CATALYSED CYANIDATION OF GOLD

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Cyanidation is the most widely used process to recover gold from its ores. In this operation, the needed gold oxidation is normally accomplished by the oxygen, in the form of air or bulk oxygen. Under most circumstances, however, the cyanidation process suffers from slow kinetic rates, mainly because of the low solubility of oxygen in water and its relative inertness. In the present work, the introduction, of an organic compound, namely anthraquinone-2-sulphonic acid (AQ), is proposed to improve the dissolution kinetics during the gold cyanidation. The major advantage of this is that the reagent is able to act as an additional and recyclable oxidizing agent, with the result that it not only increases the solution rates, but also its concentration remains constant throughout the process, playing thus the role of a catalyst. Results from experiments carried out with a rotating gold disc are also shown and a mechanism to explain the role of the catalyst on the gold dissolution is suggested.

CIANETAÇÃO CATALISADA DO OURO

Cianetação é o processo mais largamente utilizado para extração de ouro de seus minérios. Nesta operação, a necessária oxidação do ouro é normalmente efetuada pelo oxigênio do ar ou por injeção direta de oxigênio puro na polpa. Sob muitas circunstâncias, no entanto, o processo de cianetação apresenta baixa taxa de dissolução, principalmente por causa da pouca solubilidade do oxigênio na água. O presente trabalho propõe a introdução de um composto orgânico (antraquinona, AQ) a fim de aumentar a taxa de dissolução do ouro durante o processo de cianetação. A principal vantagem desta adição é que este reagente é capaz de agir como um agente oxidante adicional e reciclável, com o resultado que ele não somente aumenta a taxa de dissolução de ouro, mas também sua concentração permanece constante durante todo o processo, caracterizando portanto o papel de um catalisador. São apresentados também resultados de ensaios feitos com um disco rotativo e um mecanismo capaz de explicar o papel desempenhado pelo catalisador é sugerido.

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INTRODUCTION

Most of the gold ores processed today are treated by the cyanidation process, a technique known since the end of the last century, when in 1887 a British patent was granted to John Steward MacArthur[1]. The discovery, named "Process of Obtaining Gold and Silver From Ores", soon became known as the cyanidation process following its successful industrial application. With the use of cyanide (KCN or NaCN) in the extractive metallurgy of gold, the world output of the metal increased by more than four times in the period from 1901 to 1950 compared to the period from 1851 to 1900[2]. Throughout this century, much investigation have been carried out in order not only to achieve a deeper understanding of the process as whole or increase its efficiency, but also to look for alternative leaching reagents, such as thiourea, thiosulphate, bromine and thiocyanate, and to overcome difficulties that have arisen with the depletion of high grade ores or the exploitation of the so-called refractory gold ores (those which cannot be easily extracted by conventional means)[2,3,4,5].

Some important reviews concerning the cyanidation process and its main characteristics have been published[6,7,8,9]. The basic aspects have been established, and revealed that the rate of gold dissolution is controlled by the concentration of cyanide and/or oxygen in solution, depending on their relative concentrations, and that the optimum cyanide concentration is best attained by experiment. The dissolution process is considered to be an electrochemical reaction, in which the anodic and cathodic parts of the metallic surface are linked in short circuit. At the anode the metal gives up electrons to the latter, with further formation of the aurocyanide ion as

\[
\text{Au} + 2\text{CN}^- = \text{Au(CN)}_2^- + e^-
\]
whereas the reduction of oxygen to hydrogen peroxide takes place in the cathodic area.

$$O_2 + 2H_2O + 2e^- = H_2O_2 + 2OH^-$$

It is generally accepted nowadays that the dissolution, in aerated cyanide solution, takes place according to the following equations:

$$4Au + 4KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH$$ \hspace{1cm} 3
$$2Au + 4KCN + O_2 + 2H_2O = 2KAu(CN)_2 + H_2O_2 + 2KOH$$ \hspace{1cm} 4
$$2Au + 4KCN + H_2O_2 = 2KAu(CN)_2 + 2KOH$$ \hspace{1cm} 5

Reaction 3 was first proposed by Elsner, whereas the other two are due to Bödlander (the sum of these, as can readily be seen, gives the single Elsner’s equation)[1,10].

