

A fundamental study of the alkaline sulfide leaching of gold

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ABSTRACT

Due to the increasing concerns over the emission of sulfur dioxide from roasting and smelting, there has been an increased interest in pressure oxidation as a means of treating gold bearing ores and concentrates. One of the problems with the partial oxidation of the sulfide host matrix to form elemental sulfur is that sulfur containing streams are difficult to treat using cyanidation. In the present paper, the alkaline sulfide system was studied as an alternative to cyanide for recovering gold from elemental sulfur. It was found that the dominant lixiviant for gold in this system is sulfide, and polysulfide was ascertained to be the oxidant. The leaching reaction was determined to be chemically controlled, thus highly dependent on temperature. Other variables investigated include the effect of pH, gold purity, and the ratio of sulfide to polysulfides. It was found that each of these variables had a large impact on the system. © 2003 SDU. All rights reserved.

Keywords: Hydrometallurgy; Leaching; Gold

1. INTRODUCTION

Many gold ores are problematic as they contain metal sulfides, such as pyrite, arsenopyrite and chalcopyrite. These ores are often refractory, as the gold is encapsulated within the sulfide matrix. In order to recover the gold, the host matrix must be destroyed. Over the past 100 years, roasting or smelting has been the dominant method for oxidising sulfide bearing gold ores and concentrates. However, with the cost associated with treating SO₂ gas and the increasing concerns over emissions, many gold mines have considered other technologies such as bacterial leaching and pressure oxidation for treating sulfide containing ores. During the pressure oxidation of metal sulfides, the sulfide component can be either partially oxidised, forming sulfur as a product, or completely oxidised, forming sulfate as a product. Partial oxidation of metal sulfides has the benefit that low temperatures and pressures are required, leading to lower capital costs (Anderson and Nordwick, 1996; Anderson, 2001). The biggest problem with partial oxidation of metal sulfides is that sulfur containing streams cannot be readily treated using cyanidation, making difficult to recover the gold.

It has recently been shown that when elemental sulfur is dissolved in alkaline solutions, the solution formed is capable of leaching gold. The alkali used in these studies was either calcium hydroxide (the so called lime sulfur synthetic solution - LSSS), or sodium hydroxide (Zhang *et al.*, 1992a; Zhang *et al.*, 1992b; Anderson and Nordwick, 1996; Chen *et al.*, 1996; Fang and Han, 2002). A benefit of this process is that during the partial oxidation of the sulfide minerals, the gold tends to accumulate in the elemental sulfur (Fair and Van Weert, 1989; Barth *et al.*, 1998). Since the sulfur can be easily separated from the gangue minerals, this provides a simple way of producing a concentrated gold sample prior to leaching. It has also shown that gold can be selectively recovered from complex alkaline sulfide solutions containing a mixture of metals such as arsenic, tin, mercury and antimony. These studies showed that almost 100% of the gold could be selectively recovered using cheap solid materials for adsorption of the gold (Anderson and Nordwick, 1996). Finally the alkaline sulfide solutions which are barren of gold can be recycled for further gold leaching or further processed with low temperature oxidation to sodium sulfate, Na₂SO₄. This has been practiced in industry. The resultant sodium sulfate is further treated by purification and crystallization to

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produce high grade, marketable sodium sulfate. The sodium sulfate is then be sold to and utilized in industries such as pulp and paper, glass, ceramics, detergents, mineral feed supplements, textile dyes, bleach and photography.

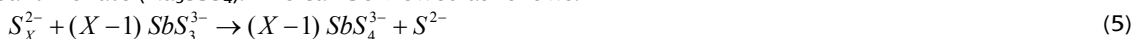
Although there has been little fundamental research into gold leaching in the alkaline sulfide system, there is some knowledge of the chemistry involved as a similar system can be used to recover metals such as antimony, arsenic, mercury and tin. In industrial practice, alkaline sulfide hydrometallurgical methods are now employed for antimony production. Antimony recovery normally calls for a two step process of leaching followed by electrodeposition. The alkaline sulfide system is employed industrially in the CIS, China and the United States (Anderson, 2000). Essentially, the lixiviant is a mixture of sodium sulfide and sodium hydroxide and when it is applied to stibnite, a solution of thioantimonite is formed. This can be illustrated as:



Dissolution of elemental sulfur in sodium hydroxide can also used as a lixiviant for alkaline sulfide leaching of antimony (Anderson and Kryš, 1993). The combination of sodium hydroxide and elemental sulfur results in the formation of metastable species other than just sulfide (S^{2-}). Both polysulfide (S_X^{2-}) and thiosulfate ($S_2O_3^{2-}$) are created along with sulfide. This is illustrated simplistically in the following scenario.



