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Elucidating the Interfacial Interactions of Copper and Ammonia with the Sulfur Passive Layer during Thiosulfate Mediated Gold Leaching

Scott R. Smith¹, Chunqing Zhou¹, Janet Y. Baron², Yeonuk Choi³, Jacek Lipkowski^{1*}

¹Department of Chemistry, University of Guelph, Guelph, ON N1G 2W1, Canada

²Barrick Gold Corporation, Goldstrike, NV 89822, United States

³Barrick Gold Corporation, Toronto, ON M5J 2S1, Canada

*Corresponding author: jlipkows@uoguelph.ca

ABSTRACT

Characterization of copper and ammonia interactions with the passive layer that impedes gold dissolution with thiosulfate based electrolytes at extended time frames was performed with electrochemistry and shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS). Generalized two-dimensional correlation spectroscopy (2DCOS) was also employed to assist interpretation of the collected SHINERS spectra. Growth of the complex passive layer mixture on a polycrystalline gold electrode immersed in a 0.10 M Na₂S₂O₃ electrolyte was found to initially proceed through formation of sulfides adsorbed to the gold electrode surface (SERS band at ca. 326 and 309 cm⁻¹) followed by rapid transformation to cyclo-S₈ (474, 218, and 152 cm⁻¹) and polysulfides/polythionates (459 cm⁻¹). After stable formation of the passive film, the addition of Cu²⁺ resulted in the partial removal of the passive layer. The removal of the components of the passive layer proceeded according to the following sequence; polysulfides were fastest, cyclo-S₈ next, followed by S_(ads)²⁻. The end product was observed to be a combination of copper and gold sulfides. In an independent study, the addition of ammonia displayed a similar ability to remove the passive layer constituents, albeit at much slower rates. From these observations it can be concluded that copper and ammonia play a vital function in preventing passive layer formation, allowing increased mass transport of thiosulfate and the oxidant across the electrode-electrolyte interface, thereby allowing a higher gold extraction efficiency.

Keywords: shell-isolated nanoparticle-enhanced Raman spectroscopy, electrochemistry, two-dimensional correlation spectroscopy, thiosulfate gold leaching, sulfur passive layer.

1. Introduction

The suitability of thiosulfate as an alternative complexing ligand in gold lixiviant solutions designed for hydrometallurgical extraction of gold is limited by the generation of passivating species that inhibit the mass transport of reactants and products across the interfacial region [1–9]. The surface enhanced Raman spectroscopy (SERS) is a surface sensitive technique that has the benefit of identifying the interfacial species in situ leading to a deeper understanding of the dissolution mechanism and to study how passive layer is formed at the gold-electrolyte interface. Previously, gold nanostructures employed to achieve sufficient Raman enhancement at the gold surface exposed to the gold lixiviant were quickly dissolved into the electrolyte [1-6]. Recently, we have shown that shell-isolated nanoparticles (SHINs), which are gold nanoparticles encapsulated in a uniform silica shell (typically 2-5 nm in thickness), are stable in typical gold leaching conditions and are capable of sustaining sufficient surface enhancement for 24 hours due to the protective silica coating that prevents dissolution of the gold nanoparticle core [10].

Using shell-isolated nanoparticle enhanced Raman spectroscopy (SHINERS) the generation of the soluble gold-thiosulfate complex as the predominant product upon initial exposure of a gold electrode to a thiosulfate lixiviant solution was observed [10]. However, the spectra collected of the SHINs modified polycrystalline gold electrode (Au/SHINs) after ~1000 mins exposure to a 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ lixiviant, see Figure 1, displays several broad and overlapping bands characteristic of many adsorbed species like thiosulfate, the gold-thiosulfate complex, sulfur/sulfides (i.e. Au_2S), cyclo- S_8 , and polysulfide/polythionate chains ($\text{S}_n/\text{S}_n^{2-}$) of varying lengths. Assignment of the bands observed in the spectra are based on a combination of; (i) previous reports of SERS spectra recorded of species adsorption from their respective pure electrolytes [1,3,6], (ii) theoretical calculations, and (iii) spectral analysis methods like Fourier self-deconvolution (FSD) or generalized two-dimensional correlation spectroscopy (2DCOS) [10]. The SERS spectra show that the thiosulfate lixiviant slowly decomposes on gold surfaces forming monoatomic adsorbed sulfur/sulfide, followed by formation of cyclo- S_8 and finally polysulfides/polythionates [6,10]. The formation of these elemental sulfur species at the gold-electrolyte interface inhibit the mass transport of reactants/products to and from the gold surface, and are therefore the primary cause for low gold extraction in industrial leaching practices.

