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An electrochemical model for the leaching kinetics of gold ore in cyanide solutions

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the anodic areas of the corroding surface. The most acceptable anodic and cathodic reactions are:

$$\text{Anodic: } 4\ Au + 8\ CN^- \rightleftharpoons 4\ Au(CN)_2^- + 4\ e^- \quad ...[14]$$

$$\text{Cathodic: } O_2 + 2\ H_2O + 2\ e^- \rightleftharpoons H_2O_2 + 2\ OH^- \text{ mainly} \quad ...[15]$$

$$2\ H_2O_2 + 2\ e^- \rightleftharpoons 2\ OH^- \text{ minor} \quad ...[16]$$

Electrochemical studies are usually conducted in such a way, that the anodic and cathodic reactions can be studied separately. This is done, by studying the change in potential-current density characteristics of the gold electrode in two separate experiments, namely:

1) Gold electrode in alkaline cyanide solution; oxygen being excluded from the system.

2) Gold electrode in alkaline solution saturated with O_2 in the absence of cyanide ions.

Habashi (1967) however warns that the results of such tests should be interpreted with care, as the application of external emf to cause dissolution, does not correspond to actual cyanidation practice. One example given by Habashi (1967), is that under these conditions, oxygen is reduced to OH^- and not to H_2O_2, as in practice. Probably this is one of the reasons for the confusion in the literature, surrounding the choice of the applicable cathodic reaction.

Once again, all the electrochemical studies referred to in this report, used pure gold and not gold in a natural ore. Some of the more thorough electrochemical studies available, are those of Kudryk et al and Cathro and it is mostly their work that are reported on in this section.

2.2.1 The cathodic reaction

Kudryk and Kellogg (1954) did some extensive electrochemical experiments, determining the cathodic reduction curve for oxygen on a gold

surface in the absence of cyanide. According to Kudryk et al, the only cathodic reaction of importance is:

$$O_2 + 2\ H_2O + 4e^- \rightleftharpoons 4\ OH^- \quad ...[17]$$

They came to this conclusion because they detected no H_2O_2. Possible reasons why they failed to detect any hydrogen peroxide were discussed in section 2.1.7.

They found that the cathodic current (i_c) increased linearly as the surface potential (E_c) was decreased, until a maximum current was reached. After that, the current stayed constant as the potential was decreased further. See figure 2.6.

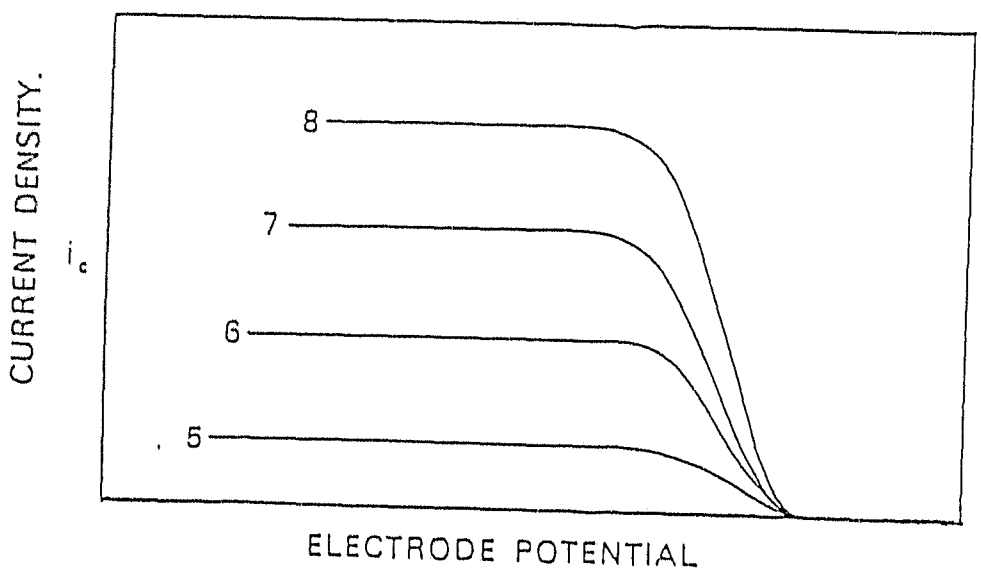

Figure 2.6: Cathodic polarization of gold in cyanide-free oxygen-containing solutions. Oxygen concentration increases in the order 5, 6, 7, 8.

This form of polarization curve is characteristic of a process which becomes diffusion limited. They concluded that the horizontal por-

tions of the polarization curves represent the maximum rate of diffusion of oxygen to the gold surface and substantiated it by the following observations:

(1) The height of the horizontal part of the polarization curves, at constant temperature and agitation speed, was found to be directly proportional to the partial pressure of oxygen over the solution.
(2) At constant oxygen pressure and constant temperature, the height of the wave increased linearly with increased speed of agitation.
(3) At constant oxygen pressure and constant agitation speed, the height of the wave increased about 2.5 % per $1^{o}C$ rise in temperature.

Cathro and Koch (1964) also conducted some very accurate electrochemical experiments. By combining the electrochemical measurements with weight loss measurements of a corroding gold disc electrode, they were able to determine the polarization curve of oxygen in the presence of cyanide ions. They divided the reduction of oxygen into two steps as given by equations 15 and 16.

Their work showed that cyanide does have an influence on the cathodic polarization curve of oxygen, in that cyanide poisons the gold surface, resulting in a separation of reactions 15 and 16. The presence of cyanide shifts the reduction curve of peroxide to much lower potentials, and that probably explains why oxygen is mostly reduced to peroxide only, in the dissolution reaction. They found the form of the polarization curve for oxygen reduction to be similar to that found by Kudryk et al.

2.2.2 The anodic reaction

Kudryk and Kellogg(1954) found exactly the same behaviour for the anodic current (i_a) with increasing potential (E_a), as for the cathodic current. They observed that the anodic current reached a maximum as the potential was increased, after which it became independent of the potential. (See figure 2.7). They concluded that the horizontal sections of these curves, resulted from the maximum rate of diffusion of cyanide to the gold electrode and substantiated it by the following observations.

(1) The height of the wave, at constant temperature and agitation speed, was found to be directly proportional to the cyanide concentration in the solution.
(2) The height of the wave, at constant cyanide concentration and constant temperature, increased linearly with increasing speed of agitation
(3) The height of the wave, at constant cyanide concentration and constant speed of agitation, increased about 2.5 % per 1°C rise in temperature (which is characteristic of a diffusion controlled process).

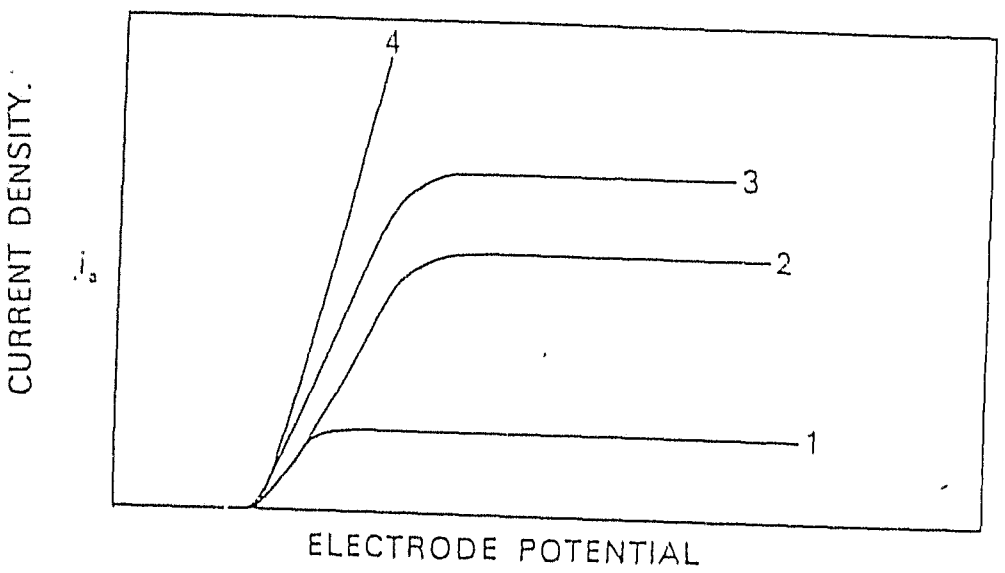

Figure 2.7: Anodic polarization of gold in deoxygenated cyanide solution. Polarization curves for a gold electrode without passivation (Kudryk and Kellogg (1954)). Cyanide concentration increases 1, 2, 3, 4.

