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

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2015-02-13
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5.1.4 Reproducibility of the gold electrode potential measurements

Difficulty was experienced with the potential measurements with the gold and the gold-silver electrodes. The procedure used in experiments 10 to 14 led to non-reproducible results. These results are given in appendix A. The redox potential measurements made in these experiment were, however, quite consistent with the measurements made in previous experiments, where only the redox potential was measured.

The experimental procedure was refined a bit by leaving the electrodes in the pulp and by using a pen recorder to record the potentials throughout the run. Conditions for experiments 10 to 14 were then repeated in experiments 15 to 19 and more satisfactory results were obtained. One problem still remained and that was, that the electrode potentials fluctuated continually over a range of ± 50 mV and therefore, an average value had to be taken every time. The pen recorder made it possible, however, to determine the average potential at a given time more accurately.

Figure 5.8 and figure 5.9 show the reproducibility of the gold and gold-silver electrode measurements respectively. The general tendencies in both the gold and the gold-silver electrode potentials seemed to be a sharp initial increase in the potential, followed by a sharp decrease between 1 and 2 hours after the beginning of the experiment. After that, the potentials remained fairly constant during the rest of the experiment. These potentials did not seem to follow the same tendencies as the redox potential.

During the experiments it was observed that the sharp drop in the potentials between 1 and 2 hours occurred together with a change in the surface appearance of the electrodes, i.e. the electrodes lost their shine at that stage. After this drop in the potential had occurred, the electrodes had a greenish colour. In experiment 19 this sharp drop in the potential of the gold-silver electrode was not observed. In this experiment the gold-silver electrode did not lose its shine either.

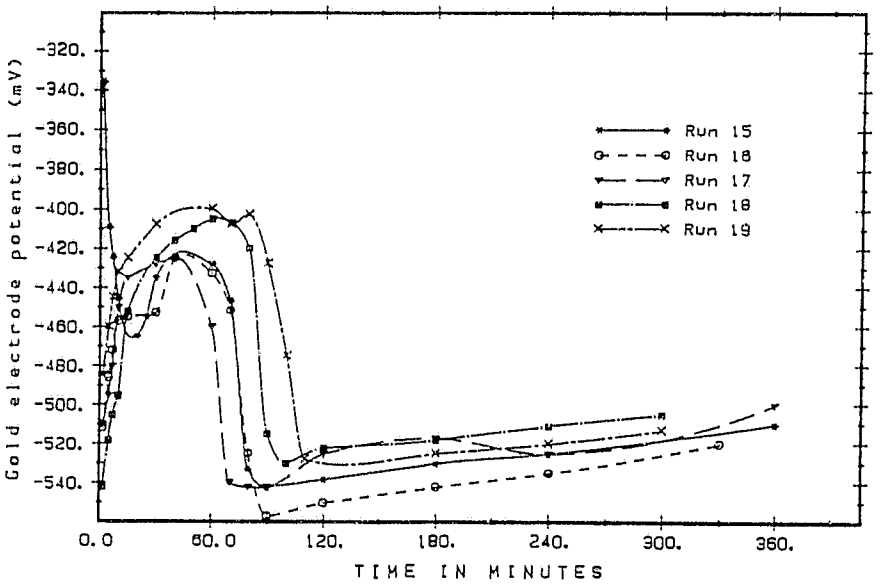

Figure 5.8: The potential measurements made with a pure gold-electrode in five leaching experiments (runs no. 15 to 19), done under exactly the same conditions, to show the reproducibility of the measurements.