Several studies investigated the potential of several additives to increase the gold extraction efficiency during thiosulfate based leaching. For example, redox couples (e.g. $\text{Cu}^{2+/+}$) [1,5], ammonia (e.g. $\text{NH}_3/\text{NH}_4^+$) [11–13], alkylthiols (e.g. RSH) [4,14], thiourea [15], sulfite [16], and ethylenediaminetetraacetic acid (EDTA) [17,18] have been suggested to improve the gold leaching kinetics in thiosulfate solutions [4,8,15,16,19–21]. In particular, the copper redox couple has been suggested as a better oxidant relative to dissolved oxygen due to increased solubility and mass transport to the gold surface in typical leaching conditions [7]. The overall leaching process, with copper as the supporting oxidant, is the combination of the electrochemical reduction of Cu^{2+} to Cu^+ and the oxidation of $\text{Au}(0)$ to $\text{Au}(\text{I})$ in the presence of excess thiosulfate [1,7,8,22]:

Amines, specifically ammonia ($\text{pK}_a = 9.24$), have also been suggested to improve the gold extraction efficiency in thiosulfate-oxygen leaching systems ($\text{pH} = 8\text{-}10$) through assisting

in surface processes like gold dissolution and transport of gold atoms into the bulk electrolyte according to [23]:

The stability constants have been previously reported to be similar for the gold-ammonia and gold-thiosulfate complexes in the bulk solution [7,23–26], but suggests free thiosulfate in solution will compete with ammonia as a ligand to form the thermodynamically favoured gold-thiosulfate complexes through [7]:

However, gold may also be leached directly into the aqueous ammonia-thiosulfate electrolyte as mixed ligand complexes according to [23]:

Nie et al. have recently suggested that the chemical interaction of ammonia with the passive layer constituents on the gold surface in thiosulfate electrolytes can significantly alter the gold leaching kinetics [13].

In addition to aiding in gold dissolution, ammonia is commonly reported as a second additive to stabilize copper(II) and prevent high rates of thiosulfate consumption [5,7,8,20,23,27,28]. In the presence of copper and ammonia the gold oxidation and subsequent dissolution in the thiosulfate leaching system is believed to occur via reduction of the copper(II) tetraammonia complex coupled with the exchange of two ammonia ligands to form a gold(I)-ammonia complex as described by:

Following Equation 3, free thiosulfate ions are then able to displace the ammonia ligands to produce the gold(I) thiosulfate complex. As been suggested by Molleman and Dreisinger [21], and more recently by Lampinen et al. [11], it is extremely important to control the thiosulfate to ammonia ratio for regeneration of the copper tetraammonia complex, Equation 6, and ensuring a high extraction efficiency of gold from the host ore.

In addition to assisting in the gold dissolution reaction, many additives may play a more complex role in gold extraction at extended time scales, by inhibiting the formation of the passive layer or by inhibiting or degrading the elemental sulfur species known to passivate the gold electrode surface. Most literature to date has focused on the cooperativity of copper and ammonia added together to the thiosulfate leaching system. Unfortunately, the reported literature has lacked direct evidence of the interaction by which each of these particular additives influence the overall gold extraction efficiency. A better understanding of the nature of copper and ammonia interactions with the sulfur passive layer formed in the interfacial region is paramount for maintaining high gold extraction efficiencies in industrial conditions. Previously, we have reported a procedure employing shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) to quantify the relative intensity changes in observed SHINERS bands related to the

formation of passive layer species under typical leaching conditions [10]. The objective of this study is to independently employ electrochemistry and SHINERS to study the effect of copper and ammonia after passive layer formation in a thiosulfate electrolyte under typical gold leaching conditions. The results presented offer added mechanistic insight into the individual roles that copper and ammonia play in assisting extraction of gold from its host ore.

2. Materials and Methods

2.1 *Materials and Substrate Preparations*

Gold nanoparticles (AuNPs, ca. 120nm dia.) were synthesized following the two step seed-mediated growth procedure and encapsulation with a thin silica layer (SiO_2 , ca. 2-5 nm thickness) as previously outlined by Li et al. [29–32]. The SERS active substrate was prepared by drop coating the SHINs under vacuum onto a freshly polished polycrystalline gold electrode (99.99% purity). Following the deposition of the SHINs, the gold electrode (Au/SHINs) was placed in a three-electrode glass electrochemical cell, and gently cleaned in an argon purged 0.1 M sodium fluoride electrolyte (NaF, Sigma Aldrich, >99%), prepared using Milli-Q water (18.2 M Ω cm), by repetitive cycling within the double layer region (-0.70 to +0.40 V vs. SCE) until a stable cyclic voltammogram characteristic of a clean gold surface was achieved. A coiled gold wire (Alfa Aesar, >99.9%) and a saturated calomel electrode (SCE, Fisher Scientific), connected to the electrolyte solution through a salt bridge, were used as the counter and reference electrodes, respectively.

Thiosulfate electrolyte solutions were prepared fresh prior to every investigation using sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, Sigma Aldrich, $\geq 99.5\%$) dissolved to a 0.10 M concentration in 100 mL of Milli-Q water (18.2 M Ω cm) and adjusted to a final pH value of 10.0 using sodium hydroxide (NaOH, Sigma Aldrich, 99.99%). The pH was routinely monitored to maintain its value constant throughout each experiment. Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Sigma Aldrich, +98%), or ammonium hydroxide (NH_4OH , Fisher Scientific, A.C.S. reagent), were studied as lixiviant additives by first dissolving them in a small aliquot of Milli-Q water, followed by slow addition directly into the thiosulfate lixiviant at $t = 0$ min or after the gold electrode had been exposed to the 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ electrolyte for 1000 mins and continuing the investigation for several additional hours.