Due to the oxidizing ability of the polysulfide ion, the major species in solution is normally sodium thioantimonate (Na_3SbS_4). This can be viewed as follows.



In the present paper, a kinetic study of gold leaching in alkaline sulfide solutions is presented. For the gold leaching system, both a complexing lixiviant and an oxidant are required to effect dissolution. It will be shown that sulfide is an effective lixiviant, and the polysulfides are effective oxidants.

2. EXPERIMENTAL

Mass changes were measured using the rotating electrochemical quartz crystal microbalance (REQCM), which is described elsewhere (Jeffrey *et al.*, 2000). This technique is the most accurate means of measuring metal leaching rates; the sensitivity is 1 ng, and the reproducibility in measuring gold leaching rates is within 5%. All experiments were carried out using solutions prepared from analytical grade reagents and Millipore Elix water. In the experiments, three different solutions were prepared, as shown in Table 1. For convenience, the terms: caustic sulfur; sulfide sulfur; and bisulfide sulfur will be used throughout the text. Unless otherwise specified, experiments were performed at 60°C and at a rotation rate of 300rpm.

Table 1
 Chemicals used to prepare the solutions used in the experiments

Name	Chemicals used in preparation
Caustic sulfur solution	4M sulfur + 9M sodium hydroxide
Sulfide sulfur solution	2M sulfur + 2M sodium sulfide
Bisulfide sulfur solution	2M sulfur + 2M sodium bisulfide

Prior to each experiment, gold was electroplated onto the platinum coated quartz electrode at 25A/m² from a solution containing 0.02M potassium dicyanoaurate, 0.23M potassium cyanide, 0.086M potassium carbonate. The gold/silver alloy was prepared by the same procedure, with the exception that 0.5mM silver nitrate was added to the solution resulting in a deposit containing approximately 5% silver by mass (which for simplicity will be referred to as gold/silver). In one experiment, a gold/silver alloy containing 20% silver by mass was prepared from a gold plating solution which contained 2mM silver nitrate.

3. RESULTS AND DISCUSSION

It is well known that sulfur disproportionates in a caustic solutions, forming sulfides, polysulfides and oxysulfur anions such as thiosulfate. A simplistic stoichiometry for this reaction is shown in Eqs. (3) and (4) (Anderson, 2001). This approach has been used dissolve gold which is associated with elemental sulfur following the partial oxidation of sulfide minerals. Both sulfide and thiosulfate form strong complexes with gold, as shown in Eqs. (6) and (7). The stability constant of the sulfide and thiosulfate complexes of gold are 2×10^{36} and 10^{26} respectively (Hiskey and Atluri, 1986).



In order to assess the rate at which the gold/silver alloy containing 5% silver dissolves in the caustic sulfur system, kinetic experiments were performed using the REQCM. A gold/silver electrode was placed in a solution which was prepared using 2M sulfur and 9M sodium hydroxide, and the kinetic plot of mass vs. time is shown in Figure 1. It can be seen that the mass of the electrode, *m*, decreases as the metal is leached, and this decrease can be related to the dissolution rate through Eq. (8),

$$r = \frac{1}{M A} \frac{dm}{dt} \quad (8)$$

where *r* is the leaching rate (mol/m²s), *M* is the atomic mass of gold (196.97g/mol), *A* is the area of the gold electrode (m²), and *t* is the time elapsed (s). Thus, the slope of the kinetic plot is a measure of the leaching rate. It can be seen from Figure 1 that the gold/silver leach rate increases as a function of time, eventually reaching a steady state value after 350s. At steady state, the leaching rate for gold/silver is calculated to be 2.3x10⁻⁵mol/m²s. The mixed potential of the gold/silver electrode is also shown in Figure 1, and it can be seen that it initially increases before reaching a steady state value of -515mV.

