



The electrochemical quartz crystal microbalance as a sensor in the gold thiosulfate leaching process

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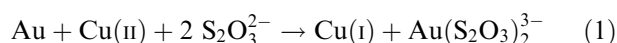
Key words: EQCM analysis, gold, hydrometallurgy, leaching, silver, thiosulfate

Abstract

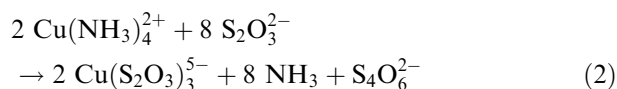
A technique was developed for measuring the thiosulfate concentration in gold thiosulfate leaching solutions containing copper and ammonia. The method, which is based on the relationship between thiosulfate concentration and the oxidation rate of silver, was firstly studied using the 'rotating electrochemical quartz crystal microbalance' (REQCM). It was found that the measured silver oxidation rate is directly related to the thiosulfate concentration. The silver oxidation rate was also shown to be unaffected by the presence of other species likely to be found in gold leach solutions. The technique was then evaluated for use as a method of flow injection analysis, utilizing a flow through 'electrochemical quartz crystal microbalance' (EQCM) cell.

1. Introduction

Cyanidation is the primary method used to recover gold from its ores, being an established technique that is both cheap and efficient. However, due to the high toxicity of cyanide, there is an increasing degree of public concern over its use in the gold leaching process. One alternative to the use of cyanide as a lixiviant is thiosulfate. It has been shown that a copper catalysed thiosulfate leaching system is a viable alternative to cyanidation for extracting gold from its ores [1–7]. The thiosulfate leach solutions are alkaline to avoid the thiosulfate reaction with acid, hence ammonia is used to stabilize the copper(II). The simplified stoichiometry by which the leaching of gold using thiosulfate solutions containing copper occurs is shown in Equation 1:

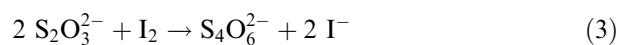


Furthermore, the gold leach rate has been shown to depend on both thiosulfate concentration and copper(II) concentration [4, 8, 9]. It has been shown that thiosulfate undesirably reacts with copper(II) as shown in Equation 2 [10]. Under typical leaching conditions in the absence of oxygen, this reaction proceeds slowly [10]. However, in the presence of oxygen, the oxidation of thiosulfate has been found to be much more rapid; this effect is known as the copper(II) catalysed oxidation of thiosulfate by oxygen [11]:



Due to the oxidation of thiosulfate in gold leach solutions, the thiosulfate concentration is constantly decreasing. Thus, a simple method for measuring and monitoring the thiosulfate concentration must be available before long term testing of the thiosulfate leaching process can proceed. However, thiosulfate is not so easily measured in these leach solutions; the reasons for this are outlined below.

There are currently several analytical methods available for the determination of thiosulfate concentration. A titrimetric based approach for the determination of thiosulfate uses the oxidation of thiosulfate to tetrathionate by iodine according to Equation 3:

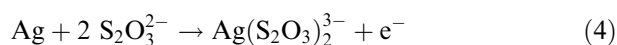


This is a simple method for determining thiosulfate concentration since the above reaction proceeds to completion under acidic conditions and the end point can be determined visually using a starch solution [12]. However, the likely presence of other species such as sulfite, and other polythionates means that one determination requires several titrations [12]. Also, the presence of copper(II) can make the end point difficult to detect visually. Furthermore, the titration is complicated by the presence of copper(I), which is generated in the leach solutions, because it too reduces iodine. This all makes the thiosulfate determination for these leach solutions very complicated.

Ion chromatography is another alternative that enables the determination of sulfite, sulfate, thiosulfate and polythionates simultaneously. This technique can

potentially provide a comprehensive solution speciation; however this method suffers from the limitation that it is relatively slow [12] and requires significant dilution that can result in a different solution speciation. Furthermore, the analytical equipment required is not robust enough for use in an industrial environment and expensive if one is only interested in measuring thiosulfate concentration.

A flow injection analysis method which uses a standard electrochemical cell with a silver working electrode and platinum counter electrode to measure thiosulfate concentration has been developed elsewhere [13]. The method is based on measuring the current due to the oxidation of silver (shown in Equation 4) while controlling the electrode potential at 0.1 V vs SCE (0.34 V vs SHE). This potential is 0.35 V more positive than the standard potential of -0.01 V for the oxidation of silver to silver thiosulfate [14]. That is,



For this technique, no correction is made for the contribution to the measured current by the reduction or oxidation of other species present in gold thiosulfate leaching solutions. At a potential of 0.34 V the oxidation of copper(I) at the silver electrode will contribute to the measured current. This could be quite significant if the gold ore contains copper, as leaching of such ores result in a high copper concentration in the leach solution. Hence, a new technique is required that is capable of easily and rapidly measuring the thiosulfate concentration in solutions used for gold leaching.

This paper presents an analytical method developed that measures thiosulfate concentration in leach solutions via the leach (oxidation) rate of a particular metal. Evaluation of the method was conducted using a rotating electrochemical quartz crystal microbalance (REQCM). The REQCM is described elsewhere [15], and has the advantage that it can measure metal oxidation rates within seconds with a sensitivity of 2 ng. The metal species was chosen such that the oxidation is dependent on the thiosulfate concentration. Gold cannot be used since its oxidation rate is largely influenced by other species in solution [8, 9].

