AN ELECTROCHEMICAL MODEL FOR THE LEACHING KINETICS OF GOLD ORE IN
CYANIDE SOLUTIONS.

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ABSTRACT

This project consisted of a literature and a laboratory study to in-
vestigate the applicability of an electrochemical model, to the leach-
ing kinetics of gold ore. The procedure was to get an approximate
measurement of the gold surface potential and then, to use only this
potential and an area term in a two parameter rate expression. The
potential measurements in a pulp, with a gold and gold-silver elec-
trode, were attempted but, the electrodes became passive. The results
showed that the rate controlling mechanism was a combination of the
rate of both oxygen and cyanide diffusion and it was concluded that
the applicability of an electrochemical model to the leaching kinetics
of gold ore, could not be ruled out. It was found that the leaching
kinetics could be modelled very accurately by using the solution
redox potential, however, no theoretical basis could be found to
explain this observation.

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1   PREFACE

1.1   Introduction

The importance of gold in the South-African economy cannot be over-emphasised. The gold industry has formed the foundation of the South-African economy for most of this century. Ironically though, is the fact that this huge and important industry has not seen as many major technological developments as have so many other sectors in South-Africa. A notable exception occurred a few years ago when the gold industry took a great step ahead with the introduction of the Carbon-in-pulp (C.I.P.) process. This development has led to a substantial increase in the recovery efficiency of many gold plants.

Despite this conspicuous lack of major technological improvements in the gold treatment process, the industry in general has never had much difficulty in showing handsome profits. Favourable gold prices, combined with relatively low running costs of gold mines, were the main factors contributing towards the prosperity of the gold industry.

This fairly easy economic situation in which the gold industry found itself and the lack of obvious methods of significantly improving the gold extraction process, inevitably reflected in the general approach towards plant design. It would not be wrong to say that the main objective of plant designers over the years, tended to be to maximise the extent of extraction of gold from the ore with cost being of secondary importance.

As a result of all this, gold plants were often considerably overdesigned. This point was illustrated by a recent research project in which two final year students at Wits University did some batch leaching experiments and were able, by applying basic chemical engineering design principles, to show that a particular plant could operate quite satisfactorily with 4 to 5 leaching tanks, instead of the 10 tanks they were running at the time (King and Greef 1986). This tendency to rather overdesign and play safe, can largely be attributed to a lack of accurate knowledge of the processes involved. So for instance, the kinetic equations needed to be able to adopt a more fundamental ap-

proach and to apply modern design techniques, have, as yet, not been fully explored.

The economic situation in the gold industry has been changing fairly rapidly during recent years and has become financially tighter in the process. With escalating capital and running costs and rapidly decreasing ore grades, improved efficiencies have become essential. All this has placed new emphasis on the search for technological advances in the gold extraction process.

The leaching process in the gold recovery circuit has long been identified as a particularly weak link which was seriously hampering the further improvement of the efficiency of the recovery process. The cyanidation leaching process has been in use for almost a century and still the kinetics and mechanisms involved in this process are not fully understood. Recently, Soviet metallurgists in particular, showed interest in finding a substitute for cyanide. Thio urea ($NH_2.CS.NH_2$) is seen as one possibility. Polysulfide ($(NH_4)_2S_x$) is also a good solvent for gold. It appears unlikely however, that any of these reagents will provide the answers, that will lead to improved commercial operation and the search for an improved leaching process must therefore be continued in all earnest.

1.2 Objective and Structure of the Research Project reported in this dissertation

With the foregoing as background, the present work was undertaken with a view to uncovering new knowledge in the field of the leaching of gold from gold bearing ore and in doing so, to inter alia provide a better understanding of the mechanisms and kinetics involved in the cyanide process. More specifically, the objective was to investigate the applicability of an electrochemical model to the leaching kinetics of gold ore.

