_4$  concentration on residual  $\text{Cu(II)}$  concentration and dissolution of colloidal gold.  $[\text{Au(c)}] = 0.1 \text{ mM}$ ,  $[\text{CuSO}_4] = 1.5 \text{ mM}$ ,  $[\text{Na}_2\text{S}_2\text{O}_3] = 10 \text{ mM}$ ,  $[\text{NH}_3 + \text{NH}_4^+] = 60 \text{ mM}$ ,  $\text{pH} = 9.5$ .

Fig. 6

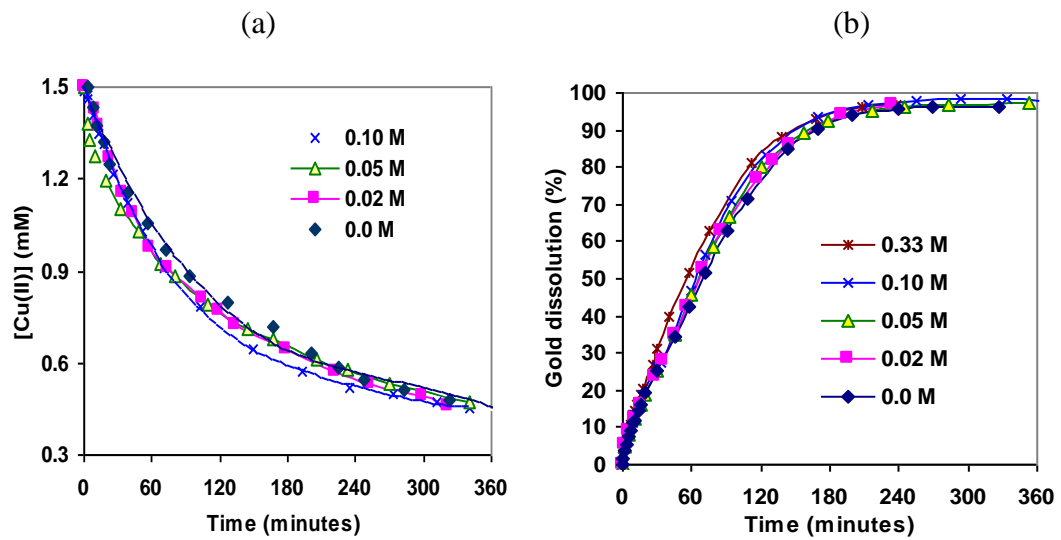


Fig.6. Effect of NaNO<sub>3</sub> concentration on residual Cu(II) concentration and dissolution of colloidal gold. [Au(c)] = 0.1 mM, [CuSO<sub>4</sub>] = 1.5 mM, [Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>] = 20 mM, [NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>] = 120 mM, pH = 9.5.

Fig. 7

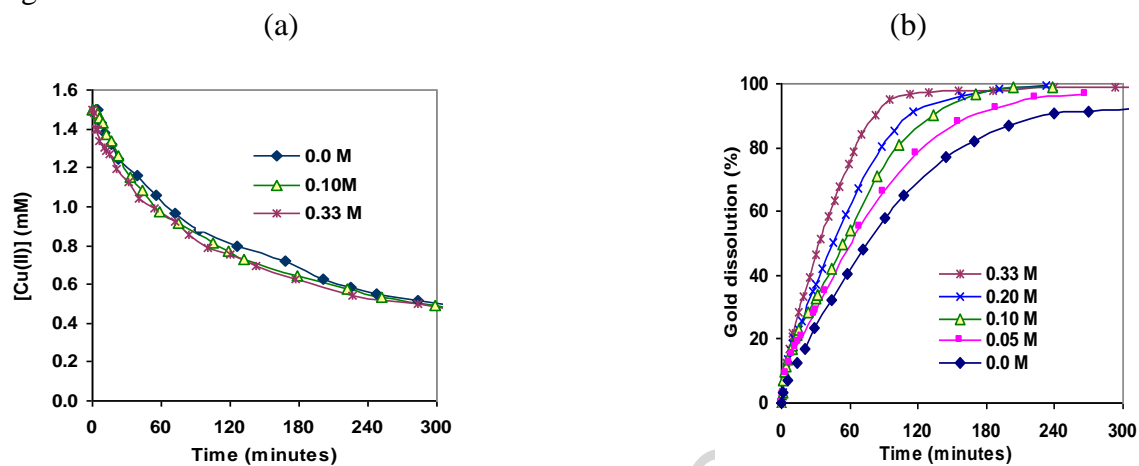


Fig.7. Effect of NaCl concentration on residual Cu(II) concentration and dissolution of colloidal gold.  $[\text{Au(c)}] = 0.1 \text{ mM}$ ,  $[\text{CuSO}_4] = 1.5 \text{ mM}$ ,  $[\text{Na}_2\text{S}_2\text{O}_3] = 20 \text{ mM}$ ,  $[\text{NH}_3 + \text{NH}_4^+] = 120 \text{ mM}$ ,  $\text{pH} = 9.5$ .