2.2 *Electrochemical Rate of Gold Dissolution*

Kinetics of gold leaching in the presence of thiosulfate was monitored using a modified electrochemical method described previously by Baron et al. which was based on a Butler-Volmer equation [7,33–35]. The gold leaching rate was observed to be extremely dependent on the preparation method of the electrode prior to each measurement. Therefore, a polycrystalline gold electrode was polished with successive grades of diamond suspension (6, 3, and 1 μm , LECO) prior to each measurement, introduced into a three electrode electrochemical cell, and then repetitively cycled between -0.90 V and +1.25 V vs. SCE in a 0.10 M NaF electrolyte using a HEKA PG590 potentiostat until a clean and stable cyclic voltammogram was obtained. The electrochemically clean, and freshly polished, gold electrode was removed from the electrochemical cell, rinsed with copious quantities of Milli-Q water, and then re-immersed into a new electrochemical cell with a freshly prepared thiosulfate lixiviant at the open circuit potential (E_{OCP}). Linear sweep voltammograms (LSV) were recorded ± 20 mV of the E_{OCP} , at a sweep rate of 1 mV s $^{-1}$, every five minutes for the first 60 mins, every 10 minutes for the

following 120 mins, and every 30 mins afterwards. After each LSV the potential was allowed to return to E_{OCP} to minimize perturbation of the passive layer and the leaching rate. The mixed leaching current, i_{M} , was calculated from the slope of the collected LSV using independently determined transfer coefficients α_{O_2} and α_{Au} of 0.53 and 0.23, respectively [9,35]. The calculated values of i_{M} were converted to the rate of gold dissolution (R_{Au} in units of nmol m^{-2}

s⁻¹) using the Faraday law and plotted as a function of exposure time of the electrode surface to the thiosulfate lixiviant.

2.3 Spectral Instrumentation and Analysis

A Renishaw Raman imaging microscope equipped with a 785 nm NIR diode laser (300 mW power) and a CCD array detector was used for all Raman investigations. A spectral resolution of approximately 1 cm⁻¹ was achieved using a holographic grating (1200 grooves mm⁻¹) and a slit width of 50 μm. The spectrometer was calibrated to the vibrational Raman band of silicon ca. 521 cm⁻¹ prior to each experiment. Complete encapsulation of the SHINs was confirmed by recording a SERS spectra of the SHINs deposited on a clean silicon wafer and immersed in a 0.01 M pyridine solution (C₅H₅N, Fisher Sci., certified ACS reagent grade) with a 100% laser power, 1 s exposure, and 3 accumulations. All gold leaching investigations were performed using a custom built Teflon spectroelectrochemical cell designed to fit the Au/SHINs electrode in an inverted configuration (180° geometry). All leaching investigations were conducted in open atmosphere to allow the exchange of dissolved oxygen in the thiosulfate electrolyte. A LEICA immersion lens (63x) was immersed directly into the electrolyte solution and focused onto the electrode/substrate surface. All SHINERS studies were collected in a single acquisition between 3200 to 100 cm⁻¹ at regular time intervals with a laser power of approximately 15 mW at the sample, exposure time of 10 s, and 3 accumulations.

The SERS intensities plotted versus time were normalized following a previously published procedure [10]. In short, a background SHINERS spectrum was recorded of the clean Au/SHINs electrode immersed in Milli-Q water. The Milli-Q water was carefully aspirated and replaced with the desired thiosulfate leaching solution. Upon lixiviant exposure, the spectral intensity of all sequentially acquired SHINERS spectra were normalized at $\nu_{t=x}$ (2883 cm⁻¹) to the $\nu_{t=0}$ (2883 cm⁻¹) of the background spectrum to remove changes in the surface enhancement effect. Background removal of the normalized thiosulfate spectrum was accomplished by subtraction of the background spectrum, followed by baseline correction. Finally, the corrected band intensities of the passive layer species were normalized to the observed intensity at $t = 1000$ min, whereas, the bands related to the gold-thiosulfate complex were normalized at $t = 0$ min.

Generalized two-dimensional correlation spectroscopy (2DCOS) spectra [36–39] were generated from the dynamic SHINERS spectra using 2Dshige © software from Shigeaki Morita, Kwansei-Gakuin University (2004-2005). Briefly, 2DCOS analysis provides a 2D spectrum generated from a collection of sequentially acquired spectra in which the band intensities changed as a function of immersion time in the thiosulfate solution. The analysis gives two types of correlations, synchronous 2DCOS spectra resulting from simultaneous changes and asynchronous 2DCOS spectra, which arise from sequential or unsynchronized changes in the measured spectral series. The autocorrelation peaks are observed as positive symmetric peaks along the diagonal, $\nu_1 = \nu_2$, in the synchronous 2DCOS spectra. These autocorrelation peaks represent variation in the spectral intensity that occurs as a function of time at that particular frequency. A strong autocorrelation peak suggests that the change in the spectral band is strong as a function of time, while weak autocorrelation peaks or the absence of an autocorrelation peak indicate that the spectra are weakly dependent on time. Cross-correlation peaks are found in the off-diagonal positions in synchronous 2DCOS spectra, $\nu_1 \neq \nu_2$. Positive cross-peaks indicate that bands at ν_1 and ν_2 increase/decrease simultaneously, while negative cross-peaks imply that one

