INFLUENCE OF SILVER ALLOYING AND IMPURITIES ON THE DISSOLUTION OF GOLD IN ALKALINE CYANIDE SOLUTIONS

By

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A dissertation submitted in partial fulfillment of the requirements for the degree of

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To Annie Nkashama and to my family for their love, encouragement and patience.

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ABSTRACT

Native gold is often alloyed with silver (about 10 %) and associated with sulphide minerals such as pyrite, marcasite and pyrrhotite. These foreign constituents may dissolve in cyanide solutions and influence cyanidation in a number of ways. To better characterise the action of silver alloying and impurities on the cyanidation of gold potentiodynamic and potentiostatic experiments were conducted within the potential range where conventional cyanidation takes place, i.e., -600 to 0 mV vs. SCE. It was found that gold presents a large passive region between –0.3 and 0 V (SCE). The presence of silver alloying is beneficial to the cyanidation process since the alloy presents a smaller passive region.

Additions of trace amounts of lead to the cyanide solutions have a favourable effect on the dissolution rate of gold. The accelerating action of lead on the gold surface was due to its soluble species and not to metallic lead as postulated by various authors. The decelerating effect of lead additions observed at high potentials and high concentrations must be due to the formation of insoluble lead species or to the formation of a more stable passive film on the gold surface.

Traces of sulphide ion decrease the anodic activity of gold between E_{corr} and –380 mV (SCE), but increase it at higher potentials where gold would normally passivate in the absence of sulphide. It is therefore possible to increase the dissolution rate of gold in cyanide solutions containing small amounts of sulphide by maintaining more oxidizing conditions on the gold surface.

The combined action of sulphide and lead ions on the dissolution rate of gold indicates that the overall effect depends on the relative concentrations in solution and the value of the open-circuit potential. From E_{corr} to approximately –380 mV (SCE), lead ions increase the dissolution of gold while sulphide ions counteract this effect. At more positive values, the opposite effect was observed.

Keywords: Gold, silver, cyanide, lead, sulphide, passivation, rate determining step, electrochemistry, potentiodynamic measurements, potentiostatic measurements.

INVLOED VAN LEGERING MET SILWER EN ONSUIWERHEDE OP DIE OPLOSSING VAN GOUD IN ALKALIESE SIANIED OPLOSSINGS

Deur

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OPSOMMING

Ontginbare goud is dikwels gelegeer met silwer (ongeveer 10 %) en is geassosieerd met sulfied minerale soos piriet, markasiet en pirotiet. Die onsuiwehede wat met die minerale geassossieer is, kan in sianiedoplossings oplos en kan die loogkarakeristieke op 'n aantal wyses beïnvloed. Potensiodinamiese and potensiostatiese ekseperimente is uitgevoer in die selfde potensiallbereik (-600 tot 0 mV vs. SCE) waarin konvensionele loging uitgevoer word om sodoende die invloed van silwerlegering en onsuiwerhede te karakteriseer. Daar is bepaal dat goud 'n groot passiewe gebied, tussen –0.3 en 0 V (SCE), besit. Die voorkoms van silwerlegerings is voordelig vir die loogproses omrede die legering 'n kleiner passiewe gebied het.

Die byvoeging van spoorhoeveelhede lood tot die sianiedoplossings, het 'n voordelige invloed op die loogtempo van goud. Die versnellende invloed van lood op die goudoppervlak is toe te skryf aan die oplosbare loodspesies en nie die metalliese lood soos deur ander outeurs gepostuleer is nie. Die vertragende invloed van loodbyvoegings by hoë potensiale en konsentrasies is toe te skryf aan die vorming van onoplosbare loodspesies of die vorming van 'n meer passiewe laag op die goudoppervlak.

Spoorhoeveelhede sulfiedione vertraag die anodiese aktiwiteit van goud tussen E_{kor} en –380 mV (SCE), maar verhoog dit by hoër potensiale waar goud normaalweg passiveer in die afwesigheid van die ione. Dit is dus moontlik om die tempo van goudloging in sianiedoplossings wat klein hoeveelhede sulfied bevat, te verhoog deur meer oksiderende toestande op die goudoppervlak daar te stel.

Die gekombineerde uitwerking van sulfied en lood-ione op die tempo van goudloging dui daarop dat die algehele effek afhang van die relatiewe konsentrasies van die spesies in oplossing en ook die waarde van die oopbaanpotensiaal. Vanaf E_{kor} tot ongeveer –380 mV (SCE), bevoordeel lood-ione in oplossing die loogtempo terwyl sulfiedione die effek neutraliseer. Daarenteen is die teenoorrgestelde effek by meer positiewe waardes weergeneem.

Sleutelwoorde: Goud, silwer, sianied, lood, sulfied, passiwiteit, snelheidsbepalende stap, elektrochemie, potensiodynamiese metings, potensiostatiese metings.

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CONTENTS

Chapter 1

INTRODUCTION

Gold is a minor component of typical gold ores compared with other elements. It is nearly always alloyed with varying amounts of silver and sometimes also associated with tellurides, sulphides, carbonaceous matter and many other minerals. Many gold-bearing and gangue minerals will also dissolve in cyanide solutions resulting in a series of metal cyanide complexes, sulphide and arsenic compounds, etc. These products may affect the leaching of gold in a variety of ways such as occlusion, scavenging of reagents and galvanic interactions. It has been speculated that gold can only be dissolved in cyanide solution when some other metals or impurities are present in the solution. In order to optimize the extraction of gold, several pre-treatment methods such as pre-aeration, pressure oxidation and roasting are used in most gold plants when direct treatment by cyanidation gives low gold recoveries. However, the compounds formed during these operations may also affect the efficiency of gold leaching. For example, the oxidation of both pyrite and marcasite to sulphur and metal ions involve large positive volume changes, i.e., the volume of sulphur produced is greater than that of the original mineral volume. This can occlude exposed gold particles and cause passivation of the mineral surface to further oxidation (Marsden, 1992). It was also found that the addition of small quantities of soluble lead salts, such as lead nitrate or lead acetate during the pre-aeration of the solution, can assist in the passivation of reactive sulphide minerals (Liddell, 1989). The lead forms an insoluble hydroxide and possibly some lead sulphate depending on the pH and the sulphate concentration of the solution. Both of these compounds are largely insoluble in dilute alkaline solutions and may screen the surface of the gold particles. This is in contrast to the accelerating effect observed during gold dissolution when lead salts are added to cyanide solutions. On the other hand, Fink and Putnam (1950) showed that sodium sulphide at a concentration as low as 1.2 mg/l can have a detrimental effect on gold leaching. In contrast, Weichselbaum et al. (1989) reported that some gold plants operate with pregnant solutions containing up to 15 mg/l sulphide without, sometimes, adding lead. Lorenzen et al. (1992) also reported that many researchers and operating staff in the minerals industry believe that the passivation of gold does not generally occur in plant solutions contrary to the predictions based on laboratory results. Although the cyanidation process has been applied for almost a hundred years, interactions of gold with foreign substances in cyanide solutions are still little understood. Many effects such as the depletion of cyanide in the leaching solutions, galvanic interactions between gold and associated minerals, formation of passive films on the gold surface and the depassivating action of heavy metals interact in the overall process of gold leaching. A better understanding of each phenomenon may result in more efficient processes leading to more complete extraction of gold during the leaching process. The thermodynamics of the Au-CN-H_2O and Au-CN-S-H_2O system does not indicate thermodynamically stable chemical compounds that may cause passivation of the gold in the potential and pH range used for gold dissolution. This is also the case for the active species of lead, which causes an accelerating or decelerating effect on the gold dissolution. The objective of the present research is to investigate the effect of impurities, especially sulphide and lead ions, on the dissolution of gold using potentiodynamic and potentiostatic techniques. It is of great interest to determine the nature of electroactive species of lead and to investigate the effect of factors such as sulphide ion concentration, potential of the electrode, time and the presence of impurities on the stability of passive films formed on the gold surface.

This study has been subdivided in three main parts:

- The first part concerns the theoretical background of the gold dissolution in cyanide solutions. A brief review of the theories proposed and the available experimental basis are discussed in this part. This then also serves as the motivation for the present work.
- The second part concerns the presentation of the results obtained during the present study and their interpretation.
- The third part concerns the conclusion, remarks and recommendations related to the investigations that have been done in the present study.

Chapter 2

THEORETICAL BACKGROUND

The dissolution of gold in alkaline cyanide solutions can be described by the following reaction:

$$4\ Au + 8\ CN^- + O_2 + 2\ H_2O \Leftrightarrow 4\ Au(CN)_2^- + 4\ OH^- \qquad [2.1]$$

The two major considerations in the dissolution of gold are:

(1) the extent to which the reaction will proceed, and
(2) the rate at which the reaction will proceed.

The former depends on the thermodynamic tendency of the chemical system, which determines the overall reaction driving force. This may be conveniently followed on potential-pH diagrams such as those shown in figures 2.1 and 2.2. The latter, the reaction kinetics, depend on a combination of physical, chemical and mass transfer factors.

From figures 2.1 and 2.2 it follows that:

- Metallic gold is highly stable in aqueous solution;
- Addition of cyanide leads to a relatively large stability region of aurocyanide in the entire pH range such that gold is destabilized to such an extent that it may be leached in aqueous solutions;
- Passivation of gold is probable at high values of potential at intermediate pH values.

As conventional cyanidation is conducted at pH 10 or above, a mild oxidation condition would be sufficient to dissolve gold at a reasonable rate. Unfortunately, that is not the case in practice and leachable gold losses during the process are a crucial problem in the industry. Disagreements between predictions made using the potential-pH diagram of the Au-CN-H_2O system and experimental results may result from the fact that:

- The potential-pH diagram shows only the predominant species;

- Thermodynamic calculations are performed by assuming a priori that all possible reactions would always be at equilibrium.

Obviously such assumptions are not invariably valid in practice since minor quantities of certain species can also affect the dissolution rate of gold and many steps such as adsorption, dissolution, precipitation and redox reactions may be involved in the leaching process of gold. These effects are difficult to predict when using only thermodynamic calculations.

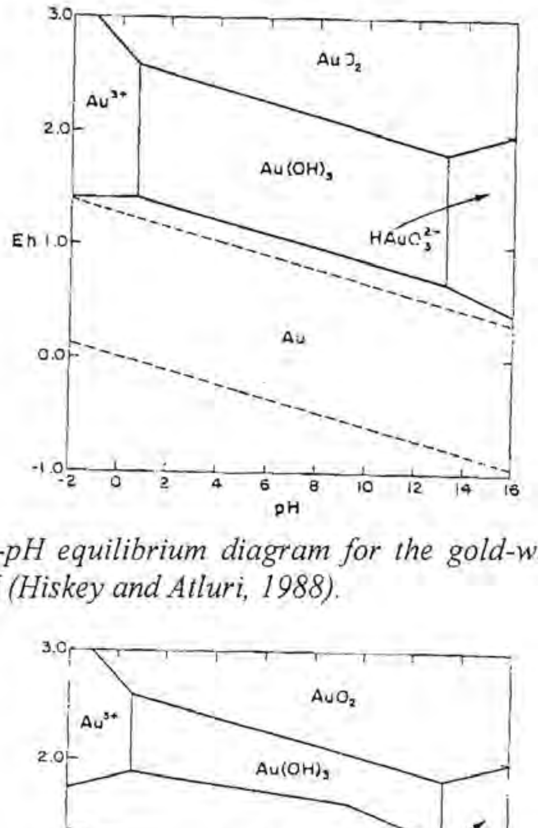


Figure 2.1. Potential-pH equilibrium diagram for the gold-water system for dissolved gold species of 10^{-4} *M (Hiskey and Atluri, 1988).*

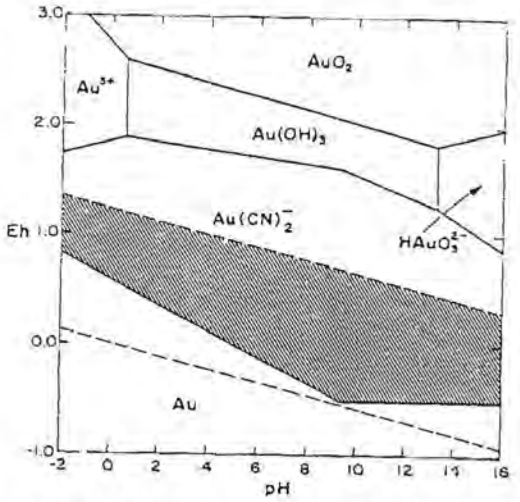


Figure 2.2. Potential-pH equilibrium diagram for the gold-cyanide-water system for [Au] =10^{-4}*M and [CN] =* 10^{-3} *M. (Hiskey and Atluri, 1988).*

Studies devoted to the mechanisms of the formation of passive layers on the gold surface are of great interest since the optimum conditions required for the extraction of precious metals can then be predicted. The formation of passive layers on the gold surface is a phenomenon observed in pure alkaline solutions and in alkaline solutions containing impurities. Since the mechanisms for the formation of these films are different, it will be discussed separately.

2.1 RETARDING EFFECTS ON THE DISSOLUTION RATE OF GOLD

2.1.1. Passivation of gold in pure cyanide solutions

The anodic characteristics of gold in cyanide solutions reveals several peaks associated with the formation of passive films on the gold surface as shown in figure 2.3.

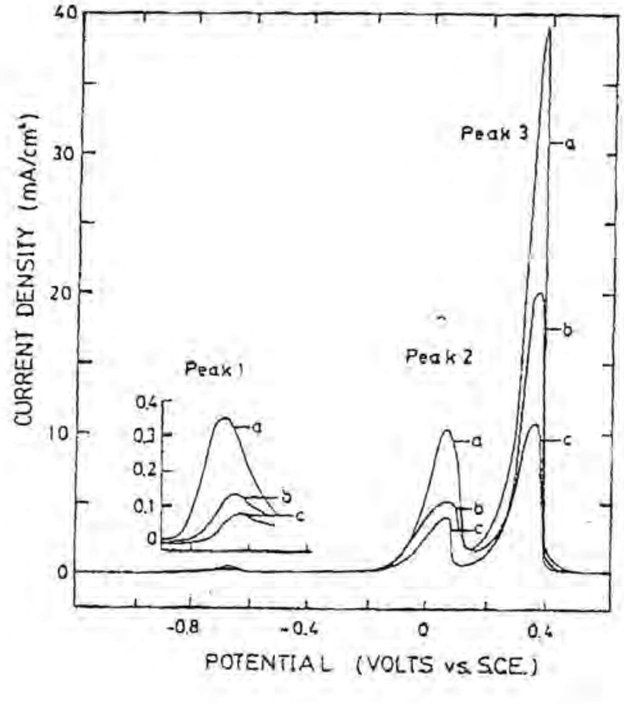


Figure 2.3. Potentiodynamic curves for gold in aqueous alkaline cyanide at 23 °C; a, 0.1 M KOH + 0.2 M KCN; b, 0.1 M KOH + 0.1 M KCN; c, 0.1 M KOH + 0.05 M KCN. Scan rate = 1 mV/s, (Kirk et al., 1978).

Most authors (Cathro and Koch, 1964; Kirk et al, 1978; Nicol, 1980) have identified three current-peaks located at approximately -400, + 300, and +600 mV (SHE). The difference in the values of potentials at which peaks appear is most likely due to the impurities in the gold specimen and in the cyanide, the metallurgical conditions and the measurement techniques used for experiments. In practice, the potential at which gold leaching occurs in aerated pulp is in the region of the first peak, i.e. -600 to -300 mV vs. SHE. This is the result of the intersection of the anodic and cathodic polarization curves in that region. It is therefore appropriate to discuss the anodic behaviour of gold in the region of the first peak in greater detail.

From thermodynamic calculations (Table 2.1), the only solid gold cyanide species appears to be AuCN. This product is not stable in alkaline cyanide solutions (Osseo – Asare et al., 1984) and is therefore unlikely to be the cause of the gold passivation.

Table 2.1. Thermodynamic data for selected cyanide complexes

Chemical formula	Quantity	State	References
$AuCN$	$\Delta G^{\circ}_{f,298} = 135$ kJ/mole	Solid	Hiskey et al., 1988
$Au(CN)_2^-$	$\log \beta_2 = 39.3$	Aqueous	Wang et al., 1990
$Au(CN)_4^-$	$\log \beta_4 = 56$	Aqueous	Wang et al., 1990
$AgCN$	$pK_{sp} = 15.66$	Solid	Wang et al., 1990
$Ag(CN)_2^-$	$\log \beta_2 = 20.48$	Aqueous	Wang et al., 1990
$Ag(CN)_3^{2-}$	$\log \beta_3 = 21.40$	Aqueous	Wang et al., 1990
$Ag(CN)_4^{3-}$	$\log \beta_4 = 21.90$	Aqueous	Wang et al., 1990

It is also possible that the cyanide ions are adsorbed on the gold surface and form products such as $(Au^+\text{-}CN^-)_{ads}$ or $(Au\text{-}CN)_{ads}$, which may screen the gold surface from the solution. Adsorption of cyanide ions on the gold surface should depend on factors such as the affinity of cyanide ions towards the gold surface, the concentration of cyanide in solution, the pH, the ionic strength of the solution and the applied potential. The transformation of the adsorbed film to the soluble species of gold, in particular $Au(CN)_2^-$, may be achieved by a series of steps involving the oxidation and dissolution of the adsorbed layers. The mechanisms proposed in the present study are based on experimental results collected from previous studies. The main conclusions of these studies were:

1. The mass transfer of the cyanide ions to the gold surface plays a significant role in the dissolution process of gold in particular at low cyanide concentrations (Kudryk and Kellogg, 1954);
2. The dissolution of gold occurs by a one-electron transfer step (Kirk, Foulkes and Graydon, 1978);
3. The adsorption of negative ions on a metal surface creates a surface dipole which assists the transfer of the metal atoms into solution (Benard, 1983).

From these conclusions, the adsorption of cyanide on the gold surface, may be represented by:

$$Au + CN^- \Rightarrow (Au^+\text{-}CN^-)_{ads} + e^- \qquad [2.2]$$

and the removal of the adsorbed cyanide, may be represented by the reaction of cyanide ions with the adsorbed species:

$$(Au^+\text{-}CN^-)_{ads} + CN^- \Rightarrow Au(CN)_2^- \qquad [2.3]$$

If the rate of the electrochemical production of the adsorbed $(Au^+\text{-}CN^-)_{ads}$ is higher than the rate at which the adsorbed species are removed as $Au(CN)_2^-$, a macromolecule layer acting as barrier may be formed on the gold surface. Guan and Han (1994) tried to identify the passive species on the gold surface in the region of the first peak using Fourier transform infrared spectroscopy, but were not successful. It may have failed because the passive species are unstable intermediates. It is also not clear why the anodic characteristics of other metals of group IB such as silver and copper, which have relatively high stability constants for cyanide solid compounds [pK_{sp} = 15.66 and 19.49

respectively for $AgCN_s$ and $CuCN_s$ (Wang and Forssberg, 1990)], do not exhibit similar passivation behaviour in alkaline cyanide solutions. Despite many investigations over many years, the mechanism of the passivation of gold in cyanide solutions is still not adequately resolved.

2.1.2 Passivation of gold in cyanide solutions containing sulphide ions

Small amounts of sulphide ions are known to reduce the dissolution rate of gold (Fink and Putnam, 1950). The existence of gold-sulfur compounds such as Au_2S, Au_2S_3, $AuS_2O_3^-$ and AuS^- has been reported (Osseo-Asare et al., 1984). However, thermodynamic calculations indicate that these compounds are not stable in cyanide solutions in the potential and pH range used for gold cyanidation. The retarding effect of sulphide ions on the dissolution rate of gold can only be explained by other factors, which can not be predicted by thermodynamic considerations. The main factors are:

- *Adsorption reaction of S^{2-} on the gold surface*:

  The coating of gold by the adsorbed sulphide layer may retard the dissolution kinetics (Fink and Putnam, 1950; Habashi, 1970; Lorenzen and Van Deventer, 1992).

- *Underpotential deposition of sulphur on gold in alkaline solutions*:

  Wierse et al. (1978) proposed that elemental sulphur formed during gold dissolution may coat exposed gold surfaces or sulphide particles and effectively occlude the mineral to prevent complete oxidation. However, the instability of elemental sulphur in alkaline solutions raises doubt about this proposed mechanism.

- *Consumption of cyanide and oxygen by sulphide minerals:*

  During the dissolution of sulphide minerals in cyanide solutions, the sulphide ions (S^{2-}) released may react with cyanide in the presence of oxygen and form thiocyanate according to the following equation:

$$S^{2-} + 1/2\ O_2 + H_2O + CN^- \Rightarrow SCN^- + 2\ OH^- \qquad [2.4]$$

This species may also be adsorbed on the gold surface. However, kinetics rather than thermodynamics limits the extent of the sulphide oxidation (Zhang et al., 1997). It has also been reported that the stability region of AuCNS is restricted only to higher potentials and relatively acidic conditions (Osseo-Asare et al., 1984). It is therefore unlikely that thiocyanate may influence the dissolution of gold in conventional cyanidation processes.

Little is known about the exact nature of the sulphide passive layers and this leads to a number of questions concerning the action of sulphide ions. Is there a competition between S^{2-} and CN^- ions on the active sites of the gold surface for the formation of passive films or is more than one film formed simultaneously on the gold surface? On the other hand, cyanide leach solutions usually also contain other anions such as OH^-, Cl^-, CO_3^{2-} and SO_4^{2-}. It is not clear why these anions are not adsorbed on the gold surface like the anions containing sulphur. A better understanding of the factors affecting the stability of the adsorbed sulphide films is of great practical interest since it can be helpful in the optimization of the gold dissolution in the presence prediction of the behaviour of the sulphide minerals during the cyanidation process of gold.

2.1.3. Passivation films formed during the galvanic interactions between gold and associated minerals

Gold is often associated with conductive minerals such as pyrite, pyrrhotite and galena. Electronic properties of selected sulphide and oxide minerals associated with gold are presented in appendix 1. The susceptibility of the different gangue minerals to oxidation in solution is dependent on their electrical resistivity, standard electrode potential, rest potential and solubility in the particular medium. The galvanic interactions between gold and associated minerals will depend on the reversible electrode potential of the process, the exchange current densities and Tafel slopes for oxygen reduction on the surface of the minerals, the relative areas and spatial distribution of gold and conductive minerals involved, and the conductivity of the solution. In fact, the galvanic interactions between gold and sulphide minerals can only take place if electronic conduction is created between the minerals involved. Due to the small amounts of gold compared with other elements in the gold ores, it is less likely that a transfer of electrons from the gold particles to the other conductive minerals will take place, unless they are embedded in those minerals. Furthermore, the situation can be more difficult to interpret if more than one sulphide or conductive mineral interact. Various authors (Mehta and Murr, 1983; Lorenzen and Van Deventer, 1992; Holmes and Crundwell, 1995) examined a number of galvanic interactions between sulphide minerals and indicated that the products of the galvanic interactions between sulphide minerals may affect the dissolution behaviour of gold in the following ways:

- More oxidizing potentials can be created on the surface of the gold if some sulphide minerals act as cathodes and stimulate the oxygen reduction reaction. In this case the open-circuit potential for gold dissolution will tend to move to more positive values and will favour either higher dissolution rates or the passivation of gold.
- The ions generated during the dissolution of gangue minerals acting as anodes in a galvanic interaction, can either accelerate or retard the dissolution of gold. For example, when arsenopyrite is in contact with pyrite, this latter mineral is galvanically protected and oxygen is preferentially reduced on its surface. Conversely, arsenopyrite acts as anode and produces Fe^{2+} and S^{2-}. Due to the high alkalinity of the solution Fe^{2+} may precipitate as $Fe(OH)_2$ on the gold surface and the sulphide ions may also form a diffusion barrier which can passivate the gold surface. A schematic representation of these effects is presented in figure 2.4. In the case of galena and pyrite in galvanic contact, galena acts as anode and produces Pb^{2+} which can accelerate the dissolution of gold.
- More reducing potentials, which could cathodically protect the gold, i.e., reduce or prevent gold dissolution, can be created on the gold by coupling with more reactive minerals, which in turn will sacrificially dissolve.

The effect of galvanic interactions on the passivation of gold depends therefore on other factors such as the distribution of gold particles in the mineral, degree of liberation and particle size. In a way, these also explain why ores from different sources may behave differently on leaching because of their different mineralogical properties and composition.

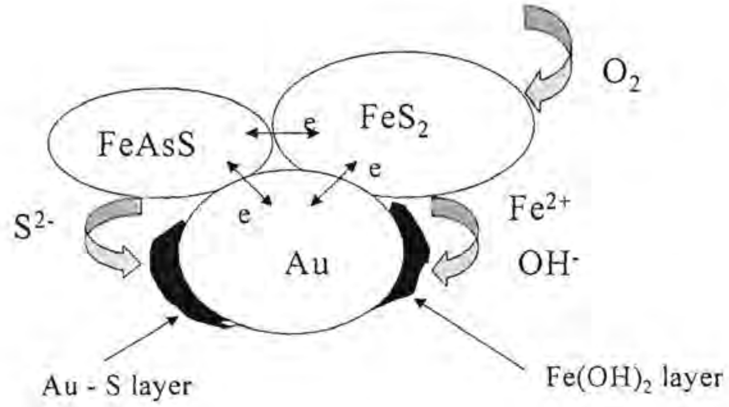


Figure 2.4. Schematic representation of the galvanic interaction between pyrite, arsenopyrite and gold and its effect on gold dissolution.