2. Experimental details

All experiments were carried out using solutions prepared from analytical grade reagents and distilled water. Mass changes were measured using an REQCM, which is described elsewhere [15]. The REQCM has already been used to study a number of electrochemical reactions such as leaching, electrodeposition and corrosion [16–20]. Use of a rotating electrode as in the REQCM means that mass transfer is reproducible and well defined; the flux of reactants to the disc surface can be calculated from the Levich equation. The change in

electrode mass, Δm , measured by the REQCM, is related to the oxidation rate through Equation 5:

$$r = \frac{\Delta m}{AM\Delta t} \quad (5)$$

where r is the oxidation rate ($\text{mol m}^{-2} \text{s}^{-1}$), A is the electrode surface area (m^2), M is the atomic mass of the metal (g mol^{-1}) and Δt is the time elapsed (s).

Platinum was sputtered onto the quartz electrodes using a Balzers SCD-050 sputter coating system. Prior to each experiment conducted with a silver electrode, the electrode was electroplated at 50 A m^{-2} from a solution containing 0.025 M silver cyanide, 0.23 M potassium cyanide and 0.11 M potassium carbonate. To prepare a copper electrode, the electrode was electroplated at 150 A m^{-2} from a solution containing 0.75 M copper sulfate and 0.25 M sulfuric acid.

Unless specified otherwise solutions contained 0.1 M Na_2SO_4 and 0.1 M NH_3 , and all REQCM experiments were conducted using a rotation rate of 300 rpm and at a temperature of 30°C . Potential scans were conducted at a rate of 1 mV s^{-1} . The Radiometer PGP201 Potentiostat was computer controlled and data was logged via the computer. To measure the thiosulfate concentrations with time for a leach solution, a thiosulfate solution was first stirred within a sealed jacketed vessel maintained at a constant temperature ($\pm 0.1^\circ\text{C}$) and purged with the appropriate gas before commencing experiments. A concentrated copper-ammonia solution was then injected into the vessel to commence each experiment. Samples were withdrawn using a syringe for thiosulfate analysis.

3. Results and discussion

3.1. Development of analytical method

To measure thiosulfate concentration via the oxidation rate of a metal, some preliminary work was conducted in order to establish a possible metal candidate. Based on the work previously conducted by Hemmati et al. [13], silver was an obvious starting choice. The REQCM was used to measure mass changes of a silver electrode, whilst the applied potential was scanned, in solutions of various thiosulfate concentrations. The change in electrode mass with time is converted to an oxidation rate using Equation 5. Figure 1 illustrates both the mass change and calculated silver oxidation rate versus applied potential for a silver electrode in 0.12 M thiosulfate. Clearly, as the electrode potential is increased the typical exponential growth in silver oxidation rate is observed; a diffusion limiting oxidation rate is not observed due to the very high concentration of thiosulfate in solution.

One factor which must be considered when analysing the frequency response of the EQCM is the surface roughness of the film of interest; it has been shown that

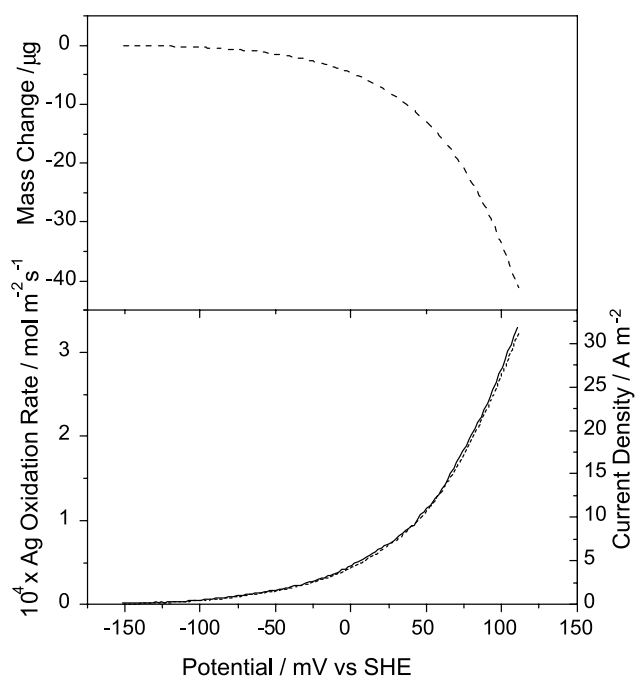


Fig. 1. Mass change of silver electrode against potential in 0.12 M thiosulfate solution. Lower part shows the silver oxidation rate (—) calculated from the rate of mass change and the current density (---).

fluid can become entrapped within rough surfaces, and hence contribute to the frequency change which is measured. For example, Zhang et al. [21] have shown that surface roughness changes may induce frequency shifts of 100 ppm (1000 Hz for a 10 MHz crystal). Since the silver surface is being oxidized, there may be a change in the morphology of the surface during the measurements. To assess the effect of surface roughness, the current measured during silver oxidation is also shown in Figure 1. In this figure, the current density axis scale is equal to the oxidation rate scale multiplied by the Faraday constant. It can be seen that the measured current density response directly matches the silver oxidation response at all applied potentials. Such a result implies that the EQCM is mainly measuring frequency changes which result from changes in mass of the silver electrode. Thus, changes in surface roughness were not considered as a major contribution to the measured frequency change.