Bearing in mind the growing importance attached to the improvement of the leaching process, as being imperative for the continued economical recovery of gold from different types of ore, it is only natural that

a great amount of theoretical and practical studies have already been carried out in this field. In the undertaking of any new studies on this subject, it would therefore have been extremely short-sighted not to take thorough cognizance of the work that had already been done and to acquaint oneself as thoroughly as possible, with all the existing knowledge on the subject.

With this in mind, it was decided to split the project in two separate phases. The first phase consisted of a very thorough study of all the work published on the subject to date. It was just possible that, by doing so, something like a common denominator might have been discovered in the results of the many studies of the past, that could lead to new perceptions.

The second phase of the project consisted of practical research work in the laboratory, with the view to substantiate and further develop existing knowledge, which was disclosed through the literature study and/or to uncover entirely knew knowledge on the subject. More specifically, the object of the practical research work would be to investigate the applicability of an electrochemical model on the leaching kinetics of gold ore.

The two phases of the project will now be reported on successively in detail in the following sections of this dissertation.

2   LITERATURE SURVEY

It appears from the literature that most of the studies done on the dissolution of gold, used ideal systems in that it studied the dissolution of pure gold. The methods used, can be divided into three groups, namely:

1) Gold foil test: The time required for a piece of gold foil to dissolve completely was measured.
2) Rotating disc or plate method: The mass loss of a rotating gold disc or plate during a specific time-span was measured.
3) Electrochemical studies: The relationship between the gold surface potential and the current density (dissolution rate) was measured.

In section 2.1 below, the results of studies using the first 2 of the above mentioned methods, are given while the results of studies, using the third method, are given in section 2.2. Unless otherwise stated, all the studies were conducted on pure gold.

2.1   Experimental studies on dissolution kinetics

2.1.1   The dissolution reaction

The first equation [1] formulated for the dissolution reaction, is known as the Elsner equation and followed after Elsner(1846) recognized that oxygen was essential for the dissolution of gold.

$$4Au + 8NaCN + O_2 + 2H_2O \rightarrow 4NaAu(CN)_2 + 4NaOH \quad ...[1]$$
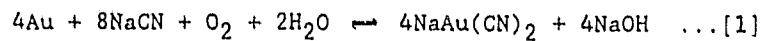
Other researchers, like Janin(1888), were unaware of the necessity for oxygen however, and postulated the following equation [2]:

$$2Au + 4NaCN + 2H_2O \rightarrow 2NaAu(CN)_2 + 2NaOH + H_2 \quad ...[2]$$
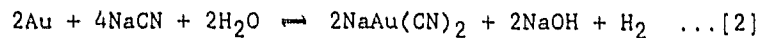
Bodländer(1896) detected hydrogen peroxide in the solution while the gold was dissolving and postulated the equation [3] that follows:

$$2Au + 4NaCN + O_2 + 2H_2O \rightleftharpoons 2NaAu(CN)_2 + 2NaOH + H_2O_2 \quad ...[3a]$$

$$H_2O_2 + 2Au + 4NaCN \rightleftharpoons 2NaAu(CN)_2 + 2NaOH \quad ...[3b]$$
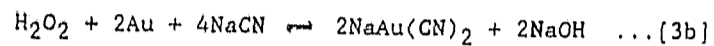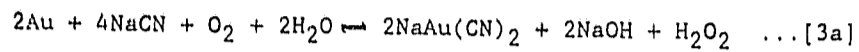
Barsky, Swainson and Hedley(1934) determined the free energy changes in the various reactions suggested. Their calculations supported the Elsner and Bodlander equations, whereas Janin's equation seemed thermodynamically unfeasible.