Fig. 8

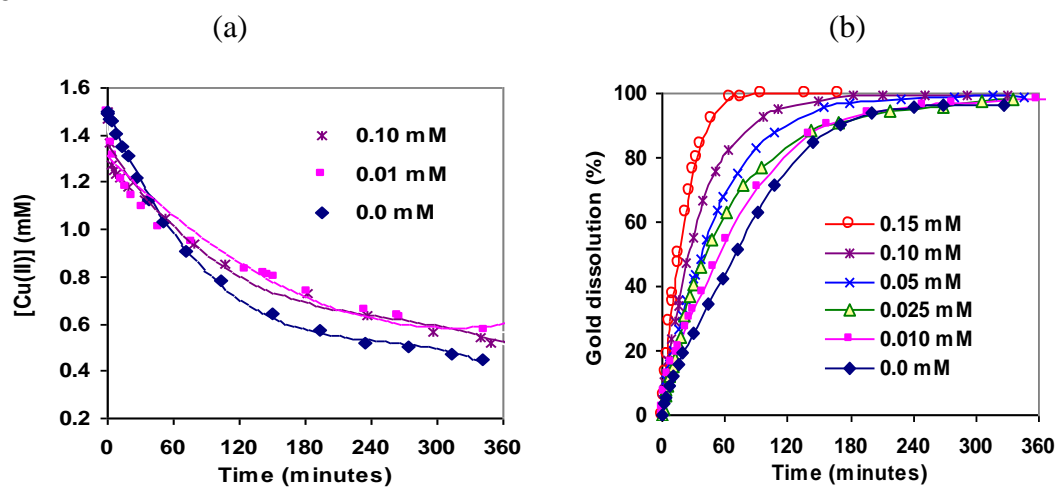


Fig.8. Effect of  $\text{AgNO}_3$  concentration on residual  $\text{Cu(II)}$  concentration and dissolution of colloidal gold.  $[\text{Au(c)}] = 0.1 \text{ mM}$ ,  $[\text{CuSO}_4] = 1.5 \text{ mM}$ ,  $[\text{Na}_2\text{S}_2\text{O}_3] = 20 \text{ mM}$ ,  $[\text{NH}_3 + \text{NH}_4^+] = 120 \text{ mM}$ ,  $\text{pH} = 9.5$ .

Fig.9.

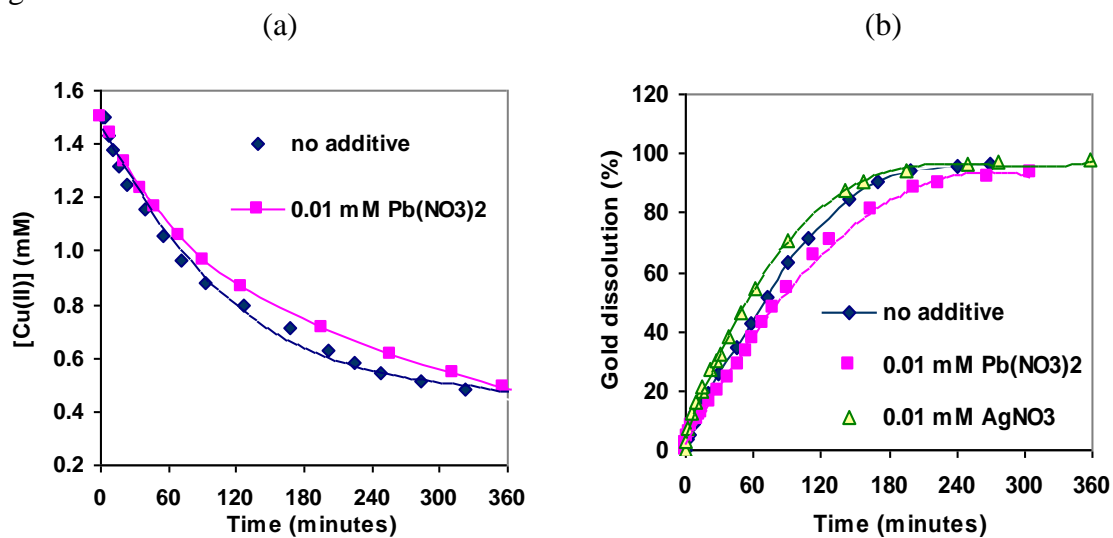


Fig.9. Effect of 0.01 mM AgNO<sub>3</sub> and Pb(NO<sub>3</sub>)<sub>2</sub> on residual Cu(II) concentration and dissolution of colloidal gold. [Au(c)] = 0.1 mM, [CuSO<sub>4</sub>] = 1.5 mM, [Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>] = 20 mM, [NH<sub>3</sub>+NH<sub>4</sub><sup>+</sup>] = 120 mM, pH = 9.5.