In order to form soluble cyanide complexes, the gold must be also oxidized: this operation is normally performed by introducing compressed air to use oxygen as the oxidizing agent. Under most circumstances the dissolution of gold may be hampered by slow kinetic rates, or even stop altogether, mainly because of the low solubility of oxygen in water. This situation is aggravated at high altitudes, with increasing temperature and during certain industrial practices, such as heap leaching for instance, where the oxygen may be almost totally absent toward the bottom of the heap. Much research has been carried out to overcome this difficulty, and suggestions include the introduction of oxygen in an already dissolved form, such as adding inorganic peroxides, or injection of compressed air where heap leaching is being used[11,12,13].

In the present work the addition of an organic compound, namely
anthraquinone-2-sulphonic acid (AQ), is proposed to improve the kinetic rate of the gold dissolution during the cyanidation process. The major advantage of using this organic compound is that it can act as an additional and recyclable oxidizing agent, with the result that it not only may increase the rate of gold dissolution, but its concentration remains practically constant throughout the dissolution process, playing thus the classical role of a catalyst. An additional feature of this cyclic reaction is that, during the reoxidation of the reduced AQ, there occurs the "in-situ" production of hydrogen peroxide, which may also act as an appropriate oxidizing agent for the process[11].

ANTHRAQUINONE: A CATALYST FOR THE GOLD CYANIDATION

Quinones are substances in which two hydrogen atoms of the benzene structure are replaced by two oxygen atoms, as in the figure below:

![Figure 1 - 1,4 benzoquinone molecular structure](image)

The quinone structure plays an important role in theories concerning the relationship of chemical constitution to colours. Anthraquinones contain the two oxygen atoms on an anthracene structure, as shown on the following page:
This is the most important quinone derivative of anthracene and the source of a large class of dyes and pigments.

When aromatic hydrocarbons or their derivatives are treated with $\text{H}_2\text{SO}_4$, they yield sulphonic acids in which a hydrogen of the benzene nucleus is replaced by the sulphonylic group $\text{SO}_3\text{H}^-$.

Anthraquinone sulphonic acids are important intermediates in the preparation of dye-stuffs. The sulphonic acid group renders the AQ soluble in water and imparts it an affinity for wool and silk.

It is well established that the most commonly used process nowadays for the production of hydrogen peroxide is the chemical autoxidation of anthraquinone derivatives, often referred to as the quinone process for hydrogen peroxide$[14,15]$. Generically, the main reactions involved in this process are:
While the possibility of using many quinone-type compounds has been mentioned, the use of products containing sulphonic acid groups is preferred and commonly used industrially because of their relatively high solubilities in water[15,16].

The diagram depicted in FIGURE 4 on the following page is the superimposed Eh - pH diagrams for the system Au-CN-H$_2$O$_2$-AQ in aqueous solution. It may be seen that it is thermodynamically feasible for
the AQ to act as an oxidizing agent in the Au-CN$^-$ system over a pH range from approximately 8.0 upwards (the diagram also discloses the region where AQ, $H_2O_2$ and Au(CN)$_2^-$ may coexist).

![Eh-pH diagram for the system Au-CN-H$_2$O$_2$-AQ-H$_2$O at 25°C; [H$_2$O$_2$]=10$^{-1}$M, [CN$^-]=10$-1M, [Au]=10$^{-4}$M, [AQ]=10$^{-3}$M.](image)

The overall reactions involved with the gold dissolution in aerated KCN and in the presence of AQ as a catalytic oxidizing agent could then be written as:

$$2Au + 4KCN + O_2 + 2H_2O = 2KAu(CN)_2 + H_2O_2 + 2KOH$$

$$2Au + 4KCN + H_2O_2 = 2KAu(CN)_2 + 2KOH$$
2Au + 4KCN + AQ + 2H₂O = 2K₂Au(CN)₂ + AQ⁻H+ + 2KOH + H⁺  

and the oxidation step

\[ \text{AQ}^- + \text{O}_2 + \text{H}^+ = \text{AQ} + \text{H}_2\text{O}_2 \]

continuously generating both oxidizing agents.

**APPARATUS AND MATERIALS**

In order to investigate the use of AQ as a catalyst for the cyanidation of gold, a system consisting of a rotating disc (1.4 cm diameter) of pure gold (99.9%), rotated by a precision speed motor (Oxford Electrodes), was chosen. This approach, for kinetic and mechanistic studies, has been the subject of extensive investigations and its use increasing widely\[17,18\].

Before each experiment, the disc was carefully polished with 1.0μ diamond compound (Hyprez Five Star), using a silk cloth and a water soluble polishing lubricant liquid. The gold disc with a mirror-like appearance was then rinsed and immersed in a strong chromic sulphate solution for about 1 minute; afterwards the disc was rinsed again with double distilled water before being used for an experiment. With this care, reproducibility could be achieved within 5% relative variation.