Boonstra(1943) was the first to recognize the similarity between the dissolution of gold and the corrosion process of metals. Thompson-(1947) did some experiments that unambiguously illustrated the electrochemical nature of the dissolution of gold particles. Today it is generally accepted that the dissolution of gold takes place by way of an electrochemical mechanism. The anodic and cathodic reactions are respectively:

Cathodic:

$$O_2 + 2H_2O + 2e^- \rightleftharpoons H_2O_2 + 2OH^- \quad ...[4]$$

$$H_2O_2 + 2e^- \rightleftharpoons 2OH^- \quad ...[5]$$

Anodic:

$$4Au + 8CN^- \rightleftharpoons 4Au(CN)_2^- + 4e^- \quad ...[6]$$
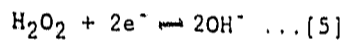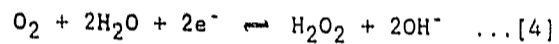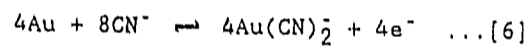
Scientists are not yet in agreement however, as to which cathodic reaction is the predominant one, or as to the actual mechanism of the anodic reaction. Recent experimental observations though, convinced many investigators that the oxygen is reduced to H_2O_2 and that only a small amount of H_2O_2 is reduced further to OH^-. Highly accurate electrochemical experiments performed by Kirk, Foulkes and Graydon(1978) tended to indicate, that the anodic reaction most probably takes place in the following sequence:

$$Au + CN^- \rightleftharpoons AuCN_{ads}^- \quad ...[7]$$

$$AuCN_{ads}^- \rightleftharpoons AuCN_{ads} + e^- \quad ...[8]$$

$$AuCN_{ads} + CN^- \rightleftharpoons Au(CN)_2^- \quad ...[9]$$
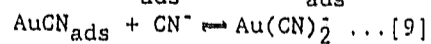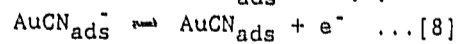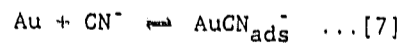
2.1.2 Effect of agitation

Many investigators, who studied the dissolution of gold in cyanide
solutions, reported that the rate of dissolution increased with in-
creasing speed of agitation. Kakovskii et al(1960) analysed the
effect of agitation quantitatively with a rotating disc. They report-
ed that the rate of dissolution increased only up to a certain speed
of agitation (150 rpm), after which it dropped again and became nearly
constant. See figure 2.1.
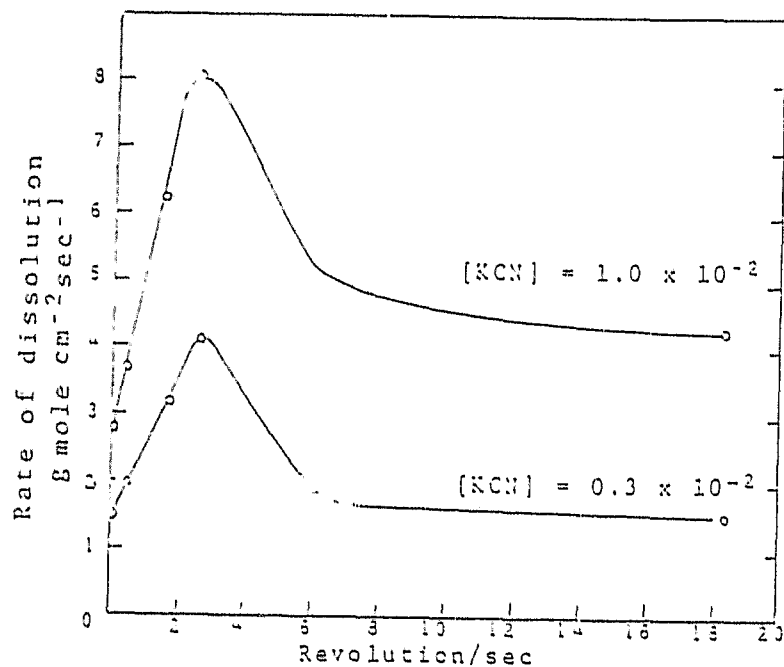
Figure 2.1: A decrease in the rate of gold dissolution was observed
at high speeds of agitation and at two different cyanide concentra-
tions. Conc. in gmole/liter. Temp 25°C, P_{O2} = 1 atm. Plotted from
data by Kakovskii et al (1960).