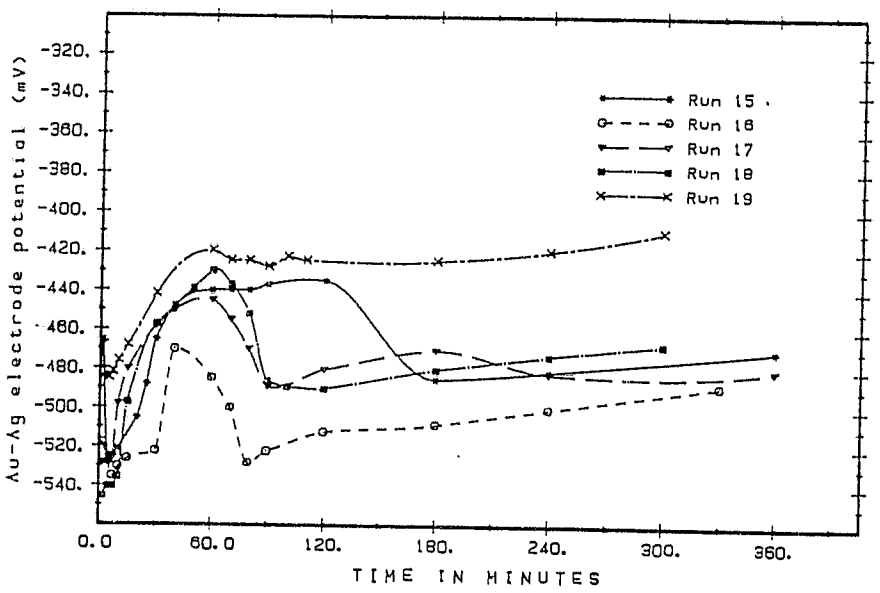

Figure 5.9: The potential measurements made with a gold-silver electrode in five leaching experiments (runs no. 15 to 19), done under exactly the same conditions, to show the reproducibility of the measurements.

5.1.5 Experiments 20 to 23

Experiment 20 was done with nitrogen as sparging medium. From the change in cyanide concentration, it was clear that leaching still took place, probably because of a small concentration of oxygen still left in the solution. The effect of the very low oxygen concentration on the potential measurements, are shown in figure 5.10 and figure 5.11. The redox potential again increased gradually during the experiment. It is significant that the redox potentials were much lower in this experiment than in the experiments where the sparging medium was air or oxygen.

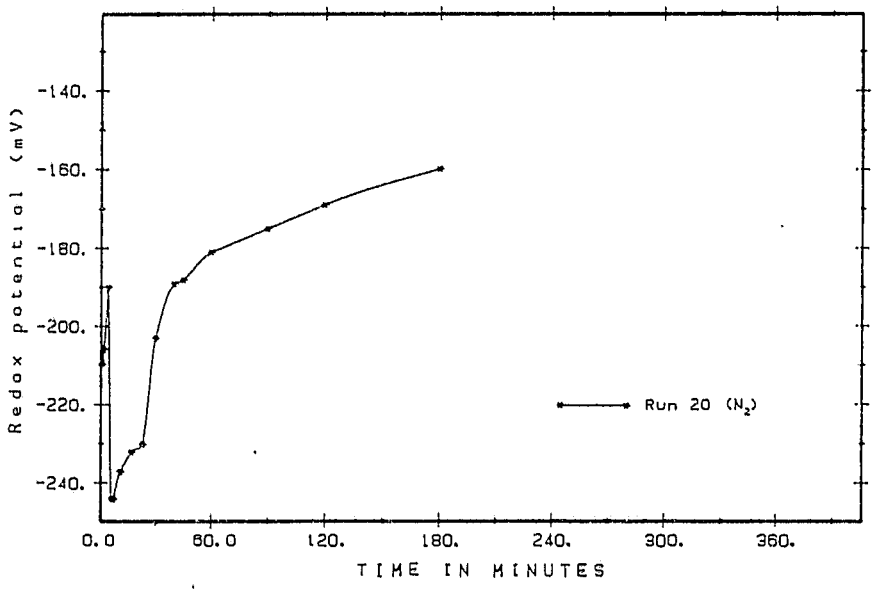

Figure 5.10: The redox potential measurements made in run 20, when the pulp solution was sparged with N_2.

There was also a significant difference between the potentials of the gold and the gold-silver electrodes in this experiment and the potentials measured in previous experiments. The gold and the gold-silver electrode potentials also shifted to lower values. Furthermore, they showed a rapid increase initially, but did not decrease again be-

tween 1 and 2 hours after the start, as they had done previously. There seemed to be a resemblance in the change of the three electrode potentials vs. time during this experiment.

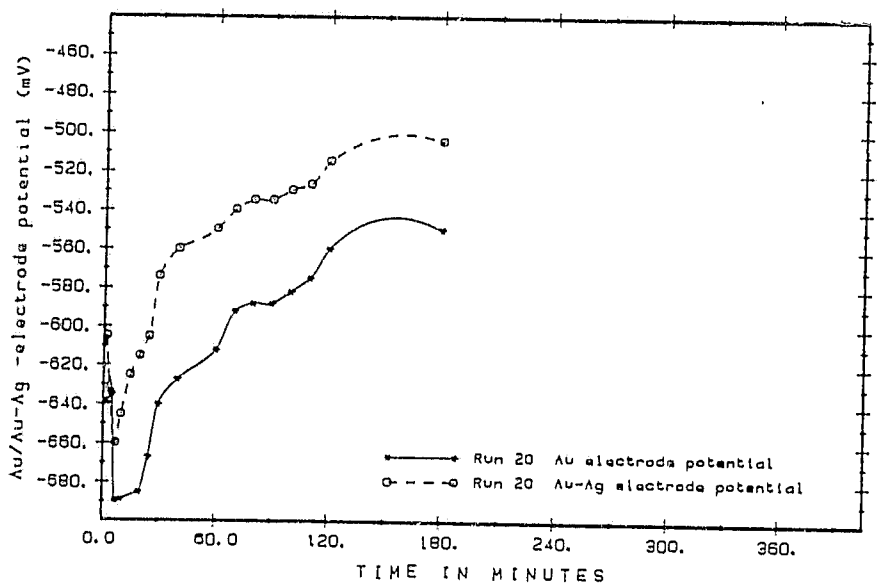

Figure 5.11: The potential measurements made in run 20 with a gold and a gold-silver electrode, when the pulp solution was sparged with N_2.