Fig. 10

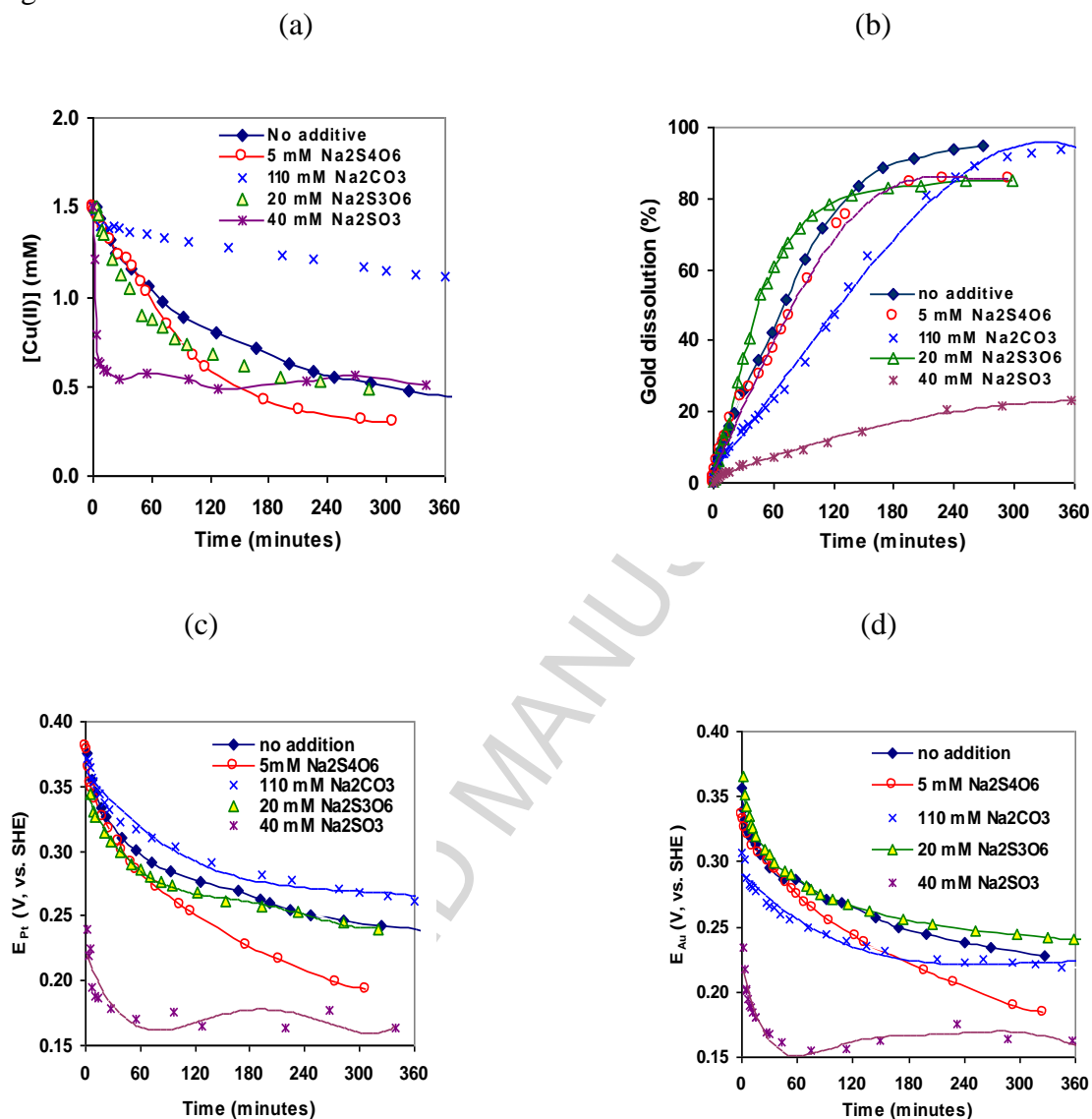


Fig.10. Effect of Na<sub>2</sub>S<sub>4</sub>O<sub>6</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>S<sub>3</sub>O<sub>6</sub> and Na<sub>2</sub>SO<sub>3</sub> on residual Cu(II) concentration and dissolution of colloidal gold. [Au(colloid)] = 0.1 mM, [CuSO<sub>4</sub>] = 1.5 mM, [Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>] = 20 mM, [NH<sub>3</sub>+NH<sub>4</sub><sup>+</sup>] = 120 mM, pH = 9.5.