band is increasing while the other band is decreasing as a function of time. A correlation square, which illustrates the existence of coherent variations in the spectral intensities at ν_1 and ν_2 , can be obtained by connecting a pair of cross-correlation peaks positioned on opposite sides of the diagonal through the corresponding autocorrelation peaks. Thus, the synchronous 2D spectrum can help remove the ambiguity in the band deconvolution procedure by providing the number of peaks and their corresponding positions. In contrast to the synchronous spectra, asynchronous spectra are antisymmetric with respect to the diagonal, and therefore, no autocorrelation peaks are observed. If the intensity variation in two Raman bands occurs completely synchronized, then no cross correlation peak will be observed in the asynchronous spectra. Again, cross-correlation peaks in asynchronous spectra can be either positive or negative as in synchronous spectra. If the sign of an asynchronous cross-correlation peak matches the sign of the synchronous cross peak, then the change of band intensity at ν_1 takes place first and is followed by the change at ν_2 . If the signs of the synchronous and asynchronous cross-correlation peaks are opposite, then the change in the band intensity at ν_2 takes place before the change at ν_1 . Therefore, the asynchronous spectrum can provide information about the sequence of spectral changes.

3. Results and Discussion

3.1 Gold leaching in thiosulfate solution with ammonia

Figures 2A and 2B display the average electrochemical mixed potentials, E_M (top panel, Figure 2A), and gold leaching rates, R_{Au} in units of $\text{nmol m}^{-2} \text{s}^{-1}$ (middle panel, Figure 2B), calculated from the current voltage curves recorded after immersing a polycrystalline gold electrode into two different electrolyte solutions during 2500 min of gold leaching. The black curves, marked with (■), plot the results for the 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ (pH = 10.0) solution. The initial E_M and R_{Au} values are $-0.112 \pm 0.014 \text{ V vs. SCE}$ and $11.5 \pm 1.5 \text{ nmol m}^{-2} \text{s}^{-1}$, respectively. Error bars were excluded from Figure 2 for clarity. The E_M and R_{Au} decrease quite quickly during the first 50 min to $E_M \approx -0.144 \pm 0.006 \text{ V vs. SCE}$ and $R_{Au} \approx 5.2 \pm 1.8 \text{ nmol m}^{-2} \text{s}^{-1}$. After this initial change, E_M increases and R_{Au} decreases slowly in a quasi linear fashion. A large variance in the gold dissolution rate has been reported in the literature due to a number of reasons which include; (i) types of reagents used, (ii) differences in reagent concentrations, pH, and temperature, (iii) presence of different additives, (iv) different substrate preparation/cleaning methods and/or (v) the analytical technique employed to measure the leaching rate. R_{Au} values ranging from 10^{-5} to $10^{-8} \text{ mol m}^{-2} \text{s}^{-1}$ [4,5,35,40,41] have been reported for thiosulfate leaching systems. The values reported here are consistent with the lower end of these rates. The observed decrease in the leaching rate corresponds very well with the previously reported decrease in the quantity of the gold-thiosulfate complex in the interfacial region and the concomitant increase in adsorbed monatomic sulfur, cyclic sulfur and polysulfides/polythionates which comprise the passive layer that is believed to inhibit the gold dissolution reaction [10].

The green curves marked with (◆) in Figures 2A and 2B plot data for the 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ + 50 mM NH_4OH (pH = 10.0) electrolyte. The E_M and R_{Au} values display similar changes to that observed for the 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ solution. Their initial values -0.118 V and $10.8 \text{ nmol m}^{-2} \text{s}^{-1}$, are within the experimental error equal to the corresponding initial values in the solution without ammonia. However, with increasing leaching time the E_M decreases to a value about 50 mV more negative, ca. -0.168 V , and correspondingly the R_{Au} value remains higher than in the 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ electrolyte, during the first 1000 min of the leaching time. At leaching times longer than 1200 min the leaching rates become equal in these two electrolytes. The increase in the R_{Au}

in the presence of ammonia relative to the $\text{Na}_2\text{S}_2\text{O}_3$ electrolyte supports the previous suggestions that ammonia plays an important but convoluted role in aiding gold dissolution [7]. However, while the observed change in the E_M upon ammonia addition appears quite significant, the relatively small change in R_{Au} is within the standard error. It is believed that after a long exposure of the gold surface to the $\text{Na}_2\text{S}_2\text{O}_3$ electrolyte multilayers of passive species are likely present at the gold surface and the addition of a small quantity of ammonia may only be able to remove a small portion of this layer which results in shifting the E_M by 50 mV but not able to change R_{Au} to a significant extent.