To explain this phenomenon, they suggested that the dissolution of

gold follows one of two mechanisms, depending on the speed of agita-
tion. Cathro(1963) also reported a decrease in dissolution rate at
higher speeds of agitation.

Further evidence, presented by Kakovskii et al (1960) for their
"two mechanism theory", is given later on in sections 2.1.4 and 2.1.5.

2.1.3   Effect of cyanide concentration on the rate of dissolution

It becomes clear from the literature that the effect of the cyanide
concentration on the rate of dissolution, is influenced by the other
variables, such as temperature, agitation speed and rate of aeration,
used in the experiments employed in determining the effect. All the
investigators observed however, that the rate of dissolution increased
linearly with increasing cyanide concentration until a maximum was
reached. Beyond this maximum, a further increase in cyanide did not
have any accelerating effect, but on the contrary, had a slight retar-
ding effect. See figure 2.2.

The concentration at which this maximum dissolution rate is reached,
depends on other variables, such as the oxygen concentration and the
agitation speed. Hence, it was reported differently by various inves-
tigators, probably because of differences in the variables and tech-
niques employed in determining these figures. Habashi(1967) gives a
summary of all these values. See table 2.1. It varies from 0.10 %
KCN (Beyer 1936) to 0.0085 % KCN (Kakovskii and Kholmanskih 1960).

Table 2.1: Cyanide concentration at which a maximum gold dissolution
rate is reached at atmospheric oxygen pressure and room temperature.

Researcher	%KCN
Maclaurin (1895)	0.25
White (1919)	0.027
Barsky and others (1934)	0.07
Beyer (1936)	0.10
Kameda (1949)	0.03
Kudryk and Kellogg (1954)	0.0175
Kakovskii and Kholmanskih (1960)	0.0085

The decrease in the rate of dissolution at high cyanide concentrations, was attributed by Habashi(1967) to the increase in the pH of the solution, due to the hydrolysis of cyanide.

$$CN^- + HOH \rightleftharpoons HCN + OH^- \quad ...[10]$$
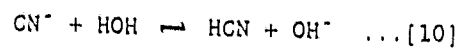
As will be seen later, the rate of dissolution decreases with increasing pH of the solution.
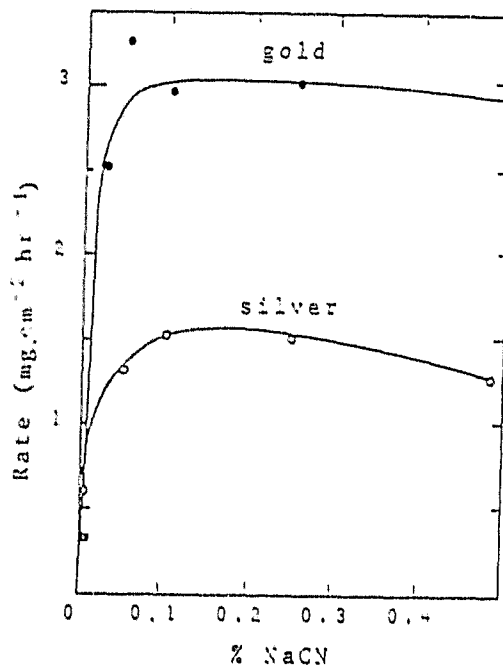
Figure 2.2: The effect of the cyanide concentration on the rate of dissolution of gold and silver. Barsky and others (1934).

2.1.4   Effect of oxygen concentration on the dissolution rate

The speed of agitation and the cyanide concentration strongly influence the effect that the oxygen concentration will have on the dis-