Cathro and Koch (1964) found a similar relationship between the anodic current and potential at potentials, more negative than ± -0.6V (vs S.C.E.). However, they observed a sharp decrease in the current as the potential was increased to more positive potentials, and found the

anodic polarization curve to be much more complex than Kudryk et al (see figure 2.8). This form of polarization curve is characteristic of metals where the surface becomes passive at a certain potential.

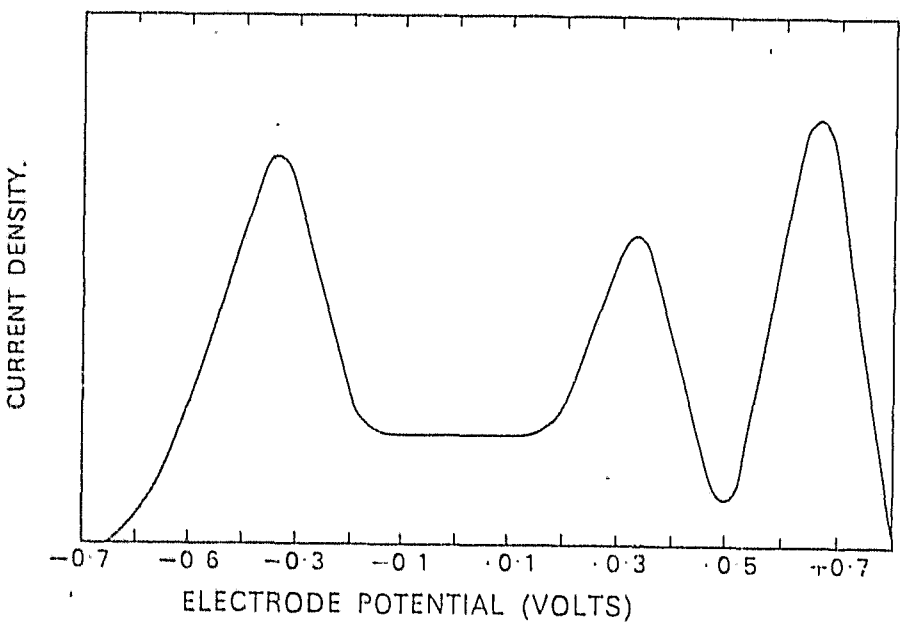

Figure 2.8: Polarization curves for a gold electrode showing passivation in cyanide solutions (Cathro and Koch(1964)).

They found the potential at the maximum current, to be a function of the pH and concluded that passivation of the gold surface at potentials more positive than ± -0.6V is due to the formation of a "basic cyanide' film (i.e. OH^- and CN^- groups must both be adsorbed on the surface). They also found that impurities present in extremely low concentrations, can prevent the formation of this film on the gold surface and thus can prevent passivation of the gold surface. They attributed the failure of Kudryk et al to observe passivation of the gold surface, to this fact.

As can be seen in figure 2.8, the gold surface becomes active again at

potentials between +0.2 and +0.3V, but because this is irrelevant to the dissolution process of gold in cyanide, it will not be discussed any further in this report.

Fink and Putnam (1950) reported many years before Cathro's work, that the presence of lead, thallium, mercury or bismuth has an accelerating effect on the dissollution of gold. Cathro and Koch (1964) examined in some detail the effect of these metals on the anodic polarization curve. The effect of thallium on the polarization curve is shown in figure 2.9. As can be seen, the presence of only a small amount of thallium, eliminates passivation of the gold surface almost completely. One can therefore expect that thallium will have an accelerating effect on the dissolution of gold.

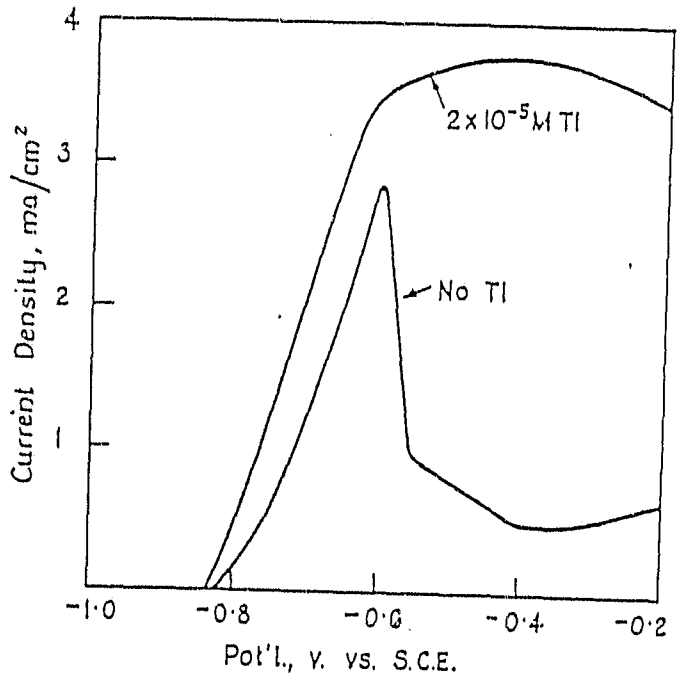

Figure 2.9: The effect of the presence of a small amount of thallium on the anodic polarization curve of gold. (Cathro et al (1964)

2.2.3 The rate controlling mechanism

It is known from the theory of corrosion, that a metal will corrode at a certain potential where the anodic and cathodic currents are balanced. Therefore, by combining the anodic and cathodic polarization curves the corrosion current and potential are obtained at the point where the two curves intersect.

Kudryk and Kellogg (1954) combined their determined polarization curves as shown in figure 2.10. They reached the conclusion that the dissolution rate is controlled by the rate of diffusion of either oxygen (curves 4 and 5 on figure 2.10) or cyanide (curves 1,2,3 and 5) to the gold surface. From the combination of the polarization curves, it appears that at low cyanide concentration, the magnitude of the dissolution rate depends on the maximum diffusion current of cyanide. As the concentration of cyanide is increased ($[CN^-]$ - 1,2,3 in figure 2.10) the diffusion current increases until the stage is reached where the diffusion current of cyanide is greater than that of oxygen. At this point, the maximum rate of diffusion of oxygen becomes the rate controlling step. Kudryk and Kellogg's electrochemical studies, therefore, provided some explanation for the experimental observations made in research work on the effects of oxygen and cyanide on the dissolution rate of gold.

Kudryk and Kellogg could explain most of the experimental observations, made by various researchers (see section 2.1). There were a few, however, which they could not explain with their mass transfer theory. It was mentioned in section 2.1 that, amongst others, Mills (1951) and Kakovskii et al (1960) observed that under certain conditions, the dissolution rate increases only up to a point with increasing agitation, whereafter it starts to decrease. Under similar circumstances, it was found that with increasing oxygen concentration, the rate at first rises proportionally and then starts rising significantly slower, or even starts to decrease. Furthermore, Kakovskii (1960) obtained two different values for the energy of activation for the dissolution reaction, under low and high agitation speeds respectively. Kakovskii concluded from these observations that the dissolution process is no longer controlled by mass transfer, but that it

becomes chemical reaction controlled at high agitation speeds or high oxygen concentrations.