A volume of 250 ml reagent grade potassium cyanide was used in all trials. The salt was dissolved in double distilled deionized water and solutions were freshly prepared shortly before each experiment. Analytical grade (BDH) 9,10-anthraquinone-2-sulphonic acid ("silver salt") (AQ) was used as the organic catalyst. A stock solution of 15mM AQ in 1mM KOH was prepared and diluted accordingly to give the concentration required for each experiment. The reactor was a 300 ml split-top, round-bottom
glass reactor, normally used in hydrometallurgical investigations of this type. FIGURE 9 on the last page of this work depicts the equipment used for these tests.

The experiments shown were carried out at a constant temperature of 25°C with the aid of a water bath. Samples were collected every 15 minutes and tests were normally run for 90 minutes, unless specifically otherwise stated. The dissolution potential observed on the gold surface (and measured against a Ag-AgCl electrode) typically changed from -420mV to -370mV for a conventional aerated solution, and from -350mV to -320mV when AQ was added to the leaching solution; pH was kept between 10.5 and 11.2. The amount of gold dissolved was analysed by atomic absorption in all cases (Perkin Elmer 1100B), and the results calculated according to the following equation:

\[
M_t = C_t (V_{t-1} - S_{t-1}) + \sum_{i=t-1}^0 S_i C_i
\]  

where

- \(M_t\) is the amount of gold dissolved at time \(t\) (mg)
- \(C_t\) the atomic absorption reading in time \(t\) (mg/l)
- \(V_t\) the solution volume in the reactor in time \(t\) (l)
- \(S_t\) the volume of the sample taken (l)

In the evaluation of the rates obtained experimentally, the use of this equation is important to make allowance for the decrease in volume at each sample withdrawal.
RESULTS

The dissolution of gold against time in 0.03M KCN is shown in FIGURE 5. The linearity of the plot of gold dissolved and time is an indication that the surface area of the gold disc remained constant throughout the leaching trial. The gold surface was examined microscopically at the end of each test and no indication of uneven attack or pitting was observed. The rate was calculated from the slope of this type of plot. All the results could be fitted by a straight line, with a correlation factor equal to or greater than 0.980 in most cases. The average rate value of the reproduced trials under 0.03M KCN and rotation speed of 10Hz reached $2.86 \times 10^{-9}$ mol/cm$^2$.s

![Graph showing gold dissolution over time](image)

**Figure 5 - Gold dissolution in cyanide 0.03M from a rotating disc (10 Hz; $P_{O_2}=2.13 \times 10^4$ Pa).**

The effect of additions of AQ on the rate of gold dissolution in a normally aerated 0.03M KCN solution is shown in FIGURE 6 on the following page:
From these results, it may be seen that an increase of up to 50% is observed, when 3.0mM AQ is present in the leaching solution. Above this AQ concentration there is no further increase in the rate of gold dissolution.

The rate dependence on KCN concentration at 3.0mM AQ is depicted in FIGURE 7. It may be seen that for the conventional system (air flowing) there is no improvement in the rate if the cyanide concentration is increased beyond 0.01M. On the other hand, when 3.0mM AQ is present in the same system, i.e., when a supplementary oxidizing agent is added, the rate increases with cyanide concentration up to 0.03M. This indicates that with a supplementary oxidizing agent in a 0.01M cyanide solution, the rate turns to be controlled by the availability of cyanide.

As may be seen from the results, the effect on the rate of gold dissolution obtained with additions of AQ were encouraging. Thus, in order to further investigate the action of AQ itself, tests were also
performed under oxygen-free atmospheres. While evident, it is important to note that, under these circumstances, AQ is the sole oxidizing agent for the process.

![Graph showing dissolution rate dependence on KCN and AQ concentration](image)

**Figure 7 - Gold dissolution rate dependence on KCN and AQ concentration (pO2=2.13 x 10^4 Pa; f=10Hz).**

**Experiments With No Oxygen**

FIGURE 8 shows the dissolution of gold in an aqueous cyanide (KCN=0.01M) solution at four different AQ concentrations. An introductory trial was carried out under nitrogen but with no AQ to test for any oxygen leaking into the reactor; in this experimental condition, as expected, no detectable gold was dissolved.