2.1.4. Passive films formed during the pre-treatment of gold ores prior to cyanidation

In some cases the compounds formed during the pre-treatment of refractory gold minerals can have a negative effect on the dissolution of gold in alkaline cyanide solutions. In the case of sulphide minerals, flotation and oxidation of sulphide minerals are common practice in most gold plants. Collectors of the thiol type (xanthate, dithiophosphate) characterised by functional groups which contain a sulphur atom bonded to a carbon or phosphorus atom are usually used for the flotation of gold-bearing sulphides. The xanthate may also be adsorbed on the surface of exposed gold particles to render the surface hydrophobic (Finkelstein, 1983). The hydrophobic particles will tend to flocculate and will be less prone to attack by the solution. A second method of pre-treatment is the oxidation of sulphide minerals to sulphur and metals ions. This can produce a greater volume of sulphur than the original mineral volume and may cause the formation of a passive layer if the reaction products are not removed faster than they are formed. The addition of small quantities of soluble lead salt during the low pressure oxidation pre-treatment or "pre-aeration" can assist the formation of an insoluble lead hydroxide, and possibly lead sulphate depending on the pH and sulphate concentration of the solution:

$$Pb^{2+} + 2\ OH^- = Pb(OH)_2(s) \qquad [2.5]$$

$$Pb^{2+} + SO_4^{2-} = PbSO_4(s) \qquad [2.6]$$

The pre-aeration of pyrrhotite in strong alkaline solutions, in the absence of cyanide, results in the following reactions (Kondos et al., 1995):

$$2\ FeS + O_2 + 2\ H_2O \Leftrightarrow 2\ Fe^{2+} + 2\ S + 4\ OH^- \qquad [2.7]$$

$$2\ Fe^{2+} + 1/2\ O_2 + H_2O \Leftrightarrow 2\ Fe^{3+} + 2\ OH^- \qquad [2.8]$$

$$Fe^{3+} + 3\ OH^- \Leftrightarrow Fe(OH)_3 \qquad [2.9]$$

The different products of reactions 2.5 to 2.9, namely $Pb(OH)_2(s)$, $PbSO_4(s)$, S and $Fe(OH)_3$, may occlude the exposed gold particles before the cyanidation process. The extraction of gold during the cyanidation process will therefore depend on the response of lead, iron and sulphide products to the cyanide solutions. Thermodynamic data indicate that iron forms both ferrous, $Fe(CN)_6^{4-}$, and ferric, $Fe(CN)_6^{3-}$, cyanide complexes. However, the high solubility of iron or iron oxides suggested by the thermodynamics, has not been observed in practice (Osseo-Asare et al., 1984). It is therefore possible that the iron products formed during the pre-aeration of the solution may coat the gold surface and retard the dissolution of gold in cyanide solutions. Sulphide ions are known to decrease the dissolution of gold and the behaviour of lead species in cyanide solutions will be discussed in the following sections. The efficiency of the pre-treatment processes will therefore depend on factors such as the alkalinity of the solution, the grade of iron and sulfur in the mineral and the hydrodynamic conditions in the solution. Studies should be conducted in order to find the optimum conditions for the pre-treatment of various minerals prior to cyanidation.

2.2. ACCELERATING THE DISSOLUTION RATE OF GOLD

The leaching reaction is heterogeneous in character and consists of several sequential steps. This situation is represented in figure 2.5 in which the steps may be considered to consist of:

1. Transport of gaseous reactants (where relevant) to the gas-solution interface and subsequent dissolution;
2. Transport of reacting species through the solution to the solid-liquid interface;
3. Reaction at the interface which may be chemical or electrochemical. The chemical reaction involves adsorption or desorption of species and the electrochemical reaction involves transfer of electrons and ions across an electrical double layer;
4. Transport of products from the interface into the bulk of the solution.

The leaching rate is dependent on which of these steps, or combination of steps, is rate controlling. In order to optimise the dissolution of gold, all parameters influencing each step should be investigated.

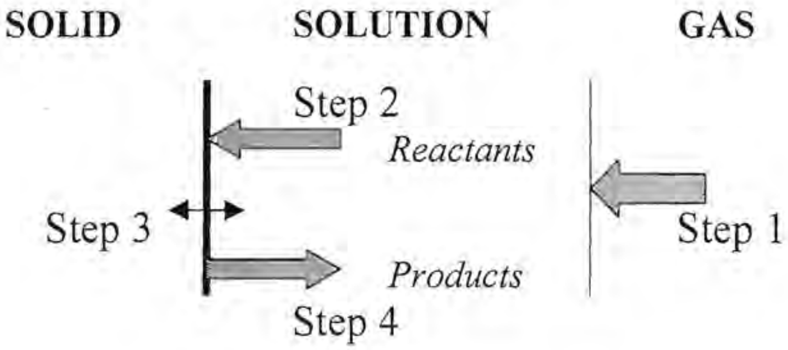


Figure 2.5. Schematic representation of the reaction steps involved in the dissolution of gold in aerated cyanide solutions.

2.2.1. Influence of the mass transfer of reagents such as cyanide and oxygen

It is generally accepted that the dissolution of gold in aerated cyanide solutions is an electrochemical process. The anodic half-reaction for gold leaching is given by:

$$Au + 2\ CN^- \Rightarrow Au(CN)_2^- + e^- \qquad [2.10]$$

and the cathodic half-reaction can be expressed by the direct 4 electron reduction:

$$O_2 + 2\ H_2O + 4\ e^- \Leftrightarrow 4\ OH^- \qquad [2.11]$$

or by two consecutive 2-electron steps which can be expressed by the equations:

$$O_2 + H_2O + 2\ e^- \Leftrightarrow HO_2^- + OH^- \qquad [2.12]$$

$$HO_2^- + 2\ e^- + H_2O \Leftrightarrow 3\ OH^- \qquad [2.13]$$

Kudryk and Kellogg (1954) established the electrochemical nature of gold dissolution in cyanide solutions by measuring the anodic and cathodic partial electrode reactions directly. They proposed that the mass transfer of oxygen and cyanide to the metal surface in separate regimes controlled the kinetics of gold dissolution in aerated cyanide solutions. A reduced rate, r (mols.cm^{-2}.sec^{-1}), may be expressed as:

$$r = \frac{dn_{Au}}{dt} = \frac{1}{2}\frac{dn_{CN}}{dt} = \frac{z\ dn_{O2}}{dt} \qquad [2.14]$$

where z is the stoichiometry factor and has the value 4 for the direct 4-electron reduction of oxygen indicating the full use of oxygen for the gold reaction, or the value 2 for the sequential reaction. Kudryk and Kellogg applied Fick's first law to equation 2.14 and coupled oxygen and cyanide diffusion

$$r_{CN} = \frac{dn_{CN}}{dt} = \frac{-D_{CN}\ A}{\delta}\ [\ (CN) - (CN)_s] \qquad [2.15]$$

$$r_{O2} = \frac{dn_{O2}}{dt} = \frac{-D_{O2}\ A}{\delta}\ [\ (O_2) - (O_2)_s] \qquad [2.16]$$

where D_{CN} and D_{O2} are the diffusion coefficient, [CN] and $[O_2]$ are the bulk concentrations, $[CN]_s$ and $[O_2]_s$ are surface concentrations, A is the area of the metal and δ is the diffusion boundary thickness. They assumed that both reactants should be diffusing at their maximum rates to the gold at the point of change-over from control by cyanide diffusion to control by oxygen diffusion. Under this condition, surface concentrations were negligible and the rate could be expressed as:

$$r = \frac{1}{2} r_{CN} = \frac{-D_{CN}}{2\,\delta} [CN] = z\, r_{O2} = \frac{-zD_{O2}}{\delta} [O_2] \qquad [2.17]$$

$$\frac{D_{CN}\,[CN]}{D_{O2}\,[O_2]} = 2z \qquad [2.18]$$

The rate of the transfer processes may be increased by either decreasing the diffusion boundary layer thickness or by increasing the diffusion coefficients, bulk concentrations or area of the interface. Increasing temperature does not necessarily increase the dissolution rate of gold because of counteracting factors such as the decomposition of cyanide above 50 °C and the decrease of the gas solubility with increasing temperature. The dissolution rate of gold increases with increasing cyanide concentration until a maximum is reached, beyond which a further increase in cyanide does not increase the amount of gold dissolved. At high cyanide concentrations a slight retarding effect may be observed on the leaching of gold. The decrease in the rate at high cyanide concentration may be attributed to one or more of the following factors: the increase in pH of the solution caused by the hydrolysis of cyanide ions, the decrease in the solubility of oxygen in the solution and/or the difficulty to transfer oxygen in the case of pulps of high viscosity. The thickness of the diffusion boundary is therefore an important variable to manipulate the rate of gold dissolution. It is a complex function of various parameters such as bulk flow, agitation, viscosity of the solution and temperature and can be reduced considerably by employing various means of agitation. According to Ettel et al. (1975), the thickness of the diffusion layer varies between ~ 0.3 mm and 0.03 mm with moderate stirring by air bubbling. In slurry containing suspended particles, increasing agitation also increases particle-particle interactions. This may enhance the dissolution kinetics of gold if the particles in contact with gold are conductive and act as cathodes. Furthermore, the passive layers formed on the gold surface may be removed by the physical abrasion caused by the particle-particle contact.

It would be of great interest to study the influence of the cyanide mass-transfer on the anodic behaviour of gold for different potential values as it may give an indication about the rate-determining step for the dissolution of gold in alkaline cyanide solutions.

2.2.2. Oxygen reduction on gold

Oxygen is typically used as oxidant in the cyanidation of gold. At high cyanide concentration the rate of gold dissolution depends only on the oxygen concentration. In figure 2.6, the plateau indicating the point of changeover between the two kinetic regimes is defined by the oxygen concentration, the relative diffusion coefficients ($D_{O2} = 2.76 \times 10^{-5}$ cm^2 sec^{-1}, $D_{CN} = 1.83 \times 10^{-5}$ cm^2 sec^{-1} , Habashi, 1970), the stirring of the solution and the temperature.

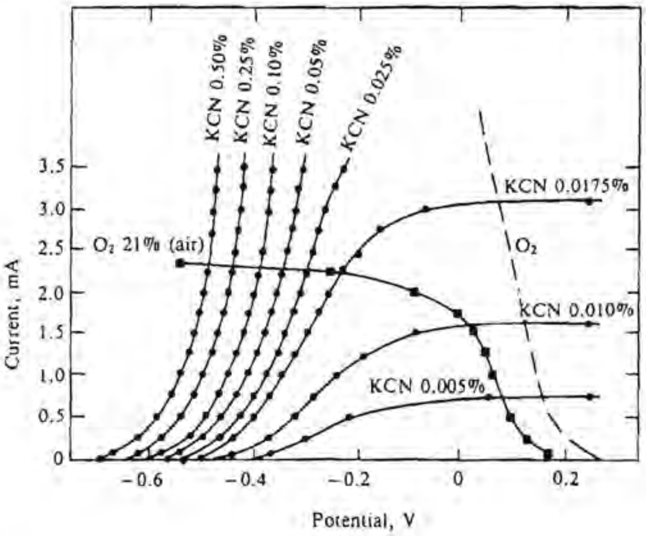


Figure 2.6. Anodic and cathodic polarization curves for gold (after Kudryk and Kellogg, 1954)

The reduction of oxygen on metals is believed to occur by the initial adsorption of O_2 at the metal surface (Fisher and Heitbaum, 1980; Adanuvor and White, 1987; Hiskey and Sanchez, 1990). Numerous studies have shown that the sequential pathway predominates on the surface of gold (Zurilla et al., 1978; Fischer and Heitbaum, 1980; Kokkinidis, 1986) and the direct 4- electron process predominates on silver (Hiskey and Sanchez, 1990). At low peroxide decomposition rates, much of the peroxide could be lost to the solution by diffusion. This implies that the first wave corresponding to reaction [2.12] may fix the dissolution rate of gold. In this particular case, the overall dissolution rate is lowered. As the decomposition rate increases, more oxygen is formed on the surface of the electrode and the limiting current is increased. At a very high peroxide decomposition rate, the limiting current becomes equal to that of the direct 4-electron process. This indicates that a good peroxide decomposition catalyst on the gold surface can accomplish the same results as in the case where the 4-electron process is applied. It is believed that underpotential deposited layers of lead, mercury, thallium and bismuth can act as catalytic surface and enhances the reduction of hydrogen peroxide. This can only be true in the activation-controlled region of the oxygen reduction, as it can not change the characteristics in the mass transfer control region. However, at low cyanide concentrations the intersection point of the anodic and cathodic branches may be situated in the active region of oxygen reduction. In this particular case, the effect of underpotential deposited metal on the oxygen reduction can be of importance. For gold-silver alloys, it is possible that with an increase in the silver concentration in the alloy, the difference in the rate of the sequential reactions (2.12 and 2.13) increases. At low silver contents in the alloy, the sequential pathway may predominate while at high silver contents, the direct path may predominate.

In order to accelerate the dissolution of gold, it is important to raise the dissolved oxygen level in the pulp whatever the mechanism for the oxygen reduction. However, the saturation of oxygen in the pulp is difficult to maintain due to the difficulty to transfer oxygen from the gas phase to the water. According to the Fick's first law (equation 2.16), the transfer of oxygen depends on the thickness of the mass transfer boundary layer, the diffusion coefficient of oxygen, the interfacial area and the concentration of oxygen. The mass transfer of oxygen is lowered by the following factors:

- the presence of two diffusion boundary layers, in the gas and in the liquid phases,
- the small interfacial area of oxygen bubbles,
- a small retention time in the liquid due to the mobility of oxygen bubbles,
- for pulps of high viscosity the boundary layer thickness will increase,

Recent work on the use of other oxidants such as H_2O_2, CaO_2 and oxone powder ($2KHSO_5.KHSO_4.K_2SO_4$) indicates that the dissolution rate of gold may be increased by using those reagents. The kinetics of CN^- oxidation to OCN^- by powerful oxidants is considered to be slow without the presence of catalysts (Stoychevski and Williams, 1993). However, most of the potential oxidants are not yet tested in gold plants because of cost.

2.2.3. Influence of heavy metals on the leaching of gold

It is well known that small amounts of heavy metals (lead, bismuth, thallium and mercury) accelerate the dissolution of gold in cyanide solutions (Fink and Putnam, 1950; Habashi, 1970). Although many fundamental studies have been performed, some contradictions still exist on the exact mechanism of the action of heavy metals, in particular lead, on the gold surface. In one mechanism, the rapid dissolution of gold in the presence of lead is proposed to be due to the alteration in the surface character of gold by alloying with lead plated onto gold (Fink and Putnam, 1950; Habashi, 1970; Kokkinidis, 1986; Mussati et al., 1997). This mechanism referred to as " Underpotential deposition of heavy metal atoms on noble metal " attracted considerable interest some years ago. It was proposed that the trace foreign metal ions which are most effective as depolarizers are those which tend to deposit uniformly on the gold surface to form an adsorbed monolayer at electrode potentials positive to those where their cathodic deposition as bulk metal begins. Some authors (Kokkinidis, 1986; Wang and Forssberg, 1990; Chimenos et al., 1997) believe that underpotential deposited layers of lead, bismuth, thallium, and mercury may enhance the electrocatalytic activity of gold in different ways, by:

- formation of a galvanic couple on the gold surface with gold acting as anode and the heavy metals as cathode.
- enhancement of the catalytic activity of gold for the reduction of oxygen by lead and thallium adatoms in alkaline medium.

However, the deposition of lead on the gold surface can only take place if lead is more noble than gold in cyanide solutions; no data is presented in the open literature to show that it is indeed so. Furthermore, the slow leaching rate of gold is probably due to the passivation of the gold, which occurs at more positive potentials. The introduction of an additional cathodic reaction such as the reduction of lead would tend to move the potential to more positive values and would thus favour passivation rather than dissolution. It is rather evident that lead, in some or other form increases the anodic reaction rate on the gold surface; this would move the open-circuit potential to more negative values. Two other factors may possibly affect the interaction of lead and gold in cyanide solutions:

- the addition of cyanide to the Pb-H_2O system may increase the solubility of lead;
- due to the high pH value typical for cyanide leach solutions the formation of $Pb(OH)_2$ or PbO could decrease the concentration of soluble lead.

It is therefore improbable that conditions in typical leach solutions would favour underpotential deposition of lead. If anything, it would rather decrease the activity of soluble lead species and make the deposition of metallic lead less favourable. In the discussion of the influence of lead on the dissolution of gold, the speciation of lead in aqueous cyanide solutions is of obvious importance. A number of studies on the speciation of lead species in aqueous solutions have been published, but disagreements still persist about the exact nature of the soluble species of lead. The Pourbaix diagram of the Pb-H_2O system reveals that PbO is the predominant species at pH 11 as indicated in figure 2.7. However, this product is solid and will tend to create a barrier on the gold surface and therefore reduce the dissolution rate of gold. Since in practice an opposite effect is observed while lead is added to the cyanide solutions , the Pourbaix diagram can not explain the action of lead on the dissolution of gold.

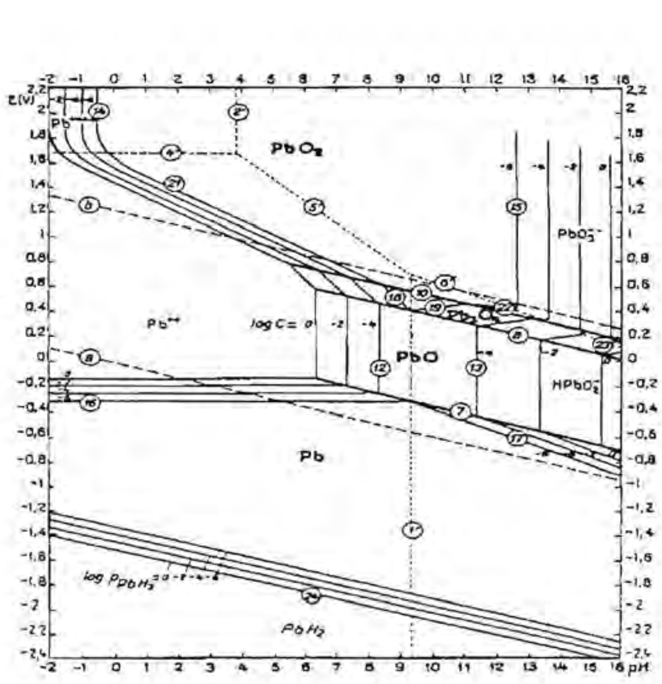


Figure 2.7. Potential –pH equlibrium diagram for the system lead – water, at 25 °C (Pourbaix, 1966).

It was found in the literature that Pb(II) forms a number of hydroxide complexes in aqueous solution such as $PbOH^+$, $Pb(OH)_2$, $HPbO_2^-$, $Pb_4(OH)_4^{4+}$, $Pb_3(OH)_4^{2+}$, PbO_2^{2-} and $Pb_6(OH)_8^{4+}$ (appendix 2) but most of these species do not appear on the Pourbaix diagram. Probably, these species were not identified or no thermodynamic data of other species were available when Pourbaix established the diagram. It is evident that a certain competition exists between the different species as one complex forms at the expense of another. This competition depends on factors such as pH, potential, concentration of lead, concentration of cyanide and interaction with other species. Rickard and Nriagu (1978) investigated the distribution of lead (II) hydroxy complexes in terms of pH for various lead concentrations in aqueous solutions and the results obtained are presented in figure 2.8.

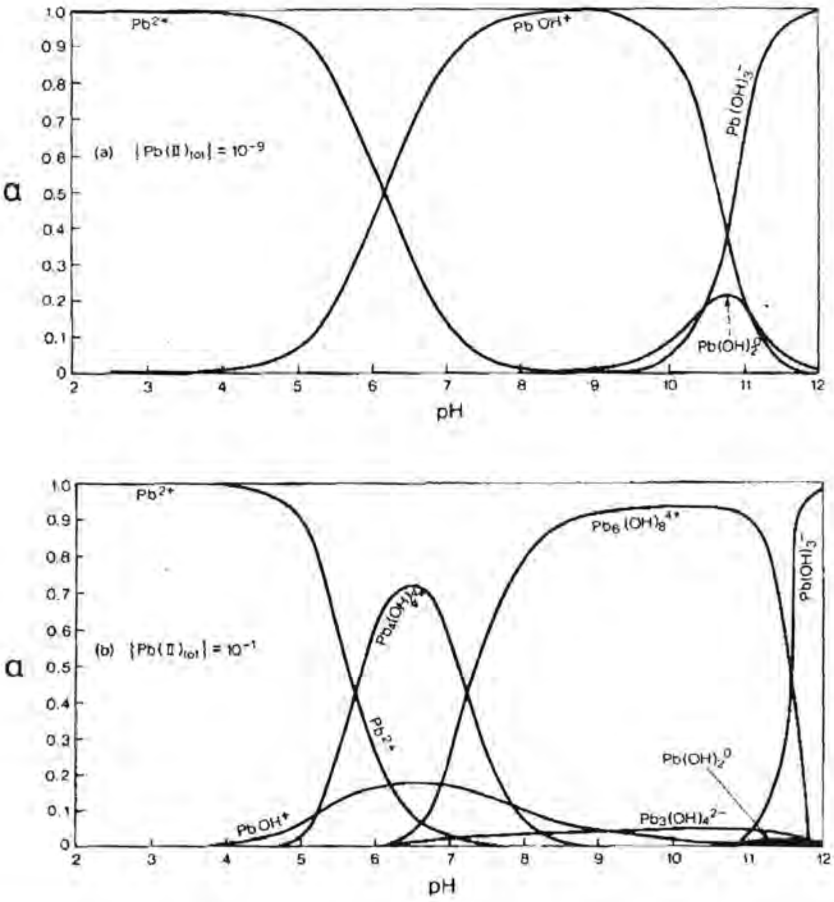


Figure 2.8 Abundance of lead species in terms of pH and α (the fraction of total dissolved lead that the species makes up). (a) For total dissolved Pb activity, {Pb(II)$_{tot}$*} = 10*$^{-9}$*; (b) for {Pb(II)*$_{tot}$*} = 10*$^{-1}$ *(Rickard and Nriagu, 1978).*

At pH 11 it can be seen that the main species are $Pb(OH)_3^-$ (60 %), $Pb(OH)^+$ (20 %), and $Pb(OH)_2$ (20 %) for 10^{-9} M Pb(II). The concentration of $Pb(OH)_3^-$ and $Pb(OH)^+$ is further decreased at pH 11 for 10^{-1} M Pb(II) while $Pb_6(OH)_8^{4+}$ represents more than 90 % of the total lead. It is possible that the abundance of a particular lead species with regard to others is dependent on the total lead (II) in solution. These different species may therefore influence the dissolution of gold in a variety of ways. We believe that the various lead species in contact with the gold particles do not have the same catalytic effect on gold leaching. The combined effects of pH and total lead (II) in solution may help to clarify the action of various lead species on the dissolution of gold in cyanide solution. It was also found in the literature that lead forms a wide variety of complexes and precipitates with other anions (appendix 3). The ions generated during the dissolution of sulphide, sulphate and carbonate minerals can react with lead by forming solid products such as PbS, $PbSO_4$ and $PbCO_3$, which may occlude the exposed gold particles. This may also reduce the abundance of lead species necessary to accelerate the dissolution of gold. Investigations on the action of various anions such as S^{2-}, SO_4^{2-} and CO_3^{2-} on the cyanidation of gold in solutions containing lead ions may contribute to optimize the process.

However, since these species are in contact with a conductive surface, their nature will depend not only on the pH of the bulk solution and the total dissolved lead but also on the potential and the concentration of the species at the surface. For a given pH, in particular the pH used in most gold plants, it would be of great interest to investigate the behaviour of lead and other impurities on gold leaching as a function of electrochemical potential.

2.2.4. Influence of alloying elements

In ores, gold is generally alloyed with other elements such as copper and silver. For example, Witwatersrand gold ores contain between 7.5 and 14.3 % silver with an average of about 10 % (Marsden and House, 1992). The greater reactivity of silver may influence the behaviour of gold in flotation, leaching and/or recovery process. According to the basic theories of corrosion, when two metals are placed in electrical contact in an electrolyte, the dissolution rate of the less noble metal is increased. This type of behaviour depends on parameters such as the composition of the two metals, the composition of the solution and the spatial distribution of the two metals. Choi et al. (1991) investigated the dissolution behaviour of silver-gold alloys. They found that the dissolution rates of the alloys were lower than those of gold and silver. They proposed that the attractive force between gold and silver atoms is higher than that between similar atoms and this may cause more difficulty in dissolution of gold and silver from the alloy. However, the net dissolution rate depends not only on the anodic characteristics of the alloy but also on the cathodic reduction of oxygen on the metal surface. No data of the oxygen reduction was given in their paper. Guan and Han (1994) also investigated the dissolution behaviour of gold-silver alloys in aerated cyanide solutions. They noted that the dissolution behaviour of silver and gold-silver alloys were very similar. The anodic dissolution of the alloys did not exhibit a passive region even at high gold content in the alloys (up to 50 % gold). This leads to a number of questions such as:

- What is the effect of the dissolution time on the composition of the alloy?
- Since gold and silver have different dissolution rates, is it possible that the less noble metal is depleted on the surface of the alloy during its dissolution process?

Knowledge of the dissolution behaviour of gold and silver in cyanide solutions may contribute to the better understanding of the leaching behaviour of gold-silver alloys.

2.3. CONCLUSIONS

The successful application of cyanidation to the extraction of gold depends not only on the dissolution behaviour of gold itself but also on the response of associated minerals to the leaching solution. Impurities in alkaline cyanide solutions may either accelerate or retard the dissolution of gold. The retarding effect on the dissolution of gold in cyanide solutions was proposed to be due to the formation of passive layers, of which the nature is still uncertain. Small amounts of sulphide ions were found to be detrimental to the dissolution of gold in cyanide solutions. However, the literature does not reveal a stability region of chemical compounds such as Au-S in cyanide solutions. Consequently, the passivation of gold may be attributed to the adsorption of anions containing sulphur on its surface. When the gold particles are embedded in conductive minerals, a galvanic interaction may exist between them. This can retard the dissolution of gold if the open-circuit potential of the couple is either moved to the passive region of gold or to more negative potentials in the active region. It is also possible that the products of the galvanic interactions between sulphide minerals may affect the dissolution of gold. The sulphide ions released may decrease the dissolution rate of gold while the liberated lead ions may accelerate the dissolution rate. The accelerating effect on the dissolution of gold depends on factors such as the mass transfer of reactants and products, the concentration of dissolved oxygen in solution, the presence of lead and the influence of alloying elements. Small amounts of lead salts are known to accelerate the dissolution of gold while high concentrations retard it. The thermodynamics of the lead-water-cyanide system can not explain the action of lead species on the gold surface. It is evident that lead must be involved directly in the surface reaction and disrupts the formation of the passive layer on the gold surface but the electroactive species of lead responsible for this has not yet been established. However, since the species accelerating or decelerating the dissolution rate of gold are in contact with the gold surface, their nature will depend not only on the pH and their concentration in solution but also on the electrochemical potential at the gold surface.

The objectives of this study were:

- To investigate the influence of the mass transfer on the dissolution of gold and a gold-silver alloy (10 % Ag) using a rotating disc electrode;
- To identify the factors that may stabilise or destabilise the passive layers formed on a gold surface. Some of these factors are the sulphide ion concentration, the potential of the gold electrode, time and the presence of other impurities such as lead in solution.
- To investigate the nature of electroactive species of lead, which increase or decrease the dissolution of gold in cyanide solutions and to study the interaction of lead with other impurities such as SO_4^{2-}, CO_3^{2-} and S^{2-} on gold leaching.
- To investigate the combined action of sulphide and lead ions which are known to have opposite effects on gold leaching.

Chapter 3

EFFECT OF SILVER ALLOYING ON THE DISSOLUTION OF GOLD IN ALKALINE CYANIDE SOLUTIONS

3.1. INTRODUCTION

Native gold grains have been known to contain up to 99.8 % gold but most vary between 85 and 95 % gold content, with silver as the main impurity (Marsden and House, 1992). Mechanisms involved in the dissolution of gold and silver have been documented (Habashi, 1970; Hiskey and Sanchez, 1990; Jun Li and Wadsworth, 1993) but the dissolution behaviour of their alloys is not well understood. The purpose of this chapter is to identify and discuss the electrochemical reaction mechanism by which the dissolution of a gold-10 % silver alloy takes place. In order to have a better understanding of the dissolution kinetics of a gold-silver alloy, experiments were first conducted with unalloyed gold and silver.