In experiment 21 the liquid portion of the pulp was replaced with distilled water. This did not seem to have any effect on the potentials. Experiment 22 was done in the liquid portion of the pulp only, while experiment 23 was done in distilled water. The same potential measurements were taken with the same electrodes. These potential measurements in the liquid portion only, were compared to those made in the pulp in previous experiments. The measured changes in the electrode potentials vs. time were quite different, as can be seen in figures 5.12, 5.13 and 5.14. In both experiments 22 and 23 much greater changes in the redox potential were observed. The redox potential increased from -150 mV to +50 mV, while the potential curve had flattened out to between -70 mV and -90 mV in the experiments done with pulp.

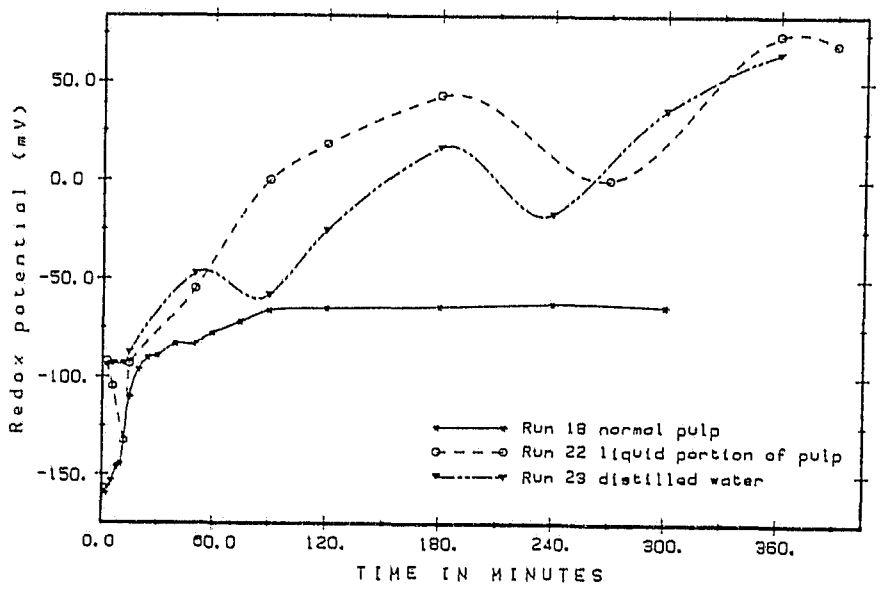

Figure 5.12: A comparison between the redox potential measurements, made in runs no. 18, 22 and 23.

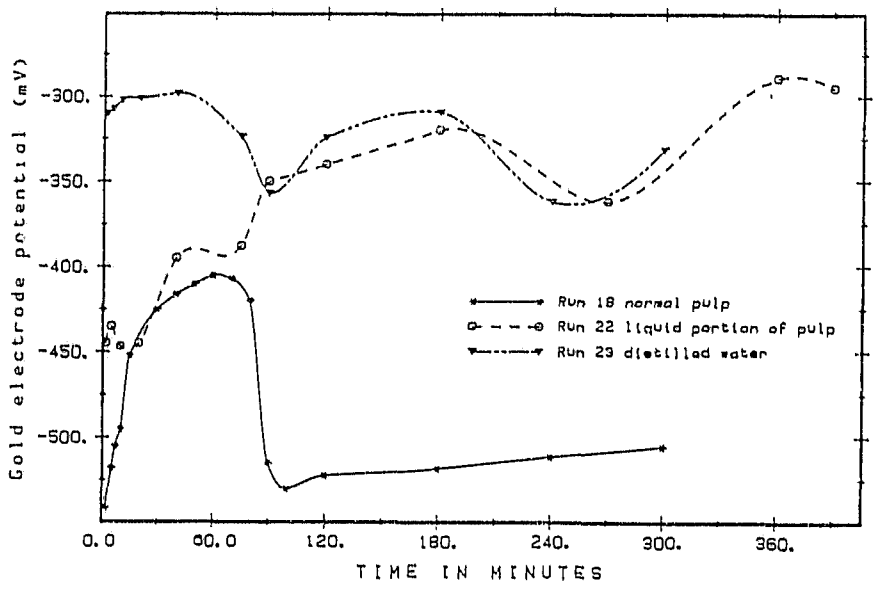

Figure 5.13: A comparison between the gold-electrode potential measurements, made in runs no. 18, 22 and 23.