solution rate. At high cyanide concentrations (above about 0.1 %
NaCN), the rate of dissolution is directly proportional to the oxygen
partial pressure. However, the rate does not increase indefinitely
with increasing oxygen pressure. There is a certain pressure beyond
which a further increase does not affect the rate any more. At low
cyanide concentrations (below about 0.1 % NaCN) and high oxygen pres-
sure, the rate of dissolution is only affected by the cyanide con-
centration.
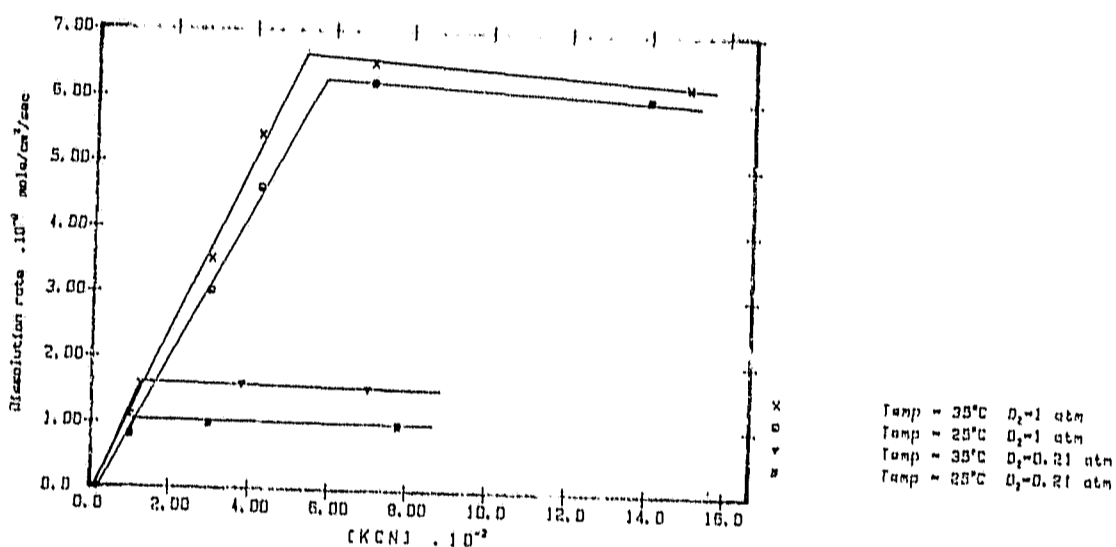
Figure 2.3: Different maximum rates of dissolution are obtained at
different oxygen concentrations as the cyanide concentration is in-
creased. (Kakovskii et al. (1960))

It was found by many investigators that, when the dissolution rate
reached a maximum value, either by increasing the [CN$^-$] or the [O$_2$],
the ratio of cyanide concentration to oxygen concentration was at a
specific value. This ratio of [CN$^-$]/[O$_2$] was found by Kakovskii et
al in 1960, to vary between 4,69 and 6,8. See figure 2.3.

From the effects that cyanide and oxygen concentrations had on the dissolution rate, it was concluded that, at low cyanide concentrations the diffusion of CN^- ions is the rate limiting factor, whereas at low O_2 concentrations, diffusion of $[O_2]$ is the rate limiting factor.

It must immediately be emphasized that the above observations were made at relatively low agitation speeds. As has been mentioned earlier on, Kakovskii et al (1960) came to the conclusion that a different reaction mechanism is applicable at high speeds of agitation. Therefore, one can expect the effect of oxygen to be different on a dissolution system which is agitated at higher speeds. Kakovskii et al (1960) observed that, at high agitation speeds, the rate was no longer proportional to the partial pressure of oxygen, but to the square root of the partial pressure, which tended to confirm that a different mechanism must be in operation at these high agitation speeds.

2.1.5   Effect of temperature

One can expect that a temperature increase will increase the rate of the dissolution reactions, but at the same time, will also decrease the oxygen content of the solution. Therefore, there should be an optimum temperature at which the dissolution rate reaches a maximum. Julian and Smart (1921) found this temperature to be 85°C (see figure 2.4), while Meyer (1931) found it to be 80°C.