An important consideration for thiosulfate analysis in ammonia solutions is that depending on the potential applied to the silver electrode and the ammonia concentration of the thiosulfate solution, silver can also be oxidized to form the amine complex, as shown in Equation 6. The standard electrode potential for this reaction is 0.372 V [14], which is significantly higher than -0.01 V for the formation of the thiosulfate complex (Equation 4). That is,

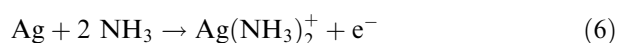


Figure 2 shows a comparison between the oxidation of silver in a 0.12 M thiosulfate solution and a 0.4 M

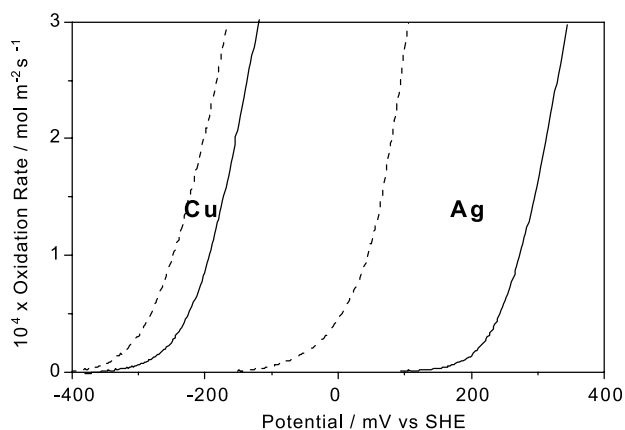


Fig. 2. Copper and silver oxidation rates against potential in either 0.12 M thiosulfate (---) or 0.4 M ammonia (—).

ammonia solution. These concentrations were chosen as they represent the typical composition of a gold thiosulfate leach solution. It can be seen from Figure 2 that the oxidation of silver in thiosulfate solutions occurs much more readily than in the ammonia solution; there is a good separation of around 200 mV between the oxidation curves. If an applied potential of 100 mV or less is utilized, then the oxidation during leaching could be expected to be limited to the formation of the thiosulfate complex.

Also shown in Figure 2 is the oxidation rate versus applied potential for copper in either 0.12 M thiosulfate or 0.4 M ammonia. In this case, it is clear that the formation of the amine complex occurs at a very similar potential to the thiosulfate complex. Hence, silver appears to be a better choice as a metal for measuring thiosulfate concentration in solutions containing ammonia. From Figure 2 it is also evident that the silver oxidation rate increases rapidly in the potential region from -100 to 50 mV. Since the oxidation reaction is chemically controlled in this potential region, it is likely that the silver oxidation rate will be sensitive to changes in temperature and the electrode surface. At potentials greater than 50 mV, the silver oxidation rate is too high for practical use, as a significant quantity of silver is consumed in every measurement.

To improve the technique for the determination of thiosulfate concentration, it was decided that the leach solution should be diluted. This would result in the silver oxidation rate being lower. The most important consideration in dilution is to maintain the solution chemistry, otherwise the concentration of thiosulfate measured in the diluted sample may not be representative of the thiosulfate concentration in the actual leach solution. There are two possible reasons why the solution chemistry could be different due to dilution. The first possibility is that the dilution could result in a significant relative increase in the reaction rate between copper(II) and thiosulfate. This would result in a lower determination of thiosulfate concentration. The second possibility is that the dilution could change the copper(I)

complex speciation. As will be shown later, the thiosulfate which is complexed with copper(I) is not measured using this technique. Thus, if the amount of thiosulfate complexed to copper(I) is varied, the free thiosulfate in the diluted solution would change. The methods used to minimise these problems are outlined below.

A number of experiments were conducted to establish what effect dilution had on the reaction between copper(II) and thiosulfate. Dilution into a 0.1 M sodium sulfate electrolyte was firstly considered. However, upon dilution of a leach solution by a factor of 10 with this solution, the copper was observed to precipitate. This is obviously undesirable for an analytical method. Therefore, dilution into an electrolyte solution containing ammonia is required. It was observed that when the ammonia concentration in the electrolyte is low, the reaction between thiosulfate and copper(II) is very rapid; 0.1 M ammonia was required to stabilize the copper(II) so as to minimize its reaction with thiosulfate. With 0.4 M ammonia in the diluent, the copper(II)-thiosulfate reaction rate is observed to almost completely cease.

An important consideration with dilution into ammonia is the relative potentials for oxidation of silver as the silver amine and silver thiosulfate complexes, respectively. Experiments were performed with a thiosulfate concentration of 6 mM thiosulfate (1 in 20 dilution) and 0.1 M ammonia. The silver oxidation rate as a function of potential is shown in Figure 3. It can be seen that the curves are nowhere near as steep as those observed for the undiluted solutions. This is advantageous for an analytical technique.

In comparison, the oxidation curve for silver in 0.1 M ammonia in the absence of thiosulfate is also shown in Figure 3. It is clear that in these solutions, the oxidation of silver does not occur at potentials more negative than 200 mV. In contrast, in solutions containing 0.4 M ammonia, it is clear from Figure 3 that the oxidation of silver occurs at potentials more positive than 130 mV. So, if the solution contained 0.4 M ammonia, the potential applied to the silver electrode would need to

be less than 130 mV to avoid the oxidation of the silver as the silver amine complex. If the solution contained 0.1 M ammonia, then a potential of 200 mV could be used. It is often beneficial to impose a higher overpotential to the silver electrode, as the reaction is likely to be less sensitive to changes in the surface state of the silver. Hence, it was decided that the dilution should result in a solution which contains 0.1 M ammonia, and a potential of 200 mV was chosen.