To demonstrate that ammonia weakens the passive layer, a third experiment was performed in which 50 mM NH_4OH were added to the 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ (pH = 10.0) electrolyte after 1000 min of leaching time had elapsed. These data are marked as (▲) in Figures 2A and B. During 500 min after the addition of 50 mM NH_4OH , E_M decreases and R_{Au} increases to values slightly above the rates observed during continuous leaching in the 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ + 50 mM NH_4OH (pH = 10.0) solution. At longer times (after 1500 min), the leaching rates become approximately equal in all three experiments. This experiment suggests that the addition of the NH_4OH plays a role in degrading the passive layer and allowing the rate of gold leaching to increase, if there is enough NH_4OH to remove a significant portion of the passive layer that exposes the underlying gold surface for further gold dissolution.

To further demonstrate the interfacial role that ammonia plays as an additive, molecular identification of the species present in the interfacial region is needed. For that purpose SHINERS was employed using a SHINs modified polycrystalline gold electrode (Au/SHINs). The spectra acquisition and analysis followed the procedure described in detail in the earlier publication [10]. The SHINERS spectra were recorded continuously before and after addition of ammonia to the 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ solution repeating experiment 3, where the data is marked as (▲) in Figures 2A and 2B. The spectra recorded during the first 1000 min of gold leaching in the 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ solution were in a very good agreement with the data presented in ref [10] and hence they are not shown here. After 1000 min exposure to a 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ electrolyte the passive layer formed at the interface is observed to predominantly consist of several sulfur species, most notably, sulfides, cyclo- S_8 , and polysulfide ($\text{S}_n/\text{S}_n^{2-}$) or polythionate ($\text{S}_n\text{O}_y^{2-}$) chains of variable length, as shown in Figure 1. The composition of the passive layer becomes stable and therefore approximately time independent after 1000 min exposure of the Au/SHINs electrode to 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$.

Here, we show only spectra acquired after addition of 50 mM NH_4OH to the 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ solution, recorded at regular intervals of time. A selected set of SHINERS spectra for the 100 – 550 cm^{-1} region are displayed in Figures 3A and 4, respectively. They are marked as a time elapsed after the addition of ammonia to the leaching solution. The overall shape of spectra in Figure 3A is similar to the spectrum shown in Figure 1 indicating that the broad envelope of these spectral features consists of bands corresponding to the components of the passive layer as assigned in Figure 1. All bands in Figure 3A decrease as a function of time, albeit at different rates, suggesting that ammonia is assisting the removal of elemental sulfur species, most notably sulfides (309 cm^{-1}), cyclo- S_8 (474, 218, and 152 cm^{-1}) and polysulfides/polythionates (459 cm^{-1}) present at the gold-electrolyte interface.

To correlate changes in the composition of the passive layer to the changes in the dissolution rate, the intensity of the selected sulfur bands are plotted in Figure 2C as a function of the dissolution time, before and after the addition of ammonia at the 1000 min mark. These bands correspond to; (▲) sulfides at 309 cm^{-1} , (●) cyclo- S_8 at 218 cm^{-1} , (■)

polysulfide/polythionate chains at 459 cm^{-1} and (♦) gold-thiosulfate complex at $\sim 379\text{ cm}^{-1}$. In order to visualize the effect of ammonia addition on the composition of the passive layer, the band intensities were normalized with respect to the intensities measured at time 1000 min, which is at just before addition of NH_4OH . The gold-thiosulfate band was normalized at $t=0$ min and only plotted to 500 min as it becomes overly convoluted with the passive layer bands at longer immersions. Further, as already discussed in our previous paper [10], the fast initial decrease of the leaching rate ($t = 0$ to 100 min) correlates well with the decrease in the surface concentration of the gold-thiosulfate complex. The results show that the decrease in the normalized intensity of all three sulfur bands after NH_4OH addition ($t > 1000$ min) correlates well with the increase in the gold dissolution rate shown in Figure 2B. This correlation suggests that ammonia removes elemental sulfur and that the presence of elemental sulfur in the interfacial region inhibits the gold dissolution reaction. The data also shows at approximately 400 min after addition of ammonia the amount of sulfur species in the passive layer starts to increase.

To explore the order by which ammonia is degrading the passive layer, generalized 2DCOS analysis of the sequentially acquired spectra (Figure 3A) was employed. This analysis can provide useful information in which order the sulfur species are removed from the passive layer by ammonia. The synchronous and asynchronous 2DCOS spectra are displayed in Figures 3B and 3C, respectively. Strong positive cross-correlation squares can be observed in Figure 3B between many of the identified bands suggesting the change in spectral intensity of all these bands occurs in the same direction. However, in the asynchronous spectrum (Figure 3C), the negative cross-correlation bands at (309, 459) and (218, 459) suggest that the changes in the spectral intensity related to polysulfides/polythionates, i.e. 459 cm^{-1} , occurs prior to that of sulfides, at 309 cm^{-1} and cylo- S_8 at 218 cm^{-1} . In addition, the positive (218, 309) band indicates that spectral changes corresponding to cylo- S_8 take place before spectral changes corresponding to sulfides. Therefore, the 2DCOS analysis revealed that after addition of ammonia the polysulfides/polythionates appear to be removed first, they are followed by the removal of cylo- S_8 and sulfides at the end. Previous research, has shown that amines and other nucleophiles such as cyanide [42], sulfides [43], phosphines [44], can cause spontaneous ring opening of cyclo- S_8 forming polysulfides which can then undergo further attack via S-S bond cleavage [45]. From these observations it could be hypothesized that additives like ammonia, under typical gold leaching conditions, may chemically interact with the elemental sulfur layer that has been formed at the gold-electrolyte interface.