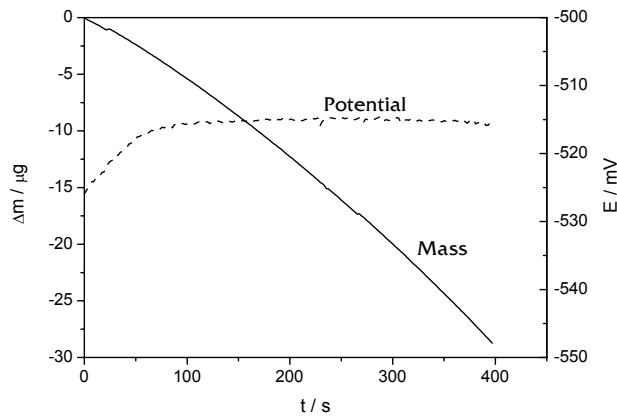


Figure 1. Kinetic plot showing the mass of the electrode during the leaching of gold/silver in a caustic sulfur solution at 60°C. Also shown is the mixed potential

In caustic sulfur solutions, there is the possibility of either thiosulfate or sulfide being the lixiviant. The standard potentials for the oxidation of gold to gold thiosulfate and gold sulfide are 0.15V and -0.46V respectively (Hiskey and Atluri, 1986). Given that the mixed potential measured during leaching was -515mV, it is likely that the lixiviant in this instance is sulfide rather than thiosulfate. Since the caustic sulfur solution also contains polysulfide, it is likely that this species is the oxidant for gold leaching. The potential of the sulfide / polysulfide system can be conveniently represented by an E-pH diagram. A metastable E-pH diagram for sulfur in alkaline solutions was generated using the StabCal thermochemistry package (Huang and Young, 1996), and is shown in Figure 2A. The only species considered in the calculations were sulfur, sulfide, bisulfide, and the polysulfides.

It can be seen that there are regions at high pH in which the polysulfides are represented. It is worth noting that this is only a metastable E-pH diagram, since all the sulfur species are ultimately oxidised to sulfate. If for instance thiosulfate is considered as a species in the thermodynamic calculations, then the polysulfide stability regions disappear at high pH, as shown in Figure 2B. It can be seen from Figure 2A that at pH 14, the potential for the reduction of S₂²⁻ to S²⁻ is -507mV. This is close to the potential measured -515mV. It is worth noting from Figure 2 that a range of different polysulfide species are able to be formed. The distribution of these species in solution is likely to be dependent on the solution composition.

3.1. Effect of gold purity

Since most naturally occurring gold usually contains at least 5wt% silver (Hurlbut and Klein, 1977), the effect of varying the silver content in the gold samples was investigated. These results are shown in Figure 3. It should be clear that the pure gold sample leaches very slowly in the caustic sulfur solution; the reaction rate is an order of magnitude lower than for the gold sample containing 5% silver. Such a result is similar to the gold cyanide leaching system, where it has been shown that gold containing small amounts of silver leaches significantly faster than pure gold samples (Jeffrey and Ritchie, 2000). It can also be seen from Figure 3 that the gold containing 20% silver leaches the fastest of the three samples studied. The reason for

this is unclear, although it could relate to the ability of sulfide ions to form a passivating underpotentially deposited monolayer on the gold surface at -600mV (Hamilton and Woods, 1983). This process has been shown to passivate gold leaching in cyanide solutions in the presence of sulfide ions (Jeffrey and Breuer, 2000). However, for pure silver, the formation of a monolayer of sulfur prior to silver sulfide formation at -450mV was not observed (Jeffrey and Woods, 2001). It is thus possible that for an alloy containing 20% silver, the passivation of the gold by sulfur is less prevalent than for pure gold samples. It was decided that for the majority of the experiments that the sample containing 5% silver should be adopted, as this represents the minimum level of silver normally found in native gold. This ensured that these experiments more closely mimicked the minimum leach rates that would be encountered in an industrial process.