3.2. EXPERIMENTAL

The experimental work was performed with gold (99.9 % Au), silver (99.9 % Ag) and gold-silver alloy (10 % Ag) electrodes which had respective surface areas of 0.24, 0.25 and 0.22 cm^2. The leaching vessel was made of glass and had a capacity of 0.5 liter. The cover of the leaching vessel had five openings which allowed insertion of the counter electrodes, the rotating electrode, the Luggin capillary and the tube for nitrogen or oxygen purging. The study on the anodic reaction was conducted in deaerated cyanide solutions while the cathodic reaction was conducted in cyanide-free oxygen containing solutions. For anodic potentiodynamic experiments, the solution was purged with nitrogen for one hour before each experiment to eliminate the effect of oxygen, and the nitrogen was kept flowing over the electrolyte during the test. The influence of the cyanide and oxygen mass-transfer may be conveniently studied with a rotating disc electrode (RDE) because its hydrodynamics is well established. According to the basic theory of the RDE as published by Levich (1962), the mass transfer limiting current $i_{l,c}$, under laminar flow conditions, is given by:

$$i_{l,c} = 0.62\, n\, F\, \omega^{1/2}\, \nu^{-1/6}\, D^{2/3}\, C_0 \qquad [3.1]$$

where ω is the angular velocity in Hz, ν is the kinematic viscosity in cm^2/s (i.e. the viscosity divided by the density), D is the diffusion coefficient in cm^2/s and C_0 is the concentration in bulk solution in mol/cm^3. All experiments were conducted at 25 °C. Cyanide concentrations of 250 and 2500 mg/l were used for the experiments. The desired cyanide concentrations were obtained by the addition of analytical grade sodium cyanide to the electrolyte. The pH of the electrolyte was adjusted to 11 with NaOH. This pH value is typically used in industrial gold leaching practice. An E.G. & G Princeton Applied Research potentiostat/galvanostat model 273 and a Pine rotating disk electrode model ASR2 were used to obtain polarization data. Polarization curves were obtained by continuously measuring the current as a function of potential between –1 and 0 V vs. SCE starting at the more negative potential. This potential range was selected because this study focused on the first peak in the anodic polarization diagram. The scan rate was 1 mV/s unless otherwise noted. Graphite was used as counter electrode and a saturated calomel electrode was used as a reference electrode. All potentials quoted in this study are with respect to the saturated calomel electrode (SCE).

3.3. RESULTS AND DISCUSSION

3.3.1. Anodic behaviour in cyanide solutions

a. Gold

The anodic polarisation curves obtained are presented in figure 3.1. A peak appears between -470 and -420 mV and the gold starts to passivate at potentials close to -350 mV. The influence of the cyanide mass transfer on the anodic behaviour of gold was investigated using different cyanide concentrations (250 and 2500 mg/l) and different rotation speeds, namely 0, 225, 450, 675 and 900 revolutions per minute (figures 3.1 and 3.2). It is clear that increasing cyanide concentration and stirring increased the dissolution of gold in the active region while dissolution in the passive potential range was less affected. To further establish if the increased rate was indeed due to better mass transfer, the variation of the peak current density i_c with $\omega^{1/2}$ was investigated at potentials corresponding to the maximum current.

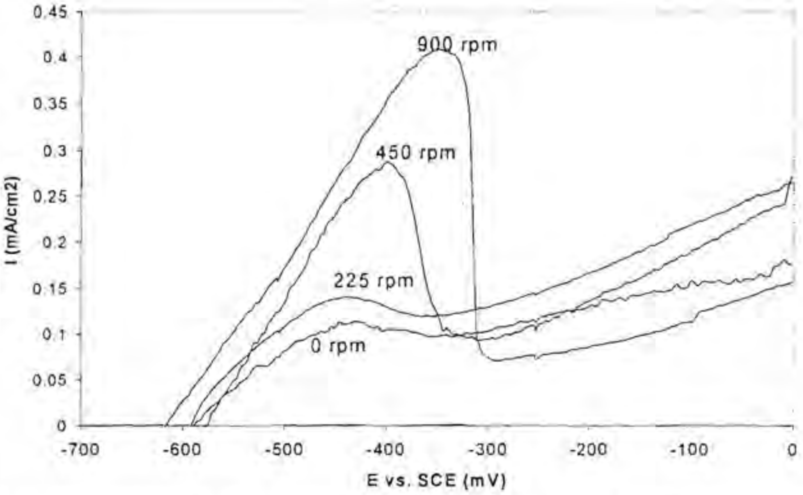


Figure 3.1. Influence of disc rotation speed on the anodic polarization curves of gold in deaerated aqueous cyanide as a function of disc rotation speeds, pH = 11; NaCN = 250 mg/l.

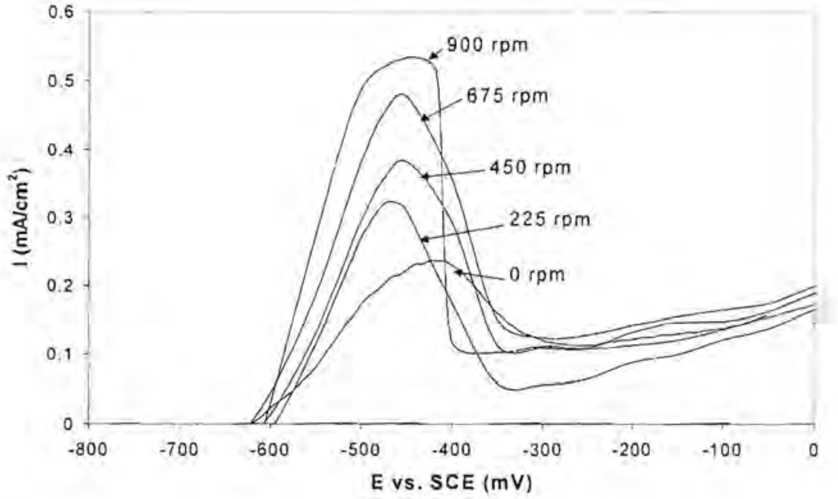


Figure 3.2. Influence of disc rotation speed on the anodic polarization curves of gold in deaerated aqueous cyanide as a function of disc rotation speeds, pH = 11; NaCN = 2500 mg/l.

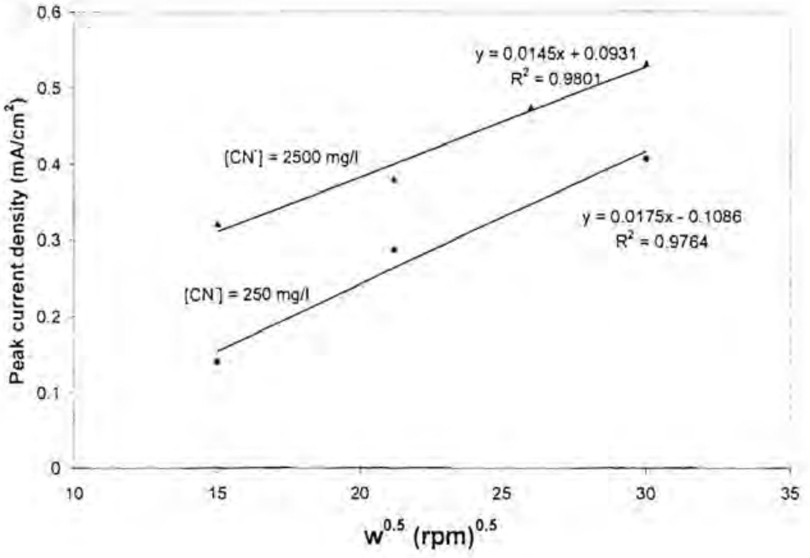


Figure 3.3. Effect of disc rotation speed on the peak anodic current densities for gold in deaerated aqueous solutions, NaCN = 250 and 2500 mg/l; pH = 11.

The approximately linear relationship between the peak current density and the square root of the rotation disc speed indicates that the dissolution of gold at these potentials is indeed controlled by the mass transfer of cyanide to the surface. However, Fick's law predicts that the dissolution rate of gold should be proportional to the cyanide concentration in the bulk when the process is diffusion controlled. The results indicate that this ratio is not achieved for the conditions used in this work. For a cyanide ratio of 10, the current density ratio was 2.3 under static conditions and 1.4 at 900 revolutions per minute. It is possible that the passivation of gold has already started at potential close to that corresponding to the peak current. A certain competition may exist between the dissolution of gold and the formation of a passive layer. The overall dissolution rate will therefore depend on factors such as the cyanide concentration and the time of contact between the gold and the cyanide solutions. Conditions during potentiodynamic polarization experiments are non-steady state and to better evaluate conditions at specific potential values, potentiostatic experiments were done to establish the influence of the cyanide concentration and time on the peak height. Potentiostatic experiments were conducted for a duration of 20 minutes at – 450 mV. This potential was chosen because the anodic polarization curves (figures 3.1 and 3.2) revealed that the peak current densities were in the range of – 350 to – 470 mV. Three different concentrations of cyanide were used namely 250, 750 and 2500 mg/l. Cyanide was added three minutes after the beginning of the experiment as shown in figure 3.4. It was found that the peak height increased with increasing the cyanide concentration. For a cyanide ratio of 10, the current density ratio was 2.4 two minutes after the addition of cyanide to the solution and 3.1 ten minutes latter. This indicates that the dissolution of gold as well as the formation of the passive film is time dependent. The increasing tendency in curve c in figure 3.4. may be explained by the removal of some or other layer from the gold surface.

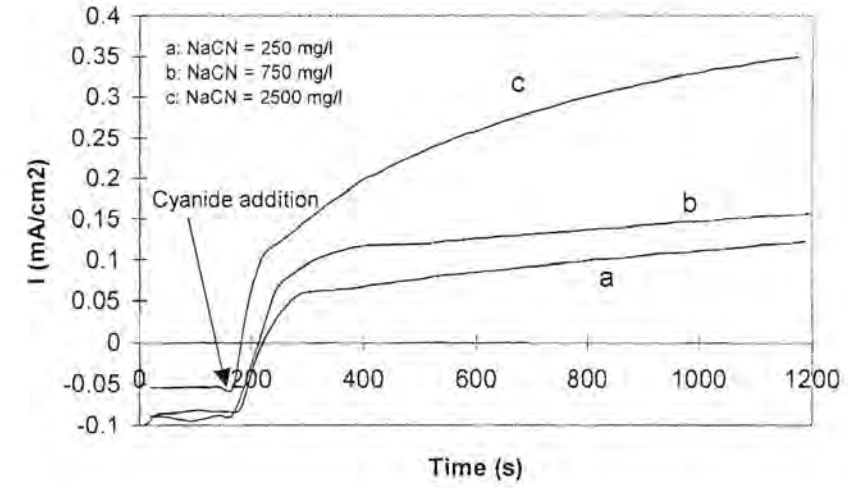


Figure 3.4. Effect of cyanide additions on the dissolution rate of gold in deaerated alkaline solutions. Constant potential E = -0.45 V; pH = 11, disc rotation speed = 225 rpm.

However, in the passive region, it appeared that a more stable passive layer was formed when the cyanide concentration and the stirring of the solution increased, i.e., when more cyanide ions were in contact with the gold. The large amount of $Au(CN)_2^-$ produced in the active region of the anodic curve, in particular at high rotation speeds and high cyanide concentrations, may create a diffusion barrier on the gold surface. A more resistant passive layer must be formed under these conditions if the $Au(CN)_2^-$ ions are not removed faster than they are formed. After the formation of a passive film on the gold surface, it was therefore important to know if the applied potential and/or the diffusion of cyanide to the gold surface could influence its dissolution. This may give an indication of the stability of the passive layer formed on the gold surface. Potentiostatic experiments were first done at –200 mV (SCE) for 20 minutes using three different rotation speeds, namely static electrode, 450 and 900 rpm in order to passivate the gold (figure 3.5). The results collected from the potentiostatic experiments confirmed those obtained from the potentiodynamic curves, i.e., the dissolution rate of gold at –200 mV (SCE) was further decreased at high rotation speeds. The influence of the mass transfer of cyanide on the reactivation of the passive film was investigated at – 450 mV (SCE). It was found that the reactivation of the passive film formed at high rotation speeds was a slow process (figure 3.6). After 45 minutes the current did not reach the steady-state, in particular at high rotation speeds, indicating that the gold surface was still covered by a passive layer. It seems that a poorer passive layer is formed at lower cyanide concentrations. The combined effect of a more positive applied potential and an ample supply of cyanide at the gold surface favours the formation of a more stable passive layer. It is therefore important to control the cyanide concentration, the stirring of the solution and the oxidation potential in the pulp such that the gold does not passivate.

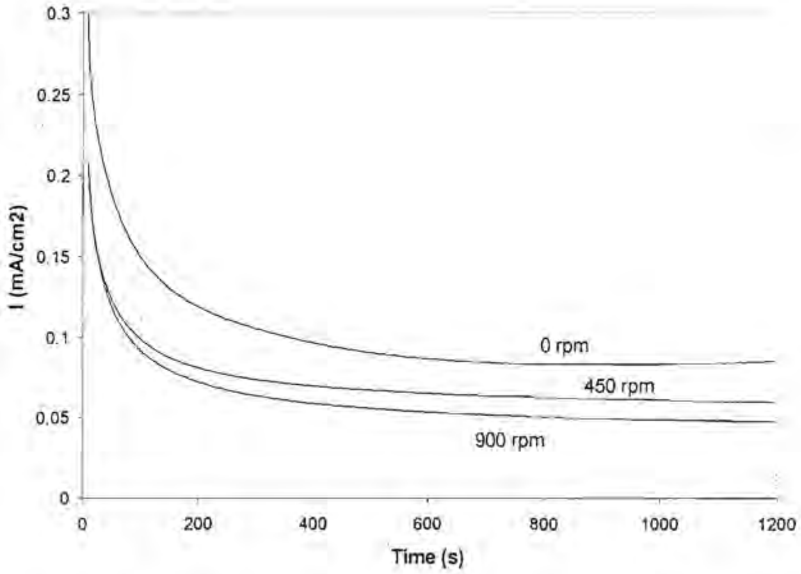


Figure 3.5. Influence of the rotation speed and time on the passivation of gold in deaerated aqueous cyanide at a potential of -200 mV (SCE), pH = 11, NaCN = 2500 mg/l.

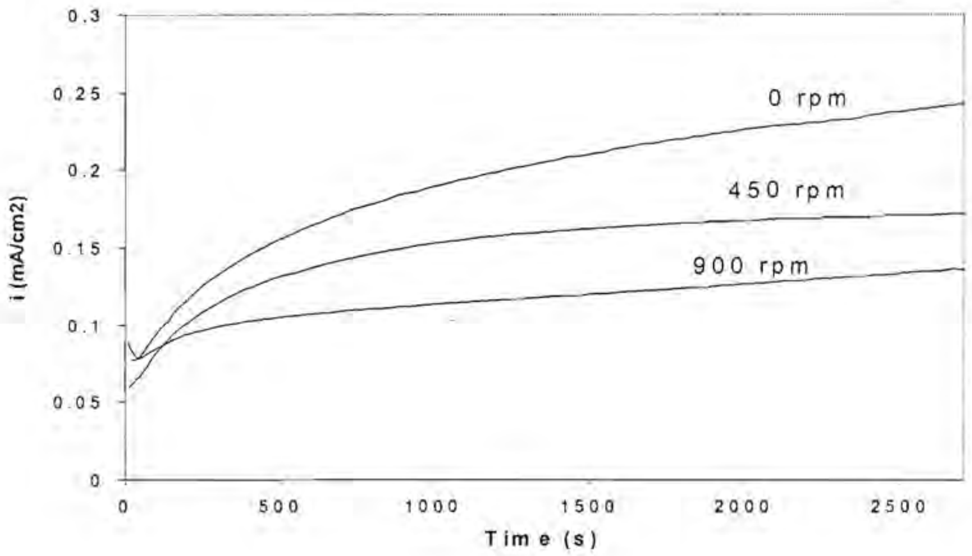


Figure 3.6. Influence of the rotation speed and time on the reactivation of the passive film formed on the gold surface at a potential of -450 mV(SCE), pH = 11, NaCN = 2500 mg/l.

b. Silver

The anodic characteristics obtained for silver in alkaline cyanide solutions are presented in figure 3.7. All of the polarization curves demonstrate similar features and indicate that the rate of silver dissolution increases with the disc rotation speed. Within the range of -1 to 0 V, the polarization curves reveal that silver does not passivate. By plotting the current density against the square root of rotation speed at –450 mV (SCE), linear relationships result as illustrated in figure 3.8. The straight line indicates pure diffusion polarization. This is in good agreement with the results of Jun Li and Wadsworth (1993). By comparing gold and silver dissolution it is clear that silver dissolves faster than gold.

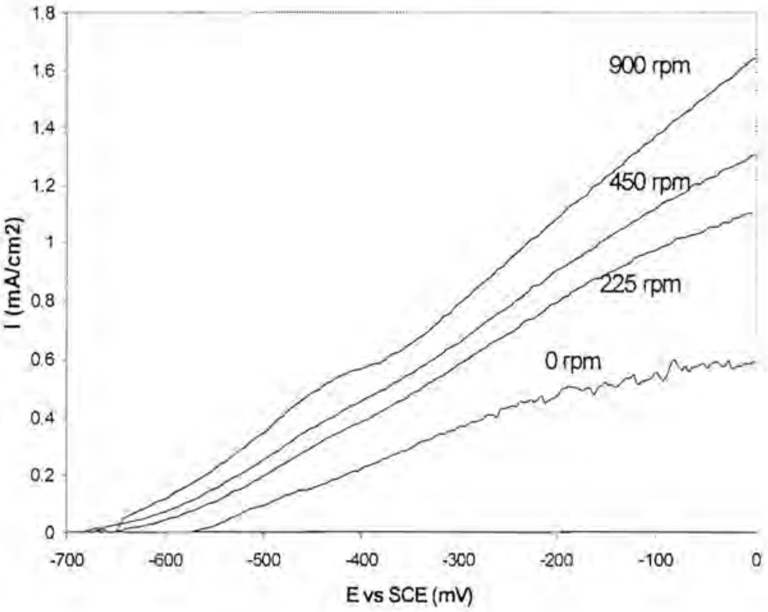


Figure 3.7. Influence of disc rotation speed on the anodic polarization curves of silver in deaerated aqueous cyanide as a function of disc rotation speeds, pH = 11; NaCN = 250 mg/l.

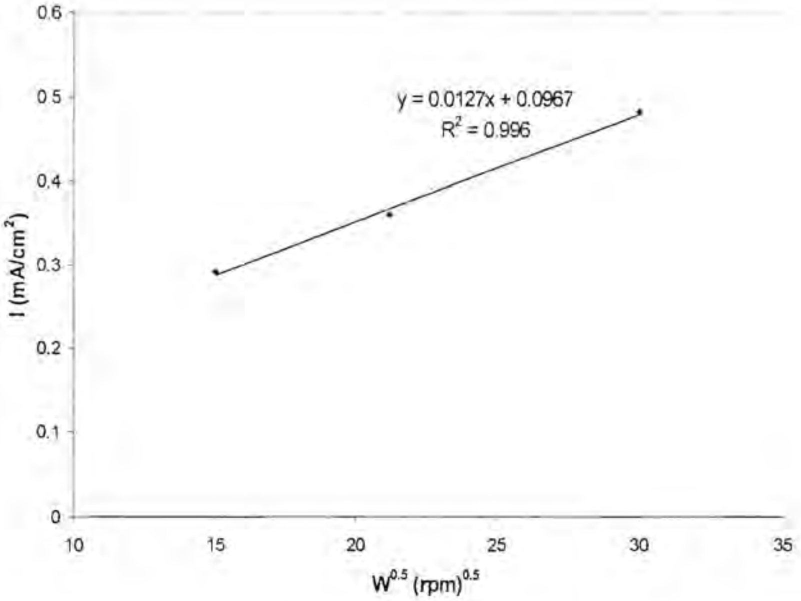


Figure 3.8. Effect of disc rotation speed on the anodic current densities at –0.45 V (SCE) for silver in deaerated aqueous solutions, NaCN = 250 mg/l; pH = 11.

c. Gold-silver alloy

The anodic dissolution of a gold-silver alloy was studied using the same conditions as previously. The curves obtained are presented in figure 3.9. The anodic polarization curves revealed a passive region, which increased at higher rotation speeds and cyanide concentrations. These curves were situated between those of gold and silver (figure 3.10). The passive film formed on the alloy surface was located in the region where gold also passivates. It was found that the current density at potentials corresponding to the peak was directly proportional to the square root of the rotation speed, as predicted by Levich's equation for a rotating disc (figure 3.11). These results indicate that the dissolution of the gold-10 % silver alloy is mainly diffusion controlled. A comparison between figures 3.3 and 3.11 indicates that the value of the current density ratio is close to that of the cyanide ratio in the case of the gold-10 % silver alloy. For a cyanide ratio of 10, the current density ratio was 7.2 under static conditions and 4.9 at 900 revolutions per minute while for gold the ratios were 2.3 and 1.3 for the same experimental conditions. The formation of a less stable passive film on the surface of the alloy, at potentials corresponding to the peak current, may explain these differences. The decrease of the current density ratio at high rotation speeds indicates that increasing the stirring favours the formation of a more passive film in the region of the peak. It can also be seen that the slopes of the curves for the gold-silver alloy are much higher than those for the gold, in particular at higher cyanide concentrations. The increasing tendency to accelerate the dissolution rate in the case of the alloy may be explained by:

(i) the removal of some or other layer from the surface,
(ii) some form of autocatalytic reaction on the surface.

Since silver dissolves faster than gold, it is possible that during the dissolution of the alloy, the surface is enriched in gold. This can explain the passive region observed on the anodic polarization curve of the alloy. To confirm this statement, the influence of time on the anodic dissolution of the alloy was investigated. Different scan rates, namely 0.1, 0.5 and 1 mV/s were used for the polarization curves (figure 3.12). It was found that at a lower scan rate (0.1 mV/s), the polarization curve revealed a clear passive region. This result supports the statement that silver is depleted on the alloy surface during its dissolution process.

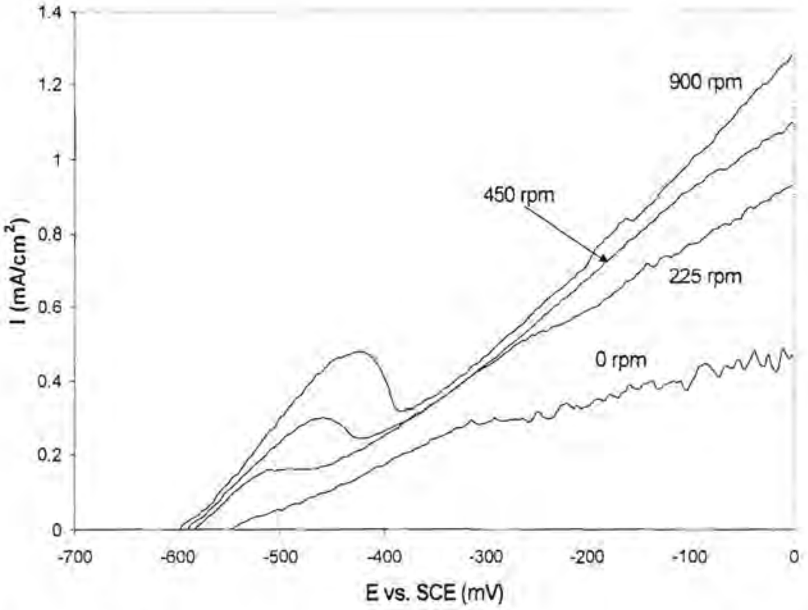


Figure 3.9. Influence of disc rotation speed on the anodic polarization curves of a gold-10 % silver alloy in deaerated aqueous cyanide as a function of disc rotation speeds, pH = 11; NaCN = 250 mg/l.

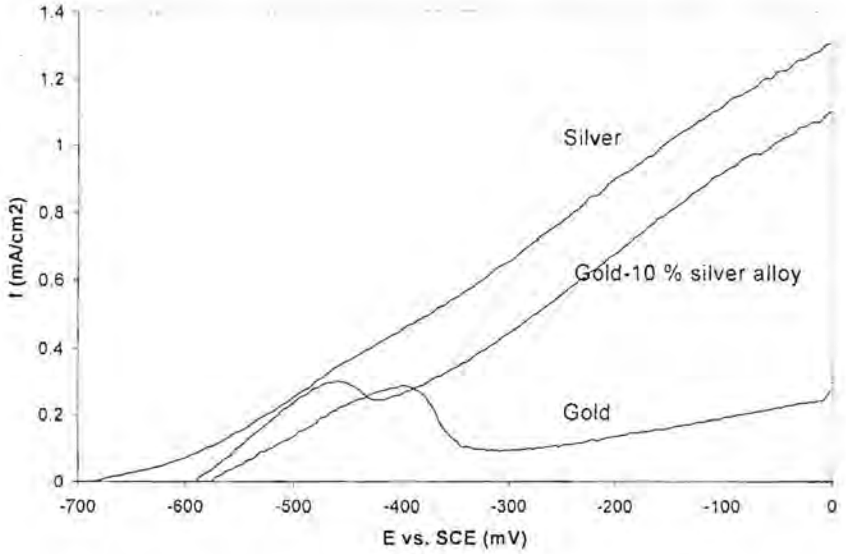


Figure 3.10. Anodic polarization curves of gold, silver and a gold-10 % silver in aqueous cyanide at a disc rotation speed of 450 rpm, pH = 11; NaCN = 250 mg/l.

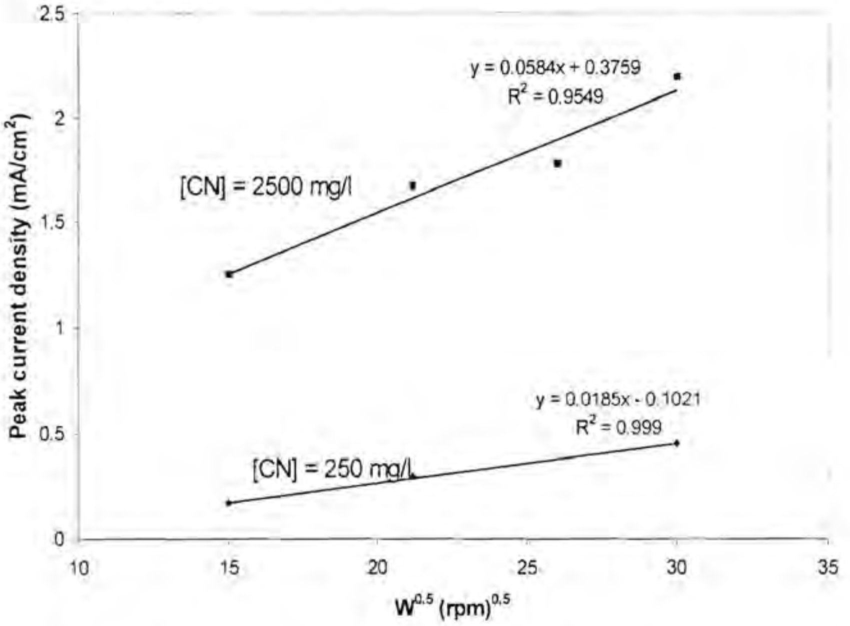


Figure 3.11. Effect of disc rotation speed on the peak anodic current densities for gold in deaerated aqueous solutions, NaCN = 250 and 2500 mg/l; pH = 11.