Some investigators were able to determine the activation energy of the process from Arrhenius plots, and found it to be in the range of 2 to 5 Kcal/mole. In table 2.2, the findings of various investigators are summarized. This value for activation energy is typical for processes controlled by diffusion. It is very important, however, to note that an activation energy of 14.1 Kcal/mol was found for gold dissolution under similar conditions, but at a high speed of agitation (1100 rpm) (Kakovskii 1960). This value is typical of processes controlled by chemical reactions. This is again convincing evidence that there must be two mechanisms for gold dissolution, depending on the speed of agitation. It seems that at low speeds of agitation, the rate is dif-

fusion controlled, whereas at high speeds the rate is chemically controlled

Table 2.2:

Temp range	P_{O2} atm	KCN%	rpm	Activation Kcal/mole	Investigator
15-40	0.21	0.03		5.245	Kameda(1949)
27-72	0.21	0.03	100-500	3.5-4.0	Kudryk and Kellogg(1954)
25-45	1.00	0.0195	100	3.487	Kakovskii et al (1960)
15-35	1.00	0.0195	1100	14.1	Kakovskii et al (1960)
30-60	1.00		200-1600	6.2	Cathro (1963)
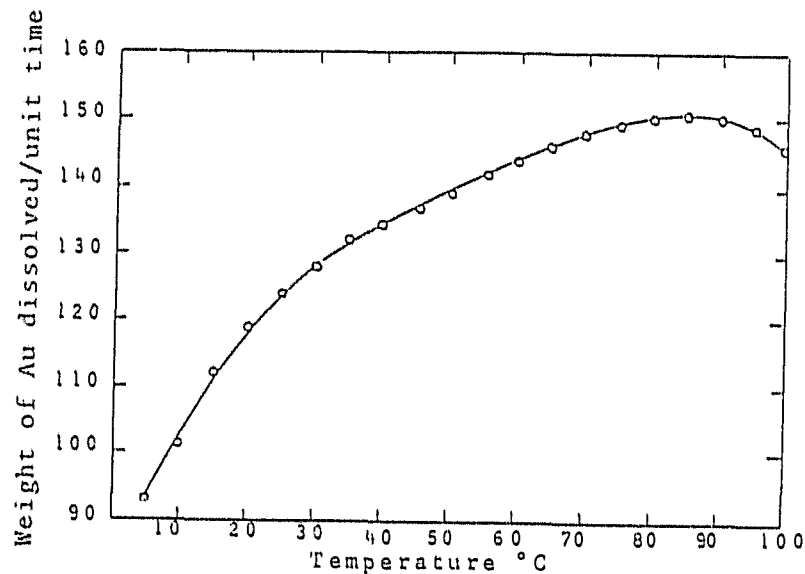
Figure 2.4: The effect of temperature on the rate of dissolution of gold in 0.25 % KCN (Julian and Smart(1921)).

2.1.6 Effect of hydrogen ion concentration

All the investigators reported a decrease in rate of dissolution as the pH was increased. See figure 2.5. Day (1967) reported that, the

retarding effect appeared to reach a maximum when the molar concentration of OH^- ions was 2-3 times the molar concentration of CN^- ions. It was also observed by researchers, that the retarding effect of lime is greater than that of sodium hydroxide when used to increase the pH. Kameda (1949) has done an extensive study on this phenomenon. He assumed the following reaction in order to give an explanation:

$$H_2O_2 + CaO \longrightarrow CaO_2\downarrow + H_2O \quad \dots [11]$$
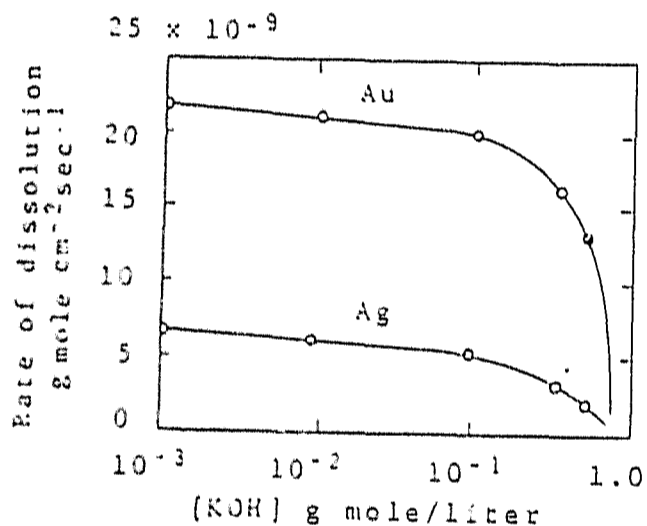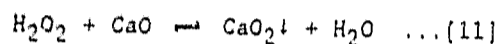
Figure 2.5: The effect of pH on the rate of dissolution of gold and silver in KCN (after Kakovskii and Kholmanskikh(1960)).