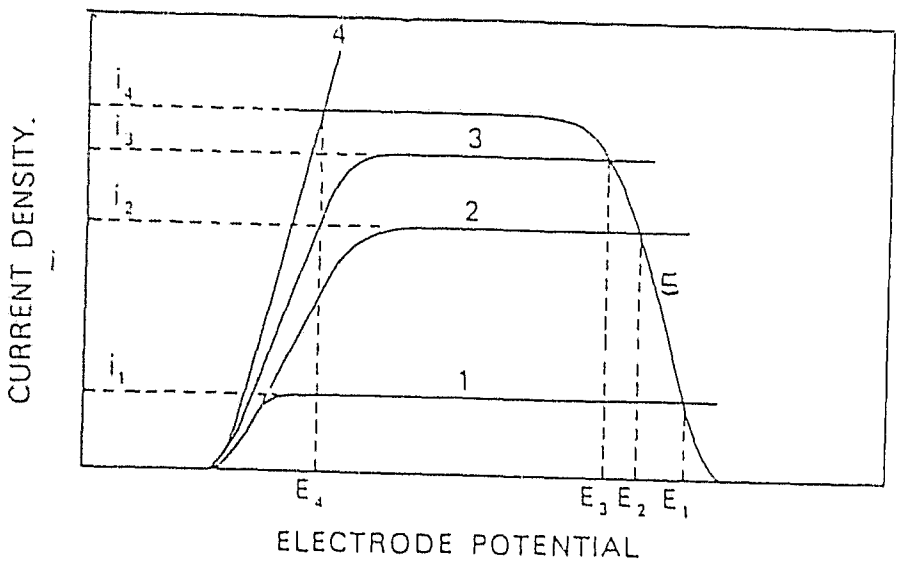

Figure 2.10: Combination of the anodic and cathodic polarization curves. The [CN^-] increases 1, 2, 3, 4. ($E_1 i_1$) represents the dissolution potential and current for the case where [CN^-] = 1, etc.

Cathro and Koch succeeded in explaining all these observations by combining their more accurate anodic and cathodic polarization curves, as showed in figure 2.11. It can be seen in figure 2.11 that, at low oxygen concentration, the cathodic polarization curve (line 2) intersects the anodic curve (line 1) at lower potentials, in the so-called active region. The rate is then controlled by diffusion of oxygen. On the other hand, at higher oxygen concentrations, the cathodic curve (line 3 and 4) intersects the anodic curve in the passive region. Now the rate is controlled by the chemical reaction and it is obvious that, the rate can actually decrease with increasing oxygen concentration.

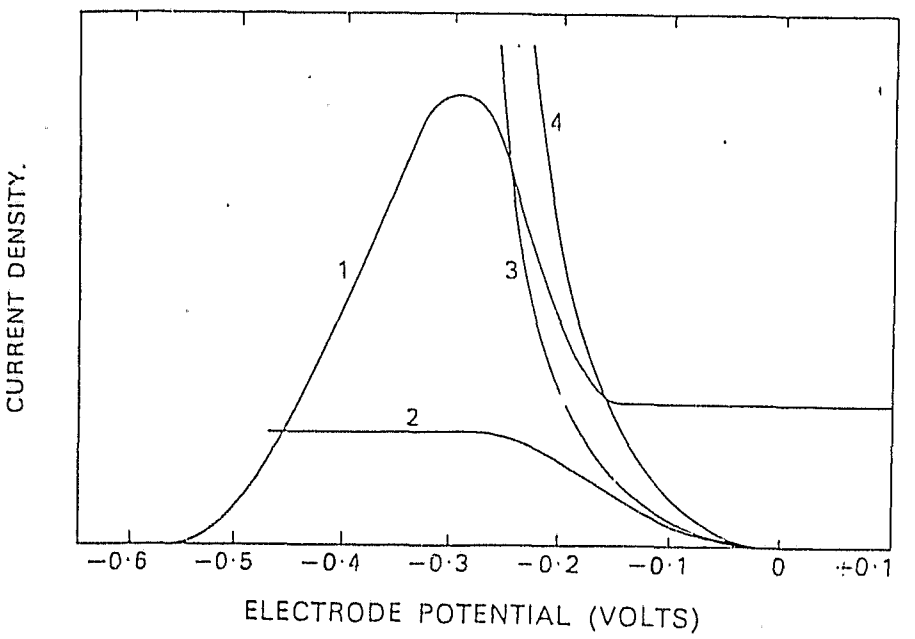

Figure 2.11: Combination of polarization curves, showing the effect of passivation on the dissolution of the gold in cyanide solutions under the influence of oxygen.
1 = anodic polarization curve of gold in cyanide solution. (Cathro)
2, 3, 4 = cathodic polarization curves of gold in solutions containing increasing concentrations of oxygen.

Cathro (1963) found the change-over point from oxygen diffusion controlled to reaction controlled occurs at ± 4 mg/l O_2 for gold spheres and at ± 16 mg/l O_2 for a gold disc. He gave a tentative explanation for this great difference in terms of the thickness of the diffusion layer. He proposed that the rate of oxygen diffusion to the spheres is ± 4 times as fast as that to the disc and hence the change-over point for spheres occurs at about one quarter of the oxygen concentra-

tion at which it occurs in the case of the disc.

As has been said before, these results were obtained from experiments done with pure gold. The question is now: what is the situation in practice? Finkelstein (1966) concluded that passivation is not merely a laboratory curiosity and that it can in fact reduce the efficiency of industrial operations. Cathro (1963) conducted experiments on calcines from two mines in Australia and showed that gold in natural ores can in fact become passive at sufficiently high oxygen concentration (Higher than 4.7 mg/l O_2). He showed how thallium can improve the efficiency of the leaching process under high O_2 concentrations, and attributed it to the fact that thallium prevents passivation of the gold surface.

2.3 Proposed leaching rate expressions in the literature

2.3.1 Habashi (1966)

Habashi's rate expression is based on the work done by Kudryk and Kellogg. He accepted that the dissolution reaction is mass transfer controlled and, by applying Fick's law for steady state diffusion, he derived the following rate expression.

$$\text{Rate} = \frac{2.A.D_{CN^-}.D_{O_2}.[CN^-].[O_2]}{\delta.(D_{CN^-}.[CN^-] + 4.D_{O_2}.[O_2])} \quad \ldots[18]$$

where: A = Total area of gold, cm^2

D_{CN^-} and D_{O_2} = Diffusion coefficients of cyanide and dissolved oxygen, cm^2sec^{-1}

$[CN^-]$ and $[O_2]$ = The concentration of CN^- and O_2 in the bulk of the solution, mol/ml

δ = The thickness of the boundary layer, cm

He showed that at low CN^- concentrations, the first term in the denominator may be neglected in comparison with the second, so that the equation simplifies to:

$$\text{Rate} = \tfrac{1}{2}\frac{A.D_{CN^-}}{\delta}[CN^-] = k_1[CN^-] \quad ...[19]$$

Similarly, when the O_2 concentration is very low, the second term in the denominator may be neglected, giving:

$$\text{Rate} = 2\frac{A.D_{O_2}}{\delta}[O_2] = k_2[O_2] \quad ...[20]$$

These results comply with experimental findings, as given in sections 2.1.2 and 2.1.4. This model will, of course, only apply to a system which is mass transfer controlled. One problem in applying this model to the leaching of gold from natural ores is that, it is very difficult to determine the diffusion coefficients and boundary layer thickness in such a system. Furthermore, these variables will probably all be a function of the percentage extraction of gold from the ore, which will make it practically impossible to use the equation.