Another important variable that must be considered is change in the ammonia concentration of the thiosulfate leach solution. Figure 3 also shows a comparison between the oxidation of silver in 6 mM thiosulfate and either 0.1 or 0.4 M ammonia. It is clear that the silver oxidation curves differ, even at low overpotentials where the formation of the silver amine complex does not occur. These results are similar to the oxidation of copper in thiosulfate solutions, where the addition of ammonia results in oxidation at more negative potentials [22]. One possible explanation for this phenomena is that silver is capable of forming a mixed thiosulfate/ammonia complex. Unfortunately, thermodynamic data on such species are not available. From a practical point of view, the results shown in Figure 3 indicate that careful control of the ammonia concentration is required. A 1 in 20 dilution was chosen so that if the ammonia concentration of the leach solution did vary, then the concentration of ammonia after dilution remains relatively constant.

Once all of the parameters for the thiosulfate analysis had been chosen, the next task was to perform a calibration. Figure 4 shows the calibration curve for silver oxidation rate (determined by applying a constant potential of 200 mV vs SHE to the electrode) versus thiosulfate concentration in solutions of 0.1 M ammonia and 0.1 M sodium sulfate. Clearly, under these conditions the silver oxidation rate varies linearly with thiosulfate concentration; the linear correlation has an R value of 0.999. This is very useful in any analytical technique, as elaborate curve fitting of the standards is

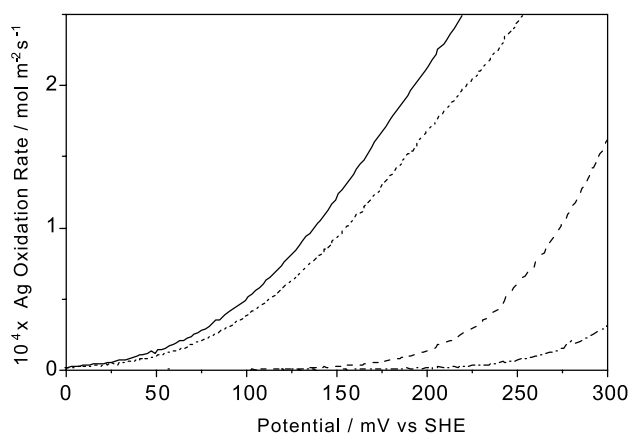


Fig. 3. Effect of ammonia concentration on silver oxidation rate in 10 mM thiosulfate solutions. Key: (—) 6 mM $S_2O_3^{2-}$ + 0.4 NH_3 ; (----) 6 mM $S_2O_3^{2-}$ + 0.1 NH_3 ; (-·-·-) 0.4 M NH_3 ; (·-·-·) 0.1 M NH_3 .

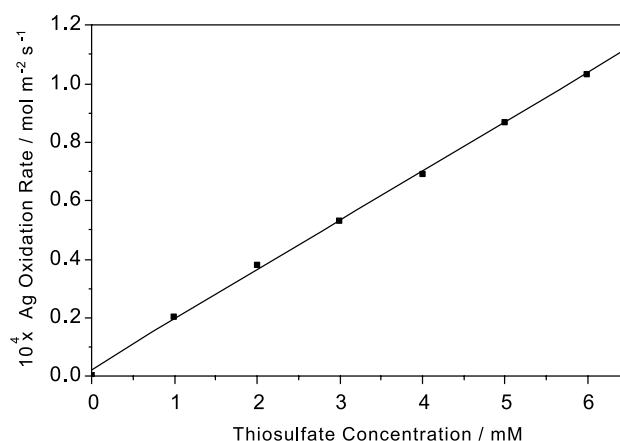


Fig. 4. Calibration curve of silver oxidation rate versus thiosulfate concentration at an applied potential of 200 mV vs SHE for the REQCM in solutions containing 0.1 M NH_3 and 0.1 M Na_2SO_4 .

not required. In addition, any change in the system variables, such as electrode surface area, can be adjusted for by using a single point reslope.

For this technique to be useful it is important that other species in the gold thiosulfate leach solution have no effect on the silver oxidation rate. It has been shown previously that the gold oxidation process is catalysed by the presence of copper(II) [23]. Hence the effect of copper(II) addition on the silver oxidation rate was investigated. An experiment was conducted where the silver oxidation rate was measured just after copper(II) + ammonia was added to a thiosulfate solution, so that very little reaction between thiosulfate and copper(II) had occurred. The silver oxidation curve is shown in Figure 5(a); it is clear that the silver oxidation rate in a thiosulfate solution is unaffected by the presence of copper(II). Experiments were also performed where tetrathionate was added to the thiosulfate solution. The data shown in Figure 5(a) indicate that the presence of tetrathionate also has no effect on the silver oxidation rate in thiosulfate solutions. This is not surprising, as silver does not form complexes with tetrathionate or other polythionates. During the experiments where the mass change was measured with the REQCM, the current was also measured. Figure 5(b) shows the current measured at the silver electrode in the solution containing thiosulfate and ammonia. In a similar manner to Figure 1, the current density response is the same as the oxidation response calculated from the mass changes. This is because, under these conditions, the oxidation of silver is the only electrochemical