Ammonia is known to adsorb on gold surfaces exhibiting SERS bands in the $700 - 600\text{ cm}^{-1}$ and $400 - 350\text{ cm}^{-1}$ regions [46]. To find spectroscopic evidence of ammonia adsorption, Figure 4 plots SHINERS spectra in the $1100 - 600\text{ cm}^{-1}$ region, recorded after the addition of NH_4OH to the $0.10\text{ M Na}_2\text{S}_2\text{O}_3$ electrolyte. The SHINERS spectra displays several distinct bands located at $1063, 1040, 1025,$ and 998 cm^{-1} , which correlate well with previously reported $\nu(\text{SO})$ values from polythionates with $n \geq 4$, the gold-thiosulfate complex, and thiosulfate [3–6,47–50]. The weak, broad band observed between $900 - 750\text{ cm}^{-1}$ which remains fairly consistent after the addition of ammonia may be associated with oxide formation, e.g. $\nu(\text{AuO}$ or $\text{AuOH})$, on the polycrystalline gold surface [52]. Upon addition of NH_4OH , a strong band at ca. 673 cm^{-1} , tentatively assigned as $\nu_s(\text{SNS})$, appears initially and grows in intensity until 21 min where it begins to decrease and eventually disappears altogether after 61 min. A second band positioned at 881 cm^{-1} appears after ~ 20 min NH_4OH addition which may correspond with $\nu_{as}(\text{SNS})$ [51]. The appearance of these bands indicates that ammonia plays a critical role by interacting

directly with the sulfur passive layer and chemically degrades and removes sulfur species from the interfacial region through direct bonding to adsorbed sulfur species.

3.2 Gold leaching in thiosulfate solutions with copper

Figures 5A and 5B compare the E_M and R_{Au} values of a freshly polished and electrochemically clean gold electrode recorded during three independent 2500 min gold leaching experiments. The black points plot the data obtained for gold leaching in 0.10 M $Na_2S_2O_3$ with pH = 10.0 (experiment 1-reference curves). The blue points represent measurements of experiment 2 performed in 0.10 M $Na_2S_2O_3$ + 10 mM $CuSO_4$ (pH = 10.0) solution. Finally, red points plot the data of experiment 3 in which 10 mM $CuSO_4$ was added to the 0.10 M $Na_2S_2O_3$ solution after 1000 min of gold dissolution. For the 0.10 M $Na_2S_2O_3$ + 10 mM $CuSO_4$ electrolyte, the initial $E_M \sim -0.010$ V vs. SCE is more positive with respect to the initial value of the solution without copper ($E_M = -0.112$ V). In the presence of copper, the initial $R_{Au} \sim 135.8 \pm 30.2$ nmol m⁻² s⁻¹ is an order of magnitude larger than in the pure 0.10 M $Na_2S_2O_3$ solution (initial $R_{Au} \sim 5.2$ nmol m⁻² s⁻¹). Within the first 60 minutes the E_M and R_{Au} values for 0.10 M $Na_2S_2O_3$ + 10 mM $CuSO_4$ solution quickly decrease reaching a minimum at -0.078 ± 0.004 V vs. SCE and 20.8 ± 0.1 nmol m⁻² s⁻¹, respectively. The E_M value increases somewhat after reaching the minimum, but over extended times remains fairly constant around -0.060 ± 0.003 V. For clarity the error bars have been omitted from Figure 5. As evidenced from the shift in the E_M and R_{Au} values the addition of Cu^{2+} significantly alters the surface chemistry. Previously, this change has been attributed to the ability of Cu^{2+} to act as a better redox couple relative to dissolved oxygen. Upon conversion of the Cu^{2+} to Cu^+ , dissolved oxygen in the bulk is able to regenerate the Cu^{2+} ion for further leaching. The E_M values are always shifted about 0.080 V more positive than in the electrolyte without copper. However, the average R_{Au} in the presence of copper rises at extended leaching times suggesting that Cu^{2+} plays a very complex role in the gold dissolution mechanism.

In experiment 3, 10 mM $CuSO_4$ (final concentration) was added into the 0.10 M $Na_2S_2O_3$ electrolyte solution after the gold electrode was exposed for 1000 min. The E_M and R_{Au} values were then continually monitored for an additional 1500 min. Upon addition of Cu^{2+} , a large positive shift in the E_M from -0.135 V to -0.032 V vs. SCE and a corresponding increase in the R_{Au} value, from 3.7 to 60.8 nmol m⁻² s⁻¹, are observed. After the initial positive shift in E_M upon Cu^{2+} addition the mixed potential quickly decreases and then slowly approaches the values measured in experiment 2 for 0.10 M $Na_2S_2O_3$ + 10 mM $CuSO_4$ solution. The addition of Cu^{2+} also causes a spike on the R_{Au} versus leaching time plot followed by a progressive increase of R_{Au} . The rates of gold dissolution after Cu^{2+} are much higher than in the pure 0.10 M $Na_2S_2O_3$, however lower than in experiment 2 where copper was present in the leaching solution since initial exposure of the gold electrode. The higher R_{Au} values in the presence of Cu^{2+} indicate that Cu^{2+} plays a complex interfacial role by; (a) promoting gold oxidation, and (b) interacting with elemental sulfur species present in the interfacial region. The shift in the mixed potential and large increase in the leaching kinetics are consistent with the previous reports of enhanced gold dissolution in the presence of copper [1,7,23,41].