2.3.2 Brittan's (1975) rate expression

Brittan's expression was derived particularly for low grade ores. Brittan appreciated the complexity of the dissolution of gold from a natural ore and took into account factors such as, the fact that some of the gold is locked up while other is coated to varying degrees by hydrated iron oxides, and that these inhibit access by cyanide. He realized that the expression would become too complex if one tried to account for each rate limiting effect separately. He therefore postulated a variable activation energy model.

In this model, all the rate limiting effects are lumped together as an Arrhenius activation energy barrier, which is related to the conversion. It is accepted that during the leaching process, the more accessible metal is leached away first, leaving behind progressively more refractory material. The model analogue of this is an increase in the activation energy during leaching, hence, the reaction rate

"constant" decreases as conversion increases.

He postulated the following expression:

The rate constant, $k = A.e^{-E/RT} = A.\exp[-E_0(1 - \alpha.[C_m])/RT]$ ...[21]

where $[C_m]$ - residual metal concentration
A - Arrhenius constant
E_0 - activation energy when $[C_m] \rightarrow 0$
R - ideal gas constant
T - temperature

This resulted in the following rate expression after simplification:

$$-\frac{d\,[C_{Au}]}{d\,t} = ([C_{Au}] - [C_{Au}]^*)\,\exp(b_1([C_{Au}]-[C_{Au}]^*)-b_2) \quad \ldots[22]$$

where $[C_{Au}]^*$ - refractory gold concentration

This expression can be used to model experimental data of leaching experiments, but it is very difficult to use this model in any design procedures.

2.3.3 Mintek expression (Stange (1986))

The Council for Mineral Technology found that the data of leaching experiments could be fitted with an empirical equation of the following form:

$$\frac{d\,C_t}{d\,t} = -k_p(C_t - C^*)^2 \quad \ldots[23]$$

where: k_p - a constant
C^* - refractory gold concentration in ore
C_t - residual gold concentration at time t

The Anglo American Research Laboratories (Stange (1986)) also use an empirical correlation of the following form:

$$\frac{d\,C_t}{d\,t} = \frac{-a.C_0}{(a + bt)^2} \quad \ldots[24]$$

where: C_0 = the initial gold concentration

Both these correlations give accurate fits for leaching data but again, because they are empirical, they cannot in general be used for design or predictive purposes.

2.3.4 Loveday, Robinson and Paynter (1984)

Loveday et al (1984) also developed a model, specifically for the leaching of low grade ores. The assumption was made that the rate of dissolution of all the individual sites could be described by zero-order rate expressions and that there was a definite distribution of these rates. The Schuhmann distribution function was used to describe the way in which the initial zero-order rate constants are distributed. They proposed the following rate expression:

$$C_t = C_0\left\{[1-C^*]\left[1 - \frac{\Phi}{\Phi + 1}(K_{max}t)\right] + C^*\right\} \text{ for } t < K_{max}^{-1} \quad \ldots[25a]$$

$$C_t = C_0\left\{[1-C^*](\Phi + 1)^{-1}(K_{max}t)^{-\Phi} + C^*\right\} \text{ for } t > K_{max}^{-1} \quad \ldots[25b]$$

where: C_0 = initial gold concentration
C_t = concentration of gold residue at time t
t = leaching time
C^* = refractory gold
Φ = Shape factor
K_{max} = Arhennius type of expression, accounting for temperature effects.

The parameter K_{max} can be represented by an Arhennius type of ex-

pression, thus accounting for temperature effects. In a constant temperature leach, K_{max} can be treated as a simple parameter.

Again this expression is semi-empirical and therefore of limited use in design procedures.

The conclusions drawn from the literature survey can be summarized as follows:

It appears that, although there has been considerable interest in the cyanidation process of gold, the work of the researchers has led, in many instances, to contradictory results and conclusions. The effects of various variables are documented very thoroughly but unfortunately most researchers have not produced mathematical models that are widely applicable but were content with presenting single independent variable effects.

Furthermore, it appears that, despite all the research work that has been done over the years, to this day very little real fundamental knowledge is available on the leaching of natural gold in gold bearing ore. It is not clear to what extent the findings, made on pure gold systems, apply to the gold bearing ore system. Although the rate limiting mechanisms at work in ideal systems are well understood, it is not clear whether these are also valid for ores.

The overall conclusion that has to be drawn from the literature study is that the answers to the problems of improving the efficiency of gold leaching processes are incomplete.

3 INTRODUCTION TO THE MODELLING APPROACH ADOPTED

It is generally accepted that gold dissolves by means of an electrochemical mechanism. The various electrochemical studies on the dissolution of gold were discussed in section 2.2. In those studies, gold dissolution was treated as a corrosion process. It was shown in section 2.2.3 how the polarization curves of the anodic and cathodic reactions determine the corrosion rate and thus the dissolution rate. At the corrosion potential the anodic and cathodic areas on the corroding metal are approximately at the same potential and the anodic and cathodic currents ought to be the same.

The well known Tafel equation gives the relationship between the anodic surface potential and the anodic current. Therefore, under conditions where the Tafel equation is applicable, one is able to determine the corrosion current, if the surface potential of the metal is known. It might therefore be possible to model the leaching kinetics of gold by using the potential of the gold surface and applying electrochemical theory.

3.1 Modelling of the leaching kinetics of base-metal sulphides

An electrochemical study into the dissolution of base-metal sulphides led to a very successful modelling of the process (See Dry (1984)). That project has had a great influence on this project and therefore a short review of some of Dry's findings are given here. In that study a leaching rate expression was derived from the Tafel equation. This expression had only an area term and the surface potential of the mineral as variables. The rate expression was as follows:

$$\text{rate} = K_1 a.\exp(k_2 E) \quad ...[26]$$

where: E = surface potential
a = surface area of the mineral

One problem experienced was to measure the surface potential accurately without any galvanic interaction between the various minerals. It was however found that in the case of the leaching of base-metal

sulphides in acid solutions, the solution redox potential gave a good approximation of the mineral surface potential. This redox potential was set by the Fe^{2+}/Fe^{3+} couple. It is shown in figure 3.1 why this approximation holds in this particular case.

As can be seen in figure 3.1 the anodic current, due to the leaching of the minerals, is much smaller than the exchange current between the Fe^{2+}/Fe^{3+} couple. Hence, the difference between the surface potential of the mineral and the solution redox potential is also quite small. This successful modelling of the leaching kinetics of base metal sulphides served as inspiration to try the same method of modelling in the leaching of gold.

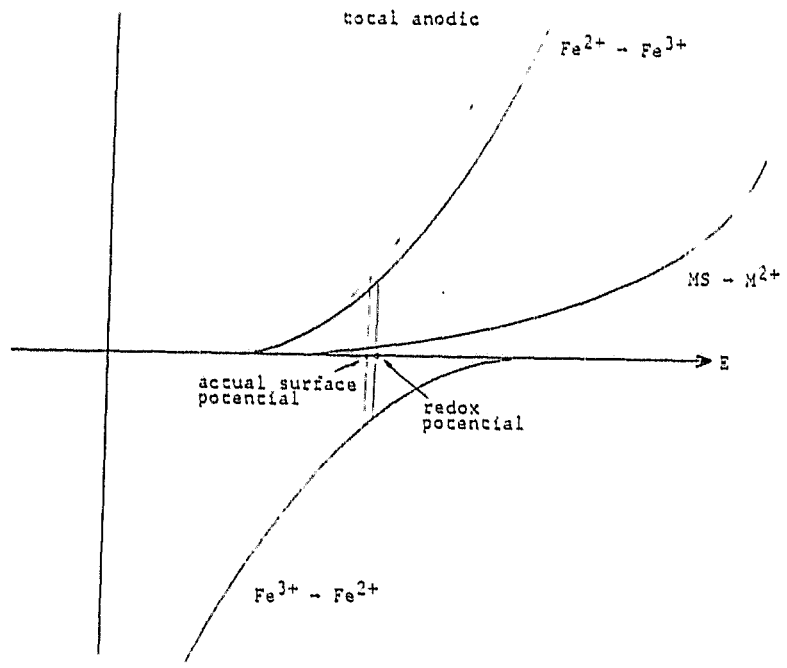

Figure 3.1: The appropriate polarization curves in the dissolution of base metal sulphides in acid solutions.