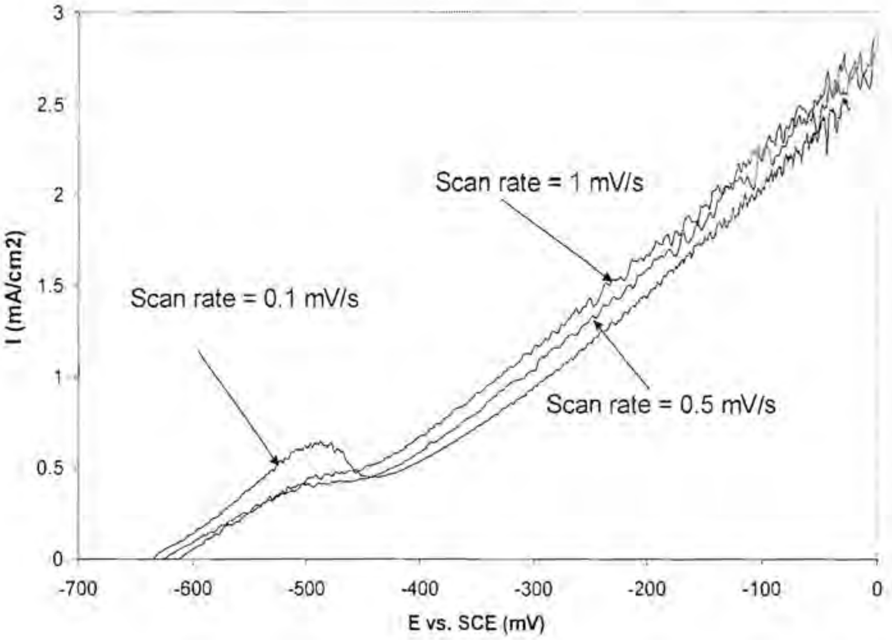


Figure 3.12. Anodic dissolution of gold-10% silver alloy in deaereted alkaline cyanide solutions at different scan rates, pH = 11, NaCN = 250 mg/l, disc rotation speed = 300 rpm.

3.3.2. Cathodic reduction of oxygen in alkaline solutions

The current-potential curves for the reduction of oxygen on pure gold, pure silver and gold-10 % silver alloy for a constant dissolved oxygen of 12 mg/l are presented in figures 3.13 a, b and c. Three rotation speeds were investigated namely, 0, 450 and 900 revolutions per minute. These curves show the trend of approaching a limiting current. In the activation kinetic region the reduction of oxygen on the silver surface is lower than that on the gold and gold-10 % silver alloy. Hiskey and Sanchez (1990) observed similar behaviour and proposed that the difference between the discharge of oxygen on silver and gold are due to:

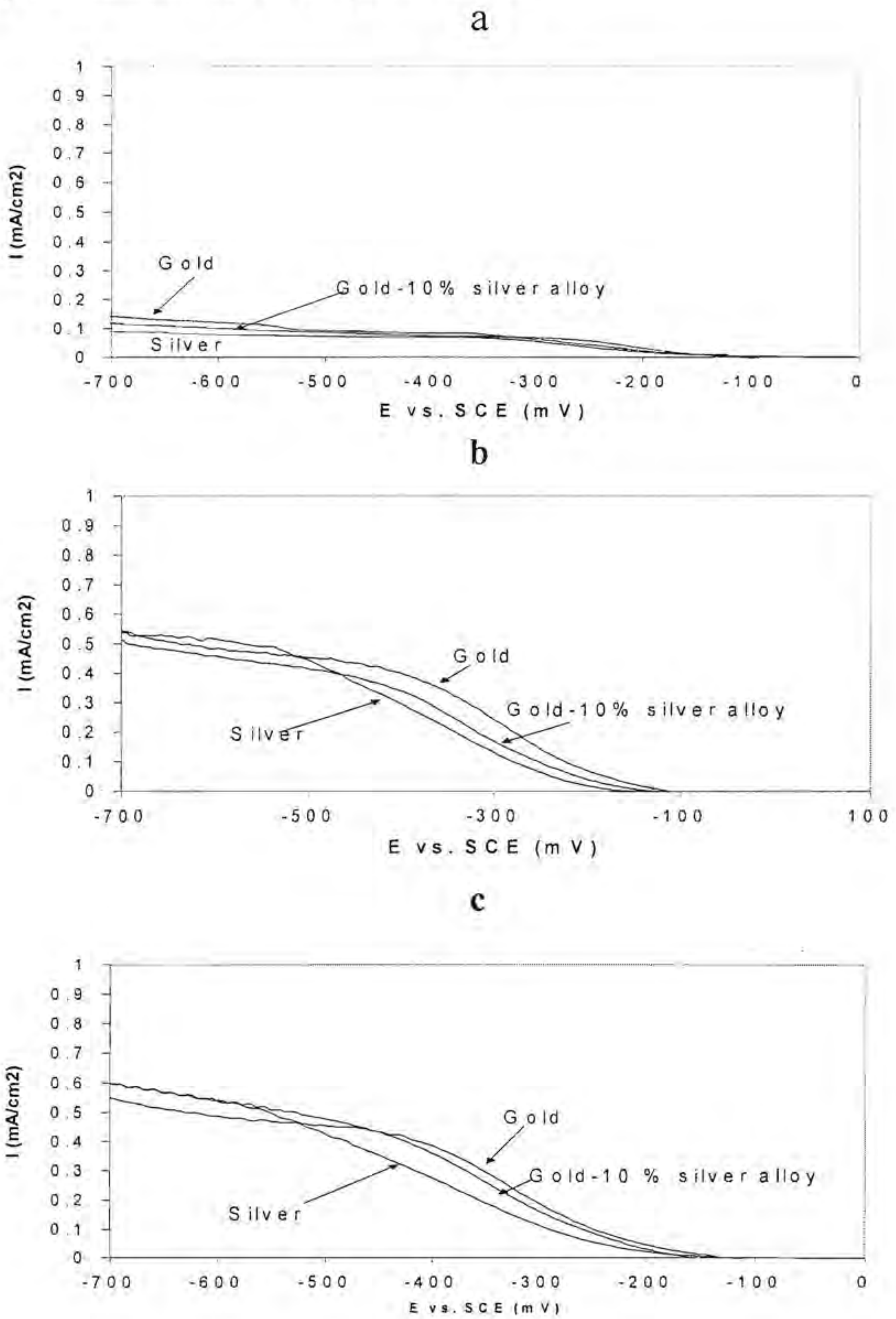
(i) silver proceeds by a four electron direct path instead of the two-electron path for gold,

(ii) oxygen adsorption appears to follow a Freundlich isotherm on silver and a Langmuir isotherm on gold,

(iii) the transfer coefficient for oxygen reduction on silver is 0.25 whereas on gold it is 0.5.

This proposed mechanism is in contradiction with the conclusions of Adanuvor and White (1988) who studied the oxygen reduction on silver in a 6.5 M caustic soda. They suggested that the sequential process with catalytic decomposition of peroxide predominates over the direct process. Whatever the mechanism, it is important from a practical point of view to compare the kinetic response of gold, silver and gold-silver alloy by overlaying the anodic dissolution curves of these metals with the curves for the cathodic reduction of oxygen on the same metals. This may give an indication about the rate-determining step and the dissolution rate of gold in aerated cyanide solutions.

Figure 3.13. Cathodic polarization curves for the reduction of oxygen on gold, silver and 10 % silver alloy at three different rotation speeds, Dissolved oxygen in solution =12 mg/l; a: Static electrode, b: 450 rpm , c: 900 rpm.



3.3.3. Combination of anodic and cathodic curves

a. Gold

According to the mixed-potential theory, the corrosion potential and the net dissolution rate can be obtained by combining the anodic and cathodic current-potential curves on so called Evans diagrams as shown in figures 3.14 to 3.16. Under static conditions the intersection point for gold leaching is located in the active region on the anodic curve and in the oxygen diffusion limiting region on the cathodic curve (figure 3.14). This indicates that under the experimental conditions, the mass transfer of oxygen is the limiting step. At 450 rpm, the anodic and cathodic curves intersect in the passive region of the anodic curve and in the activation region of the cathodic curve. This implies that the overall dissolution rate is controlled by the formation of a passive layer on the gold surface. At 900 rpm, there are three intersection points. The first intersection point is located in the passive region of the anodic curve. A passive film is formed at this point. The second point is in the transpassive region and the third point is in the active region corresponding to a high dissolution rate. A situation like this often leads to unusual results (Fontana, 1967), although all the three of these points meet the basic requirement of the mixed-potential theory. This system may exist in either the passive or active state. It can be seen that the position of the cathodic curve fixes the rate of the overall process.

b. Silver

From figure 3.15 it follows that there is only one intersection point for each combination of the cathodic and the anodic curves at different rotation speeds. Under static conditions this point is located in the oxygen-diffusion-limiting region on the cathodic curve and in the active region on the anodic curve. In this case, the rate of silver dissolution is oxygen-diffusion controlled. At higher rotation speeds, the intersection points are situated in the active region of both curves. Since silver does not passivate in the potential range used for the experiments, the metal will dissolve faster if the agitation and/or the dissolved oxygen is increased.

c. Gold-10 % silver alloy

It is interesting to note that the alloy can passivate at high rotation speeds and high cyanide concentrations but the extent of passivation is smaller compared to that of gold. Under static conditions and at 450 rpm there is one intersection point (figure 3.16). The dissolution of the alloy is oxygen-diffusion controlled under static conditions and mixed controlled at high rotation speeds. An ample supply of oxygen will increase the dissolution of the metal. However if the concentration of silver decreases in the alloy, the extent of the passive region will also increase and the behaviour of the alloy will be similar to that of gold.

3.4. CONCLUSIONS

The kinetics of dissolution of gold, silver and gold-10 % silver alloy have been studied using potentiodynamic and potentiostatic methods. The anodic polarization study showed that gold presents a large passive region between –0.3 and 0 V (SCE). Although the results showed an approximately linear relationship between the peak current density of the gold and the square root of the rotation disc speed, the ratios of the currents and the cyanide in the bulk were not proportional as predicted by the Fick's law. It is possible that the passivation of gold has already started at potentials close to that corresponding to the maximum current. In the passive region it appeared that a more stable passive layer was formed when the cyanide concentration and the stirring of the solution increased. It has been proved that the mass transfer of aurodicyanide ions was slower than that of cyanide ions. This implies that the large amount of $Au(CN)_2^-$ produced in the active region, in particular at high rotation speeds and high cyanide concentrations, may screen the gold surface and create a more resistant diffusion barrier. For silver, the polarization curves indicate that silver does not passivate in the potential range used in this study. The anodic behaviour of the gold-10 % silver alloy presents a smaller region of passivation compared to that of pure gold. However, at high cyanide concentrations and higher rotation speeds, the extent of passivation is increased. It was also found that the ratios of the currents and the cyanide in the bulk were much higher than those calculated for gold. This confirmed the statement that a less stable layer is formed on the alloy surface. The reduction of oxygen on silver was found to be lower than that of gold and the gold-10 % silver alloy in the activation controlled region. These results were in good agreement with the findings of Hiskey and Sanchez (1990). Contradictions still persist about the exact mechanism of the oxygen reduction on noble metals. The combination of anodic and cathodic polarization curves revealed that dissolution of gold, silver and gold-10 % silver alloy was predominantly diffusion controlled under static conditions and activation controlled at high rotation speeds. Due to the fact that silver did not exhibit a passive region, the net dissolution rate of silver was found to be the highest, followed by that of the gold-10 % silver alloy. In a solution containing 250 mg/l NaCN oxygen was found to be the limiting reactant. The position of the cathodic curve fixed the rate of the overall process. In practice it is therefore important to control the dissolved oxygen level in solution since the passivation of the gold occurs at more positive potentials. The solutions used in this chapter were "pure", while in practice the cyanide solutions generally contain numerous impurities. When impurities are present, it is possible that the anodic and/or the cathodic reaction may be affected. Mechanisms such as adsorption of an impurity on the surface, precipitation of an insoluble film at the gold surface and activation of the surface of the gold may move the intersection of the anodic and cathodic curves in a direction which favours the dissolution or the passivation of gold. It would be of interest to study the influence of impurities on the anodic and cathodic polarization curves of gold and the gold-10 % silver alloy. This is discussed in the next chapter.

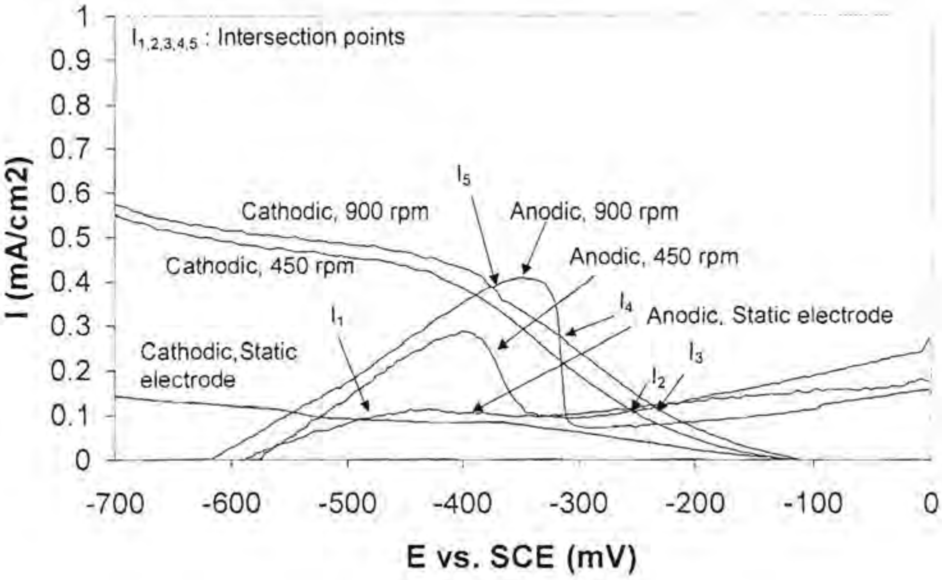


Figure 3.14. Evans diagrams for a gold rotating disc electrode in oxygenated aqueous cyanide solutions containing 250 mg/l NaCN, dissolved oxygen = 12 ppm, pH = 11.

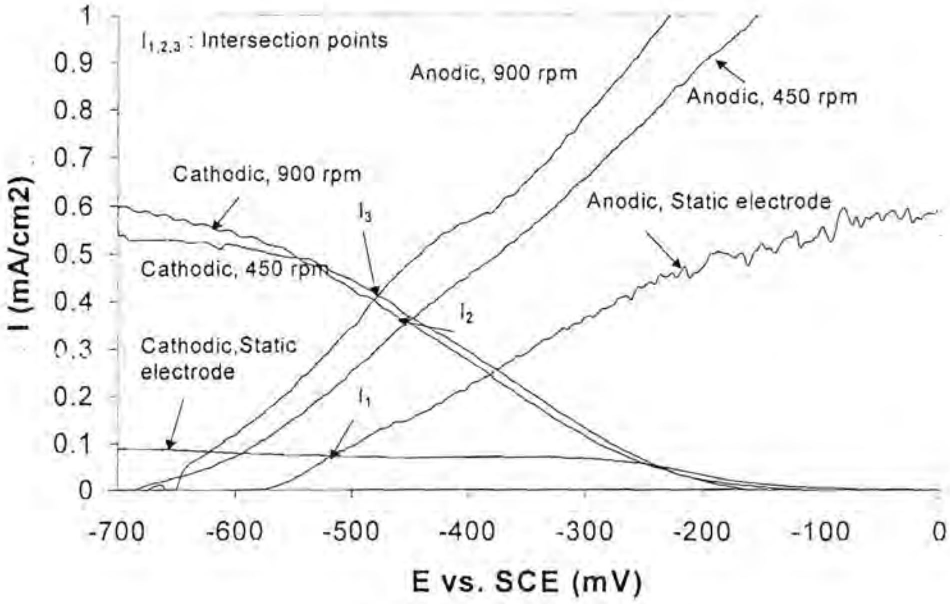


Figure 3.15. Evans diagrams for a silver rotating disc electrode in oxygenated aqueous cyanide solutions containing 250 mg/l NaCN, dissolved oxygen = 12 ppm, pH = 11.

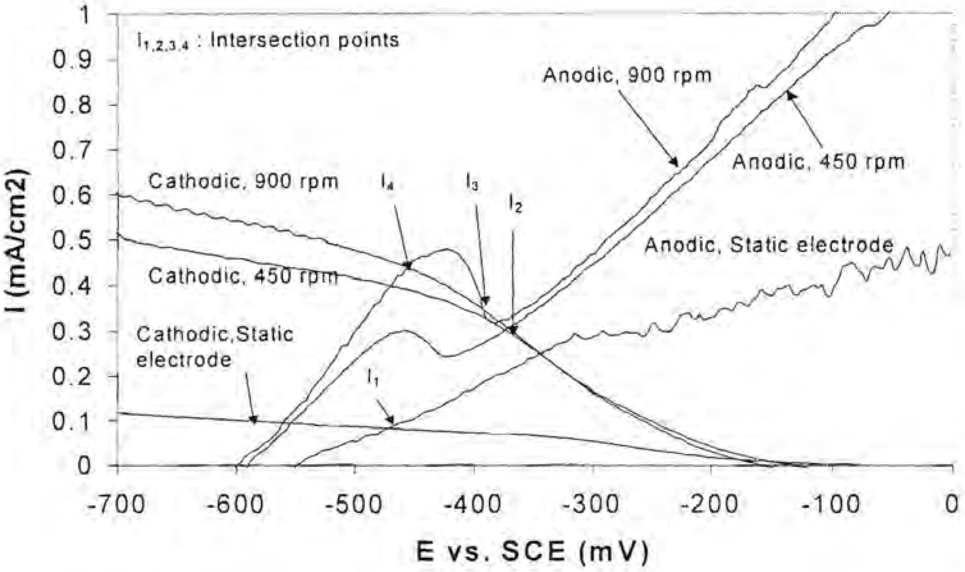


Figure 3.16. Evans diagrams for a gold-10 % silver alloy rotating disc electrode in oxygenated aqueous cyanide solutions containing 250 mg/l NaCN, dissolved oxygen = 12 ppm, pH = 11.

Chapter 4

INFLUENCE OF LEAD ON THE LEACHING RATE OF GOLD AND A GOLD- 10 % SILVER ALLOY IN CYANIDE SOLUTIONS

4.1. INTRODUCTION

Studies devoted to the role of trace impurities such as lead, thallium, bismuth and mercury on the leaching rate of gold have always been of interest since the extraction of gold in their presence could be improved significantly. Salts of lead are generally used to increase the dissolution rate of gold but, as described previously, the exact nature of the electroactive species of lead is not yet known. The thermodynamic diagram of the Pb-H_2O-CN system was not found in the literature and this raises speculation about the nature of lead species in alkaline cyanide solutions and the mechanism of their action on the gold surface. However, from an engineering point of view the kinetics of gold leaching is of more importance. Moreover, a kinetic study may give an indication of the presence of soluble and solid species, which interact at the metal surface. The purpose of this chapter is to investigate the behaviour of gold and a gold-silver alloy in cyanide solutions containing salts of lead as a function of electrochemical potentials using potentiodynamic and potentiostatic techniques.

4.2. EXPERIMENTAL

The experimental work was conducted with gold (99.9 % Au) and a gold-silver alloy (10 % Ag) and lead (99.9 % Pb) electrodes which had respectively surface areas of 0.24, 0.22 and 1 cm^2. Two graphite rods were used as counter electrodes and a saturated calomel electrode connected via a Luggin tube to the cell was used as a reference electrode. The leaching vessel was made of glass and had a capacity of 0.5 liter. The cover had five openings which allowed insertion of the counter electrodes, the rotating electrode, the Luggin capillary and the tube for nitrogen or oxygen purging. Cyanide concentrations of

250, 1000 and 2500 mg/l were used for the experiments. Cyanide was added as NaCN to the solution. The pH of the electrolyte was adjusted to 11 with NaOH. The desired lead concentrations were obtained by the addition of analytical grade $Pb(NO_3)_2$ to the electrolyte. The effects of S^{2-} , SO_4^{2-} and CO_3^{2-} on the anodic characteristics of gold were investigated by adding analytical grade Na_2S, Na_2SO_4 and $CaCO_3$ to the solution. Three different lead to anion ratios were used for the experiments namely 0.31, 0.21 and 0.15. Since the stoichiometry indicates that 1 mol of Pb^{2+} reacts with 1 mol of S^{2-}, SO_4^{2-} or CO_3^{2-}, the anions were therefore in excess. An E.G. & G Princeton Applied Research potentiostat/galvanostat model 273 and a Pine rotating disk electrode model ASR2 were used to obtain polarization data. Polarization curves were obtained by continuously measuring the current as a function of potential between –1 and 0 V vs. SCE starting at the more negative potential. The scan rate was 1 mV/s unless otherwise noted. All potentials quoted in this study are with respect to the saturated calomel electrode (SCE). Current density vs. time curves for the oxidation of gold with and without impurities were obtained in potentiostatic experiments. The reduction of the added lead on the gold surface was avoided by polarizing the electrode to a potential 100 mV positive to the lead corrosion potential before addition of the lead nitrate. Each potentiostatic experiment had a duration of twenty minutes and impurities were added three minutes after the beginning of the experiment in order to clearly distinguish their effect on the dissolution of the gold. All experiments were done at room temperature.

4.3. RESULTS AND DISCUSSION

4.3.1. Behaviour of gold in cyanide solutions containing lead

Lead nitrate additions have a pronounced effect on the anodic characteristics of gold in cyanide solutions as indicated by the polarization diagrams shown in figure 4.1. At more negative potentials, the current density increased with the anodic potential and at about – 400 mV (SCE) the current density reached its maximum value. This value is in a good agreement with the results of Mussatti et al.(1997). Significant passivation was observed as the applied potential approached -250 mV (SCE). In the passive region the anodic activity of the gold is even further decreased when lead is added to cyanide solutions. Two assumptions can be made to explain this behaviour. First, it is possible that a passive film of lead is also formed on the gold surface at potentials more positive than -250 mV. Second, due to the higher peak current densities reached when lead ions are used, it is possible that a more protective passive layer is formed, as was indeed found in earlier experiments.

The peak anodic current densities for gold in cyanide solutions containing traces of lead were highly dependant on the rotation disc speed as shown in figure 4.2. Increasing the concentration from 0 to 0.5 mg/l lead at 900 rpm resulted in an increase of the peak-height by a factor of 11 (Figure 4.2). The peak-height increases for concentrations above this value then became asymptotic. This indicates that the mass transfer of the cyanide to the gold surface was becoming the rate determining step.

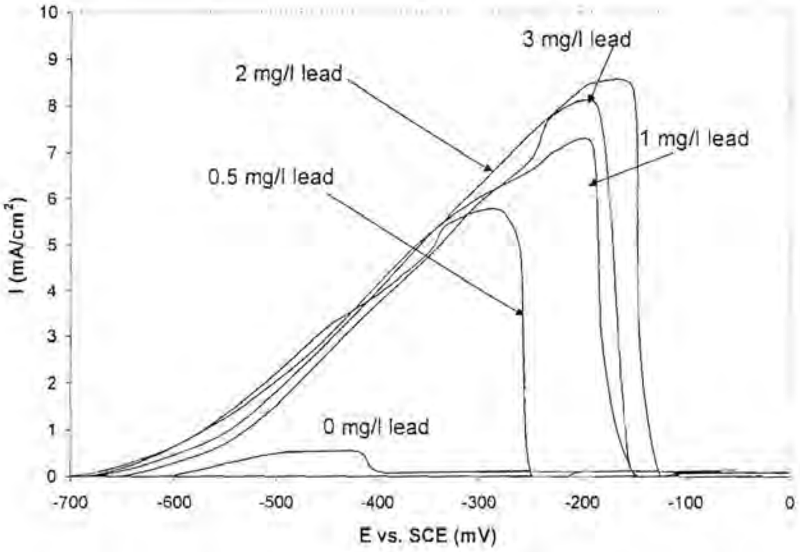


Figure 4.1. Effect of lead additions on the anodic dissolution of gold in deaerated aqueous cyanide solutions. Temperature: 25°C; pH = 11.0; NaCN = 2500 mg/l; disc rotation speed = 900 rpm.

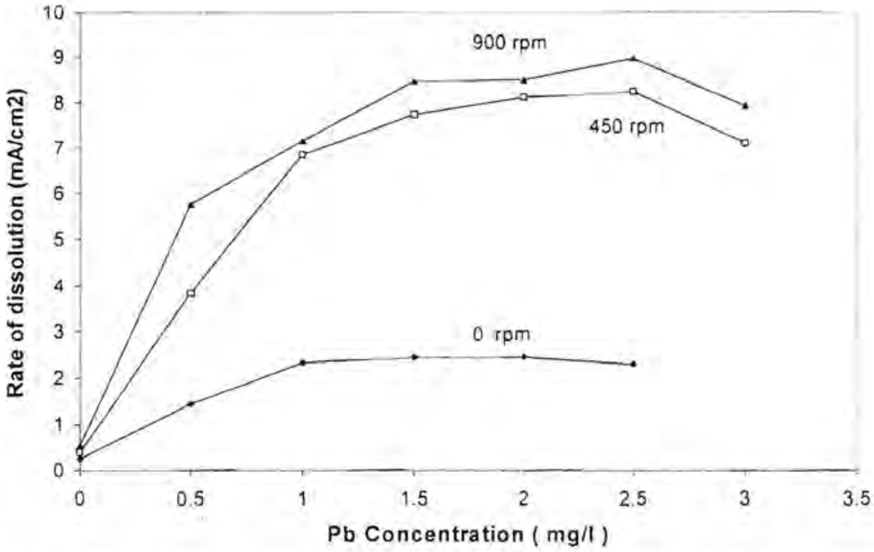


Figure 4.2. Peak anodic current densities measured for gold in deaerated aqueous cyanide solutions as a function of lead concentration and disc rotation speed. pH = 11.0; NaCN = 2500 mg/l.