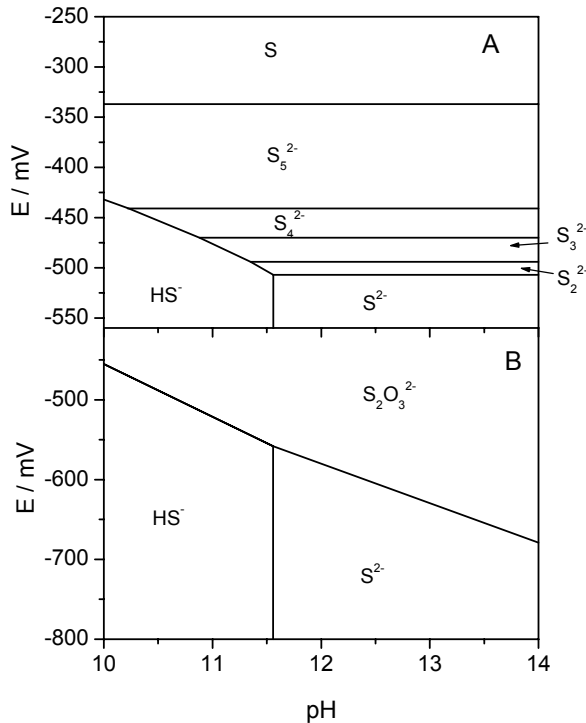


Figure 2. E-pH diagrams generated for the S-H₂O system using Stabcal, calculated for [S] = 4M, T = 60°C. For diagram A, the only species considered were sulfur, sulfide, bisulfide, and the polysulfides, whilst for diagram B, thiosulfate was also included as a species

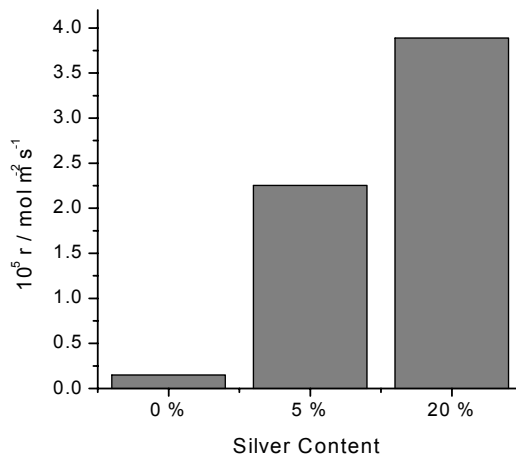


Figure 3. The effect of silver content in the gold sample on the leach rate in a caustic sulfur solution at 60°C

3.2. The rate limiting step

As the leaching of gold is a heterogeneous reaction, the reaction rate is ultimately limited by the mass transfer of reactants to the gold surface. If the leach rate is the same as the flux of one of the reactants, then the reaction is diffusion controlled, and for a rotating disc electrode, the rate will vary linearly with the square root of the rotation rate of the disc. Initially experiments were performed at a variety of rotation rates, and it was found that the gold/silver leach rate was independent of rotation rate, hence implying that the reaction is chemically controlled. This was verified by measuring the reaction rate as a function of temperature, and an Arrhenius style plot of $\ln(r)$ vs. $1/T$ is shown in Figure 4. From the slope of the data, it can be determined that the activation energy of the gold/silver leaching reaction is 75kJ/mol. Such a finding is consistent with the reaction being chemically controlled, since diffusion controlled reactions usually have activation energies of less than 25kJ/mol (Power and Ritchie, 1975).