3.2 Proposed model for gold leaching

In accordance with the above mentioned project, the same general form of an electrochemical rate expression was proposed as a probable rate expression for the leaching of gold. The assumption was made, that the gold surface area is directly proportional to the leachable gold left in the solid; an assumption which usually holds fairly well in the case of low grade ores. Hence, the proposed rate expression had the following form: (See Appendix D for more details on the derivation of this equation)

$$\frac{d[Au]_s}{d\,t} = -k_1([Au]_s - [Au]_s^{\infty})\exp(k_2 E) \quad \ldots[27]$$

where: $[Au]_s$ - gold concentration in the solids
$[Au]_s^{\infty}$ - refractory gold concentration
E - gold surface potential

Difficulty was foreseen in measuring the gold surface potential accurately because gold ore is non-conducting. Although the surface potential could be measured with a gold electrode, it is uncertain how applicable this method is. It was also decided to measure the solution redox potential in the hope that it would be possible to describe the solution parameter (see Appendix D) in this way. It must, however, be stressed that in the case of gold leaching, no theoretical grounds exists on the basis of which the solution redox potential can be taken as an approximation for the gold surface potential. It was only hoped that a relationship between the two could be established.

In the next chapter, the experimental procedures used in this project are discussed. In the subsequent chapters the results are given and discussed and certain conclusions are drawn.

4 EXPERIMENTAL PROCEDURES

The experimental work can be divided into two parts namely, the leaching experiments and the measuring of potentials in artificial solutions. The leaching experiments were planned specifically to collect data to test the applicability of an electrochemical model. The second batch of experiments was planned, to investigate which factors influenced the measured redox potential.

4.1 Description of the gold bearing pulp used in the experiments

Pulp for the leaching experiments was obtained from various industrial plants. A few experiments were done with pulp obtained from Vaal Reef's no 9 shaft, while all the remaining experiments were done with pulp from Kloof mine. The pulp was collected from the thickener underflow of the plant, prior to the cyanide being added. Lime had already been added at this point of the process. The physical properties of the leach solutions used, are given in table 4.1.

Table 4.1 Physical properties of the leach solutions

Physical property	Vaal Reef	Kloof
Grade (av) (g/t)	5.08	11.2
Solid/liquid-ratio	1:1	1.33:1
Density (g/l)	1500	1544
pH	10.7	11.2

4.2 Leaching experiments

4.2.1 Equipment

The batch leaching apparatus available in the department of Chemical Engineering, was found to be quite adequate for use in this project. A schematic representation of the apparatus is shown in figure 4.1. It consists of a fibre glass stirred tank reactor, used as a leaching

vessel. The reactor is open to the atmosphere. Inside the reactor is a stirrer for agitation. Aeration is accomplished through a cylindrical air sparger, fixed to the bottom centre of the reactor, below the paddle. The reactor has a volumetric size of 17 litres. The major dimensions of the reactor are given in a detailed diagram of the reactor in figure 4.2, which were also used by King and Greeff (1986) in their report.

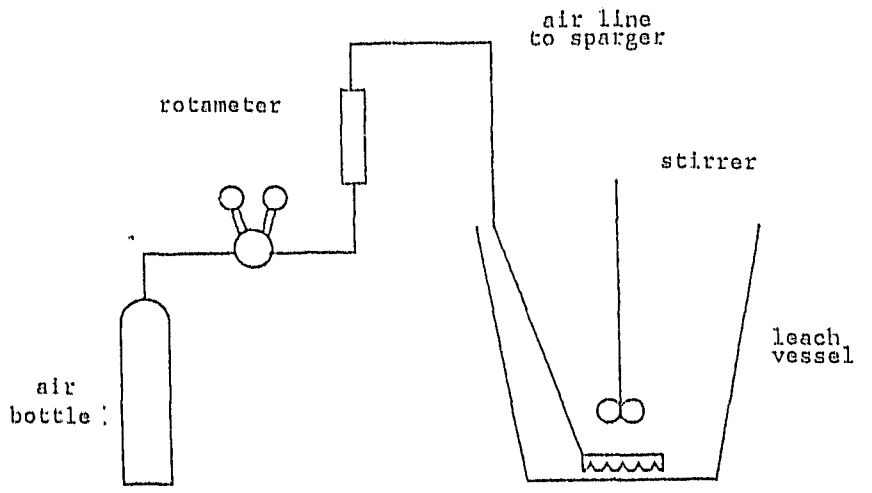

Figure 4.1: Schematic representation of experimental apparatus.

Inside the reactor, the following electrodes were installed: a pH probe, a platinum, a pure gold, a gold-silver alloy electrode and a calomel electrode. The potentials of all the electrodes were measured against the calomel electrode. The calomel electrode was connected to the solution through a KCl salt bridge to protect the calomel electrode from getting poisoned by the cyanide ions in solution. Metrohm 632 pH meters were used in the pH and potential measurements.

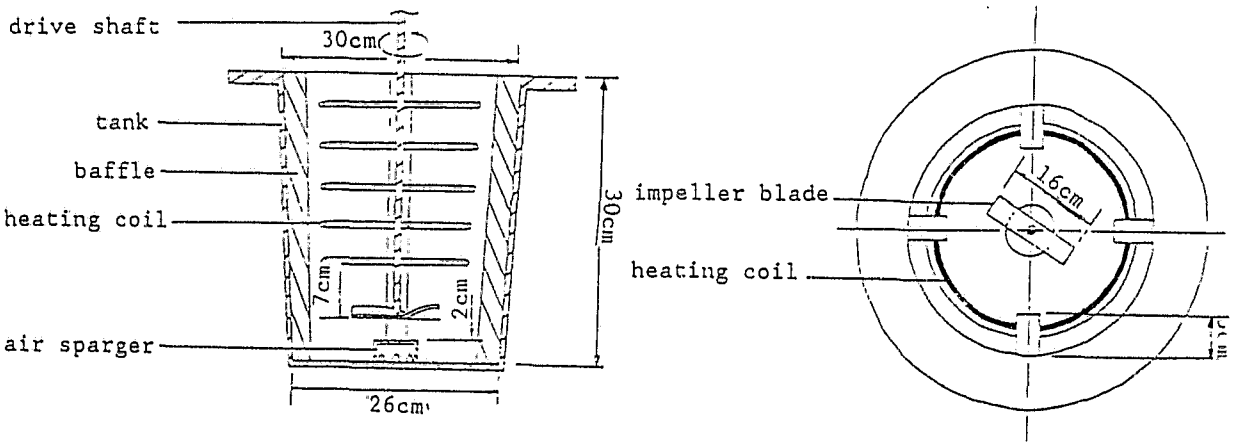

Figure 4.2: Detailed drawing of stirred tank reactor showing major dimensions.