Table 1. Effect of additives and pH on initial dissolution rates of gold colloid

Set	Additive		[Cu(II)]	[Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ]	pH	[NH <sub>3</sub> ] <sub>total</sub>	[NH <sub>3</sub> ] <sub>free*</sub>	Initial rate R <sub>Au</sub>		
	Salt	mM	mM	(mM)		(mM)	(mM)	$\mu\text{mol L}^{-1} \text{min}^{-1}$	$\mu\text{mol m}^{-2} \text{s}^{-1}$	
A	NaNO <sub>3</sub>	0	1.5	20	9.5	120	73.6	2.1	0.12	
		50						2.1	0.12	
		100						2.1	0.12	
		200						2.2	0.12	
		330						2.1	0.12	
B	NaCl	50	1.5	20	9.5	120	73.6	2.5	0.14	
		100						2.8	0.16	
		200						3.0	0.17	
		330						3.4	0.19	
C	AgNO <sub>3</sub>	0.01	1.5	20	9.5	120	73.6	2.5	0.14	
		0.025						2.9	0.16	
		0.05						3.2	0.18	
		0.1						3.9	0.22	
		0.15						4.2	0.23	
D	none		2.0	40	8.90	240	68.3	2.1	0.12	
					9.05			86.4	2.6	0.14
					9.30			120	3.0	0.17
					9.60			160	3.2	0.18
					10.0			200	3.2	0.18
					11.0			235	3.1	0.17
E	None	0	1.5	20	9.5	120	73.6	2.1	0.12	
	Na <sub>2</sub> S <sub>4</sub> O <sub>6</sub>	5						1.7	0.094	
	Na <sub>2</sub> S <sub>3</sub> O <sub>6</sub>	20						1.7	0.094	
	Pb(NO <sub>3</sub> ) <sub>2</sub>	0.01						1.8	0.10	
	Na <sub>2</sub> CO <sub>3</sub>	110						2.0	0.11	
	Na <sub>2</sub> SO <sub>3</sub>	40						0.4	0.022	

20 nm gold colloids, 25°C under nitrogen.

\* represent the values calculated using Eq. 5.

Table 2

Formation constants of mixed ammonia-thiosulphate complexes of Cu(II)

Reaction	log K
$\text{Cu}(\text{NH}_3)_4^{2+} + \text{S}_2\text{O}_3^{2-} = \text{Cu}(\text{NH}_3)_2(\text{S}_2\text{O}_3)^0 + 2\text{NH}_3$	0.18, 0.71
$\text{Cu}(\text{NH}_3)_4^{2+} + \text{S}_2\text{O}_3^{2-} = \text{Cu}(\text{NH}_3)_3(\text{S}_2\text{O}_3)^0 + \text{NH}_3$	0.55
$\text{Cu}(\text{NH}_3)_4^{2+} + 2\text{S}_2\text{O}_3^{2-} = \text{Cu}(\text{NH}_3)_2(\text{S}_2\text{O}_3)_2^{2-} + 2\text{NH}_3$	1.42, 1.96
$\text{Cu}(\text{NH}_3)_4^{2+} + \text{OH}^- = \text{Cu}(\text{NH}_3)_3(\text{OH})^+ + \text{NH}_3$	2.20

Derived from kinetic data at 25°C (Senanayake, 2004)

Table 3. Calculated  $E^\circ\{\text{Cu(II)/Cu(I)}\}$  from stability constants at 298 K

Abbreviation: Redox couple	$E^\circ/\text{V}$
A4/S3: $\text{Cu}(\text{NH}_3)_4^{2+}/\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$	0.24 (0.22)
A4/S2: $\text{Cu}(\text{NH}_3)_4^{2+}/\text{Cu}(\text{S}_2\text{O}_3)_2^{3-}$	0.16 (0.14)
A3/S3: $\text{Cu}(\text{NH}_3)_3^{2+}/\text{Cu}(\text{S}_2\text{O}_3)_3^{5-}$	0.36 (0.36)
A3/S2: $\text{Cu}(\text{NH}_3)_3^{2+}/\text{Cu}(\text{S}_2\text{O}_3)_2^{3-}$	0.26 (0.20)

$E^\circ$  calculated using  $E^\circ\{\text{Cu}^{2+}/\text{Cu}^+\} + 0.059 \log\{\beta_{\text{Cu(I)}}/\beta_{\text{Cu(II)}}\}$  and formation constants of relevant complexes of  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  ( $\beta_{\text{Cu(II)}}$  and  $\beta_{\text{Cu(I)}}$ ) from Hogfeldt (1982); values in parentheses were reported by Muir and Aylmore (2005).