He had in fact detected a small amount of CaO_2 precipitate. His theory was that the hydrogen peroxide formed in Bodlaender's second equation [3a] is precipitated as CaO_2 by the addition of lime; so that Bodlaender's second equation [3b] would hardly take place. This is not a very convincing explanation, since experiments by Boonstra (1943) showed that the second reaction of Bodlaender proceeds very slowly and, therefore, does not contribute very much to the overall

dissolution rate. See section 2.1.8 for further discussion of this matter. The decrease in the dissolution rate of gold, at high pH levels, was attributed by Kakovskii et al (1960) to the kinetic difficulties, arising with oxygen reduction in strongly alkaline solutions.

2.1.7   Effect of H_2O_2 concentration

Kameda (1949) and other investigators quantitatively studied the liberation of H_2O_2 during the dissolution of gold. As has been said, their experiments strongly supported the Bodlaender equations (3a,b). The hydrogen peroxide which is formed, may undergo catalytic decomposition according to equation [12] below during the dissolution process.

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2} O_2 \quad ...[12]$$
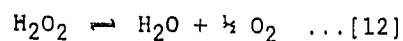
This may take place, either heterogeneously on the surface of the metal, or homogeneously because of the presence of certain ions in solution, e.g. Cl^-. This probably explains why Kudryk and Kellogg (1954) were unable to detect H_2O_2 in their experiments, because they added KCl to their solutions.

If the Bodlaender mechanism were correct, then gold should dissolve in cyanide solutions in the absence of oxygen, when only hydrogen peroxide is present. Boonstra (1943) found however, that under these conditions the dissolution rate was very slow. Kameda (1949) reported that $0,6*10^{-2}$ to $0,9*10^{-2}$ moles/liter H_2O_2 had an accelerating effect on the dissolution of gold, but more than $1,2*10^{-2}$ moles/liter H_2O_2, practically stopped the dissolution. He attributed the retarding effect to the oxidation of KCN (eq. 13).

$$KCN + H_2O_2 \rightarrow KCNO + H_2O \quad ...[13]$$
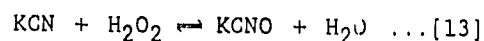
Lund (1951) confirmed the formation of potassium cyanate by the action of H_2O_2 on KCN.

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2.1.8   Effect of foreign ions

Native gold metal in natural gold ores is associated with many other minerals which are, to some extent also soluble in alkaline cyanide solution. With the exception of a few ions, such as Na^+, K^+, Cl^-, NO_3^- and SO_4^{2-}, which have no effect on the rate of dissolution of gold in cyanide solutions, foreign ions may have either an accelerating or a retarding effect.

Because the dissolution process is composed of two simultaneous reactions, the effects of foreign ion on the anodic and cathodic reactions respectively, are studied separately, as will be explained in section 2.2. The general tendencies found by many investigators are reported here.

Haden (1938) reported that small amounts of lead and mercuric salts accelerate the dissolution. This was confirmed by Kameda (1949) and Fink and Putnam (1950). Fink and Putnam further found that bismuth and thallium salts also accelerate the dissolution of gold. From calculations of electrode potentials in cyanide solutions, they concluded that gold metal can, in fact, only displace the ions of these four metals.

To explain the accelerating effect of these metals on gold dissolution, they suggested that it was due to alterations of the surface character of gold by gold alloying with the displaced metals. Kameda (1949) proposed a similar explanation for the accelerating effect of lead salts.