The observed changes in the gold electrode potential in these two experiments also differed from those observed in previous experiments. In both experiments the potential curves were shifted to higher values. Furthermore, the gold electrode potential showed an initial increase in experiment 22 (liquid portion of pulp) and an initial decrease in experiment 23 (distilled water) (see figure 5.13). After these initial changes the potential stayed more or less constant during the rest of the experiments in both cases.

The observed changes in the gold-silver electrode potential in these two experiments were also different from those observed previously. Although the potential curves were not shifted in this case, the gold-silver electrode potential also showed an initial increase in experiment 22 and an initial decrease in experiment 23. Again there was no rapid decrease in the potential between 1 and 2 hours after the start of the experiment, as was observed in potential measurements in pulp.

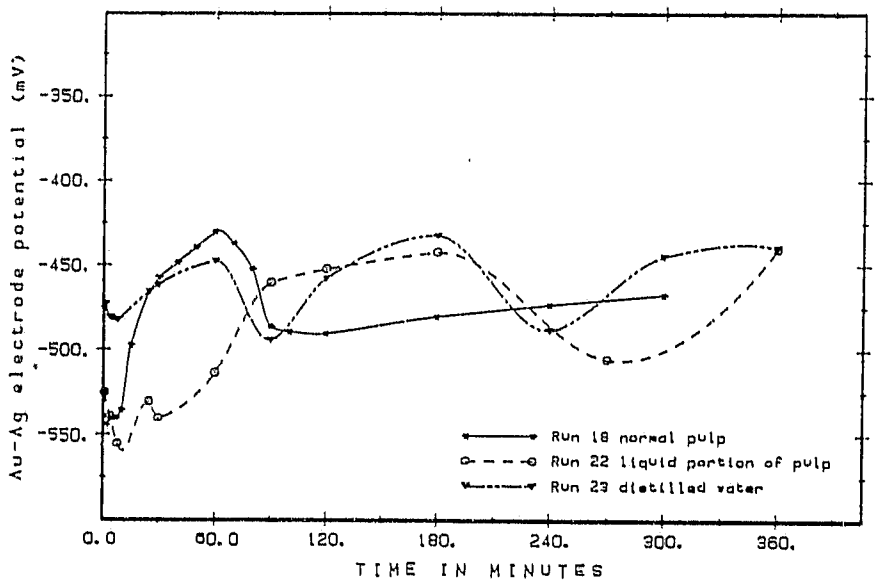

Figure 5.14: A comparison between the gold-silver electrode potential measurements, made in runs no. 18, 22 and 23.

Finally, there was another remarkable resemblance between the three electrode potential curves, as was the case in experiment 20 when nitrogen was used as sparging medium. The significant differences between the potential curves measured in these two experiments and those obtained in a pulp, gave an indication that the electrode potentials were influenced by the ions that dissolved from the ore during the experiments.

Other observations made in these two experiments were that the gold and gold-silver electrodes did not lose their shine during these experiments. Furthermore, the cyanide concentration decreased more in experiment 22 than in experiment 23. The dissolution rate of gold from the electrodes seemed to be slower in the clear cyanide solution used in these experiments, than in the cyanided pulp. This can be seen from the fact that the gold concentration in the clear cyanide solutions in these experiments, was only in the range of 0.7 ppm after 6 hours, while in the case of a pulp, the presence of the electrodes increased the gold concentration in the liquid from ± 15 ppm to ± 24 ppm after 6 hours.

5.1.6 Effect of agitation speed

Experiments 7, 24 and 25 were done under exactly the same conditions except that different agitation speeds were used. The extraction curves of these three experiments are compared in figure 5.15. In figure 5.15 the initial slopes of the extraction curves appear to have increased as the agitation speed increased. This indicates that a higher agitation speed resulted in a higher leaching rate. This fact will be discussed in more detail in section 6.1.

5.1.7 Effect of thallium

In experiment 26 a small amount of thallium was added to investigate the possibility of the gold surfaces in the ore having been passivated in the experiments. Cathro (1963) showed how the addition of a small amount of thallium could accelerate the leaching rate under certain conditions by preventing passivation of the gold surface.