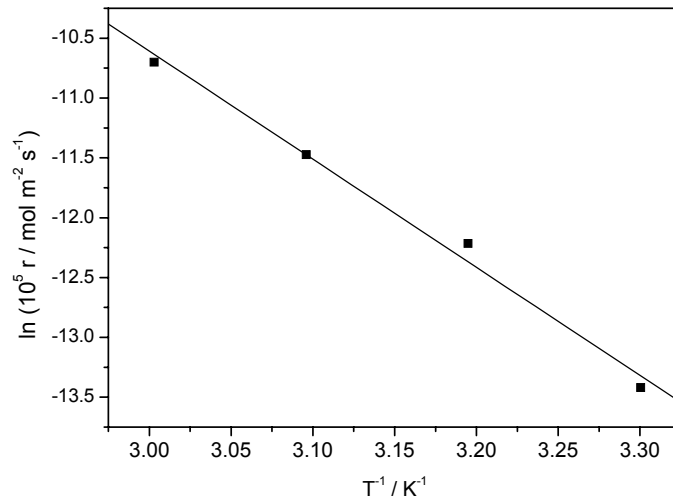


Figure 4. Arrhenius plot for gold/silver leaching in a caustic sulfur solution

3.3. The sulfide/sulfur system

Initial sulfide leaching experiments were carried out using a 2M sulfide solution in the absence of polythionates, and it was found that the gold/silver did not leach at all. Hence the presence of the polysulfides are necessary for the gold leaching reaction to occur. An alternative method for preparing a polysulfide solution is to dissolve sulfur in a concentrated sulfide solution. In this instance, sulfide and polysulfides are the sole reaction products and hence less reagents are required to form the same quantity of sulfide and polysulfide. Leaching experiments were performed using a solution prepared from 2M sulfur and 2M sulfide, and the gold/silver leach rate in this solution was measured as a function of temperature. The Arrhenius plot for the sulfide sulfur system is shown in Figure 5.

It should be clear that the data exhibits a linear relationship, and the activation energy calculated from the slope is 72kJ/mol. The data for the caustic sulfur system is also overlaid in Figure 5, from which it can be seen that the leaching behaviour is very similar for both systems. Such a result implies that the thiosulfate and other oxy-sulfur anions formed in the case of the caustic sulfur system do not play a role in the dissolution of gold.

3.4. Effect of pH

It is well known that the bisulfide ion, HS^- , is also capable of forming a strong complex with the aurous ion, as shown in Eq. (9). The standard potential for the oxidation of gold to the gold bisulfide complex is -90 mV (Zhang, 1997).



In the caustic sulfur system, when excess hydroxide was used, almost all of the sulfide exists as S^{2-} rather than HS^- . However, for the sulfide sulfur system, there will be some HS^- in solution. To evaluate what effect HS^- has on the leaching of gold/silver, a solution was prepared using 2M S and 2M HS^- . In this instance, the majority of the sulfide exists as HS^- . Figure 6 shows a comparison in the gold/silver leach rate between the caustic sulfur system, the sulfide sulfur system, and the bisulfide sulfur system. It should be clear that the

measured gold/silver leach rate in the bisulfide sulfur system is significantly lower than either the caustic sulfur or sulfide sulfur systems. These results are hardly surprising given that the potential for the formation of the gold bisulfide complex is significantly higher than that of the gold sulfide complex.

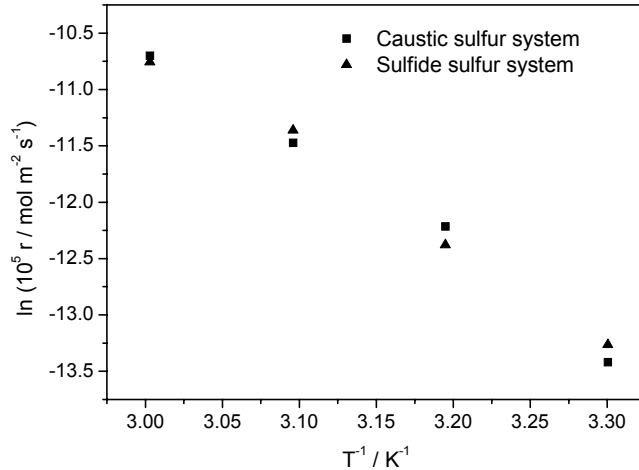


Figure 5. Arrhenius plot for gold/silver leaching in a sulfide sulfur solution. The data for the caustic sulfur solution is also overlaid for comparison