The following metallic cations, when present in solution, may have a retarding effect:

Fe^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Ca^{2+} and Ba^{2+}

[Beyers (1936), Plaksin and Sulova (1936), Plaksin and Suvorovskii (1938) and Kameda (1949).]

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Suvorovskii (1938) and Kameda (1949).]

Contrary to the accelerating effect of Pb^{2+}, when present in small

amounts, Beck and Gartell (1935), Beyers (1936) and Thompson (1947) also reported a retarding effect of Pb^{2+} when present in larger amounts. Sulfide ions also have a retarding effect on the rate [Julian and Smart (1921), Kameda (1949) and Fink and Putnam (1950)]. It was also found that certain flotation agents, such as xanthate ions, which are sometimes used to concentrate the sulfide with which gold is associated, decrease the rate of dissolution.

Many explanations or reasons for this retarding effect of ions on gold dissolution have been proposed by various investigators and are given here as summarized by Habashi (1967).

1. Consumption of oxygen from solution.
Oxygen is an essential reagent in the dissolution reaction and there-fore, any side reaction in which the cyanide solution is deprived of its oxygen content, will lead to a decrease in the rate of dissolu-tion. An example is pyrrhotite (FeS), which decomposes to ferrous hydroxide, which is then easily oxidized by oxygen to ferric hydro-xide. The sulfide ions, that come in solution due to this decompo-sision, can be oxidized to thio-sulfate and polysulfide and again, oxygen is used.

2. Consumption of free cyanide from solution.
Due to the decomposition and dissolution of metal minerals, metal ions are liberated in the solution. These ions are great cyanide consu-mers, because they form several cyanide complexes in cyanide solu-tions. Sulfide ions liberated in solution, also react with cyanide ions to form thio-cyanate. Zablotskaya (1955) also reported cyanide losses, due to adsorption of cyanide ions on gangue materials like quartz, alumino-silicates or other silicates.

3. Film formation on the surface of the metal.
It is known that sulfide ions, present in concentrations as low as 0,5 ppm, retards the dissolution. As this cannot be accounted for by the depletion of the reagents, because it is too small, it is believed that an insoluble aurous sulfide film is formed on the gold, which protects it from further dissolution.

Kudryk and Kellogg (1954) conducted some electrochemical experiments to investigate the retarding effect of small amounts of sulfide ions. They came to the conclusion that the trace sulfides poisons the gold surface towards the cathodic reduction of oxygen, but does not affect the anodic reaction.

As mentioned in section 2.1.6, Kameda (1949) suggested that the retarding effect of Ca^{2+} at high alkalinity, is due to the formation of calcium peroxide (CaO_2). Although his explanation was not entirely correct, he was definitely on the right track. Deitz and Halpern (1953) confirmed the formation of a CaO_2 layer on the gold surface in high alkaline $Ca(CN)_2$ solutions by means of X-ray diffraction analysis. This CaO_2 layer probably prevents the reaction of gold with cyanide. They found the same behaviour for Ba^{2+}, which explains why high alkaline $Ba(OH)_2$ cyanide solutions also have a retarding effect on the dissolution rate.

Insoluble cyanides may also precipitate on the gold surface and slow the reaction down. Thompson (1947) attributed the retarding effect of Pb^{2+}, when present in high concentrations, to an insoluble film of $Pb(CN)_2$, deposited on the gold surface.

The retarding effect of xanthate, is probably due to the formation of an insoluble gold xanthate film, formed on the gold surface. Kameda (1949) reported that the gold surface turned reddish when xanthate ions were present in the solution, which certainly suggests the formation of a gold xanthate film. Barbin (1961) confirmed this suggestion by using potassium xanthate marked with S^{35}.

This brings us to the end of the pure chemical studies. In the next section the electrochemical studies are discussed.

2.2 Electrochemical studies

As has been said, it is today generally accepted that the mechanism for the dissolution of gold in cyanide solutions is electrochemical in nature. The dissolution of gold can be explained by the electrolytic theory of corrosion, according to which the metal will dissolve from

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