As discussed in section 2.2.3, many mechanisms were proposed to explain the action of lead ions on the gold surface. Some authors (Kokkinidis, 1986; Chimenos et al., 1997; Mussatti et al., 1997) believe that underpotential deposited layers of metallic lead may enhance the anodic activity of gold. However, according to the potential – pH diagram of the Pb-H_2O system (figure 2.9), the predominant species at pH = 11, for lead (II) concentrations higher than 10^{-4} M (21 mg/l) is PbO. For lead (II) concentrations lower than 10^{-5} M (2.1 mg/l) lead would be present as $HPbO_2^-$. Since the optimum lead concentration was found to be less than 5 ppm, it is necessary to consider the reduction of $HPbO_2^-$ to metallic lead. In this case, the reversible potential of the $HPbO_2^-$/Pb couple can be expressed by (Pourbaix, 1966):

$$E = 0.702 - 0.0885\,\text{pH} + 0.0295 \log [HPbO_2^-] \qquad [4.1]$$

At pH = 11 and for a concentration of 2 mg/l $HPbO_2^-$ (8 μM) this potential is –0.42 V vs. SHE (-0.66 V vs. SCE). This potential is more negative than the mixed potential for gold dissolution (-0.48 V vs. SCE) in 250 mg/l cyanide solution containing 12 ppm dissolved oxygen (figure 3.14). On the other hand, the addition of lead in the system may move the open-circuit potential to lower potentials. Jeffrey et al. (1996) found that the mixed potential for gold dissolution in 1 g/l cyanide solutions saturated with air and containing 1 ppm lead, to be $\cong$ -0.4 V vs. SCE. In view of this, an underpotential value of more or less 260 mV is required to deposit metallic lead on the gold surface from a solution containing 1 ppm lead salts. It is therefore improbable that conditions in typical leach solutions would favour the deposition of metallic lead on the gold surface. Whatever the mechanism on the gold surface, it would rather decrease the activity of soluble lead species and make the deposition of metallic lead less favourable. It is possible that lead reacts only very weakly with cyanide and forms unstable Pb-CN compounds, which will react with OH^- to form stable hydroxide compounds. It was also found in the literature that lead forms a wide variety of complex salts with different anions such as Cl^-, F^-, I^- and SO_4^{2-}, but none of these complexes is a Pb-CN compound (Appendix 2).

In order to clear up these contradictions, it was decided to investigate the anodic behaviour of the metallic lead in alkaline cyanide solutions. It was found that lead is anodically more active than gold in aqueous cyanide but that it also passifies, although at a slightly more positive potential (figure 4.3). The anodic characteristics of metallic lead and gold shown in figure 4.3 indicate that depending on the potential:

- Both lead and gold are active;
- Lead is active and gold passive;
- Both lead and gold are passive.

To determine if the action of the lead was influenced by the lead species in solution, the influence of 0.5 mg/l lead nitrate additions on the anodic behaviour of gold held at various potentials in both the active and passive regions of gold and lead was investigated (figure 4.4).

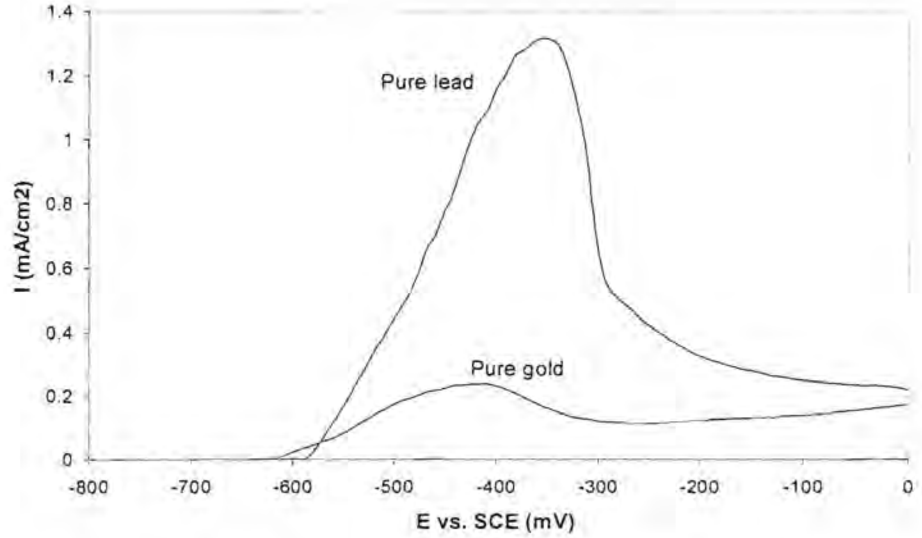


Figure 4.3. Anodic polarization curves of gold and lead in deaerated cyanide solutions, pH = 11.0, NaCN = 2500 mg/l, Static conditions.

4.3.1.1. Lead and gold in the active region

Lead and gold are both active in the voltage range -0.6 to -0.4 V. The effect of 0.5 mg/l lead on the dissolution of gold was investigated using two constant potentials namely -0.5 and -0.43 V. Both cases show a profound change in the gold dissolution after the addition of lead ions (figure 4.4). The rate of gold leaching was 3 to 4 times faster than for the other experimental conditions using solutions free of lead. The dissolution rate of gold reached a maximum after which it started to decrease again. It is possible that the lead and the cyanide are consumed at a higher rate during this process. If the mass transfer of cyanide is the rate determining step, a decrease in the cyanide concentration will imply a decrease in the dissolution rate of gold.

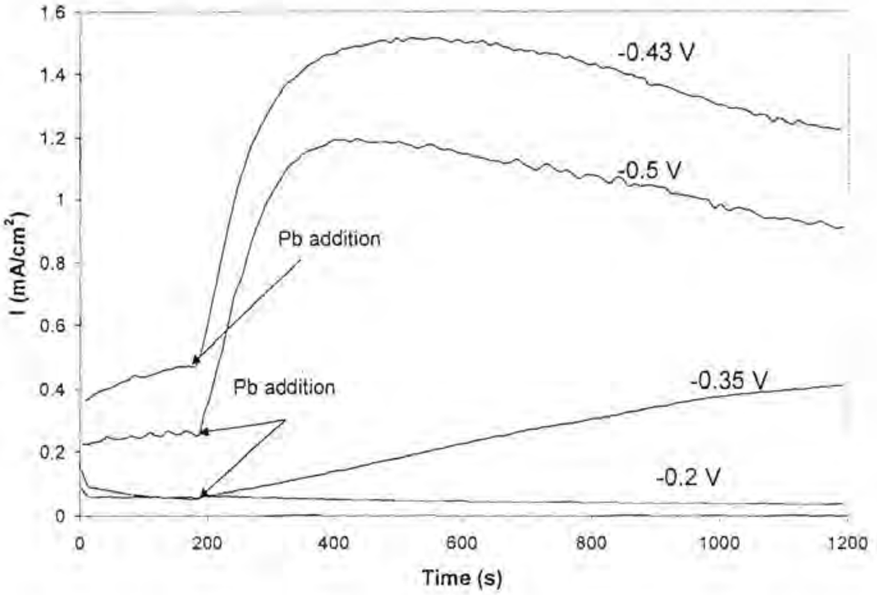


Fig 4.4. Potentiostatic curves for gold in alkaline cyanide solutions with addition of 0.5 mg/l lead. Temperature: 25 °C, pH = 11, NaCN = 2500 mg/l, disc rotation speed = 225 rpm.

The accelerating effect of lead in this first potential range must be due to the lead species in solution and not to metallic lead since the reduction of the added lead on the gold surface was avoided by polarizing the gold to potentials more positive than the lead corrosion potential (~ -0.58 V vs. SCE). The literature reveals more than fifteen lead species in solution (Appendix 3). At pH 11 and for a total lead concentration of 0.5 mg/l (1.7×10^{-6} M) the most probable species is $Pb(OH)_3^-$ according to figure 2.8.a. This first potential range is of interest since in practice the dissolution of gold in aerated cyanide solutions takes place between –350 to –600 mV (SCE).

4.3.1.2. Lead in the active region and gold in the passive region

This situation occurs within the potential range -0.4 to -0.325 V. The effect of lead was investigated for a constant potential of -0.35 V. After the addition of lead, the dissolution of gold increases relatively slowly with time (Figure 4.4). After twenty minutes the steady state was not reached, indicating that lead ions disrupt the formation of a passive layer on the gold surface but its removal is a slow process. Supplementary factors such as the temperature and the agitation of the solution may give more details about the action of lead ions in the process of breaking down the passive film on the gold surface.

4.3.1.3. Lead and gold in the passive region

This situation occurs in the region of -0.325 to 0 V. The effect of lead was investigated for a constant potential of -0.2 V. It was observed that the anodic activity of the gold was even further decreased when lead was added to the solution (figure 4.4). This could be due to the lowering of the lead in solution by the formation of insoluble lead species or to a more stable passive film on the gold surface. The results also indicate that the depassivation of the gold is a relatively slow process especially at the more positive potentials where the passive layer on gold will presumably be better developed.

4.3.2. Behaviour of gold-silver alloy(10 % Ag) in cyanide solutions containing lead

The anodic behaviour of the alloy in an aqueous cyanide solution is different from that of pure gold as indicated by the polarization diagrams shown in figure 4.5. A slight increase in the dissolution rate of the gold-silver alloy is observed when lead is added to the solution, in particular at low rotation speeds. The effect of the lead concentration on the anodic dissolution rate of the alloy was studied using 0.5 mg/l increments ranging from 0 to 2 mg/l lead. As for gold the peak height became asymptotic above the addition of 0.5 mg/l lead to the solution.

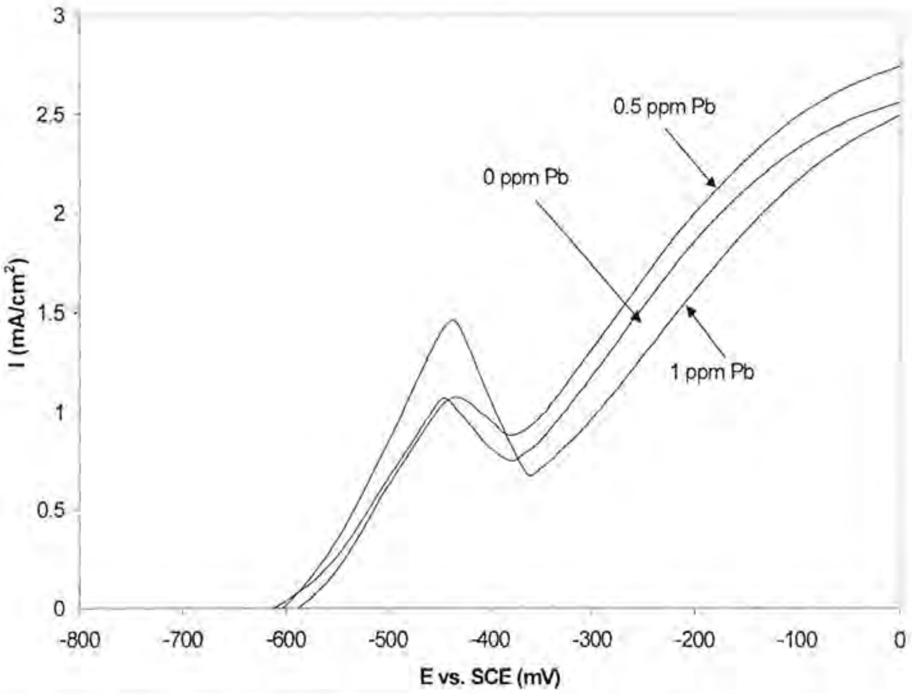


Figure 4.5. Effect of lead additions on the dissolution rate of gold-10 % silver alloy in alkaline cyanide solutions. Temperature: 25 °C; pH = 11.0; NaCN = 2500 mg/l; scan rate: 1 mV/s; static conditions.

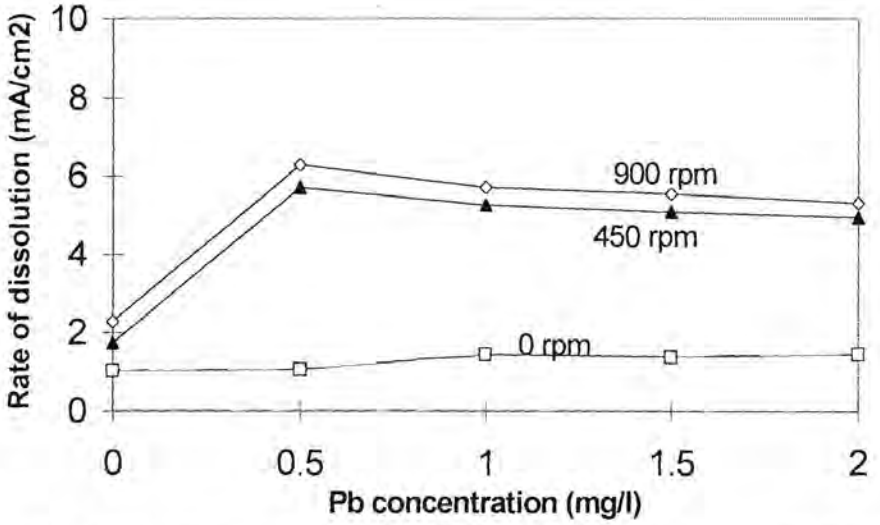


Figure 4.6 Peak anodic current densities measured for gold-10 % silver alloy in deaerated aqueous cyanide solutions as a function of lead concentration and disc rotation speed. pH = 11.0; NaCN = 2500 mg/l.

The anodic characteristics of gold-10 % silver alloy and pure lead are presented in figure 4.7. The dissolution of metallic lead and gold-10 % silver alloy revealed three cases where different species of both metals co-exist (figure 4.7):

- Lead and gold-silver alloy are both active;
- Lead is active and gold-silver alloy is passive;
- Lead is passive and gold-silver is active.

We have also used potentiostatic measurements to study each case.

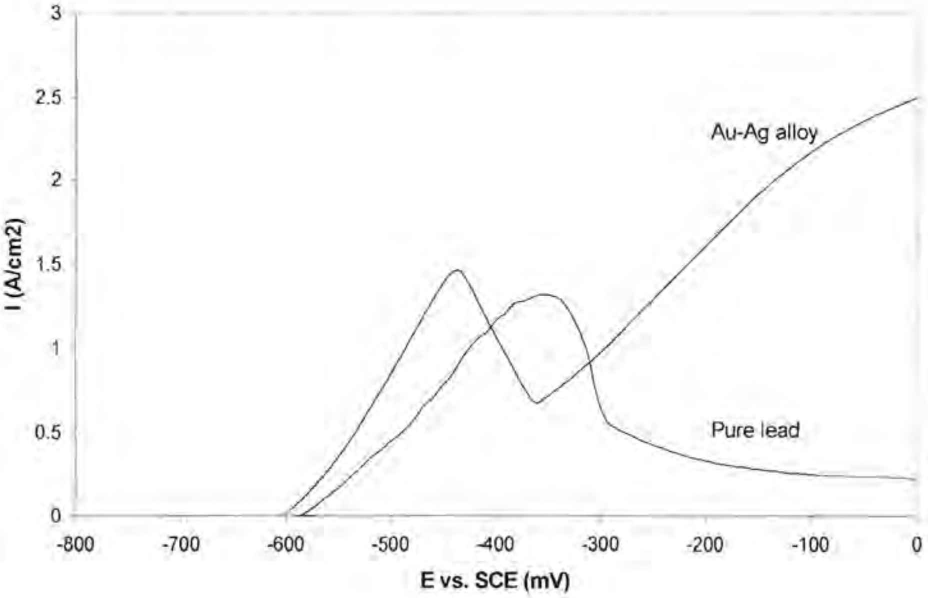


Figure 4.7. Anodic polarization curves of gold-10 % silver alloy and lead in deaerated cyanide solutions. pH = 11.0; NaCN = 2500 mg/, Static conditions.

4.3.2.1. Lead and gold- 10 % silver alloy in the active region

The potential range for this case is -0.6 to -0.4 V. This study was conducted for a potential of -0.5 V (Figure 4.8). It was found that after the addition of lead ions in cyanide solutions, the dissolution rate of the gold-silver alloy was increased. As for pure gold, the accelerating effect of lead in this first potential range is likely to be due to the lead species in solution.

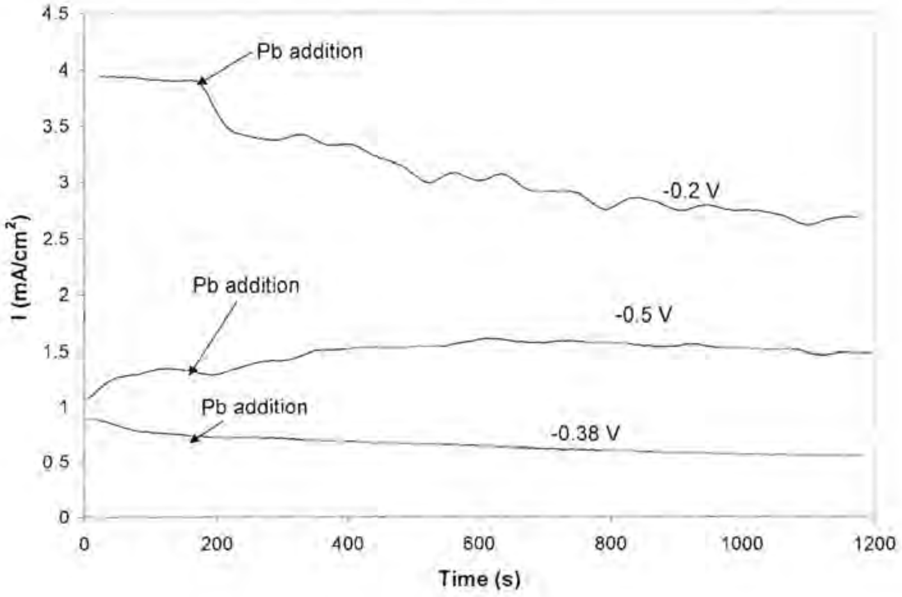


Figure 4.8. Potentiostatic curves for gold – 10 % silver alloy in alkaline cyanide solutions with addition of 0.5 mg/l lead. Temperature: 25 °C; pH = 11.0; NaCN = 2500 mg/l; disc rotation speed = 225 rpm.

4.3.2.2. Lead in the active region and gold-silver alloy in the passive region

The passive region of the alloy is narrow, from -0.425 to -0.35 V. The action of lead was investigated for a potential of -0.38 V (Figure 4.8). It was found that the dissolution of the alloy was not affected after the addition of lead. This indicates that lead ions have a slight or negligible effect on the removal of the passive film on the surface of the alloy.

4.3.2.3. Lead in the passive region and gold-silver alloy in the active region

This situation occurs in the region of -0.35 to 0 V. The effect of lead was investigated for a constant potential of -0.2 V (Figure 4.8). As predicted, after the addition of lead the leaching rate of the alloy is reduced. This indicates the formation of insoluble lead species on the surface of the alloy. There is in this case competition between the dissolution of the alloy and the formation of a passive film on the surface of the alloy. The overall effect depends on the surface covered by the film and its stability.

Since the lead species in solution are found to accelerate the dissolution of gold, it is more relevant for an engineering point of view to investigate the parameters that can affect the abundance of lead species in cyanide solutions.

4.3.3. Effect of pH on the efficiency of lead additions

The peak anodic current density for gold in cyanide solutions with 2 mg/l lead decreased with an increase in pH as indicated in figure 4.9. The highest gold dissolution rate was found at pH 10.5. The decrease of the anodic activity of gold at higher pH values was more pronounced in solutions containing lead. These results are in good agreement with the results of Kondos et al. (1995). It is possible that the different species of lead do not have the same catalytic effect on the gold surface. The species formed at low pH (10.5 - 11) seem to be more active than those formed at higher pH (above 11).

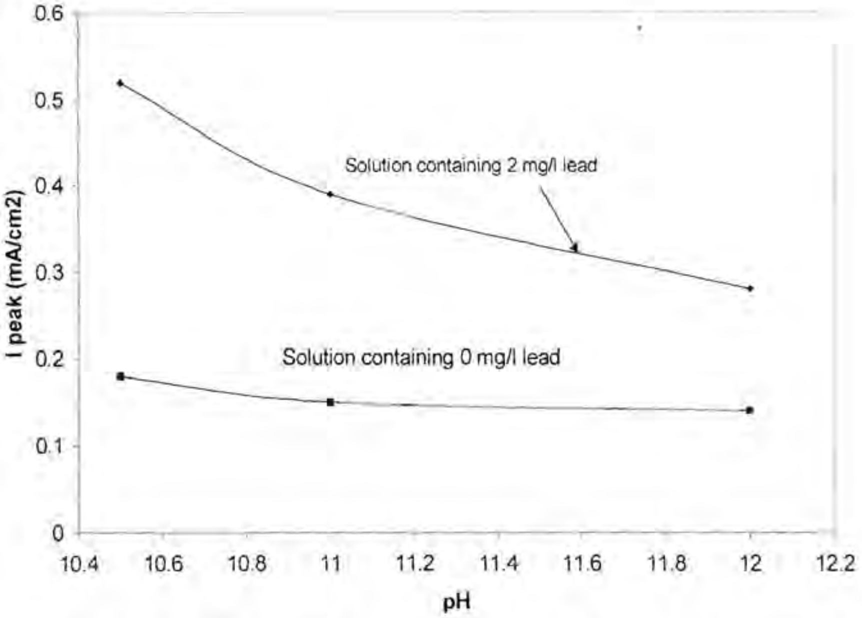


Figure 4.9. Effect of pH on the peak anodic current densities for gold in deaerated aqueous cyanide solutions, NaCN = 250 mg/l, disc rotation speed = 225 rpm.

4.3.4. Effect of cyanide with lead additions

The anodic dissolution of gold in cyanide solutions containing 2 mg/l lead is increased with increasing cyanide concentration as indicated by the polarization curves shown in figure 4.10. In the absence of lead, the ratio of the currents divided by the ratio of the cyanide concentration at 225 rpm gave 0.23 (figure 4.11) while the same ratio in cyanide solutions containing 2 mg/l gave the value 1.1. The almost direct proportionality obtained indicates that the anodic dissolution of the gold is probably determined by the rate of mass transfer of cyanide to the surface of the gold. A much stronger dependency on cyanide concentration was observed in solutions containing lead, which is indicative of the absence of a diffusion barrier on the gold surface when lead is present. In other words, the dissolution of gold in cyanide solutions containing lead is less affected by the formation of a passive layer at potentials close to that corresponding to the current peak.

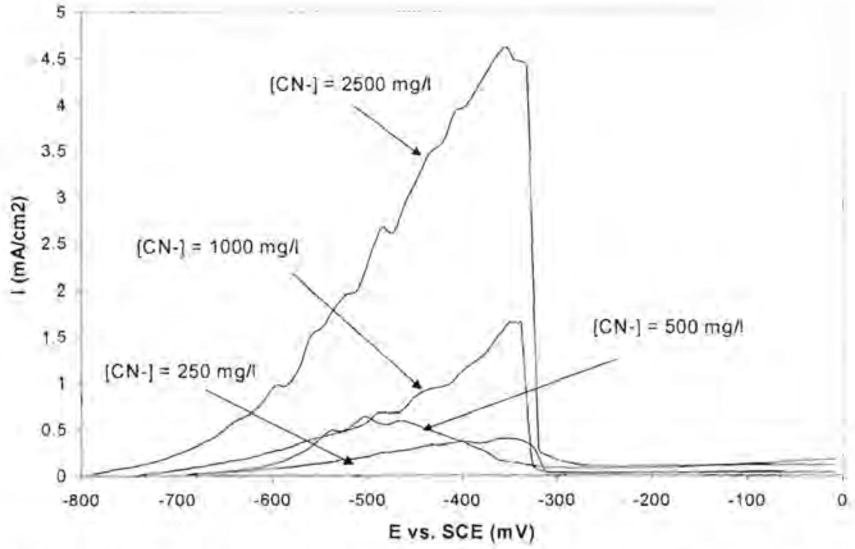


Figure 4.10. Effect of cyanide concentrations on the polarization curves of gold in alkaline cyanide solutions containing 2 mg/l lead, [NaCN] = 250 mg/l, pH =11, disc rotation speed = 225 rpm.

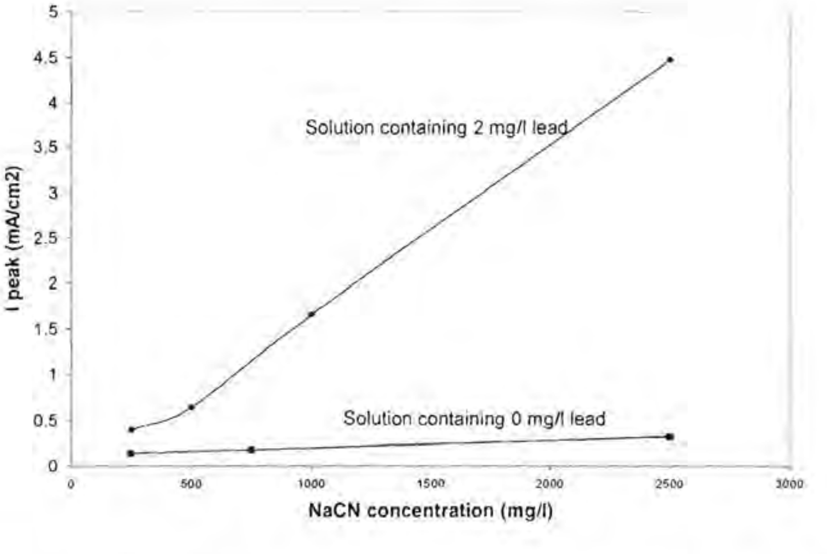


Figure 4.11. Effect of cyanide concentration on the peak anodic current densities for gold in deaerated aqueous cyanide solutions, pH = 11, disc rotation speed = 225 rpm

4.3.5. Effect of other impurities in cyanide solutions containing lead

During the dissolution of gold ores the gangue minerals may also dissolve in cyanide solutions and release anions which can react with the lead added to the solution. The main anions are S^{2-} , SO_4^{2-} and CO_3^{2-}. These anions, when reacting with lead, may decrease the available lead necessary to accelerate the dissolution rate of gold. However, it was found that the reaction of lead and others anions can not be predicted by the stoichiometric equation. For example, 2 mg/l lead can only precipitate 0.31 mg as PbS. However, it was found that 2 mg/l lead can fully counteract the poisonous effect of 20 mg/l sulphide (Weichselbaum et al., 1989). It was then important, for an engineering point of view, to investigate the effect of those anions in a cyanide solution containing 2 mg/l lead. Since the three anions named above have the same state of oxidation (-2) it was therefore necessary to use molar ratio rather than mass ratio in order to better compare the results. The lead will react with sulphide, sulphate and carbonate ions according to the following reactions:

$$Pb^{2+} + S^{2-} \Rightarrow PbS \qquad [4.3]$$

$$Pb^{2+} + SO_4^{2-} \Rightarrow PbSO_4 \qquad [4.4]$$

$$Pb^{2+} + CO_3^{2-} \Rightarrow PbCO_3 \qquad [4.5]$$

The influence of sulphide, sulphate and carbonate additions on the anodic behaviour of gold in aqueous cyanide are shown in figure 4.12. Sulphide additions were found to have the most detrimental effect on gold leaching while sulphate and carbonate additions also decreased the anodic activity of the gold but to a much lesser extent. Raw water typically contain 60 mg/l $CaCO_3$ (0.6 x 10^{-3} M) and 5 mg/l sulphate (0.052 x 10^{-3} M) (Brits et al., 1998). If 5 mg/l lead (0.015 x 10^{-3} M) are added as $Pb(NO_3)_2$ to a cyanide solution containing the same amount of carbonate and sulphate ions as described earlier, the Pb^{2+}/CO_3^{2-} and Pb^{2+}/SO_4^{2-} molar ratios are respectively 0.025 and 0.288. The accelerating effect of 5 mg/l lead may be reduced by 10 % in industrial waters containing 5 mg/l sulphate and by 90 % in industrial waters containing 60 mg/l $CaCO_3$. The required lead addition to accelerate the dissolution rate of gold would thus depend on the amount of lead present in the ore and the presence of lead consumers such as carbonate and sulphate in the ore.