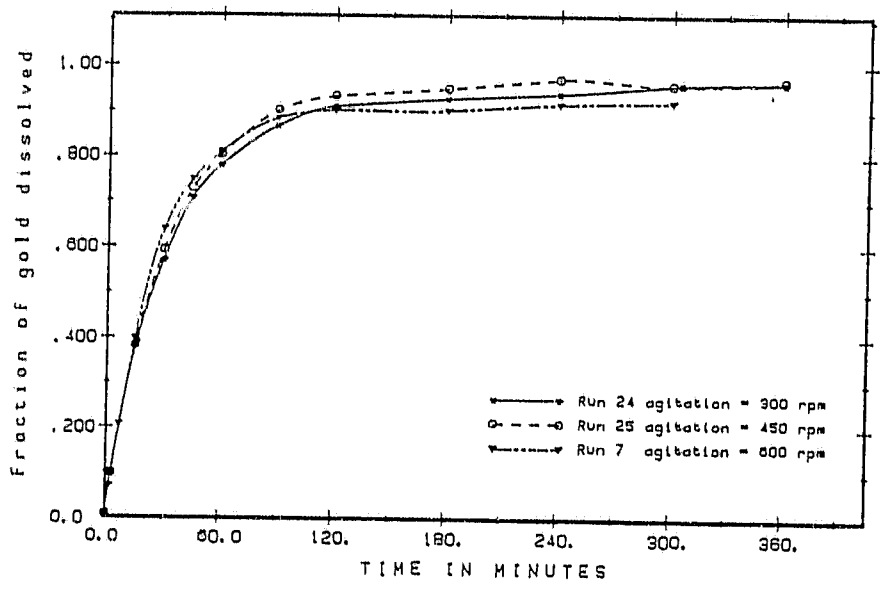

Figure 5.15: The dissolution curves of runs no 7, 24 and 25, done with three different agitation speeds, to show the effect of the agitation speed on the leaching rate.

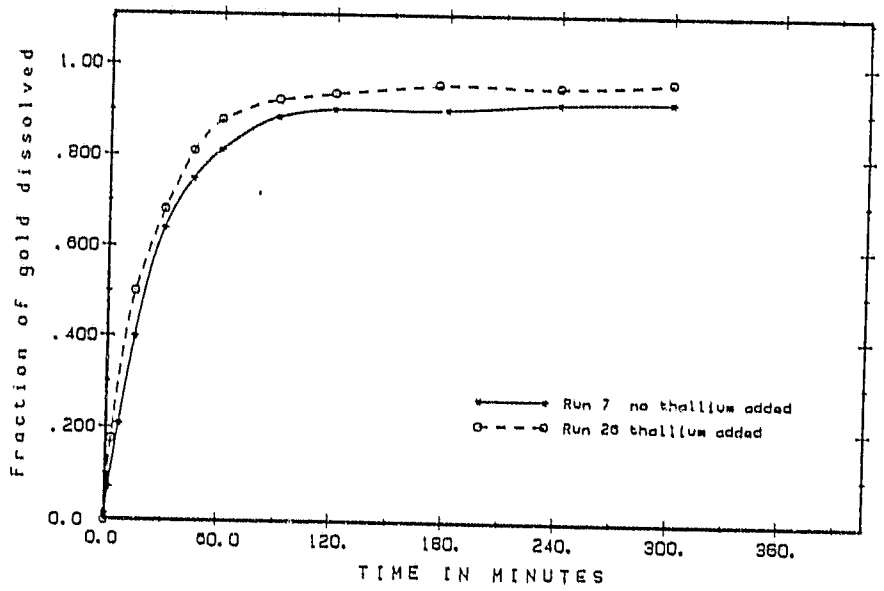

Figure 5.16: The dissolution curves of runs 7 and 26, to show the effect of thallium on the leaching rate.

In figure 5.16 the extraction curves of experiments 7 and 26 are compared to observe the effect of thallium. From the fact that the curve of experiment 26 lies above the curve of experiment 7 in figure 5.16, it is obvious that the thallium had a slight accelerating effect on the leaching rate. The accelerating effect is, however, not as distinct as one would have expected after studying Cathro's work. The deductions made from these experimental results are discussed in detail in section 6.1.

5.2 Potential measurements in artificial solutions

5.2.1 Experiment A1: The effect of cyanide ions

In this experiment the effect of the cyanide concentration on the redox potential was investigated. After each addition, 10 to 20 minutes had to be allowed for the potential to stabilise. It was, however, clear that an increase in the cyanide concentration resulted in a decrease in the redox potential. The stabilised potential was plotted against the cyanide concentration as shown in figure 5.17.