4.2.2 Procedures

15 litres of pulp was used in each experiment. Before an experiment was started, the pulp was first aerated for 20 - 30 minutes. The experiment was then started by adding the cyanide. King and Greeff (1986) checked the degree of mixing and found the density gradient of the pulp, from the top to the bottom of the leaching tank, to be negligible.

Samples of about 50 ml were taken at gradually increasing time intervals and immediately filtered and washed through a pressure filter. The liquid portion was kept and analysed for gold and cyanide. In some instances the solid portion was also kept for analysis for gold. Most of the experiments were run for 24 hours, except where it was regarded as unnecessary.

Every time a sample was taken, potential measurements were made and the pH was measured. In experiments numbers 10 to 14 the three electrode potentials were measured on the same voltmeter by inter changing the input plugs. This, however, led to non-reproducible results. In

experiments 15 to 19, the three electrode potentials were measured with three different voltmeters and in addition, the potentials were recorded continuously on a pen recorder. This led to more reproducible results.

The conditions used in each experiment are summarized in table 4.2. The first three experiments were done with pulp from Vaal Reefs to test the reproducibility of the redox potential measurements. Experiment 4, which was also done with Vaal Reefs pulp, tested the effect of a higher O_2 concentration on the leaching kinetics and redox potential. Experiments 5 and 6 were done under exactly the same conditions as experiment 4, but this time with pulp from Kloof mine. Experiments 5 and 6 were done to observe the differences in measurements between the types of pulps and also, to determine the reproducibility of experiments done with pulp from Kloof.

The next three experiments, nos 7, 8 and 9, were done with different initial cyanide concentrations to determine the effect of the cyanide concentration on the kinetics and potential measurements. The next few experiments, nos 10 to 14, were done to determine the reproducibility of the gold and gold-silver potential measurements. The results from these experiments were, however, found to be non-reproducible for the reasons as explained above. Experiments no 10 to 14 were repeated in experiments 15 to 19, while using the more accurate measuring system as described above.

Experiment 20 was done with nitrogen as sparging medium to see what effect O_2 had on the potentials. Experiment 21 was done with Kloof pulp of which the liquid portion had been replaced with distilled water. Experiment 22 was done to investigate whether the potential was influenced by something that occurred in the solids or in the liquid. Experiment 23 was done with only distilled water.

Experiments 24 and 25 were done at different speeds of agitation to investigate the possibility that the rate is diffusion controlled. Finally experiment 26 was done with the addition of a small amount of thallium to investigate the possibility that the rate is chemical reaction controlled.

Table 4.2: Conditions used in each experiment

Exp no	Vol pulp(l)	Aera-tion	Stirrer speed(ppm)	NaCN added (g)	Pulp	Remark
1	15	air	600	7.31	VR	
2	15	air	600	7.31	VR	
3	15	air	600	7.31	VR	
4	15	O_2	600	7.31	VR	
5	15	O_2	600	7.31	K	
6	15	O_2	600	7.31	K	
7	15	air	600	4.50	K	Test effect of
8	15	air	600	2.25	K	cyanide conc.
9	15	air	600	1.13	K	
10	15	air	600	4.50	K	
11	15	air	600	4.50	K	Measure all three
12	15	air	600	4.50	K	potential on the
13	15	air	600	4.50	K	same meter
14	15	air	600	4.50	K	
15	15	air	600	4.50	K	
16	15	air	600	4.50	K	
17	15	air	600	4.50	K	Use pen recorder
18	15	air	600	4.50	K	
19	15	air	600	4.50	K	
20	15	N_2	600	4.50	K	Use nitrogen
21	15	air	600	4.50	K	
22	15	air	600	9.00	Liquid	Only liquid frac.
23	15	air	600	9.00	Water	Only dist. water
24	15	air	300	4.50	K	Test effect of
25	15	air	450	4.50	K	agitation speed
26	15	air	600	4.50	K	Add 0.24g TlCl

4.2.3 Analysis

As previously indicated, the samples taken during the leach experiments were filtered immediately. The liquid portions were kept in sealed specimen tubes while the solids were dried. Atomic absorption techniques were used to analyse the liquid samples for gold. The cyanide concentration was also determined in some instances by titration with $AgNO_3$ (the method is described by Kolthoff and Sandell (1952)).

The gold concentrations in the solids were determined by the Analyti-

cal Division at Mintek, using standard assay techniques.

4.3 Potential measurements in artificial solutions

These experiments were done to get a better understanding of what factors were influencing the solution redox potential. The objective was to establish a relationship between the solution redox potential and the overall leaching rate of the gold (or the gold concentration in solution). These experiments were done in a 600 ml glass beaker, using the same Pt electrode that was used before in the redox potential measurements. A magnetic stirrer was used for agitation.

The procedure was basically to make up a clear solution with a certain CN^- concentration and pH. Another substance was then added with a burette, while the Pt redox potential was measured, to see what effect this substance had on the potential. Because the Pt potential responded slowly to the addition of any substance, the potential was measured at various times after each addition of substance. The next quantity of substance was added only after the potential had stabilized. The conditions were kept as close as possible to those used in the leach experiments. Therefore, air was also bubbled through the solution all the time.

4.3.1 Conditions

Experiment no A1: This experiment was done to test the effect of CN^- concentration on the redox potential. The pH of 400 ml of distilled water was adjusted to ± 10, by the addition of sodiumhydroxide. The water had been saturated with air before the experiment was started. A NaCN solution, with a concentration of 0.6703 mol/l, was then added 1 ml at a time. After each addition, the potential was measured at 1 minute time intervals, until it had stabilized. After 5 ml of the cyanide solution had been added, the cyanide concentration in the beaker was about the same as the initial cyanide concentration used in most of the leach experiments.

Experiment A2: This experiment was done to test the effect of gold

concentration on the solution redox potential. A clear solution was made up, with the initial cyanide concentration close to the cyanide concentration used in the leaching experiments. Because a small amount of copper was found to be dissolved in the leach solution, a small amount of copper, in the form of $CuSO_4$, was also added to the solution in this experiment. The initial concentrations were as follows:

400 ml H_2O
pH ≈ 10
Cu ≈ 3.5 ppm
CN^- ≈ 0.0084 mol/l

After the solution had been saturated with air a solution of $KAu(CN)_2$ was added, 1 ml at a time. After each addition, the potential was measured. The concentration of the $KAu(CN)_2$ solution was 0.0025 mol/l.

Experiment A3: This experiment was done to investigate the effect of an increasing concentration of Cu in the solution. A clear solution was made up with a CN^- concentration of 0.0084 M and a pH of ± 10. A $CuSO_4$ solution of 0.00446 M was then added, 1 ml at a time. With each addition of $CuSO_4$, a proportionate amount of $KAu(CN)_2$ was added to simulate the same conditions as during the leach experiments. After the addition of 5 ml $CuSO_4$ and 10 ml $KAu(CN)_2$, the solution had the same gold and copper concentrations as the final solutions in most of the leach experiments. Again, after each addition, the redox potential was measured at 1 minute time intervals until it had stabilized.

Experiment A4: It was realized that in experiment A3, it was not only the Cu concentration which was changed with the addition of $CuSO_4$, but also the CN^- concentration. That is because the Cu^{++} ions form a complex with CN^- ions. Therefore, the changes observed in the potential measurements in experiment A3 could have been as a result of the effect of a decrease in the cyanide concentration. Hence, experiment A4 was conducted to investigate the effect of a decrease in CN^- concentration on the redox potential. The cyanide concentration was reduced by the addition of $AgNO_3$. Ag^+ ions also form a complex

with CN^- ions. A clear solution was made up with a cyanide concentration of 0.75 mmol/l and a pH of ± 10.

After the potential had stabilized, silver nitrate (0.0282 M) was added, 1 ml at a time. After 5 ml $AgNO_3$ had been added, the free cyanide concentration had fallen to zero. The potential was measured after each addition, at 1 minute intervals, until it had stabilized.

