

# A study of gold anodic behavior in the presence of various ions and sulfide minerals in cyanide solution

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## Abstract

Gold mostly occurs in nature in the metallic form and is usually associated with sulfide minerals. In most cases, these minerals have a retarding effect on gold leaching rates in cyanide solution. This negative effect could be attributed to different factors such as galvanic effect or chemical and electrochemical interference.

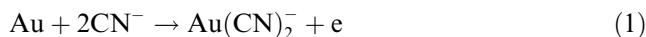
In this investigation, the anodic dissolution of gold in pure and contaminated cyanide solution and in the presence of sulfide minerals was studied. The potentiodynamic method was used to study the anodic dissolution reaction. It was found that the anodic reaction of pure gold was inhibited due to the passivation, which resulted from various ions and sulfide minerals. A minor amount of silver in gold disturbs the passivation mechanism and the reaction rate is controlled by mass-transfer mechanism. The results of this investigation indicate that sulfide ions have serious negative effects on gold anodic dissolution, accompanied by antimony ions. Metal ions such as copper, iron and lead, did not have significant negative or positive effect on gold anodic reaction. Among those sulfide minerals studied, stibnite had a very strong deleterious effect on gold anodic behavior. Gold anodic reaction in the low overpotential range was almost unaffected in the presence of galena. Under the same conditions, pyrite, pyrrhotite and chalcopyrite decrease the activity of gold toward the anodic reaction.

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## 1. Introduction

Over the last few decades, cyanide has remained the main lixiviant for gold leaching. The advantages of cyanide other lixivants have been discussed elsewhere (Fleming, 1992). As early as 1900, Christy suggested that gold dissolution in cyanide solution is electrochemical in nature (Mills, 1951). Thompson (1947) proved that the gold cyanidation process proceeds via an electrochemical mechanism. As a result, an electrochemical approach can be used to investigate the influence of solution compositions on gold leaching behavior. The gold anodic reaction proceeds according to the following reaction:



On the other hand, gold cathodic reaction involves oxygen reduction on the cathodic area. This reaction may proceed through 2 or 4 electron transfer as follows:

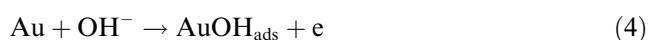


Gold anodic behavior has been the subject of several publications (Mills, 1951; Kudryk and Kellogg, 1954; Cathro and Koch, 1964). Examining the Eh–pH diagram for gold in cyanide solution, one will realize that a stable gold complex,  $\text{Au}(\text{CN})_2^-$ , forms in a wide pH range of alkaline solution. This means that gold is soluble in cyanide solution; however, the kinetic of this reaction can not be predicted by using such a diagram. On the contrary, except in one case (Kudryk and Kellogg, 1954), it was reported that the anodic profile of pure gold (99.99%) in cyanide solution indicated a passive region. Woodcock was one of the first researchers who realized that a pure gold electrode does not exhibit a normal current–voltage curve in cyanide solution

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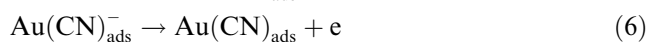
(Mills, 1951). He found a normal current–voltage curve with a limiting current proportional to cyanide concentration with a silver rotating electrode. However, with a gold electrode the curve became complicated. The curve showed normal behavior up to  $-500$  mV, then the current suddenly dropped. Using the potentiodynamic method, Kirk et al. (1978) identified three different maxima in the gold anodic curve at  $-650$ ,  $40$  and  $380$  mV vs. SCE. This behavior was not due to the diffusion limitation of reactants or products (since in either case the limiting current plateaus) and no current peaks would be expected. By employing rapid sweep cyclic voltammetry, he suggested that the adsorption of hydroxide ions on the gold surface through the Reaction 4 was responsible for gold passivation before the last peak (Kirk et al., 1980a,b):



In his hypothesis, different crystal planes are susceptible to passivation by the formation of the hydroxide layer at different potentials that are responsible for three passive zones in the anodic curve. Mills (1951) also suggested that hydroxide ions might adsorb on the gold surface and cause passivation. The adsorption of hydroxide ions at potentials more cathodic than those of oxide layer formation was also reported by Cordova et al. (1979). However, Kirk et al. (1980a,b) reported the formation of such a layer at much lower potential. The formation of an oxide layer,  $\text{Au}_2\text{O}_3$ , is believed to passivate the gold surface at the region of peak three, the most anodic one. This mechanism of passivation at potentials higher than the last peak is accepted almost by all researchers.