To characterize changes in the composition of surface species upon the addition of Cu^{2+} , a freshly prepared Au/SHINs electrode was exposed to a 0.10 M $Na_2S_2O_3$ electrolyte for 1000 min and characterized with SHINERS (measurements complementary to experiment 3). Figure 6A displays the sequentially acquired SHINERS spectra upon addition of 10 mM $CuSO_4$. After

addition of Cu^{2+} , a very rapid decrease in the spectral intensity of the polysulfide bands, ca. 459 cm^{-1} , and those related to cyclo- S_8 , ca. 474 , 218 and 152 cm^{-1} , are observed.

To allow comparison of the changes in surface composition to the changes in E_M and R_{Au} , the normalized SERS intensities due to polysulfide chains (459 cm^{-1}), gold sulfide (309 cm^{-1}), cyclo- S_8 (218 cm^{-1}) and copper sulfide (140 cm^{-1}) are plotted in Figure 5C. Upon addition of copper, the passive layer bands corresponding to polysulfide chains and cyclo- S_8 rapidly decrease to approximately 10% of their intensity. The gold-sulfide band also decreases by about 30%. The SHINERS spectra reveal a new band at 140 cm^{-1} that could be assigned to the presence of covellite (CuS) at the surface [53–56]. The data indicates that long polysulfides/polythionates and cyclo- S_8 are quickly converted to short chains, with n less than 4. The gold and copper sulfides appear to be the predominant components of the stable passive layer at longer times, $t > 200$ mins after Cu^{2+} addition.

More information about the sequential changes of these bands is provided by the 2DCOS analysis. The synchronous and asynchronous 2DCOS spectra generated from the time dependent spectra recorded after addition of Cu^{2+} are represented as Figure 6B and 6C, respectively. Strong positive cross-correlation squares drawn in the synchronous spectrum (Figure 6B) between (459 , 474), (459 , 218), and (459 , 152) indicate that these bands change in the same direction. In contrast, negative cross correlation bands between 140 cm^{-1} and all other observed features in the spectrum indicates the 140 cm^{-1} band (covellite) change in the opposite direction relative to the other spectral features. In fact Figure 6A shows that the spectral variation at 140 cm^{-1} increases while other features decrease with time. In the asynchronous, spectrum Figure 6C, the cross correlation bands at 140 cm^{-1} are positive. Since the corresponding cross correlation bands in the synchronous spectrum, Figure 6B, were negative, the intensity variation related to covellite follows after the change of all other features in the spectrum. In other words, the cyclo- S_8 , long and short chain polysulfides are removed first before covellite is formed. Further, in the asynchronous spectrum the cross correlation bands present at 218 cm^{-1} , 400 and 426 cm^{-1} (short chain), and 459 cm^{-1} (long chain polymeric sulfur) are also positive. These cross correlation bands are also positive in the synchronous spectrum indicating that changes in the 218 cm^{-1} band are taking place before changes of the polysulfide bands. This means that the cyclo- S_8 is removed by addition of Cu^{2+} before polymeric sulfides. Finally, the (309 , 459) and (426 , 459) bands are negative in the asynchronous spectrum while they are positive in the synchronous spectrum. This behaviour indicates that the changes of the long chain polysulfide band (459 cm^{-1}) take place before changes of the AuS band (309 cm^{-1}) and short chain polysulfide band (426 cm^{-1}). Thus the 2DCOS analysis provided unique information that addition of Cu^{2+} to the thiosulfate solution removes first cyclo- S_8 , followed by long-chain polysulfides, then by removal of short chain polysulfides from the passive layer. However, a new species CuS appears in the surface layer. The formation of CuS on the gold surface would be of concern during a typical gold leaching process as Cu^{2+} is consumed to form CuS . However, since the leaching rate slowly increases when the amount of CuS increases with time, the data suggests that formation of CuS on the surface does not have as significant of a passivating effect.

4. Conclusions

Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), generalized two-dimensional correlation spectroscopy (2DCOS), and electrochemistry were used to investigate the gold leaching kinetics and understand the role copper and ammonia play in the interfacial

region. Consistent with previous reports the overall kinetics of gold leaching were found to be higher in the presence of ammonia and copper. However, addition of ammonia after 1000 min of exposure of a polycrystalline gold electrode to a 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ electrolyte was found to significantly increase the leaching rate. Characterization with SHINERS revealed direct evidence of degradation of the elemental sulfur species, i.e. cyclo- S_8 , polysulfide chains, and adsorbed sulfides, by ammonia. Exposure of a similar passive layer to copper cations displayed reduction of cyclo- S_8 and polysulfide species to form a stable layer of CuS . Ammonia and copper play a convoluted mechanism of preventing passive layer formation and increasing the oxidation of gold to achieve higher gold extraction efficiencies. The observed decrease in passive layer species present in the interfacial region and the simultaneous increase in the gold dissolution rate, R_{Au} , with the additives present during gold leaching experiments supports previously reported observations of beneficial effects towards the gold leaching kinetics in the presence of Cu^{2+} and ammonia in thiosulfate lixiviants.