It may be seen from the figure that the amount of gold dissolution increases with the AQ concentration, up to a maximum beyond which the effect starts to influence in the opposite way (i.e., less gold is dissolved with 12.0 mM AQ than with 6.0 mM AQ). However, the dissolution of gold in the complete absence of oxygen indicates that the oxidation reaction...
necessary for the process was carried out by the AQ. This may be represented by

$$2\text{Au} + 4\text{CN}^- + \text{AQ} + 2\text{H}_2\text{O} = 2\text{Au(CN)}_2^- + \text{AQH}^+ + 2\text{OH}^- + \text{H}^+$$

which means that, if AQ is present in the cyanide system, the dissolution of gold is possible, even in the complete absence of oxygen. This is an interesting fact indeed, for it shows for the first time that an oxidizing agent other than oxygen or inorganic peroxides is possible to be used in the cyanidation of gold.

![Graph](image)

**Figure 8 - Amount of gold dissolved, under an oxygen-free atmosphere and different AQ concentrations (KCN=0.01M; f=10Hz).**

Under the normal aerated situation, it has been seen that the reoxidation of the reduced form of AQ, the so-called anthraquinol, leads to the "in-situ" production of hydrogen peroxide. In the present case the reaction may be represented by

$$\text{AQH}^+ + \text{O}_2 + \text{H}^+ = \text{AQ} + \text{H}_2\text{O}_2$$
Hydrogen peroxide is a strong enough oxidant to oxidize gold and promote the formation of the soluble complex $\text{Au(CN)}_2^-$

$$2\text{Au} + 2\text{CN}^- + \text{H}_2\text{O}_2 = 2\text{Au(CN)}_2^- + 2\text{OH}^-$$

Equations 12, 13 and 14 show that $\text{AQ}$ is not only capable of oxidizing gold in a cyanide solution but also that it may be continuously regenerated. The $\text{AQ}$ concentration was monitored after and during some experiments (through on-line UV-visible spectroscopy) and no variation could be detected, showing that its concentration is indeed kept constant throughout the leaching process. This confirms the catalytic role played by the $\text{AQ}$ during the cyanidation of gold, since, as seen earlier, there has been an increase in the rate of dissolution of gold when this reagent is added to the leaching solution.

Moreover, it should be pointed out that while the rate enhancement observed in these tests may be attributed to the system outlined above, this outcome is probably better understood by examining a mechanism of molecular adsorption on the metal surface. The character of the reactions taking place on the gold dissolution in the leaching system comprised of cyanide + oxygen + anthraquinone is said to be probably regulated by the adsorptive nature of each one of these components[19,20,21]. This would characterize a picture of "competitive adsorption"[22], where the reacting molecules would displace each other from sites on the gold surface. Such a mechanism might possibly to explain the results obtained where the benefit caused by the addition of $\text{AQ}$ shows an optimum, beyond which either no further enhancement is achieved (Figure 6) or a decrease in the rate actually occurs (Figure 8). This aspect of the system is currently under investigation and will be published shortly.
CONCLUSIONS

According to the currently accepted mechanism of gold cyanidation and the production of hydrogen peroxide, and from the experimental results obtained in this work it may be concluded that: 1-the rate of gold dissolution in the cyanidation process may be definitely enhanced by about 50% with the addition of AQ, at concentration up to 3.0mM in a 0.03M KCN solution; 2-this effect is noticed up to a certain AQ concentration, beyond which no further enhancement is observed; 3-tests performed under an oxygen-free atmosphere demonstrated that AQ is indeed able to oxidize gold in a dilute cyanide solution; the gold may be then dissolved by forming the auro-complex. Apart from oxygen and hydrogen peroxide, this was the first alternative (and recyclable) oxidizing agent that was successfully used in the cyanidation process; 4-under the conventional aerated situation, the reoxidation of the reduced AQ is readily achieved by oxygen, with the regeneration of the original AQ and simultaneous "in-situ" production of hydrogen peroxide; 5-the oxidizing effect of AQ is, therefore, a cyclic one with the continuous produced hydrogen peroxide also being able to act as an additional oxidizing agent; 6-while the rate enhancement may be attributed to the presence of an additional oxidizing agent in the system, the mechanism is probably better understood by examining the adsorptive nature of the reactions occurring on the gold surface during cyanidation; 7-the addition of AQ to the gold cyanidation process may prove interesting in some extreme situations such as at high altitudes, with increasing temperature, and during heap leaching, for instance, where the dissolution of gold may be hampered by slow rates, mainly because of the decreasing oxygen solubility in water, or even stop altogether due to the complete absence of oxygen toward the bottom of the heap.
REFERENCES


Figure 9 - Scheme representing the equipment used in this work: 1-rotating disc; Ag-AgCl electrode; 3-frit; 4-nitrogen outlet; 5-thermostat; 6-rotating disc speed controller; 7-water bath.