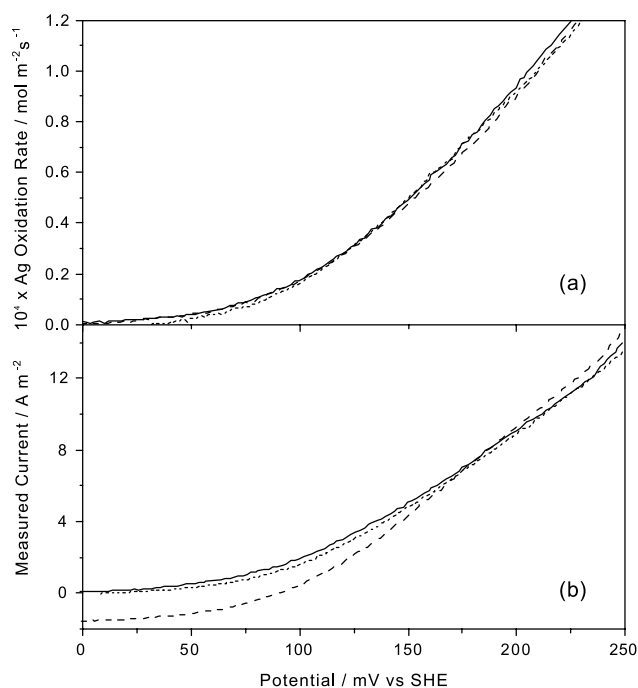


Fig. 5. Effect of copper(II) and tetrathionate on the silver oxidation rate (a) and the measured electrode current (b) in solutions containing 6 mM Na₂S₂O₃, 0.1 M NH₃ and 0.1 M Na₂SO₄. Key: (—) no Cu(II) or K₂S₄O₆; (---) 0.5 mM Cu(II); (- - - -) 1.5 mM K₂S₄O₆.

reaction that occurs, and hence the current directly relates to the rate of mass change. However, in the presence of copper(II), the measured current is lower at potentials less than 180 mV due to the reduction of copper(II) at the electrode surface contributing to the measured current. At potentials above the solution E_h , the oxidation of copper(I) to copper(II) will also contribute to the measured current. This clearly highlights the limitation to the method proposed by Hemmati et al. [13]. Tetrathionate is shown in Figure 5(b) to have no effect on the measured current as tetrathionate is neither oxidized nor reduced on silver in this potential region.

During gold leaching in thiosulfate solutions, a proportion of the copper is always present as copper(I). Hence the effect of copper(I) on the silver oxidation rate was also studied. This is more complex than the addition of copper(II), as both thiosulfate and ammonia can complex with copper(I). Shown in Figure 6 is the silver oxidation curve obtained at a rotation rate of 300 rpm for a solution containing 6 mM thiosulfate and 0.1 M ammonia to which 1.5 mM copper(I) thiocyanate was added (a stable source of copper(I) – the addition of 1.5 mM potassium thiocyanate had no effect on the measured silver oxidation rate at these potentials). The silver oxidation rate curve for thiosulfate plus ammonia is also shown for comparison. The measured silver oxidation rate is much lower where 1 mol of copper(I) has been added for each 4 mol of thiosulfate. At 200 mV the measured silver oxidation rate is 64% of that measured in the absence of added copper(I) thiocyanate. Such a result is consistent with a proportion of the thiosulfate forming a complex with copper(I), and then this thiosulfate not being available for the oxidation of the silver. In this solution it would appear that, on average, about 1.5 mol of thiosulfate are complexed with each mol of copper(I). It is possible that some of the copper is also complexed as the copper(I) amine or as a mixed copper(I) amine-thiosulfate complex.

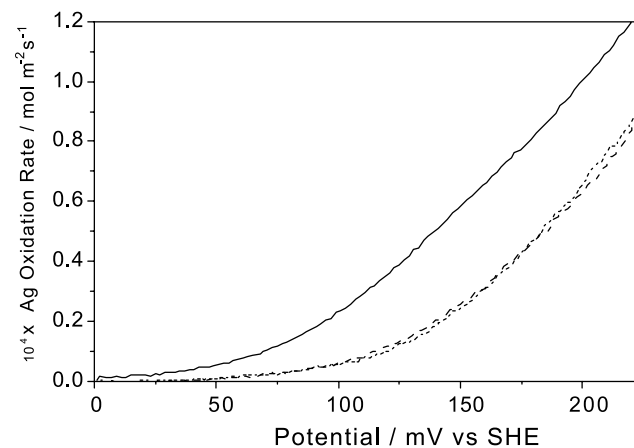


Fig. 6. Effect of copper(I) on the silver oxidation rate in solutions containing 6 mM Na₂S₂O₃, 0.1 M NH₃ and 0.1 M Na₂SO₄. Key: (—) no Cu; (---) 1.5 mM CuSCN; (- - - -) 1.5 mM CuSCN + 1.5 mM Cu(II) amine.

However, the speciation of copper(I) in solutions containing ammonia and thiosulfate is uncertain as there are no thermodynamic data available for the mixed ammonia-thiosulfate complexes of copper(I). An experiment was also conducted for a solution containing 1.5 mM copper(I) and 1.5 mM copper(II). As can be seen from Figure 6, for solutions containing copper(I), there is no difference in the silver oxidation rate in the presence or absence of copper(II). This is consistent with results for copper(II) addition in the absence of copper(I).