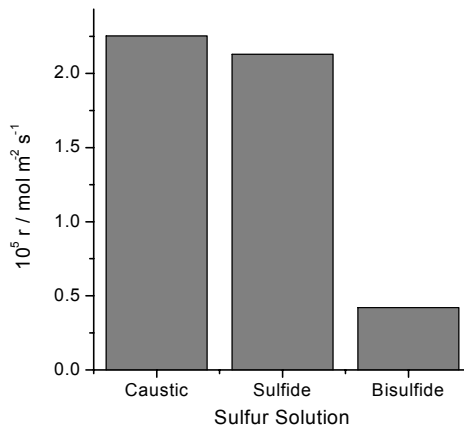


Figure 6. Comparison of gold/silver leaching in the caustic sulfur, sulfide sulfur, and bisulfide sulfur systems

3.5. Effect of sulfur: sulfide ratio

In the sulfide/sulfur system, one of the most important variables is the ratio of polysulfides to sulfide. This ratio can be effectively controlled by varying the amount of sulfur added to the sulfide solution. Experiments were carried out where the gold/silver leach rate and mixed potential were measured for solutions prepared with varying amounts of sulfur added; in each of the experiments, the sulfide concentration was fixed at 2M. It can be seen from Figure 7 that when 1M sulfur was used, the gold/silver leach rate is very low, and the mixed potential is more negative than for the other solutions. Such a result is hardly surprising, as the potential of the sulfide/polysulfide redox couple becomes more negative with increasing sulfide to polysulfide ratio. As the amount of sulfur used to prepare the solutions is increased, the ratio of polysulfide to sulfide increases, which gives rise to the increase in the mixed potential for gold/silver leaching. However, it can be seen from Figure 7 that when the sulfur addition is increased from 2M to 3M, the leach rate decreases even though the potential is more positive. Such a result is consistent with sulfide being the lixiviant and the decrease in the sulfide concentration at high S additions causing a decrease in the rate of the gold oxidation half reaction. From an industrial point of view, one is interested in the minimum amount of sulfide required to dissolve the sulfur produced from the partial oxidation of sulfides. In this instance, a ratio for sulfur to sulfide of 1.5 gives a lower sulfide requirement whilst maintaining an adequate gold leach rate.

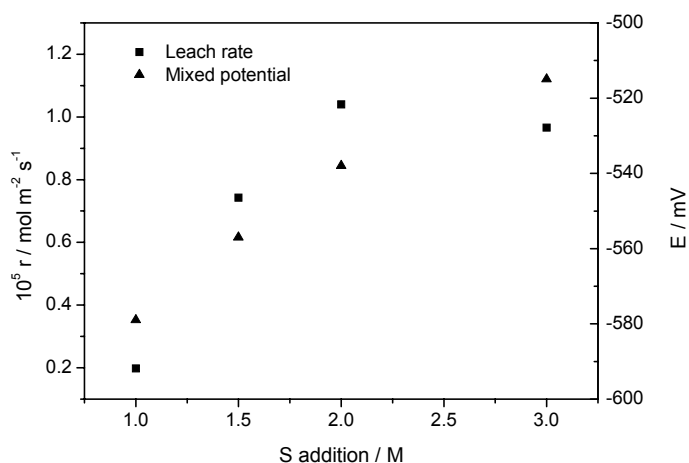


Figure 7. The effect of sulfur addition to a solution containing 2M sulfide on the leach rate and mixed potential of gold/silver

4. CONCLUSIONS

It has been shown that the alkaline sulfide system leaching system is an effective means of recovering gold from elemental sulfur formed during the partial oxidation of metal sulfides. When treated with either concentrated hydroxide or sulfide solutions, the sulfur dissolves forming polysulfides and sulfide. Sulfide is able to act as a lixiviant for the process, and the polysulfide is the oxidant. The leaching reaction was found to be chemically controlled for both the hydroxide and sulfide systems. It was also shown that gold leaching is very slow when either pure gold samples are used, or when hydrosulfide is used in place of sulfide ions. For the sulfide sulfur system, the optimum ratio of sulfide to sulfur was found to be 1:1, however adequate leach rates were still obtained at a ratio of 1 sulfur to 1.5 sulfide.

5. ACKNOWLEDGEMENTS

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