It now follows that the speciation of lead and its subsequent influence on the dissolution rate of gold is a complex function of various parameters such as those discussed in this section. The requirements to optimize the anodic dissolution of gold are: a high concentration of cyanide, a pH of around 10.5 and a high molar ratio of lead to anions consuming lead.

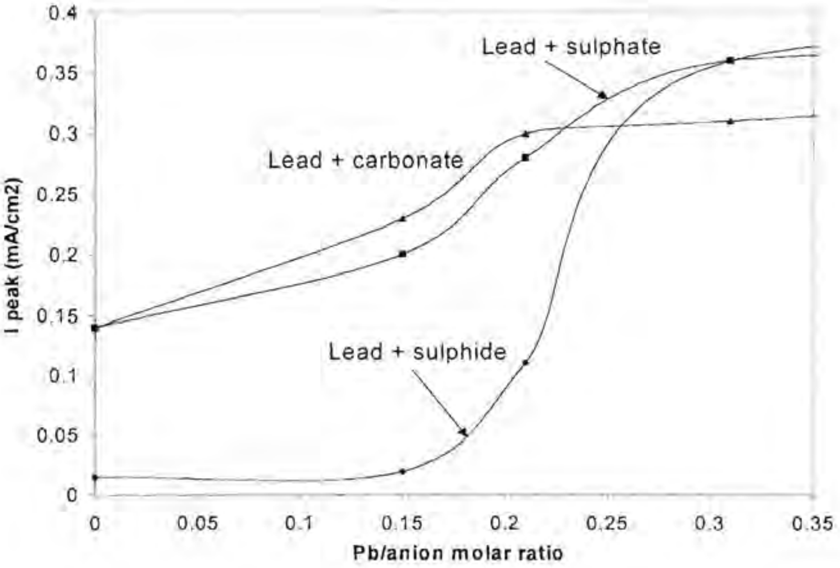


Figure 4.12. Peak anodic current densities measured for gold in deaerated aqueous cyanide solutions containing 2 mg/l lead as a function of lead to anions molar ratio, disc rotation speed = 225 rpm, NaCN = 250 mg/l, pH = 11.

4.3.6. Combination of cathodic reduction of oxygen and anodic dissolution of gold and gold- 10 % silver alloy in the presence of lead

As described previously, combining the anodic and cathodic curves will give the net dissolution rate and the corrosion potential. It was observed that many factors may change the trend of the anodic curve of gold in cyanide solutions containing lead. From a practical point of view it was more appropriate to determine the net dissolution rate of gold in those conditions so that the cyanidation of gold may be optimized. The typical anodic and cathodic combination current-potential curves are shown in figures 4.13 to 4.18. A cyanide solution containing 2 mg/l lead at pH 11 was used for all the experiments. The dissolved oxygen in solution was kept at 12 mg/l.

4.3.6.1. Effect of cyanide concentration

It can be seen that, the intersections of anodic and cathodic polarization curves occur in the oxygen diffusion limiting region on the cathodic curve (figure 4.13). This implies that an increase in the cyanide concentration would not increase the leaching rate of gold as cyanide is not involved in the rate limiting step. Much effort should be spent to achieve better aeration rather than increasing the cyanide concentration.

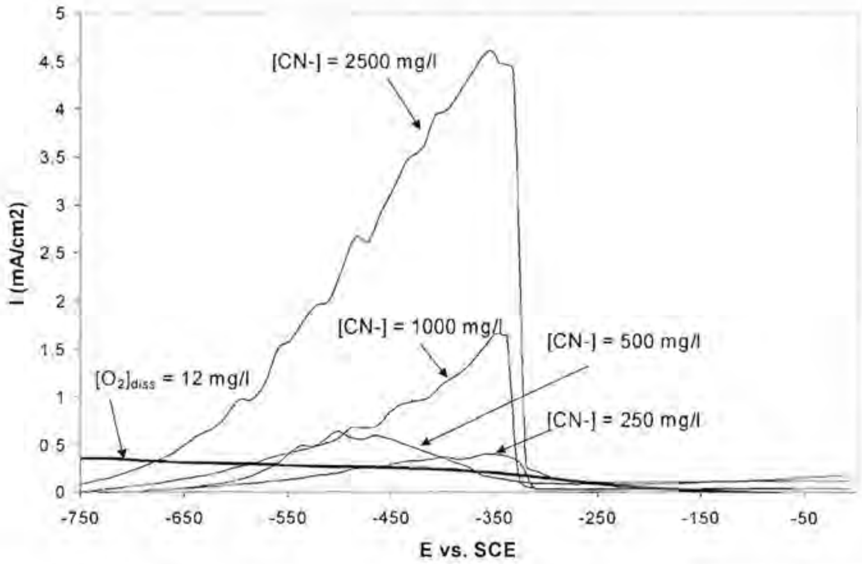


Figure 4.13. Combination of anodic and cathodic polarization curves for gold in solutions containing 2 mg/l lead at various cyanide concentrations, dissolved oxygen = 12 mg/l, pH = 11, rotation disc speed = 225 rpm.

4.3.6.2. Effect of sulphide additions

The intersections of anodic and cathodic curves revealed two cases (figure 4.14):

a. In the absence of sulphide ions or when the lead to sulphide molar ratio was 0.31, three intersection points could be identified. These points were situated in the active region of the oxygen reduction curve. The data shown in figures 4.13 and 4.14 indicate that the mass transfer of cyanide to the gold surface is probably the rate limiting step.

b. When the lead to sulphide molar ratio was 0.21 or below this value, only one intersection point was observed. The intersection point was located in the active regions of both the cathodic and the anodic curves. As the sulphide concentration increased, the open-circuit potential moved to more positive values and the dissolution rate of gold was further decreased. This implies that gold ores liberating high concentrations of sulphide in solution can only dissolve in more oxidizing conditions.

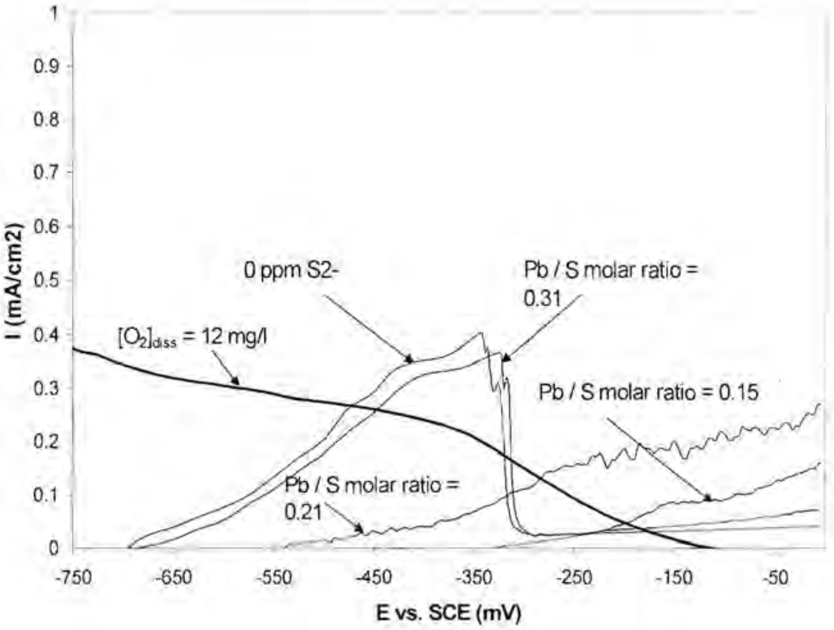


Figure 4.14. Combination of anodic and cathodic polarization curves for gold in solutions containing 2 mg/l lead at various lead to sulphide molar ratios, [NaCN] = 250 mg/l, dissolved oxygen = 12 mg/l, pH = 11, rotation disc speed = 225 rpm.

4.3.6.3. Effect of sulphate additions

Three intersection points were found when the lead to sulphate molar ratios were 0.31 and 0.21 (figure 4.15). The first point was located in the active region corresponding to a high dissolution rate, the second point in the transpassive region and the third point in the passive region. This system may exist in either the active or passive state. At lower molar ratio (0.15) only one intersection point was located in the passive region of gold. In this case the dissolution of gold is mainly controlled by the formation of the passive film.

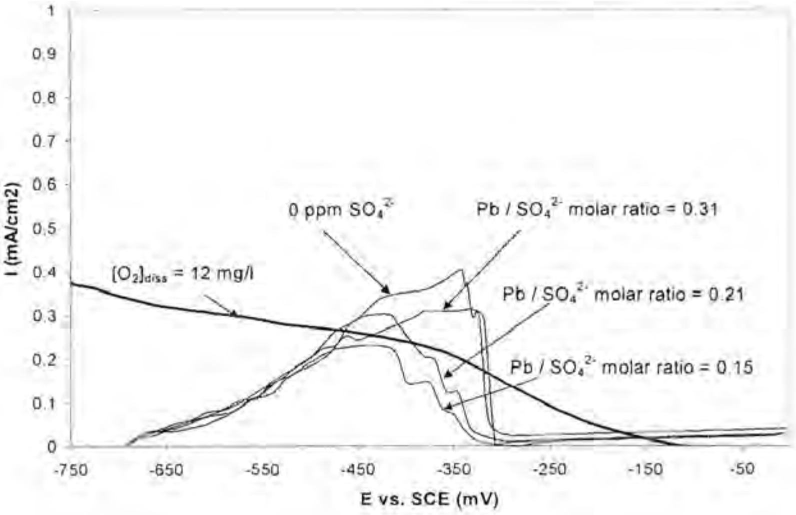


Figure 4.15. Combination of anodic and cathodic polarization curves for gold in solutions containing 2 mg/l lead at various lead to sulphate molar ratios, [NaCN] = 250 mg/l, dissolved oxygen = 12 mg/l, pH = 11, rotation disc speed = 225 rpm.

4.3.6.4. Effect of carbonate additions

The results found for carbonate were almost similar to those presented previously for sulphate as indicated in figure 4.16. The conclusions are therefore the same.

To better visualize the action of anions added to the cyanide solutions containing lead, the net dissolution rate of gold was expressed as a function of the lead to anions molar ratios as shown in figure 4.17. For the cases where two or three intersection points were found when combining the anodic and cathodic curves, the highest dissolution rate was selected. It can be seen that the dissolution rate of gold decreased by a factor of 13 when decreasing the value of the lead to carbonate or sulphate molar ratios from of 0.21 to 0.15. Above that ratio the oxygen mass transfer mainly controls the dissolution of gold. In the case of sulphide additions, the increase of the current in the "passive" region of gold raises doubt about the mechanism occuring on the gold surface. Details concerning the action of sulphide on the gold surface will follow in the next chapter.

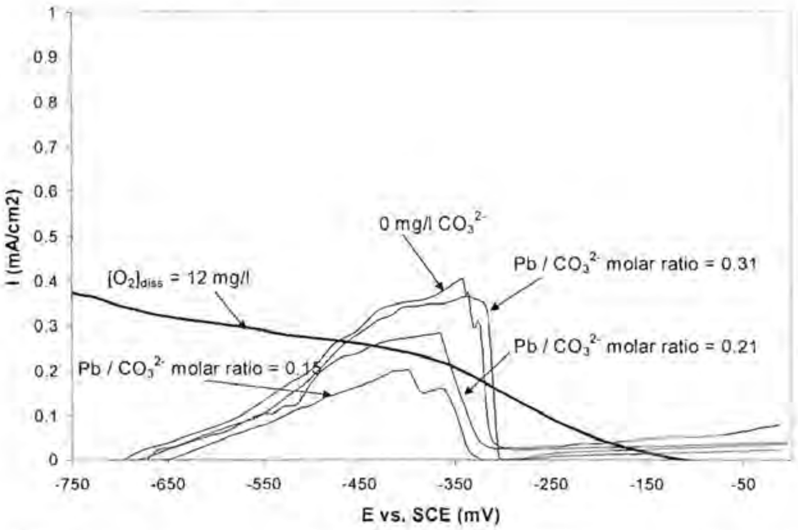


Figure 4.16. Combination of anodic and cathodic polarization curves for gold in solutions containing 2 mg/l lead at various lead to carbonate molar ratios, [NaCN] = 250 mg/l, dissolved oxygen = 12 mg/l, pH = 11, rotation disc speed = 225 rpm.

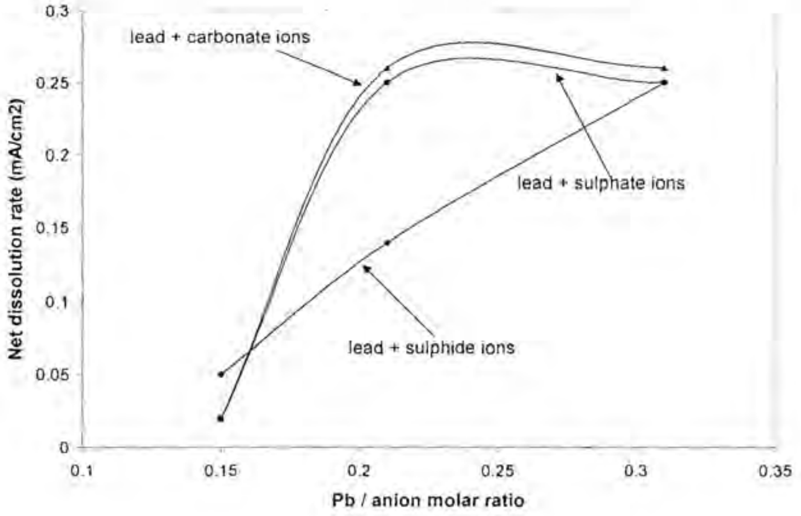


Figure 4.17. Plot of the dissolution current density at the intersection points of the anodic and cathodic curves as a function of the lead to anions molar ratios, pH = 11, [NaCN] = 250 mg/l, rotation disc speed = 225 rpm.

4.4. CONCLUSIONS

The addition of lead nitrate accelerates gold cyanidation only for trace amounts of lead and retards it slightly for higher concentrations. Concerning the mechanism of the action of lead it was demonstrated that:

- The deposition of metallic lead on the gold surface is unlikely in alkaline cyanide solutions containing trace amounts of lead.
- The accelerating effect of lead is due to one or more of its ionic species.
- Passivation of lead that occurs at high potentials and high concentrations reduces the leaching rate of gold and gold-silver alloys significantly. The nature of the lead passive film is not well understood and cannot be correlated directly with the Pourbaix diagram.
- The speciation of lead in cyanide solutions plays a crucial role in its effect on the dissolution of gold. The predominance of lead species depends on factors such as total concentration of lead in the solution, pH, cyanide concentration and the presence of anions, which may reduce the amount of lead available. The sulphide ions were found to be the most poisonous anion for the dissolution of gold in cyanide solutions. The combined action of lead and anions involves a change in the surface character of the gold since high leaching rates were observed even with an excess of anions in the solution.
- The combination of the cathodic reduction of oxygen and the anodic dissolution of gold in the presence of lead indicates that the overall leaching rate of gold is limited by the diffusion of oxygen to the gold surface. However, the presence of other anions in cyanide solutions containing lead reduced the net dissolution rate of gold for lead to anions molar ratio below 0.2. As the sulphide concentration increased, the open-circuit potential moved to more positive values. However, the presence of small amounts of sulphide ions in solution seems to depassivate the gold at higher potentials where gold would normally passivate in the absence of sulphide. In order to clear up this contradiction, it was decided to investigate the action of sulphide ions on the gold surface using potentiodynamic and potentiostatic techniques. This work is reported in the next chapter.

Chapter 5

INFLUENCE OF SULPHIDE IONS ON THE DISSOLUTION OF GOLD AND A GOLD-10% SILVER ALLOY IN CYANIDE SOLUTIONS

5.1. INTRODUCTION

The presence of small amounts of sulphide ions is known to be detrimental to the dissolution of gold in alkaline cyanide solutions. Fink and Putnam (1950) found that traces, even 0.5 ppm, of sulphide ion retard the dissolution of gold. The retarding effect of sulphide minerals in gold ores on the leaching rate of gold is generally attributed to the following factors:

- Galvanic interaction between the gold and the sulphides may move the open-circuit potential to more positive potentials where gold passivates.
- The liberation of sulphide ions to the pulp which interact with the gold to form a passive layer on the gold surface.
- Consumption of cyanide by the released sulphide ions to form thiocyanate and thiosulphate in alkaline cyanide solutions which starves the gold surface of cyanide.

Due to the small amounts of gold particles in the ores, there is not necessarily galvanic contact between the gold particles and the associated minerals unless the gold is embedded in the sulphide. Therefore, the galvanic interaction between gold and conducting minerals is not the main cause for the decrease in the rate of gold dissolution. On the other hand, Wang and Forssberg (1990) showed that the formation of thiocyanate from sulphur and cyanide had very little effect on the stability of $Au(CN)_2^-$. Osseo-Asare et al.(1984) reported the existence of gold–sulphur compounds such as Au_2S, Au_2S_3, $AuS_2O_3^-$ and AuS^-, but these were not stable under the metallurgical conditions used in conventional cyanidation. It is believed that the sulphide ions are adsorbed on the gold surface during the cyanidation process (Wierse et al., 1978; Lorenzen and Van Deventer, 1992). However, many researchers and operating staff in the minerals industry believe that such passivation occurs only in laboratory experiments with clear solutions and rotating disc electrodes (Lorenzen and Van Deventer, 1992). Weichselbaum et al. (1989) also reported that some gold plants operate with pregnant solutions containing up to 15 mg/l sulphide without, sometimes, adding lead to their leach circuit. The only explanation at this stage seems to be the presence of lead or any other of the beneficial elements such as bismuth, thallium and mercury in the ore. The beneficial effect of lead addition was investigated in the previous chapter. However, the dissolution behaviour of gold in cyanide solutions containing traces of S^{2-} was difficult to interpret at higher potentials due to an increase in the anodic activity of gold. In order to have a better knowledge of the combined action of lead and sulphide ions, it would also be of interest to better characterize the action of the sulphide ions on the gold surface. This effect has been reported in many studies (Fink and Putnam, 1950; Weichselbaum et al., 1989; Lorenzen and Van Deventer, 1992; Kondos et al., 1995) but few authors have focused their investigations on the electrochemical study of the sulphide action on the gold dissolution. Some parameters affecting the formation and stability of the sulphide film, such as the concentration of sulphide ions and the applied potential, were investigated in this chapter.

5.2. EXPERIMENTAL

The experimental work was conducted with gold (99.9 %) and gold-silver alloy (10 % Ag) electrodes which had respectively surface areas of 0.24 and 0.22 cm^2. Two graphite rods were used as counter electrodes. Potentials were measured against a saturated calomel reference electrode connected to the cell via a Luggin tube. An E.G. & G Princeton Applied Research potentiostat/galvanostat model 273 and a Pine rotating disk electrode model ASR2 were used to obtain polarization data. The anodic dissolution of gold and the gold-10 % silver alloy in deaerated aqueous solutions was studied using a scan rate of 1 mV/s. The experiments were conducted at a pH of 11 and the desired sulphide concentrations were obtained by the addition of analytical grade Na_2S to the electrolyte. Gold concentrations in the solution were analyzed by atomic absorption spectrophotometry.

5.3. RESULTS AND DISCUSSION

The influence of sulphide ions on the dissolution rate of gold and gold-10 % silver alloy was studied with five different sulphide concentrations, namely, 0, 0.5, 2, 4 and 10 mg/l sulphide as S^{2-}. Polarization curves obtained are presented in figures 5.1 and 5.2.

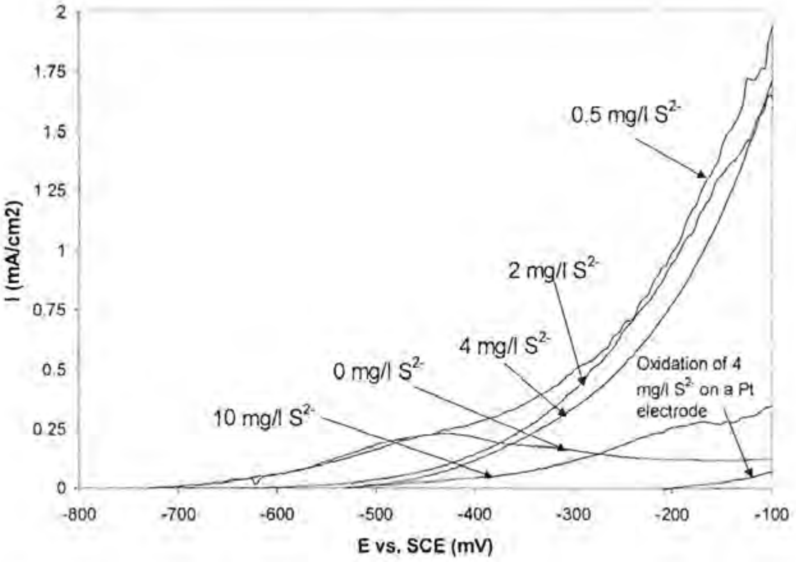


Figure 5.1. Influence of sulphide ions on the anodic characteristics of gold and oxidation of 4 mg/l S^{2-} on a platinum electrode, NaCN = 2500 mg/l, pH = 11, disc rotation speed = 225 rpm.

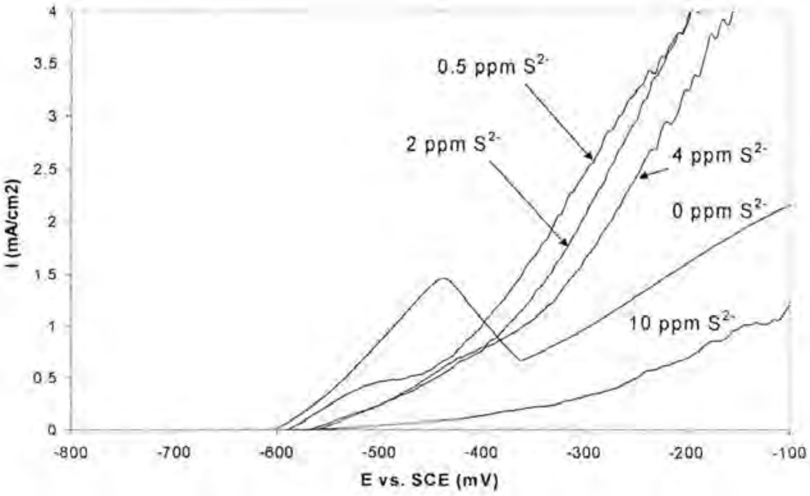


Figure 5.2. . Influence of sulphide ions on the anodic characteristics of a gold–10 % silver alloy, NaCN = 2500 mg/l, pH = 11, disc rotation speed = 225 rpm.

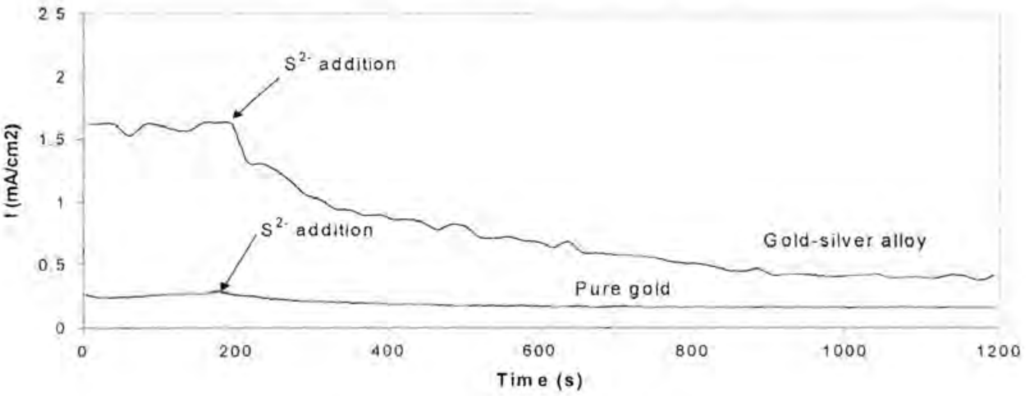
These curves revealed two regions:

a. From E_{corr} to – 380 mV (SCE).

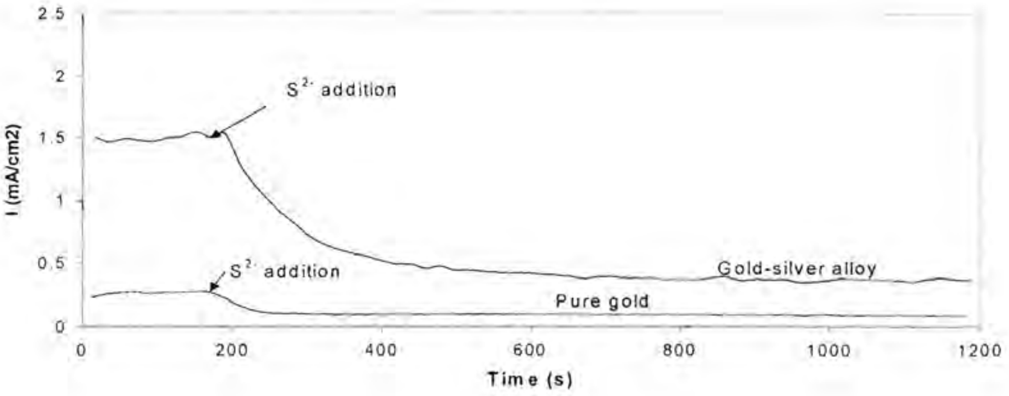
The anodic dissolution rates of gold and gold-10 % silver alloy are reduced within that potential range by the addition of sulphide ions at a concentration higher than 0.5 mg/l sulphide. The anodic characteristics of gold are almost similar within that potential range for 0 and 0.5 mg/l sulphide. This is in contrast to the influence reported by Fink and Putnam (1950). This difference may result from a difference in cyanide concentrations (A cyanide concentration of 1000 mg/l was used by Fink and Putnam and 2500 mg/l cyanide was used in this present work) and the techniques used to evaluate the dissolution rate of gold (Potentiodynamic curves were used in this work and a technique based on the determination of the time required to dissolve a known volume of gold was used by Fink and Putnam). Lower potentials decrease gold dissolution and are associated with the formation of a gold-sulphide layer on gold. If the intersection points of the anodic and cathodic polarization curves are situated in that potential range, the dissolution rate of gold should be reduced. This may explain the retarding effect on the dissolution rate of gold observed in gold plants operating with a low level of dissolved oxygen. Since the formation and the stability of the passive films depend on factors such as the sulphide concentration and the time of exposure of gold in the solution, potentiostatic experiments were conducted at a potential corresponding to peak current density in the absence of sulphide. These curves revealed that the drop in the dissolution rate of the two metals as a function of time was highly dependent on the sulphide concentration in the solution (Figures 5.3 a, b and c). A drastic decrease of the dissolution rate of gold was observed for high sulphide concentrations just after their addition to the solution. Table 5.1. gives the percentage of reduction of the dissolution rate of gold after twenty minutes. The results indicate that a severe decrease is observed in the case of the gold -10% silver alloy. It is possible that sulphide ions adsorb more strongly on the gold-silver alloy. These results are in good agreement with the observations of Osseo-Asare et al. (1984).