Applying cyclic voltammetry and galvanostatic methods, Mac Arthur (1972) suggested that the reaction at low overpotentials, up to  $-300$  mV, would be controlled chemically by the dissolution of the intermediate product,  $\text{Au}(\text{CN})_{\text{ads}}^-$ . He believed that there was no true passive region in his work when the gold potential was less than  $450$  mV since an abrupt decrease in current did not happen.

It is generally believed that gold dissolution in cyanide solution proceeds through several stages instead of a single step, Eq. (1). McIntyre and Peck (1976) and Kirk et al. (1978) proposed the following mechanism:



Kirk proposed that the reaction mechanism is the same for the first and second anodic peak. Nicol (1980) postulated that since only one electron transfer is involved in this reaction, it cannot explain the formation of more than one peak. Kirk and Foulkes (1980) tried to remove this doubt and suggested that the presence of various peaks is due to different planes in the gold crystal and

each plane is active at a certain potential. Such an argument without further clarification would be difficult to believe. The fact that gold cyanidation proceeds through an intermediate species,  $\text{Au}(\text{CN})_{\text{ads}}$ , has also been confirmed by other researchers (Sawaguchi et al., 1995) using in situ scanning tunneling microscopy (STM). This compound is known to have polymeric structure with an infinite linear chain. In conclusion, as pointed out by Cathro and Koch (1964), the dissolution of gold in aerated cyanide solutions would be controlled by the diffusion rate of dissolved oxygen if the surface was unaffected by the reaction products (active surface), but would be controlled by the anodic dissolution rate of gold if it were passive. The proceeding reactions can be interfered with the silver ions in the cyanide solution as discussed by Wadsworth and Zhu (2003).

Several researchers (Thompson, 1947; Kameda, 1949; Cathro, 1964, 1965; Nicol, 1980; Deschenes et al., 1998; Deschenes et al., 2000; Tshilombo and Sandenbergh, 2001; Wadsworth and Zhu, 2003) have examined the effect of different ions, such as silver, lead, thallium, mercury and sulfide ions, on gold electrochemical behavior in cyanide solution. Thompson (1947) reported that an immediate white precipitate formed where lead ions successively added to cyanide solution until finally the gold electrode attained a potential positive to calomel electrode. He suggested that this effect was due to cyanide removal from the solution due to lead cyanide formation. However, the formation of such a compound and the mechanism for cyanide depletion is under question. Kameda (1949) postulated that lead is more electronegative to the gold in cyanide solution; therefore, lead ion deposition on gold surface would be possible. Later, McIntyre and Peck (1976) and Adzic et al. (1980) indicated that lead is able to form an adsorbed monolayer on the gold surface even at a potential which is more positive to its reduction potential. This is referred to as underpotential deposition. As has been pointed out by Omar et al. (1993), “This phenomenon is commonly considered as the manifestation of a stronger bonding of the metal adatom to the foreign substrate than to its own bulk phase.” The formation of lead or lead alloy on the gold surface has also been confirmed by Deschenes et al. (2000) using XPS method.

Both Mills (1951) and Cathro (1964, 1965) reported that the adsorption of thallium on the gold surface would prevent the gold from becoming passivated. Nicol (1980) also postulated that the addition of minor amounts of mercury or lead increased the height of the anodic peak in the potential region  $-400$  mV significantly. It appears from his work that the gold anodic character in the presence of those ions, at more positive potential, is essentially unaffected. Since a passive area still exists in such an anodic curve, depending on gold cathodic behavior, it may not explain the pronounced effect of lead ions on the gold dissolution rate.

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