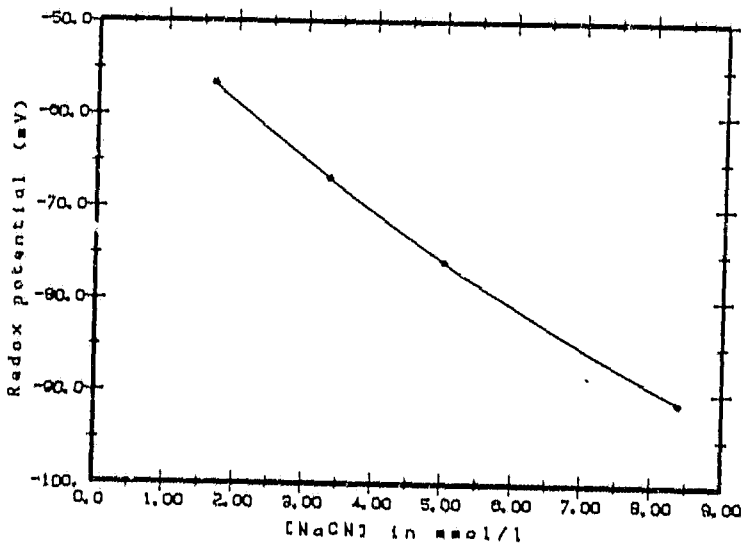

Figure 5.17: The solution redox potential vs. the cyanide concentration as measured in experiment A1.

It was also found that, at a specific cyanide concentration, the redox potential decreased as the pH increased.

5.2.2 Experiment A2: The effect of gold in solution

This experiment was planned to investigate the effect of the gold concentration in solution on the redox potential. It was found that, at a specific cyanide concentration, the gold concentration had very little effect on the redox potential. As the $KAu(CN)_2$ solution was added, only a slight increase in the redox potential was observed.

5.2.3 Experiment A3: The effect of copper ions

In this experiment the effect of an increasing copper concentration on the redox potential was investigated. After each addition of $CuSO_4$, 10 minutes had to be allowed for stabilisation of the redox potential. The potential increased with an increase in the copper concentration. The stabilised potentials were plotted against the copper concentration in figure 5.18.

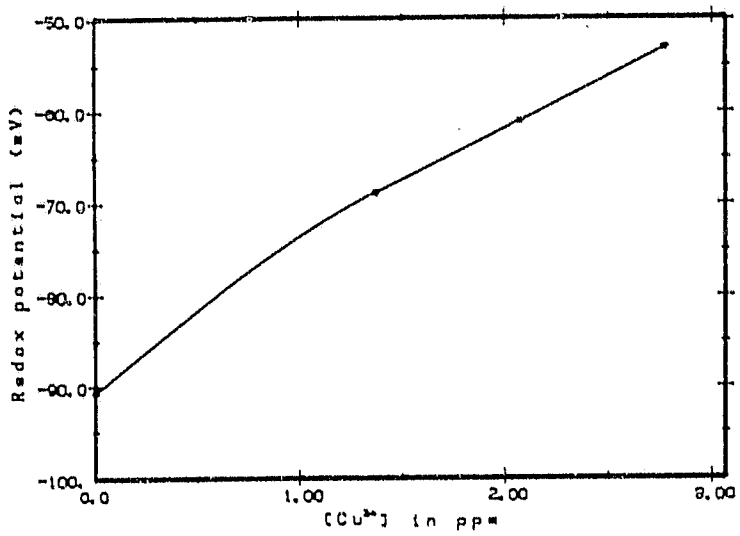

Figure 5.18: The solution redox potential vs. the Cu^{2+} concentration, as measured in experiment A3.

As one would have expected, the cyanide concentration also decreased as copper was added, because of complex formation between the cyanide and the copper. A plot of the stabilised potential vs. the cyanide concentration is given in figure 5.19.

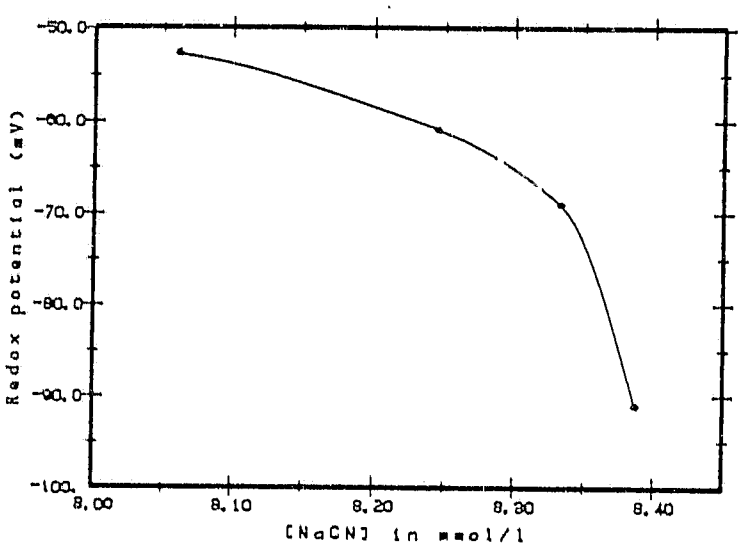

Figure 5.19: The solution redox potential vs. the cyanide concentration as measured in experiment A3.