Another consideration with the presence of copper(I) is the possibility that the amount of thiosulfate complexed by the copper(I) changes when the solution is diluted into 0.1 M ammonia. In order to confirm that under these conditions this effect is minimal, an additional experiment was conducted where the silver oxidation rate was also measured in undiluted leach solutions at a rotation rate of 60 rpm and an applied potential of 200 mV. It was found that when 25 mM copper(I) is added to 100 mM thiosulfate, the same ratio as used in the diluted solution presented in Figure 6, the silver oxidation rate decreases by 36%. This decrease is identical to that measured for the diluted solution. Hence, it can be concluded that the conditions selected for the analysis of thiosulfate concentration are very good, with the measured silver oxidation rate being directly proportional to the thiosulfate concentration and unaffected by the presence of copper(II) and tetrathionate. In addition, in the presence of copper(I), the silver oxidation rate measured reflects the thiosulfate which is available for gold leaching; that is, not including the thiosulfate which is complexed with copper(I).

3.2. Development of a flow injection analysis technique using an EQCM cell

Although the REQCM is capable of determining thiosulfate concentration by measuring silver leach rate, this instrument is not commercially available and the procedure is time consuming in terms of individual solution preparation and cleanup for each sample. Thus, a flow injection analysis (FIA) method utilizing an EQCM was investigated as a means of simply and rapidly measuring thiosulfate concentration for gold thiosulfate leaching solutions. The application of QCM [24] and EQCM [25–27] in flow cells is not new; this method has been used in a number of analytical techniques in the past few years.

The FIA system is shown in Figure 7. A sample is firstly charged into the injection loop of the injection valve and then is switched such that the sample is flushed into the system with carrier solution. The sample is then diluted with a separate carrier solution stream in a mixing tee before passing through the EQCM cell. The carrier solution contained 0.1 M Na_2SO_4 and 84 mM NH_3 ; under these conditions, when a sample containing

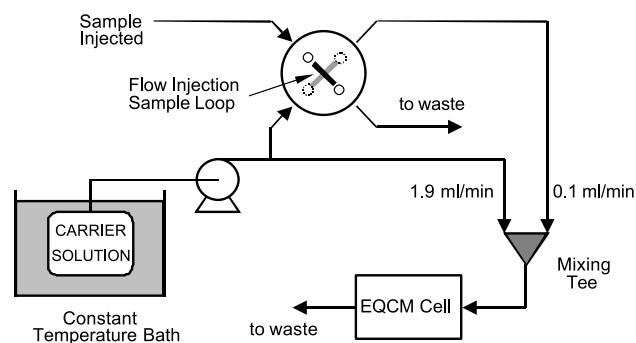


Fig. 7. Flow diagram of FIA system using EQCM cell.

0.4 M ammonia is diluted 1 in 20, the mixed solution entering the EQCM cell contained 0.1 M NH_3 . The constant temperature bath was held at 30 °C.

The EQCM cell used in our studies is shown in Figure 8 and was purpose built to utilize the same electrodes as the REQCM. This had the advantages of simple replacement and the simplicity to electroplate silver onto the electrode using the REQCM. The electrode could have been electroplated with silver within the cell by pumping the same plating solution through the cell and applying a constant current. However this would require either changing the carrier to a plating solution, or utilizing an additional pump and a bypass for the plating solution.

Pump selection was also very important as unsteady solution flow was also found to have a large effect on the EQCM response. Recording of the electrode mass began at the time of sample injection and continued until the effect of the injected sample ceased. Figure 9 shows the recorded mass change for the EQCM during an injection of solution containing 0.1 M sodium thiosulfate and 0.4 M ammonia. Clearly, the mass of the silver electrode is unchanged initially. As soon as the injected sample reaches the cell the measured mass of the silver electrode begins to decrease, reaching a maximum rate about 60 s after the sample was injected. The rate of mass change then decays away as the injected sample is flushed out of

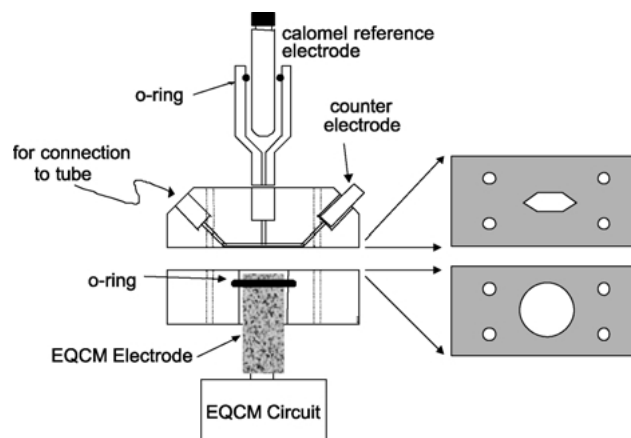


Fig. 8. Diagram of EQCM cell used for FIA.