The raw experimental results are given in appendix A. In the next chapter, these results will be discussed and the important observations will be highlighted.

5 RESULTS OF EXPERIMENTAL WORK

5.1 Leaching Experiments

The observations made in the leach experiments, are reported here. The deductions made from these results are reported in subsequent chapters.

5.1.1 Reproducibility

In the first three experiments, pulp from Vaal Reef's no. 9 shaft was used to test the reproducibility of the experimental procedures. Only the redox potential was measured with a Pt electrode in these three experiments. Figure 5.1 shows the leaching data obtained from these three experiments, plotted on the same graph. Figure 5.2 shows the redox potential measurements. The reproducibility of the measurements was reasonably satisfactory. The redox potential seemed to increase in much the same way as the gold concentration increased.

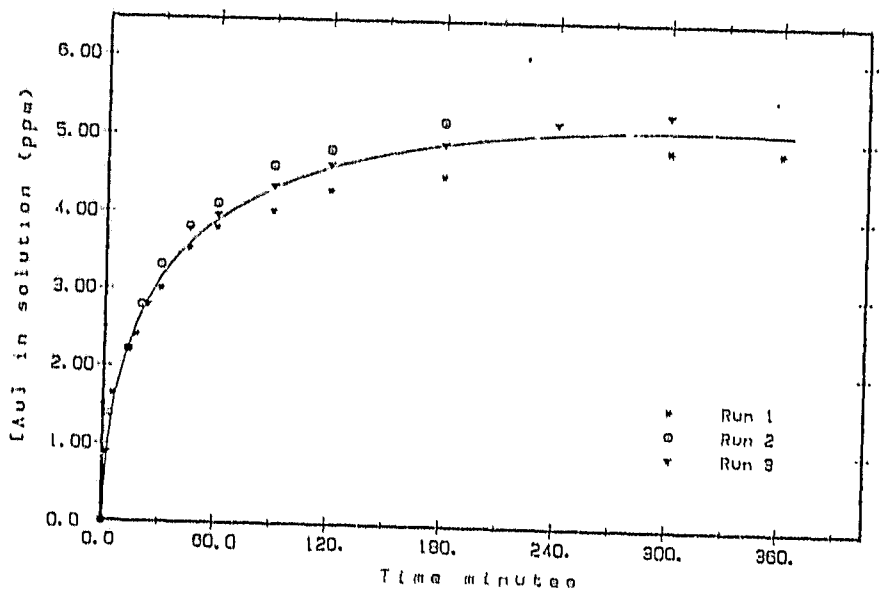

Figure 5.1: [Au] in solution vs. time for the first 3 experiments.

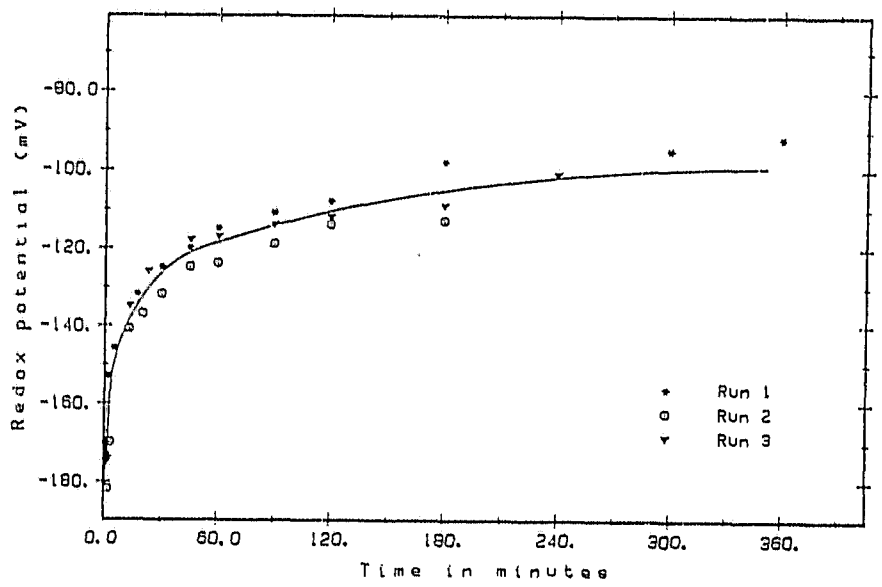

Figure 5.2: Solution redox potential vs. time for the first 3 experiments.

5.1.2 Effect of oxygen

Experiment 4 was also done with pulp from Vaal Reef, but in this experiment the pulp was aerated with oxygen. A much faster leaching rate resulted, due to the higher oxygen concentration as can be seen in figure 5.3, where experiments 1 and 4 are compared. The higher oxygen concentration also had a noticeable effect on the redox potential as can be seen in figure 5.4. Again there appears to be a connection between the redox potential and the gold concentration, because the redox potential seemed to increase in much the same way as the gold concentration.

Experiments 5 and 6 were done with pulp from Kloof under the same conditions as experiment 4. Figure 5.5 shows that the potential measurements in the two experiments followed the same trend. There was, however, a constant difference of ± 20 mV between the two curves.

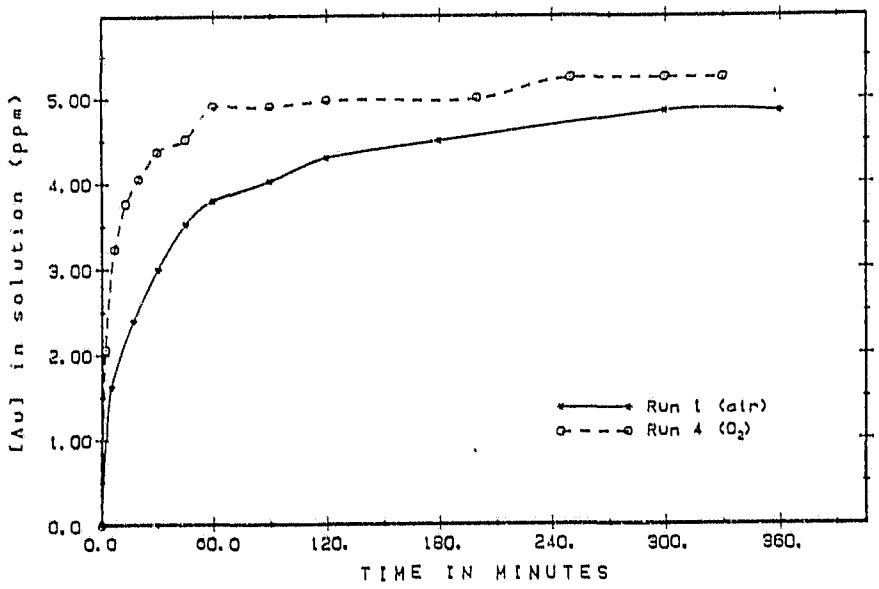

Figure 5.3: The dissolution curves of runs 1 and 4 to show the effect of a higher oxygen concentration on the leaching rate.