If one compares figure 5.19 and figure 5.17, it is obvious that the rate at which the potential decreased, with an increase in the cyanide concentration, was much greater in experiment A3 than in experiment A1. In experiment A1 the potential decreased from - 50 mV to - 90 mV, as the cyanide concentration increased from 0 to 8 mmol/l. However, in experiment A3, more or less the same change in potential was observed, while the cyanide concentration increased only marginally from 8 to 8.4 mmol/l. This shows that the copper ions must also have had an effect on the solution redox potential.

5.2.4 Experiment A4

In this experiment the cyanide concentration was reduced by adding silver nitrate. The potential increased slightly after each addition of silver nitrate. As the free cyanide concentration tended towards zero, the potential became more sensitive to the addition of silver nitrate. When the stoichiometric point was reached, where the cyanide concentration was zero, the potential suddenly jumped by ± 100 mV. When a small amount of NaCN was added to the solution again, the potential jumped back. The change in potential, due to a change in the free cyanide concentration, is shown graphically in figure 5.20.

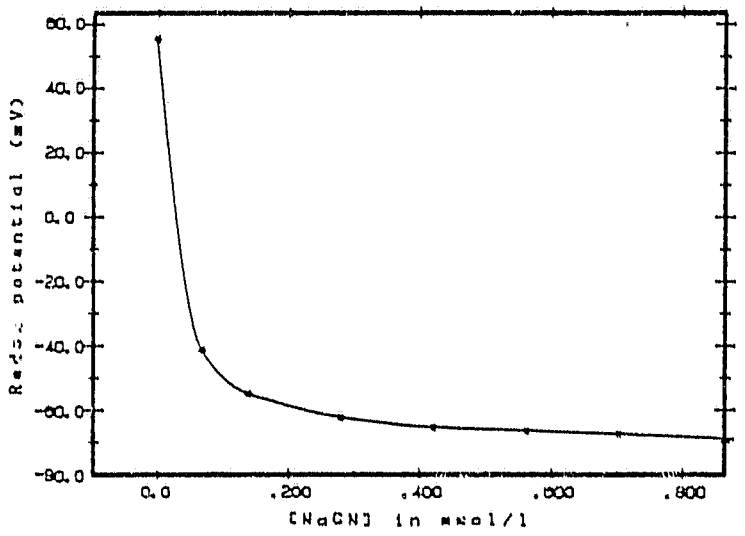

Figure 5.20: The solution redox potential vs. the cyanide concentration as measured in experiment A4.

It is important to note that, with the addition of silver to the cyanide solution, the potential showed only a large change near the stoichiometric point, while with the addition of copper, a large change was observed after the addition of the first drop of copper. This indicated that both copper and cyanide ions played a role in setting the solution redox potential.

6 MERITS OF AN ELECTROCHEMICAL MODEL

In this chapter the merits of using an electrochemical model in simulating the leaching kinetics of gold ore, are taken into consideration. Both the knowledge obtained from the literature and the experimental work are used.

6.1 Rate controlling mechanism

The proposed leach equation, eq 27 in section 3.2, is founded on the general leach equation (see appendix D):

$$\text{Rate} = Ka\psi \quad ...[28]$$

where: K = constant
a = area term
ψ = solution parameter

The functional form with which the solution parameter can be described, depends primarily on the rate controlling mechanism. When a process is modelled on the basis of its electrochemical nature, the functional form of the solution parameter is derived from the Tafel equation as shown in appendix D. The functional form of the solution parameter is then:

$$\psi = k_1 \exp(k_2 E) \quad ...[29]$$

where: k_1 and k_2 = constants
E = surface potential of the dissolving metal

In using the above functional form for the solution parameter, one actually makes the assumption that the leaching process is controlled by the chemical reaction. Hence, in considering the merits of an electrochemical model, it is necessary to take a closer look at the rate controlling mechanisms in operation in the leaching of gold ore.

From the literature it appears that three possible rate controlling steps should be considered, namely:

1) Diffusion of the cyanide ions to the gold surface.
2) Diffusion of oxygen to the gold surface.
3) Chemical reaction when the gold surface is passivated.