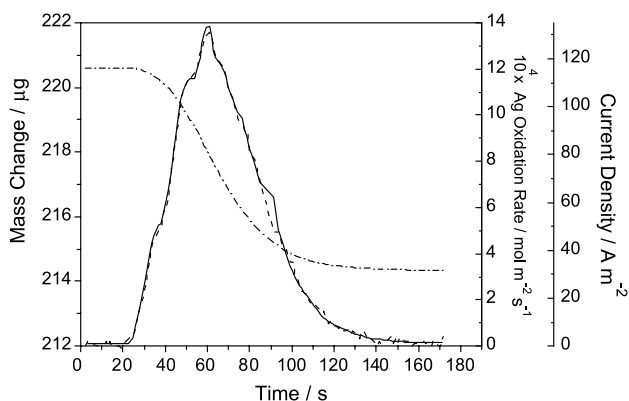


Fig. 9. Recorded electrode mass for EQCM cell during injection of a solution containing 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.4 M NH_3 at an applied electrode potential of 200 mV vs SHE. The differentiation of this curve is also shown as silver oxidation rate. Key: (.....) mass; (---) rate; (—) current density.

the cell. The rate of silver oxidation can again be calculated using Equation 5 and is also shown in Figure 9. This bell shape curve is typical of flow injection analysis measurements.

For the EQCM cell the electrode is stationary and it is the solution flow which results in mass transfer of the thiosulfate to the silver surface. Unlike the REQCM, the mass transfer under these conditions is not well defined. Since the mass sensitivity varies spatially across the crystal surface, it is important that the concentration of thiosulfate across the silver electrode is as uniform as possible. Hence, the flow channel was designed with a 7 mm width, and the silver surface of the crystal was placed centrally in the flow channel. This minimizes edge effects on the flow of the solution over the silver surface. To test that the EQCM response in the flow through cell also conformed to the Sauerbrey equation, the current was measured during the injection of the thiosulfate sample, and the response has been overlaid in Figure 9. In a similar manner to Figure 1, the current density axis scale is equal to the oxidation rate scale multiplied by the Faraday constant. It should be clear that the oxidation rate curve calculated using the Sauerbrey equation is very similar to the current density curve. Such a result indicates that the response of the EQCM is close to ideal, and that there is very little spatial variation in the silver oxidation rate.

Having achieved a FIA-EQCM set-up that gave a measurable response to the presence of thiosulfate in sample solutions, the reproducibility and relationship between mass change and thiosulfate concentration were investigated. Figure 10 shows a calibration curve for measurements of mass change (obtained from the solid line in Figure 9) versus thiosulfate concentration. This relationship was found also to be linear ($R = 0.995$), as observed for the silver oxidation rate measured using the REQCM. Clearly, the scatter in the data for multiple injection of the same solution was very small. Thus, the FIA-EQCM gives a simple and rapid analysis technique

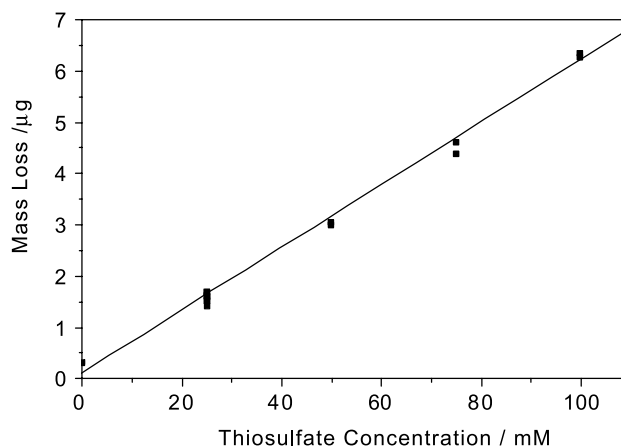


Fig. 10. Calibration curve of mass loss versus thiosulfate concentration for EQCM cell at 200 mV vs SHE applied potential.

for measuring the available thiosulfate concentration for leaching in gold thiosulfate leaching solutions.

3.3. Application of FIA-EQCM for thiosulfate measurement

As identified in the introduction, it has been previously found using oxygen consumption measurements that the oxidation of thiosulfate is significantly increased in the presence of oxygen. Hence it was decided to test the FIA-EQCM for measuring the effect of oxygen on the thiosulfate consumption in a gold leaching solution. Figure 11 shows the measured thiosulfate concentration as a function of time for separate solutions maintained under an atmosphere of varying oxygen concentrations. In the presence of argon, only a very small change in the thiosulfate concentration was measurable after 2 h. In comparison, when the solution is sparged with air, the thiosulfate consumption rate is significantly increased.

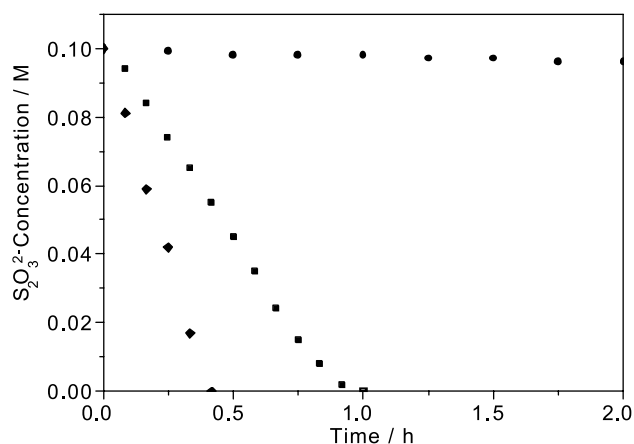


Fig. 11. Thiosulfate measurements for leach solutions, initially containing 0.4 M ammonia, 0.1 M thiosulfate and 10 mM copper sulfate, sparged at 1 l min^{-1} with gas of various oxygen concentrations. Key: (◆) oxygen sparged; (■) air sparged and (●) argon.