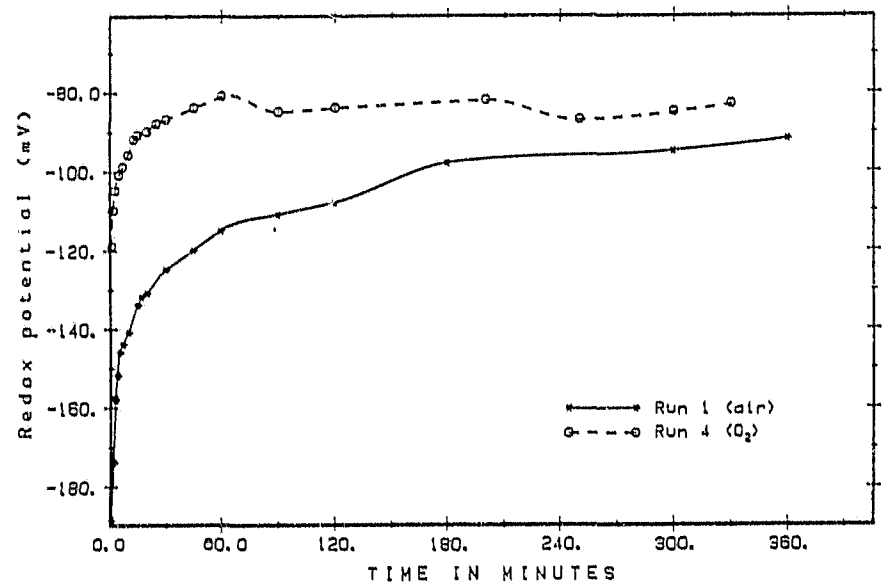

Figure 5.4: The redox potential measurements made in runs 1 and 4, to show the effect of a higher oxygen concentration on the solution redox potential.

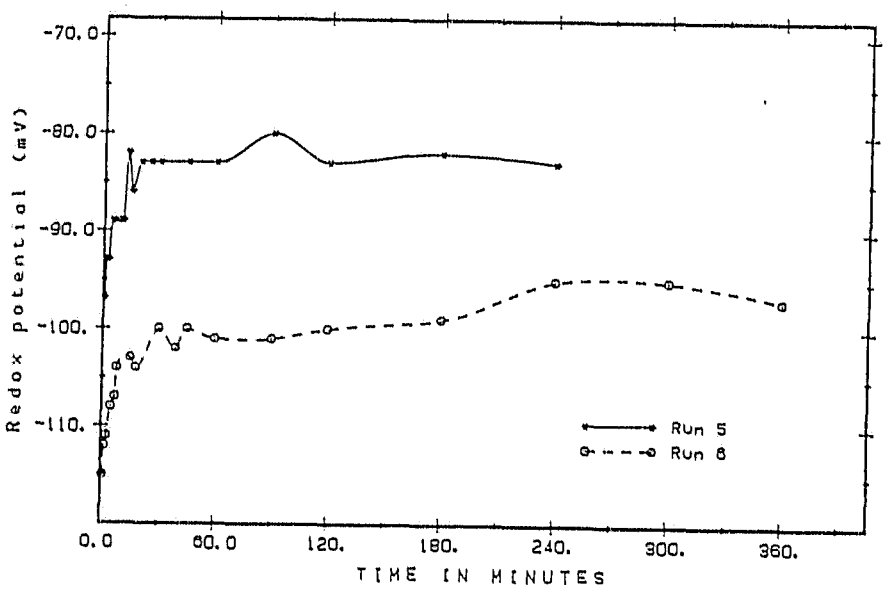

Figure 5.5: The redox potential measurements made in runs 5 and 6, to show the reproducibility of the redox potential measurement in pulp from Kloof and when the pulp was sparged with O_2.

5.1.3 Effect of cyanide concentration

Figure 5.6 shows the effect of different initial cyanide concentrations on the leaching rate. The cyanide concentration was decreased from run 7 to 9. From this figure it can be seen that the higher the cyanide concentration, the greater was the initial slope of the leaching curve. This means that a higher cyanide concentration resulted in a higher initial leaching rate. The overall leaching efficiency was, however, not affected by the cyanide concentration.

The cyanide concentration did not seem to effect the solution potential in any noticeable way, as can be seen in figure 5.7. On closer examination, however, it appears that a greater initial slope in the potential vs. time curve was obtained when the initial cyanide concentration was lower.

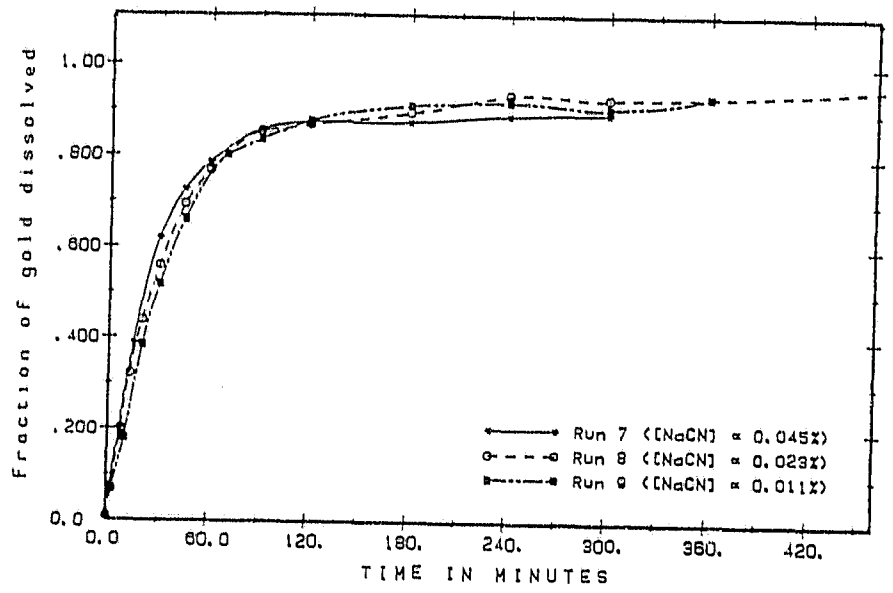

Figure 5.6: The dissolution curves for runs 7, 8 and 9, done with three different initial cyanide concentrations, to show the effect of the cyanide concentration on the leaching rate.

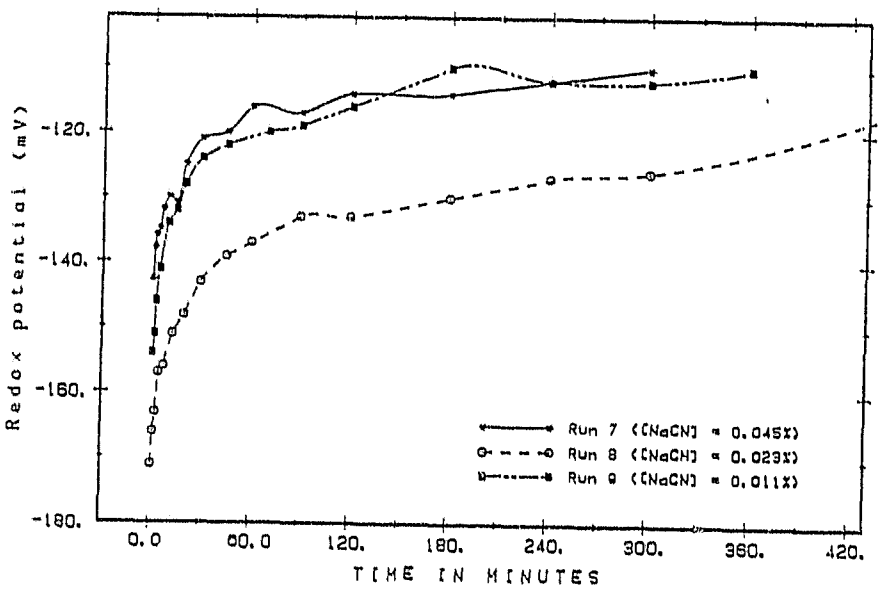

Figure 5.7: The redox potential measurements made in runs 7, 8 and 9, done with three different initial cyanide concentrations, to show the effect of the cyanide concentration on the redox potential.

Author Conradie P J
Name of thesis An Electrochemical model for the leaching Kinetics of gold ore in Cyanide solutions 1988

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