Figure 5.3. Effect of sulphide additions on the dissolution of gold and gold- 10 % silver alloy in cyanide solutions. [CN] = 2500 mg/l, pH = 11, constant potential E = -0.45 V, disc rotation speed = 225 rpm.

a. Addition of 0.5 ppm S^{2-}



b. Addition of 2 ppm S^{2-}



c. Addition of 4 ppm S^{2-}

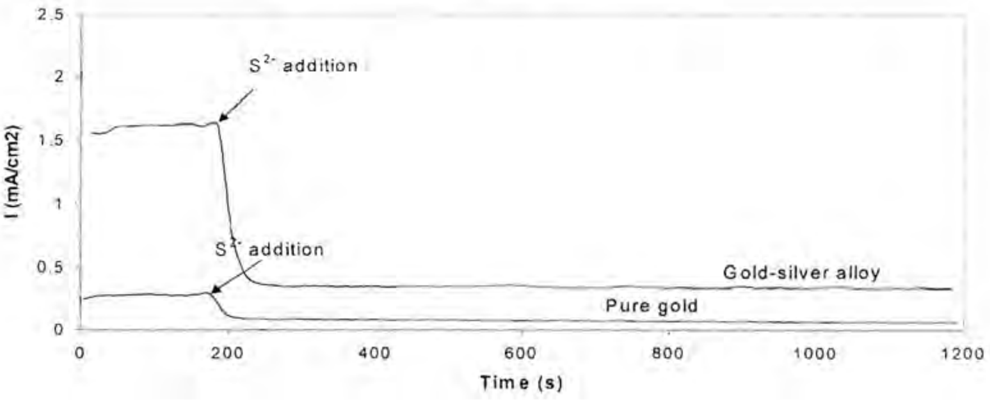


Table 5.1. Decrease of the dissolution rate of pure gold and gold- 10 % silver alloy 20 minutes after the addition of sulphide ions to the solutions.

	0.5 ppm S^{2-}	2 ppm S^{2-}	4 ppm S^{2-}
Gold	56.7 %	35.8 %	22.0 %
Gold- 10 % silver alloy	26.1 %	24.2 %	20.4 %

It can be seen that there is a slight difference at low sulphide concentration (0.5 mg/l) between potentiodynamic and potentiostatic results. This is due to the fact that the formation of a passive layer is not an instantaneous process. There is a competition between the formation of the passive layer and the dissolution of the metal. The overall reaction depends on the highest reaction rate. During the potentiodynamic scan, a sulphide layer is formed as soon as the potential, which allows such passivation is reached. In this particular case the stability of the film will depend on the scan rate of the potentiodynamic experiment. This may explain the difference between the results of the potentiodynamic and potentiostatic experiments. This difference may be reduced if the scan rate of the potentiodynamic experiment is reduced or if the concentration of sulphide concentration in solution is high.

b. From –380 to 0 mV (SCE)

For potentials more positive than –380 mV (SCE) the current density increased with increasing anodic potentials. In this case, either a supplementary oxidation reaction, such as the oxidation of the sulphide film, takes place or traces of sulphide ions increases the anodic dissolution of gold in that potential range. According to the potential-pH diagram of the S-H_2O system, the oxidation of sulphide to sulphate at a pH of 11 becomes thermodynamically possible at – 630 mV vs. SCE (figure 5.4). However, the extent of the sulphide oxidation also depends on the kinetics.

To establish the possible contribution of sulphide oxidation to the anodic current measured the oxidation of sulphide ions on an inert electrode such as platinum in alkaline solutions was determined. This result was then compared to the anodic characteristics of gold in cyanide solutions containing sulphide as indicated in figure 5.1.

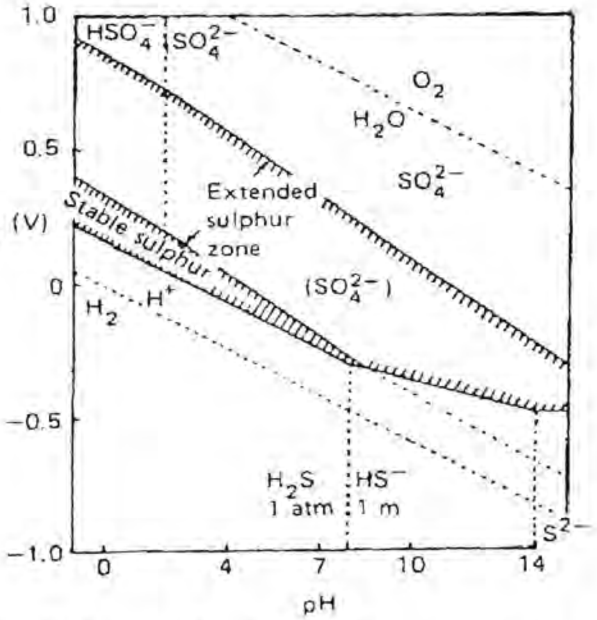


Figure 5.4. Potential- pH diagram for the S-H_2O system, showing the region of sulphur stability and the extended stability that is realized by a 300 kJ/mole barrier in the formation of SO_4^{2-} (Marsden and House, 1992).

Based on figure 5.1, a few observations can be made. First, the oxidation of 4 mg/l sulphide ions from the solution became significant at approximately -200 mV (SCE). This potential is some 400 mV more positive than that where sulphide oxidation becomes thermodynamically feasable (-630 mV vs. SCE). Secondly, the anodic current density of the sulphide oxidation obtained on the platinum electrode is much lower than that obtained for the oxidation of gold in cyanide solutions containing 4 mg/l S^{2-} as indicated in figure 5.1. The much lower anodic currents generated under these conditions indicate that the contribution of sulphide oxidation to the total current is insignificant.

To further confirm that the anodic dissolution of gold is stimulated by the presence of sulphide, it was decided to conduct potentiostatic experiments within the potential range –380 to 0 mV (SCE) and then to analyze the solution by atomic absorption spectrophotometry (AAS). Potentiostatic experiments were conducted at –200 mV for

two hours and the gold content of the solution at different sulphide levels were determined. The results are presented in figures 5.5 and 5.6. There was no major difference between the values obtained from the potentiodynamic curves at –200 mV in figures 5.1 and 5.2 and the values obtained from the potentiostatic curves. Samples were collected at the end of each experiment and then analyzed by AAS. The gold dissolved was then compared with the predicted values using Faraday's law.
According to the Faraday law's the mass loss can be expressed by:

$$M\ calc = \frac{I \times Time \times Mw}{n \times F} \qquad [5.2]$$

where Mw is the molecular mass of gold (g/mol), n is the number of electrons and F is the Farady constant (96487 C/mol). The current used in Faraday's law was obtained by the integral method using the data from the potentiostatic experiments.

The results shown in figures 5.7 and 5.8 indeed indicate a good correlation between the predicted and analysed values.

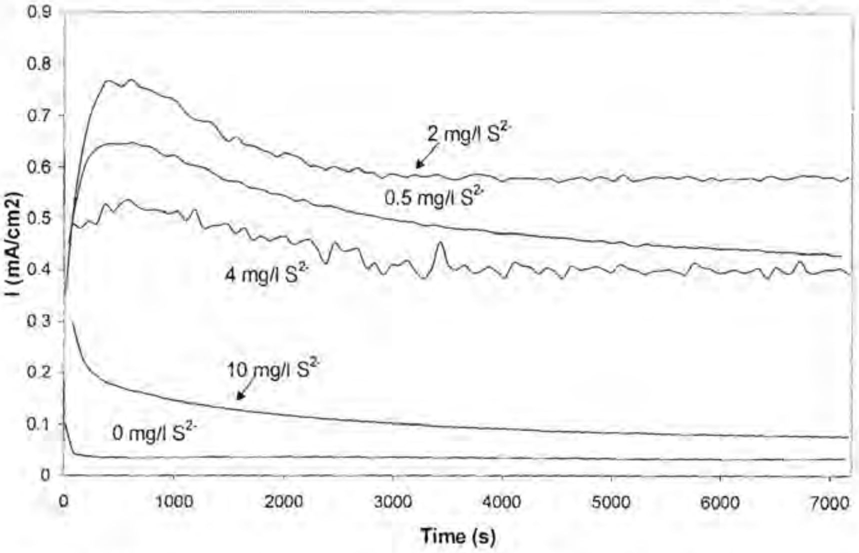


Figure 5.5. Potentiostatic curves for gold in cyanide solutions containing sulphide ions, pH = 11, constant potential E = -200 mV (SCE), disc rotation speed = 225 rpm.

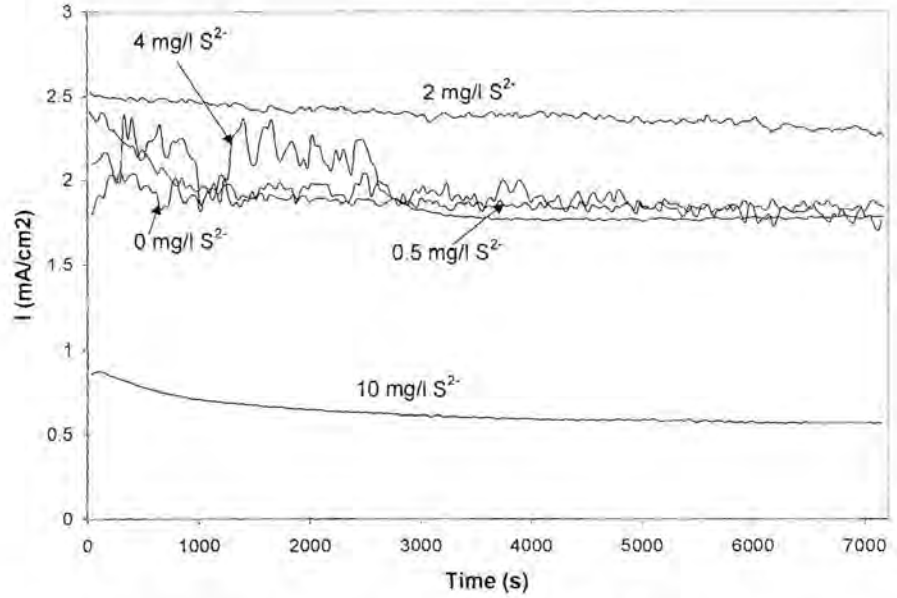


Figure 5.6. Potentiostatic curves for gold-10 % silver alloy in cyanide solutions containing sulphide ions, pH = 11, constant potential E = -200 mV (SCE), disc rotation speed = 225 rpm.

It follows that the presence of sulphide in aqueous cyanide solutions decreases the active dissolution of the gold but depassivates the gold at higher potentials where gold would normally passivate in the absence of sulphide. At higher sulphide concentrations the activity of the gold at higher potentials is again suppressed. The maximum current was obtained with 2 mg/l S^{2-}. The presence of a sulphide layer on the gold surface at high sulphide concentrations was confirmed by analyzing the gold surface with EDS in a scanning electronic microscope (SEM). The gold and gold -10 % silver alloy were polarized at –200 mV (SCE), for two hours, in cyanide solutions containing 10 mg/l S^{2-}. The results of the analysis at the SEM are reported in table 5.2.

Table 5.2. EDS analysis of the gold and gold-silver alloy surfaces polarized at –200 mV for three 3 hours in cyanide solutions containing 10 mg/l S^{2-}.

	Au (Wt %)	Ag (Wt %)	S (Wt %)
Gold	99.3	0	0.7
Gold-silver alloy	90.6	8.6	0.8

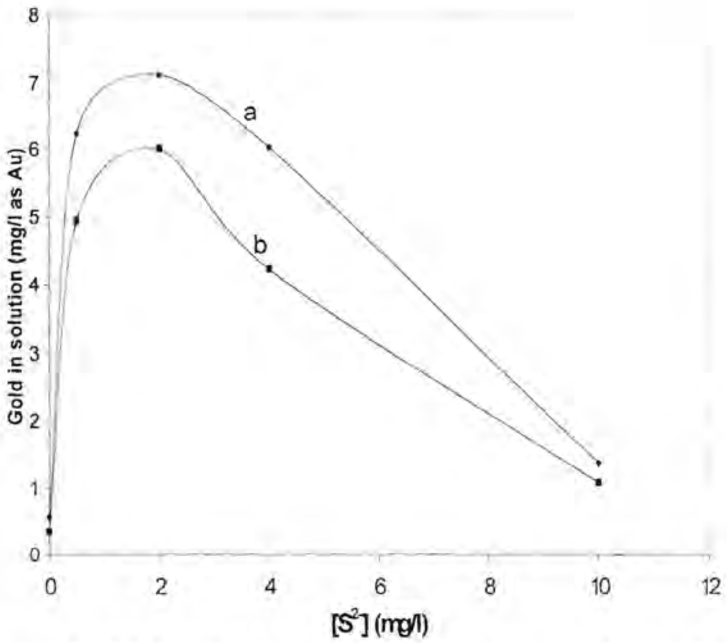


Figure 5.7. Mass of gold dissolved for two hours in deaerated cyanide solutions, pH =11, NaCN = 2500 mg/l, Constant potential E = -200 mV (SCE), disc rotation speed = 225 rpm. a. Mass analyzed by AAS

b. Mass calculated using Faraday's law

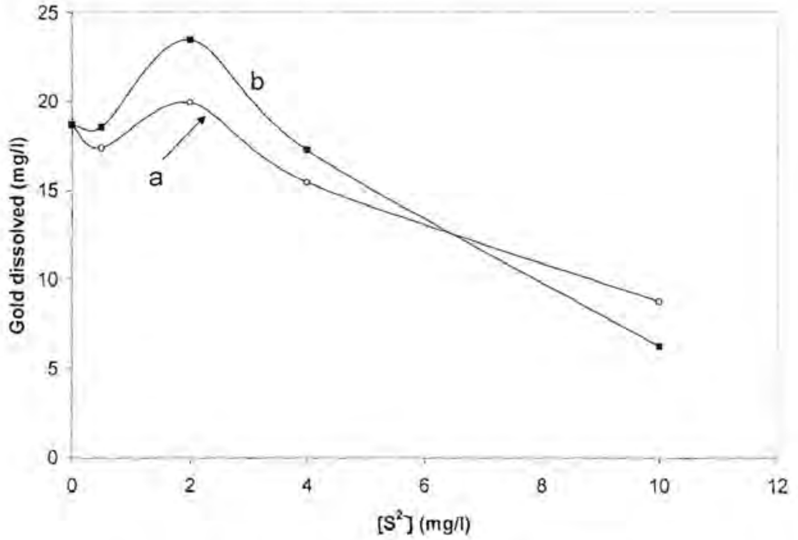


Figure 5.8. Mass of gold dissolved for two hours from the gold-10 % silver alloy in deaerated cyanide solutions, NaCN = 2500 mg/l, pH =11, Constant potential E = -200 mV (SCE), disc rotation speed = 225 rpm.

a. Mass analyzed by AAS

b. Mass calculated using Faraday's law

5.3.1. Influence of cyanide with sulphide additions

The anodic characteristics of gold in cyanide solutions containing 4 mg/l sulphide is increased by increasing the cyanide concentration as indicated in figure 5.9. This indicates that the anodic dissolution of gold in cyanide solutions containing sulphide is mainly dependent on the mass transfer of cyanide to the surface of the gold. The negative effect of sulphide on gold dissolution may possibly be overcome by using higher cyanide concentrations.

5.3.2. Influence of oxygen on the dissolution of gold in aqueous cyanide containing sulphide

Since traces of sulphide may prevent passivation at higher potentials the leaching rate of gold in the presence of sulphide may be increased if more oxidizing conditions can be created on the gold surface. The dissolved O_2 level (DO) is therefore an important factor to consider in the dissolution of gold in cyanide solutions containing sulphide. The practical implications of sulphide on the dissolution rate of gold may be conveniently followed if the polarization curve for oxygen reduction is also indicated as is done in figure 5.10. The rate of gold dissolution in an oxygen containing solution is then defined on these diagrams by the intersection of the gold anodic polarization curve with that of the oxygen reduction reaction. An increase in DO from 4 to 25 mg/l enhanced gold dissolution as indicated in figure 5.11 to 5.13. It can be seen that the net current density reached its maximum value between 0.5 and 1 mg/l sulphide. At lower cyanide concentrations the intersection points are situated below the density current where gold becomes passive as indicated in figure 5.11. The results reveal that the anodic and cathodic curves intersect in the active region of the cathodic curve. As discussed previously, the sulphide minerals may increase the cathodic reduction of oxygen when they are in contact with the gold particles. On the other hand, it has been shown that the dissolved sulphide also prevents passivation of the gold at higher potentials. The combination of these two effects may significantly increase the leaching rate of gold. Similar results were observed by Stoychevski and Williams (1993), who studied the influence of strong oxidants such as hydrogen peroxide and oxone on the dissolution of gold from pyrite ore. They found that the optimum conditions for pyritic gold ores were obtained within the potential range –50 to 0 mV (SCE). At potentials higher than 0 mV it is possible to oxidize the cyanide ions to cyanate and to be situated in a more stable passive region on the anodic curve

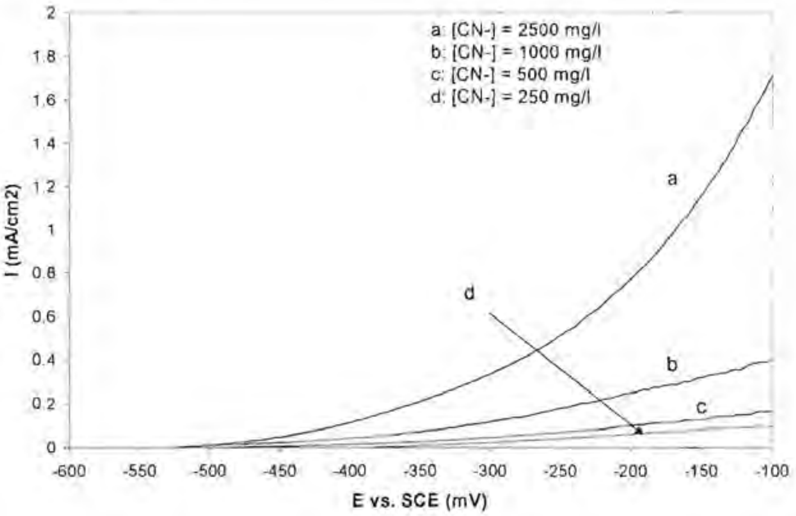


Figure 5.9. Effect of cyanide concentration on the polarization curves of gold in deaerated cyanide solutions containing 4 mg/l sulphide as S^{2-}, pH = 11, disc rotation speed = 225 rpm.

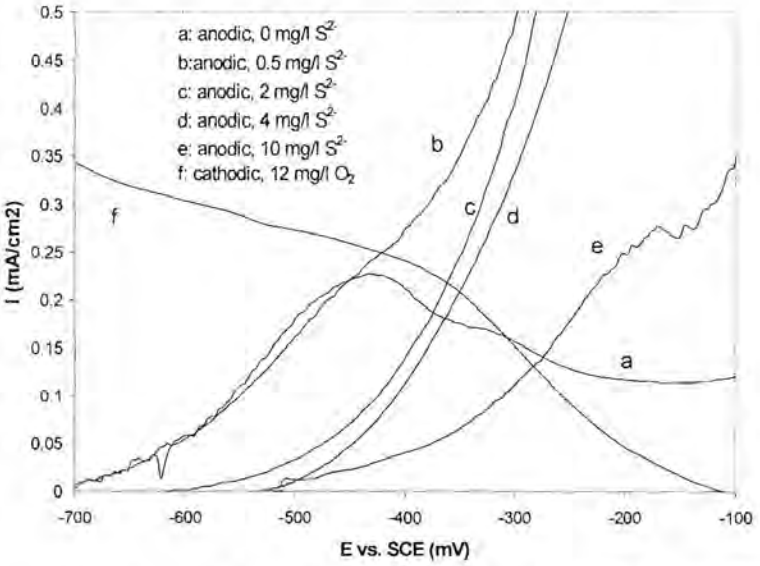


Figure 5.10. Evans diagram for gold in oxygenated cyanide solutions containing sulphide ions, pH = 11, NaCN = 2500 mg/l, dissolved oxygen = 12 ppm, disc rotation speed = 225 rpm.

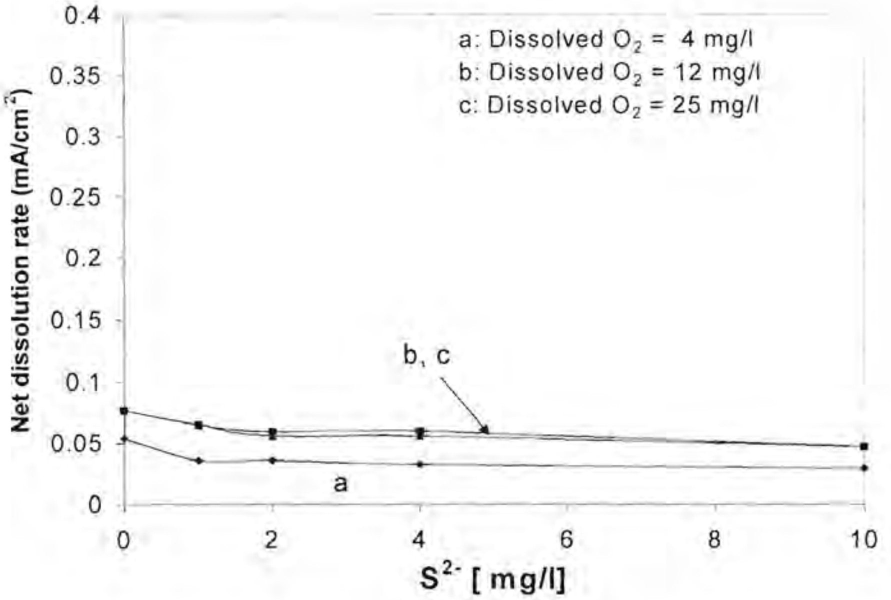


Figure 5.11. Dissolution rate of gold as determined from the intersection of the anodic and cathodic polarization curves as a function of sulphide and dissolved oxygen content, NaCN = 250 mg/l, pH = 11, disc rotation speed = 225 rpm.

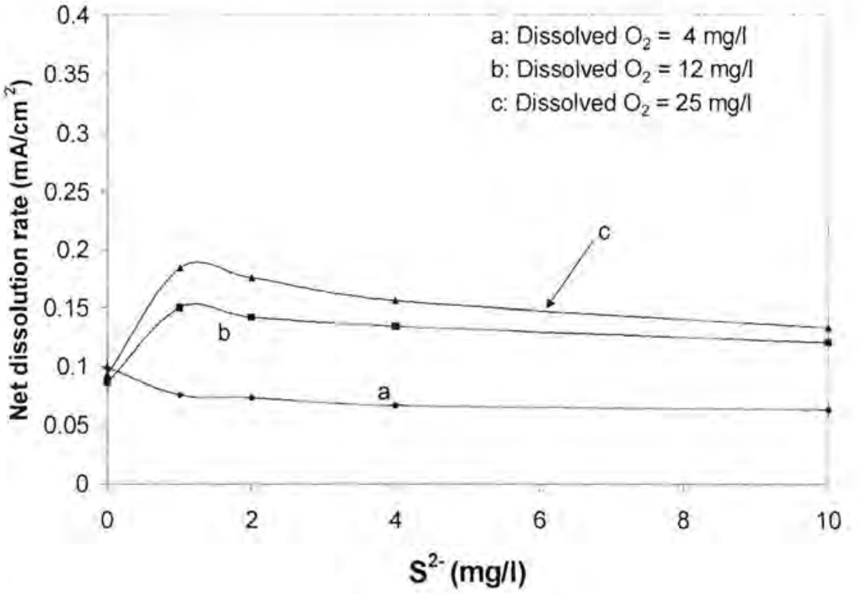


Figure 5.12. Dissolution rate of gold as determined from the intersection of the anodic and cathodic polarization curves as a function of sulphide and dissolved oxygen content, NaCN = 1000 mg/l, pH = 11, disc rotation speed = 225 rpm.

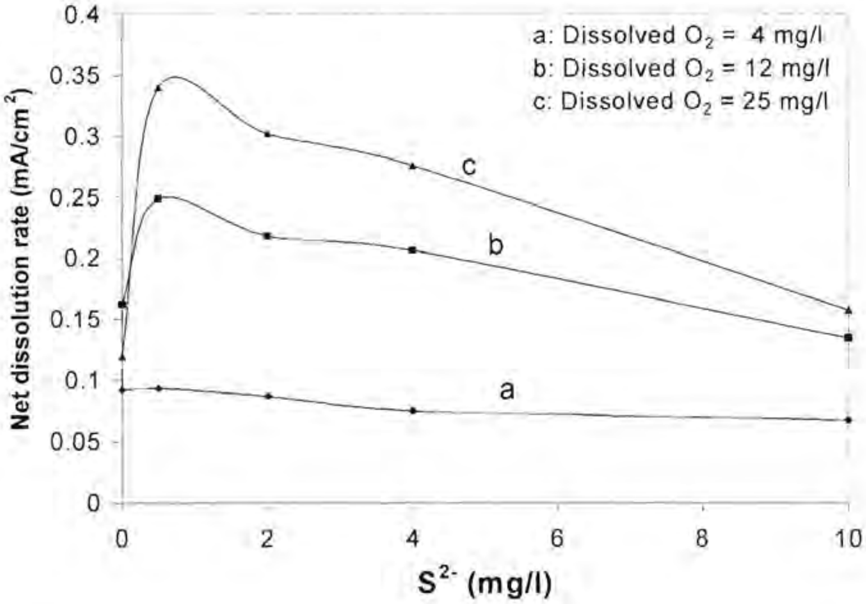


Figure 5.13. Dissolution rate of gold as determined from the intersection of the anodic and cathodic polarization curves as a function of sulphide and dissolved oxygen content, NaCN = 2500 mg/l, pH = 11, disc rotation speed = 225 rpm.