Within 1 h, all the 0.1 M thiosulfate is oxidised when the solution is sparged with air, whereas less than 5% of the thiosulfate is oxidised when the solution is maintained under argon. This confirms the results of Byerley et al. [11] that the presence of oxygen significantly increases the rate of thiosulfate oxidation. The importance of a simple and rapid technique for thiosulfate measurement in gold leaching solutions is thus apparent and is achievable by the analytical technique presented.

4. Conclusions

A method for measuring the thiosulfate concentration in solutions applicable to gold leaching has been successfully developed based on the measurement of the oxidation rate of silver in a diluted leach solution. The measured thiosulfate concentration was shown to be a measure of the available thiosulfate for leaching, and did not include the thiosulfate that was complexed with copper(I). Other solution species likely to be present were also shown to have negligible effect on the silver oxidation rate. A rapid FIA technique was developed which utilized the electrode mass change as the measure of the available thiosulfate concentration for leaching. This method allowed for the analysis of thiosulfate consumption in gold thiosulfate leaching solutions under different oxygen partial pressures. It was demonstrated that the thiosulfate oxidation rate is significantly increased when the solution contains oxygen. This method is of importance to the ongoing research into thiosulfate leaching of gold as an alternative to cyanide.

References

1. C. Abbruzzese, P. Fornari, R. Massidda and F. Veglio, *Hydromet.* **39** (1995) 265.
2. C. Cao, J. Hu and Q. Gong, in *Randol Gold Forum '92*, Vancouver (Randol International, Golden, Co., 1992), p. 293.
3. Q. Gong, J. Hu and C. Cao, *Trans. Nonferr. Met. Soc. China* **3** (1993) 30.
4. J.W. Langhans, K.P.V. Lei and T.G. Carnahan, *Hydromet.* **19** (1992) 191.
5. R.Y. Wan, in *World Gold '97*, The Australasian Institute of Mining and Metallurgy, Carlton, Victoria (1997), p. 159.
6. D. Zipperian, S. Raghavan and J.P. Wilson, *Hydromet.* **19** (1988) 361.
7. J. Li, J.D. Miller, R.Y. Wan and K.M. Le Vier, in *19th Proceedings of the International Mineral Processing Congress*, Vol. 4 (Society for Mining, Metallurgy and Exploration, Littleton, CO, 1995), p. 37.
8. P.L. Breuer and M.I. Jeffrey, *Miner. Eng.* **13** (2000) 1071.
9. M.I. Jeffrey, *Hydromet.* **60** (2001) 7.
10. J.J. Byerley, S.A. Fouda and G.L. Rempel, *J. Chem. Soc. Dalton Trans.* (1973) 889.
11. J.J. Byerley, S.A. Fouda and G.L. Rempel, *J. Chem. Soc. Dalton Trans.* (1975) 1329.
12. T. Koh, *Analyt. Sci.* **6** (1990) 3.
13. M. Hemmati, J.L. Hendrix, J.H. Nelson and E.B. Milosavljevic, in *Extraction Metallurgy '89 Symposium* (Institute of Mining and Metallurgy, London 1989), p. 665.
14. E. Högfeldt, 'Stability Constants of Metal-ion Complexes: Part A. Inorganic Ligands' (Pergamon, Oxford, 1982).
15. M.I. Jeffrey, J. Zheng and I.M. Ritchie, *Meas. Sci. Technol.* **11** (2000) 560.
16. P. Kern and D. Landolt, *J. Electrochem. Soc.* **147** (2000) 318.
17. P. Kern and D. Landolt, *J. Electrochem. Soc.* **148** (2001) B228.
18. J. Zheng, I.M. Ritchie, S.R. Labrooy and P. Singh, *Hydromet.* **39** (1995) 277.
19. M.I. Jeffrey and I.M. Ritchie, *J. Electrochem. Soc.* **147** (2000) 3257.
20. M.I. Jeffrey, W.L. Choo and P.L. Breuer, *Miner. Eng.* **13** (2000) 1231.
21. C. Zhang, S. Schranz, R. Lucklum and P. Hauptmann, *IEEE Trans Ultrason. Ferroelectr. Freq. Control* **45** (1998) 1204.
22. W.L. Choo and M.I. Jeffrey, *Hydromet.* (2001), submitted.
23. P.L. Breuer and M.I. Jeffrey, *Hydromet.* **65** (2002) 145.
24. M. Muratsugu, F. Ohta, Y. Miya, T. Hosokawa, S. Kurosawa, N. Kamo and H. Ikeda, *Anal. Chem.* **65** (1993) 2933.
25. A.L. Briseno, F. Song, A.J. Baca and F. Zhou, *J. Electroanal. Chem.* **513** (2001) 16.
26. K.L. Gering and J.J. Rosentreter, in *C.A. Young, L.G. Tidwell, and C.G. Anderson (Eds), 'Cyanide: Social, Industrial and Economic Aspects'*, (Minerals, Metals and Materials Society, Warrendale, PA, 2001), p. 141.
27. C.K. O'Sullivan and G.G. Guilbault, *Biosens. Bioelectron.* **14** (1999) 663.