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

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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 to 11 which enhances residual Cu(II) and E_H. The beneficial effect of additives follows the descending order: $AgNO_3 > NaCl > Na_2SO_4 > $ no additives $\sim Na_2CO_3 > NaNO_3 > Pb(NO_3)_2 > Na_2S_4O_6 \sim Na_2S_3O_6 > Na_2SO_3$. The two reagents $AgNO_3$ and $NaCl$ do not affect the residual Cu(II) concentration, E_H or E_{mix} but enhance gold dissolution ($\sim 100\%$ 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 ($\sim 85\%$ 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 ($\sim 85\%$ 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 ($\sim 20\%$) after 6 h.

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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 $Au + Cu(II) = Au(I) + Cu(I)$ involves the electrochemical half cell reactions: $Au = Au(I) + e^-$ (anodic) and $Cu(II) + e^- = Cu(I)$ (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 (Feng and van Deventer, 2002; Jeffrey, 2001; 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), $S_2O_3^{2-}$, NH_3 and 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, in press).

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 (Hindmarsh and Nicol, 2001; McCarthy et al., 1998; 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

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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$_3$, Na$_2$SO$_4$, NaCl, Na$_2$CO$_3$, AgNO$_3$, Pb(NO$_3$)$_2$, Na$_2$SO$_3$, Na$_2$S$_4$O$_6$, Na$_2$S$_3$O$_6$ 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 (McCarthy et al., 1998; Pal and Ganguly, 1987) 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 Na$_2$SO$_4$ according to Eq. (1), where c and z represent the concentration and valency of ions respectively.

$$I = 0.5\{c_{Na^+} \cdot \left(z_{Na^+}\right)^2 + \left(c_{SO_4^{2-}} \cdot \left(z_{SO_4^{2-}}\right)^2\right\}. \tag{1}$$
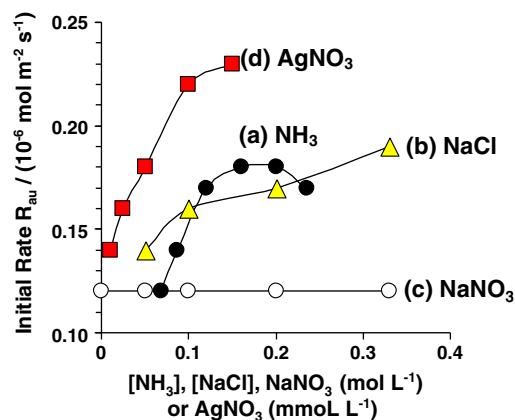

Fig. 1. Effect of NaNO$_3$, NaCl, AgNO$_3$ or free NH$_3$ on initial dissolution rate of colloidal gold at 25 °C and particle size 20 nm: (a) pH change from 8.9 to 11.0, [NH$_3$ + NH$_4^+$] = 0.24 M, [Na$_2$S$_2$O$_3$] = 40 mM, [Cu(II)] = 2 mM (b,c,d). pH 9.5, [NH$_3$ + NH$_4^+$] = 0.12 M; [Na$_2$S$_2$O$_3$] = 20 mM, [Cu(II)] = 1.5 mM.

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

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

Set	Additive		[Cu(II)] mM	[Na$_2$S$_2$O$_3$] (mM)	pH	[NH$_3$]$_{total}$ (mM)	[NH$_3$]$_{free}$[a] (mM)	Initial rate R$_{Au}$	
	Salt	mM						μmol L^{-1} min^{-1}	μmol m^{-2} s^{-1}
A	NaNO$_3$	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$_3$	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$_2$S$_4$O$_6$	5						1.7	0.094
	Na$_2$S$_3$O$_6$	20						1.7	0.094
	Pb(NO$_3$)$_2$	0.01						1.8	0.10
	Na$_2$CO$_3$	110						2.0	0.11
	Na$_2$SO$_3$	40						0.4	0.022

20 nm gold colloids, 25 °C under nitrogen.
[a] Represents the values calculated using Eq. (5).