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Figure 1: Deconvolution of the passive layer constituents formed on a SHINs modified polycrystalline gold electrode (Au/SHINs) after immersion in a 0.10 M Na₂S₂O₃ electrolyte (pH = 10.0) for 1000 min.

Figure 2: Average (A) E_M and (B) R_{Au} values measured as a function of immersion time of freshly polished polycrystalline gold electrode in electrolyte solutions of; (■) 0.10 M Na₂S₂O₃ (pH = 10.0) for 2500 min, (◆) 0.10 M Na₂S₂O₃ + 50 mM NH₄OH (pH = 10.0) for 2500 min, and 0.10 M Na₂S₂O₃ (pH = 10.0) for 1000 min followed by the addition of (▲) 50 mM NH₄OH for a sequential 1500 min. (C) Normalized average SERS intensities of; (■) polysulfide/polythionate chains at 459 cm⁻¹, (▲) gold sulfide at 309 cm⁻¹, and (●) cyclo-S₈ at 218 cm⁻¹, recorded at the surface of the Au/SHINs electrode immersed in a 0.10 M Na₂S₂O₃ electrolyte (pH = 10.0) for 1000 min, followed by a subsequent 1500 min after the addition of 50 mM NH₄OH.

Figure 3: (A) Baseline corrected SERS spectra, 600-100 cm⁻¹ region, of the Au/SHINs electrode collected upon the addition of 50 mM NH₄OH after immersion in a 0.10 M Na₂S₂O₃ electrolyte (pH = 10.0) for 1000 min. Corresponding (B) synchronous and (C) asynchronous 2DCOS spectra generated as a function of immersion time; red – positive correlation bands, blue – negative correlation bands. Time-averaged spectra included for reference.

Figure 4: Baselined corrected SERS spectra, 1100-600 cm^{-1} region, of the Au/SHINs electrode collected upon the addition of 50 mM NH_4OH into the lixiviant after the gold electrode had been immersed into the 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ electrolyte (pH = 10.0) for 1000 min.

Figure 5: Averaged (A) E_M and (B) R_{Au} values measured as a function of immersion time in electrolyte solutions of; (■) 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ (pH = 10.0) for 2500 min, (●) 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ + 10 mM CuSO_4 (pH = 10.0) for 2500 min, and 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ (pH = 10.0) for 1000 min followed by the addition of (♦) 10 mM CuSO_4 for a sequential 1500 min. (C) normalized average SERS intensities of; (■) polysulfide chains (i.e. $n < 4$) at 426 cm^{-1} , (♦) covellite at 140 cm^{-1} , (▲) metal-sulfur at $\sim 300\text{ cm}^{-1}$, and (●) cyclo- S_8 at 218 cm^{-1} .

Figure 6: (A) Baseline corrected SHINERS spectra of the Au/SHINs electrode recorded upon the addition of 10 mM CuSO₄ after immersion in a 0.10 M Na₂S₂O₃ electrolyte (pH = 10.0) for 1000 mins; (B) synchronous and (C) asynchronous 2DCOS spectra generated as a function of immersion time from the SERS spectra (Figure 6A) recorded after CuSO₄ addition; red – positive correlation bands, blue – negative correlation bands. Time-averaged spectra included for reference on the two axes.

Table 1: Summarized band positions of observed interfacial species with corresponding band assignments.

Vibrational Mode Assignment	Chemical Identity	Observed Band Positions (cm ⁻¹)		
		Au/SHINs 0.1M Na ₂ S ₂ O ₃ (≤ 600 mins)	Au/SHINs 0.1M Na ₂ S ₂ O ₃ + 50mM NH ₄ OH (≥ 1080 mins)	Au/SHINs 0.1M Na ₂ S ₂ O ₃ + 50mM CuSO ₄ (≥ 1080 mins)
δ (SSS)	CuS	-	-	140
δ_{as} (SSS)	cyclo-S ₈	151	152	152
δ_s (SSS)	cyclo-S ₈	218	218	218
δ_s (SSS)	S ₄ O ₆ ²⁻ / S ₃ O ₆ ²⁻	266, 309	248, 268, 309	268, 309
ν (CuS) / ν (Au _x S _y)	CuS / Au _x S _y / [Au(S ₂ O ₃) ₂] ³⁻			
ν (AuS)	Au _x S _y	326	-	-
ν_s (SS)	[Au(S ₂ O ₃) ₂] ³⁻	378	-	-
	S ₄ O ₆ ²⁻ / S ₃ O ₆ ²⁻ / polymeric S _{3,4} / S _{3,4} ²⁻	408	400	400
	S ₂ O ₃ ²⁻ / polymeric S _{3,4} / S _{3,4} ²⁻	430	426	426
	polymeric S _{n>4} / S _{n>4} ²⁻	459	459	459
	cyclo-S ₈	474	474	472
ν (SS)	CuS	-	-	469