5.4. CONCLUSIONS

From the results presented in the chapter, it can be concluded that, depending on the sulphide concentration and the applied potential on the gold or the gold-silver alloy surface, the anodic dissolutions of these two metals can either be accelerated or retarded in the presence of sulphide ions. From Ecorr to approximately –380 mV (SCE), traces of sulphide ions were found to decrease the dissolution rates of gold and a gold-silver alloy. Further decreases were observed at higher sulphide concentrations. For potentials more positive than -380 mV, an accelerating effect was observed on the dissolution rate of gold and the maximum current was obtained with 1 mg/l S^{2-}. The action of sulphide ions was similar to that of lead ions and is likely due to a change of the surface character of the gold. However, a drastic decrease of the dissolution rate of gold was observed for sulphide concentrations above 10 mg/l. From an engineering point of view, the accelerating or retarding effects of sulphide minerals in gold ores will depend on their solubility in cyanide solutions. When the sulphide ions exceed a certain amount, it will significantly retard gold dissolution. Better control of the sulphide ions concentration in solutions and the use of high cyanide concentrations and more oxidizing conditions may accelerate the dissolution of gold and gold-silver alloys during the cyanidation process. The galvanic interaction between sulphide minerals and gold may also be beneficial if the cathodic reduction of oxygen is increased (more oxidizing conditions on the gold surface) and if the released sulphide ions depassivate the gold.

Chapter 6

THE COMBINED ACTION OF SULPHIDE AND LEAD IONS ON THE DISSOLUTION OF GOLD IN CYANIDE SOLUTIONS

6.1. INTRODUCTION

The results obtained in the previous chapters indicated that both lead and sulphide might accelerate or retard the dissolution rate of gold. The behaviour of these two ions depend on their concentrations in solutions and the electrochemical potential of the metal surface. It has been shown in the previous chapters that:

- From Ecorr to approximately –380 mV (SCE), traces of lead accelerate the dissolution rate of gold while traces of sulphide retard it.
- From –380 mV to 0 V (SCE), traces of sulphide accelerate the dissolution rate of gold while traces of lead retard it. Within this potential range gold would normally passivate in the absence of sulphide.

Since lead and sulphide ions co-exist in most gold cyanide solutions, it was important to investigate the combined action of these two ions as a function of their relative concentrations and the applied potentials. This may help to optimize the dissolution of gold in the presence of impurities such as lead and sulphur compounds.

6.2. EXPERIMENTAL

The experimental work was performed with a rotating disc gold electrode (99.9 % Au) which had a surface area of 0.24 cm^2. Two graphite rods were used as counter electrodes and a saturated calomel electrode connected via a Luggin tube to the cell was used as a reference electrode. The leaching vessel was made of glass and had a capacity of 0.5 liter. The cover had five openings which allowed insertion of the counter electrodes, the rotating electrode, the Luggin capillary and the tube for nitrogen or oxygen purging. For anodic potentiodynamic experiments, the solution was purged with nitrogen for one hour before each experiment to eliminate the effect of oxygen, and the nitrogen was kept flowing over the electrolyte during the test. Cyanide concentration of 2500 mg/l was used for the experiments. The pH of the electrolyte was adjusted to 11 with NaOH. Freshly prepared solutions of $Pb(NO_3)_2$ and Na_2S were used to obtain the desired lead and sulphide concentrations. Polarization curves were obtained by continuously measuring the current as a function of potential between –1 and 0 V vs. SCE starting at the more negative potential. Each potentiostatic experiment had a duration of 20 minutes and impurities were added 3 minutes after the beginning of each experiment. The scan rate was 1 mV/s unless otherwise noted. Good reproducibility of the results was obtained with a disc rotation speed of 225 rpm. All experiments in this chapter were therefore done at 225 rpm.

6.3. RESULTS AND DISCUSSION

To better observe the action of lead and sulphide on the dissolution of gold it was decided to work with a relatively high concentration of cyanide (2500 mg/l) in solution. Lead ions can react with the sulphide ions according to the following reaction:

$$Pb^{2+} + S^{2-} \rightarrow PbS \qquad [6.1]$$

This equation reveals that 1 mg of Pb^{2+} can precipitate 0.15 mg S^{2-} as PbS. The effects of sulphide and lead additions were investigated for the following combinations:

- 2 mg/l sulphide (S^{2-}) + 1 mg/l lead (Pb^{2+})
- 2 mg/l sulphide (S^{2-}) + 2 mg/l lead (Pb^{2+})

For both these two cases the sulphide ions were in excess with respect to the stoichiometry of equation 6.1. Kinetic plots for these two cases are shown in figures 6.1 and 6.2. As can be seen, the additions of sulphide and lead ions have a pronounced effect on the dissolution of gold in alkaline solutions. For the first case (S/Pb = 2/1), the dissolution rate of gold was retarded in the potential range –600 to –390 mV (SCE) but was accelerated above this potential range. It was found that the anodic polarization curve for this case is situated between those of S/Pb = 0/1 and S/Pb = 2/0. The trend of the curve was the same as for the case where only sulphide ions were present in the solution (S/Pb = 2/0). A slight increase of the anodic dissolution of gold was observed while lead was added to the cyanide solution containing sulphide ions. The consumption of a certain amount of sulphide ions by lead may explain this increase if we consider that the maximum dissolution rate of gold in the presence of sulphide is reached for [S^{2-}] lower than 2 mg/l as described in the previous chapter. For the second case (S/Pb = 2/2), the opposite effect was observed, i.e., the dissolution rate of gold was accelerated in the potential range –600 to –380 mV (SCE) but was retarded at more positive values. It was observed that the anodic current in the second case was higher than that of the first case within the potential range –600 to –380 mV (SCE) and lower within the potential range –380 to 0 mV. The increased lead concentration enhanced the dissolution rate of gold in particular at lower potentials. Based on the results of the two studied cases, it follows that a potential range fixes the overall effect of the interactions between lead and sulphide ions. The first ranges from –600 to –380 mV (SCE) and the second from –380 to 0 mV (SCE). As described previously, conditions during potentiodynamic polarization experiments are non-steady state. The process of formation of the passive films or its re-dissolution in the presence of impurities is also time dependent. To better evaluate the stability of the passive films and their re-dissolution after the addition of impurities, potentiostatic experiments were done within the two potential ranges.

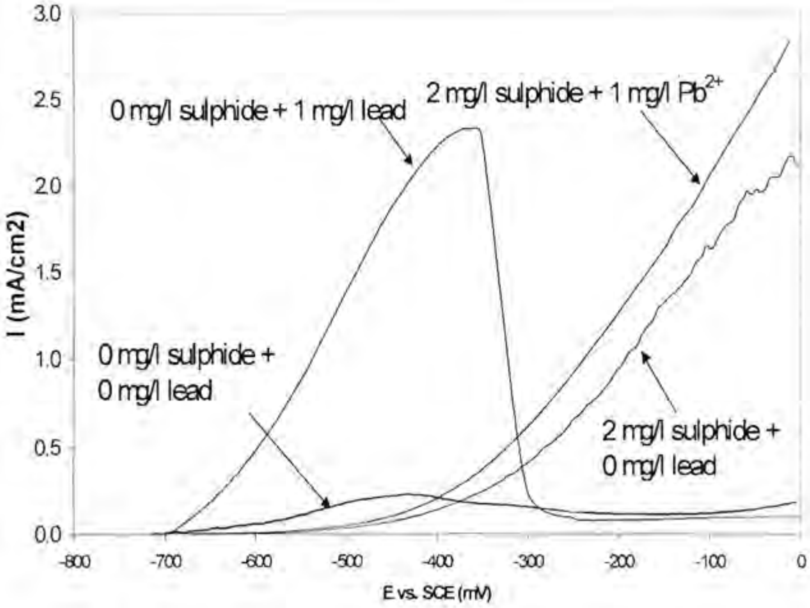


Figure 6.1. Potentiodynamic anodic polarization curves obtained on a rotating gold disc electrode in aqueous cyanide solutions containing 2500 mg/l NaCN to which 2 mg/l sulphide and 1 mg/l lead were added, pH = 11 and the disc rotation speed was 225 rpm.

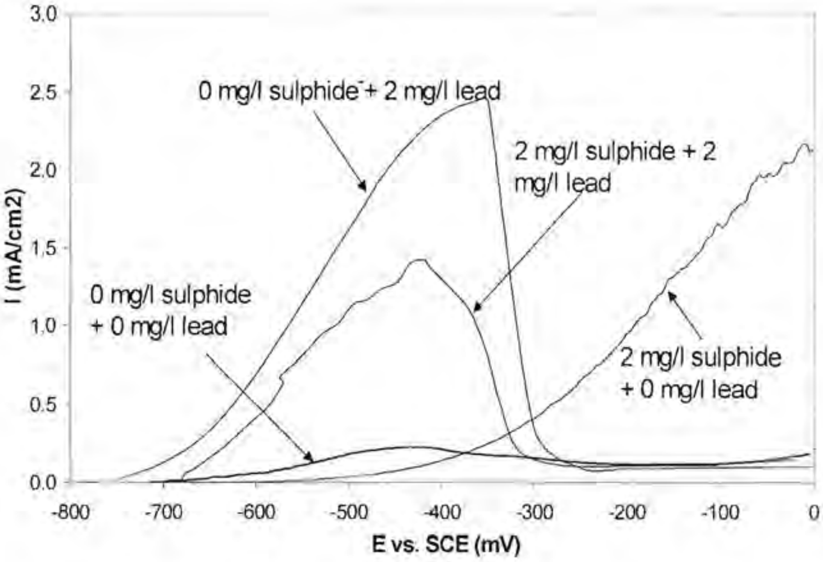


Figure 6.2. Potentiodynamic anodic polarization curves obtained on a rotating gold disc electrode in aqueous cyanide solutions containing 2500 mg/l NaCN to which 2 mg/l sulphide and 2 mg/l lead were added, pH = 11 and the disc rotation speed was 225 rpm.

6.3.1. Potentiostatic experiments conducted in the potential range –600 to -380 mV (SCE)

Experiments were conducted at –450 mV (SCE) with cyanide solutions initially containing 2 mg/l sulphide to which various concentrations of lead were added three minutes after the beginning of each experiment. Two different lead concentrations were used to study this case, namely 1 and 2 mg/l (figure 6.3). It was observed that, when the concentration of sulphide and lead are respectively 2 and 1 mg/l, the lead ions seem to be inactive on the gold surface. No change was observed on the anodic curve after the addition of lead ions. In this particular case, the passive film formed before the addition of lead ions seems to be very stable. The stoichiometry of equation 6.1 indicates that 1 mg/l Pb^{2+} can precipitate 0.15 mg/l S^{2-}. There is therefore 1.85 mg/l of "free" sulphide ions which can react with the gold surface and render it passive within this first potential range.

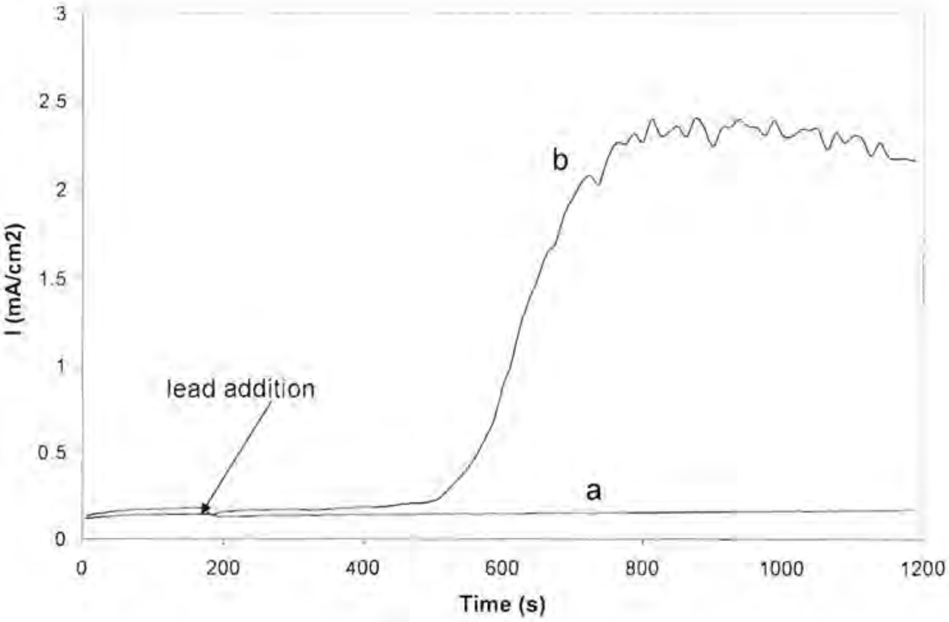


Figure 6.3. The combined effect of lead additions on the potentiostatic polarization curves obtained on a rotating gold disc (225 rpm) at a potential of –450 mV (SCE) in an aqueous cyanide solution (2500 mg/l NaCN) initially containing 2 mg/l sulphide.(a) 1 mg/l lead added , (b) 2 mg/l lead added.

However, when the concentration of sulphide and lead ions are both 2 mg/l, a drastic increase of the dissolution is observed five minutes after the addition of lead to the solution. It seems that during the first five minutes the lead interacted with the sulphide surface and removed the passive layer. After the removal of the passive film the lead ions reacted with the "clean" gold surface and accelerate its dissolution rate to levels close to that corresponding to the maximum current peak in solutions containing only lead. The role of lead in this case was not only to counteract the poisonous action of sulphide ions but also to accelerate the dissolution of gold. From stoichiometric calculations it follows that 2 mg/l lead may remove 0.62 mg sulphide as PbS. This indicates that the solution still contains some sulphide in solution. The maximum current is not reached because some active sites on the gold are probably still occupied by the sulphide ions. This process is therefore dependent on the time as well as the sulphide and lead concentrations.

6.3.2. Potentiostatic experiments conducted in the potential range –380 to 0 mV (SCE)

Experiments were conducted at –200 mV (SCE) with cyanide solutions initially containing 2 or 4 mg/l lead and to which various amounts of sulphide ions were added three minutes after the beginning of each experiment. Four different sulphide concentrations were used to study this case, namely 0.5, 1, 3 and 4 mg/l (figure 6.4). The following combinations were investigated and the excess of one ion with regard to the other was calculated according to equation 6.1.

a. 4 mg/l lead and 0.5 mg/l sulphide, i.e., deficit of 19.3 % in sulphide
b. 4 mg/l lead and 1 mg/l sulphide, i.e., excess of 61.2 % in sulphide
c. 4 mg/l lead and 3 mg/l sulphide, i.e., excess of 383.9 % in sulphide
d. 2 mg/l lead and 4 mg/l sulphide, i.e., excess of 1190.3 % in sulphide

The anodic current density of the gold was not decreased by relatively small additions of sulphide to the lead containing solution, which decreased the gold dissolution rate significantly when added at its own. Larger additions of sulphide increased the anodic current density as would be expected if the inhibiting effect of the lead is counteracted. The time required for the restoration of the anodic activity of the gold was dependant on the excess of sulphide added and ranged from 500 s for 384 % excess of sulphide to 200 s for 1190 % excess of sulphide.

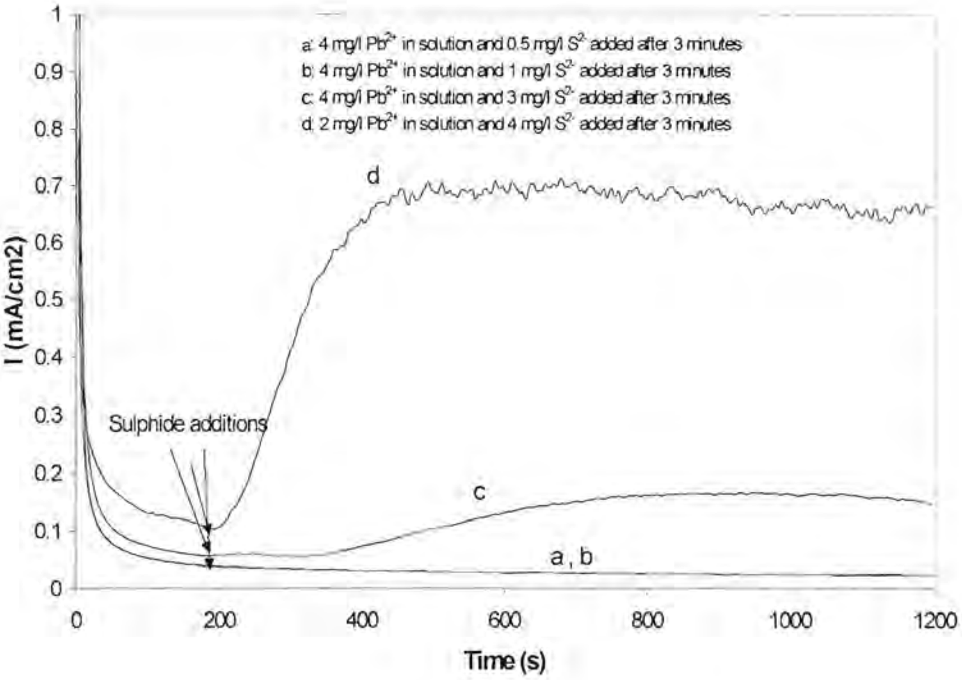


Figure 6.4. Effect of sulphide additions on the anodic current density obtained on a gold disc electrode rotating at 225 rpm, held at a constant potential of –200 mV (SCE) in an aqueous solution at a pH of 11, containing 2500 mg/l NaCN.

6.4. CONCLUSIONS

Traces of lead and sulphide ions were found to play a crucial role on the anodic dissolution of gold in alkaline cyanide solutions. From Ecorr to approximately -380 mV (SCE), lead ions increased the dissolution of gold while sulphide ions counteracted this effect. At more positive values, the opposite effect was observed. The overall effect was dependent on the relative concentrations. Under mildly oxidative conditions it is appropriate to add lead ions to the solution when a retarding effect is observed due to the presence of sulphide minerals. The use of strong oxidants in gold cyanidation can accelerate the dissolution rate of gold in cyanide solutions containing traces of sulphide ions (< 5 mg/l). For this effect to be efficient, the open-circuit potential should be more positive than -380 mV (SCE).

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

The literature survey indicated that the introduction of impurities prior or during the cyanidation process of gold might affect its dissolution rate. The main elements, which are usually present in most gold ores, are silver and sulphide minerals. Lead ions are commonly added to counteract the poisonous effect of sulphide ions. Interactions of gold with these elements are difficult to predict using only thermodynamics calculations. Many steps such as transport of reactants in the solution, adsorption and precipitation of species on the gold surface, dissolution and redox reactions may be involved in the leaching process. The process becomes more difficult to control when it is under mixed control. It was therefore important to study the behaviour of impurities on the kinetics of gold leaching. The following specific conclusions can be drawn from the kinetic study:

a. The presence of silver in the alloy significantly increases the anodic dissolution rate of gold. The cathodic curves appear to be very similar, in particular within the potential range of –350 to –600 mV (SCE) which is of interest in the leaching of gold. However, at high rotation speeds and higher partial pressure of oxygen, the dissolution rate of gold-10 % silver alloy is higher than that of pure gold since the alloy presents a smaller passive region.

b. Additions of trace amounts of lead ions to the cyanide solutions have a favorable effect on the dissolution rate of gold. The deposition of metallic lead on the gold surface is unlikely to occur in alkaline cyanide solutions containing traces of lead. The accelerating effect of lead is probably due to its soluble species. The concentration of lead species in solution depends on factors such as the total concentration of lead in the solution, pH, cyanide concentration and the presence of anions consuming lead. The sulphide ions were found to be the most poisonous anion for the dissolution of gold in cyanide solutions. The decelerating effect of lead additions observed at high potentials and high concentrations must be due to the formation of insoluble lead species or to the formation of a more stable passive film on the gold surface.

c. Traces of sulphide ions affect the dissolution of gold in a variety of ways. Between Ecorr and –380 mV (SCE) the sulphide ions decrease the dissolution rate of gold by apparently forming a sulphur rich layer on the gold surface. At more positive potentials, i.e., at potentials where gold would normally passivate in the absence of sulphide, the sulphide ions accelerate the dissolution rate of gold and this must be due to a change of the surface character of the gold and the gold-silver alloy. At higher sulphide concentrations the activity of the gold at higher potentials is again suppressed.

d. The combined action of sulphide and lead ions on the dissolution rate of gold indicates that the overall effect is dependent on their relative concentrations in solution. From Ecorr to approximately -380 mV (SCE), lead ions increase the dissolution of gold while sulphide ions counteract this effect. At more positive values, the opposite effect was observed.

Based on these conclusions a few recommendations can be made:

- Native gold grains containing high concentrations of silver dissolve relatively easily in alkaline cyanide solutions and will not passify at higher potentials. It is therefore appropriate to dissolve the native gold grains containing silver under more oxidizing conditions.
- The accelerating effect of trace amounts of lead can be affected by the presence of anions consuming lead in industrial waters. For example, the accelerating effect of 5 mg/l lead may be reduced by 10 % in industrial waters containing 5 mg/l sulphate and by 90 % in industrial waters containing 60 mg/l $CaCO_3$. In such cases, purification of the water used for the cyanidation or higher lead additions may be beneficial.
- In industrial practice the cyanide solutions usually contain sulphide ions. Addition of lead salts to the solution counteract the poisonous effect of sulphide on gold leaching within the potential range used in conventional cyanidation of gold, i.e., from –600 to -350 mV (SCE). However, a minimum amount of lead is required to achieve this. This value depends on the sulphide concentration, the agitation of the solution and the open-circuit potential. It was found that small concentrations of sulphide ions (< 5 mg/l) increase the dissolution rate of gold at potentials more positive than –380 mV.

To optimize the dissolution rate of gold at more positive potentials two conditions must be fulfilled. First, a pre-treatment of the mineral before the cyanidation process must be done to reduce the sulphide content in solution to concentrations lower than 5 mg/l. Secondly, a relatively high concentration of free cyanide and a high level of dissolved oxygen are required to obtain high dissolution rates of gold in cyanide solutions containing sulphide ions.

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APPENDIX 1.

Electronic properties of selected sulphide and oxide minerals (Marsden, 1992)

Formula	Name	Resistivity (Ωm^{-1})
Cu_5FeS_4	Bornite	10^{-3} - 10^{-6}
Cu_2S	Chalcocite	4×10^{-2} - 8×10^{-5}
$CuFeS_2$	Chalcopyrite	2×10^{-4} - 9×10^{-3}
CuS	Covellite	8×10^{-5} - 7×10^{-7}
PbS	Galena	1×10^{-5} - 7×10^{-6}
MoS_2	Molybdenite	$(7.5 - 8) \times 10^{-3}$
FeS_2	Pyrite	3×10^{-2} - 1×10^{-3}
ZnS	Sphalerite	3×10^{-3} - 1×10^{-4}
SnO_2	Cassiterite	10^{2} - 10^{-2}
Fe_2O_3	Hematite	2.5×10^{-1} - 4×10^{-2}
Fe_3O_4	Magnetite	2×10^{-4} - 4×10^{-5}
MnO_2	Pyrolusite	10^{-1} - 10^{-3}
UO_2	Uraninite	$(4 - 20) \times 10^{-1}$

APPENDIX 2.

Critical thermodynamic data for dissolved lead species at 25 °C (Rickard, 1978)

Species	Stability constant (log)	ΔG^0_f kJ	Comments
Pb^{2+}		-24.4	generally accepted
$PbOH^+$	K_1 7.83	-226.4	
$Pb(OH)_2$	β_2 10.8	-400.8	
$Pb(OH)_3^-$	β_3 13.9	-575.7	
$Pb_3(OH)_4^{2+}$	β_{43} 32.7	-888.7	0.3 M NaClO4
$Pb_4(OH)_4^{4+}$	β_{44} 36.7	-936.4	0.3 M NaClO4
$Pb_6(OH)_8$	β_{86} 69.4	-1802.5	0.3 M NaClO4
Pb^{4+}	pe 28.6	-302.5	
PbF^+	k_1 1.25	-310.5	very uncertain value
PbF_2	β_2 2.56	-596.7	very uncertain value
$PbCl_+$	k_1 1.61	-164.8	
$PbCl_2$	β_2 1.80	-297.1	
$PbCl_3^-$	β_3 1.7	-408.4	
$PbCl_4^{2-}$	β_4 1.4	-557.3	
$PbClO_3^+$	k_1 -0.32	-25.9	
$Pb(ClO_3)_2$	β_2 -0.61	-27.6	
$PbBr^+$	k_1 1.8		
$PbBr_2$	β_2 1.44	-24.1	very uncertain value
$PbBr_3^-$	β_3 1.19	-343.1	very uncertain value
PbI^+	k_1 2.0	-64.4	
PbI_2	β_2 3.15	-109.2	
PbI_3^-	β_3 3.92	-132.2	
PbI_4^{2-}	β_4 4.47	-204.6	
$PbSO_4$	k_1 2.7	-784.5	
$Pb(NO_3)^+$	k_1 1.07	-141.8	
$Pb(P_2O_7)^{2-}$	k_1 11.2	-2007.5	
$PbHPO_4$	k_1 3.1	-1131.4	

Critical thermodynamic data for dissolved lead species at 25 °C (Rickard, 1978)

Species	Stability constant (log)	ΔG^0_f kJ	Comments
$Pb(HPO4)_2^{2-}$	β_2 2.37	-2216.3	inconsistent value
$PbH_2PO_4^+$	k_1 1.5	-1163.2	
$PbCO_3$	k_1 6.4	-588.7	
$Pb(CO3)_2^{2-}$	β_2 9.8	-1136.0	
$PbSCN^+$	k_1 0.89	63.2	
$Pb(SCN)_2$	β_2 1.15	154.4	

APPENDIX 3.

Selected soluble species of lead in aqueous solutions.

Species	*References*
Pb^{2+}	Pourbaix (1966)
$HPbO_2^-$	Pourbaix (1966)
PbO_2^{2-}	Pourbaix (1966)
PbO_4^{4-}	Pourbaix (1966)
PbO_3^{2-}	Pourbaix (1966)
$Pb_2(OH)^{3+}$	Lapidus (1995)
$Pb_3(OH)_4^{2+}$	Lapidus (1995)
$Pb_4(OH)_4^{4+}$	Lapidus (1995)
$Pb_6(OH)_8^{4+}$	Lapidus (1995)
$Pb(OH)_3^-$	Mussatti (1997)
$PbOH^+$	Mussatti (1997)
$Pb(OH)_3^-$	Rickard (1978)
Pb^{4+}	Rickard (1978)
$PbSCN^+$	Rickard (1978)