To investigate the possibility that the dissolution rate of gold was controlled by the chemical reaction in the leach experiments, the effect of thallium on the leaching rate was investigated. The results (see figure 5.16) showed that thallium had a slight accelerating effect on the rate, but that the acceleration was not as distinct as one would have expected.

If one looks at the effect that thallium has on the anodic polarization curve, as given by Cathro (see figure 2.9), it becomes clear that the observed effect of thallium in experiment 26, does not necessarily indicate that the gold in the ore became passive in the absence of thallium. Apart from the fact that thallium prevents passivation of the gold surface, it also increases the magnitude of the maximum obtainable anodic current. Because the increase in the leaching rate observed in experiment 26, was not as large as one would have expected in the case where the gold was passive before the addition of thallium, it seems more probable that this accelerating effect was caused by the increase in the maximum anodic current. Therefore, it is concluded that the leaching rate is probably not controlled by the chemical reaction.

If diffusion of either oxygen or cyanide forms the rate limiting step, an increase in the agitation speed will increase the leaching rate. Experiments 24 and 25 were done to test the effect of the agitation speed on the leaching rate. The fact that in these leach experiments, agitation was produced not only by the stirrer, but also by the aeration, made it difficult to quantify the level of agitation.

A comparison between the extraction curves of the three leach experiments, done with three different agitation speeds (figure 5.15), showed that an increase in the agitation speed resulted in an increase

in the leaching rate. That is an indication that the leaching rate was probably controlled by a mass transfer operation. No quantitative deductions were, however, possible from these experiments. Better results were obtained in the experiments which investigated the effect of the oxygen and cyanide concentration respectively.

The results of experiment 4 (see figure 5.3) show very clearly the accelerating effect that a higher oxygen concentration had on the leaching rate. In the case where the leaching rate is controlled by the rate of oxygen diffusion, one expects the leaching rate to be directly proportional to the oxygen concentration. The initial slopes of the extraction curves can be taken as an indication of the dissolution rate per unit area. The average slope of the extraction curves obtained in experiments 1, 2 and 3 is 0.4 ppm/min. The slope of the extraction curve obtained in experiment 4, when pure O_2 was used as sparging medium, was 1.03 ppm/min. Thus the rate increased by a factor of 2.54, while the oxygen concentration increased by a factor of 5. The leaching rate was thus not directly proportional to the oxygen concentration and, therefore, it appears as if the dissolution rate was not controlled by the rate of oxygen diffusion only.

The effect of the cyanide concentration on the leaching rate was also investigated. A comparison between the extraction curves of experiments 7, 8, and 9 (figure 5.6) shows clearly that an increase in the cyanide concentration resulted in an increase in the leaching rate. Again the initial slopes of the extraction curves were taken as an indication of the dissolution rate. In the case where the leaching rate is controlled by the rate of cyanide diffusion, one expects the leaching rate to be directly proportional to the cyanide concentration. The relationship between the initial cyanide concentrations and the initial slopes of the extraction curves as found in figure 5.6, is given in table 6.1.

When the cyanide concentration was increased by 100 %, from 2.29 to 4.58 mmol/l, the initial slope of the leach curve increased by 33 %. When the cyanide concentration was increased by a further 100%, from 4.58 to 9.17 mmol/l, the initial slope increased by 35%. It therefore seems as if a proportionality exists between the rate and the cyanide

concentration, but because it is not a direct proportionality, it is concluded that the rate is not controlled only by the rate of cyanide diffusion either.

Table 6.1: Slopes of extraction curves vs. initial [CN^-]

Exp.no.	[CN^-]mmol/l	Slope ppm/min.	Conc. norm.	Slope norm.
7	9.17	0.473	4	1.79
8	4.58	0.351	2	1.3
9	2.29	0.264	1	1

From the discussion above, it appears as if the rate controlling mechanism in these experiments, was a combination between the diffusion of oxygen and the diffusion of cyanide. The question now still remains whether an electrochemical model can be used to model the leaching kinetics of gold ore. Let's look separately at the two possibilities; first of all where the rate is controlled by only the rate of oxygen diffusion and secondly, where the rate is controlled by only the rate of cyanide diffusion.

When the rate is controlled by the rate of oxygen diffusion only, the polarization curves have the form shown in figure 6.1. In figure 6.1, two anodic polarization curves are shown for two different cyanide concentrations and it can be seen that the corrosion potential increases when the cyanide concentration decreases. It is important, however, to note that no change in the corrosion current occurs simultaneously with this change in the gold surface potential, because the corrosion current is set by the rate of oxygen diffusion only. Thus in this case no relationship exists between the gold surface potential and the leaching rate and an electrochemical model is unlikely to be applicable.

If one assumes that the gold surface does not become passive, the polarization curves will have the form shown in figure 6.2, when the rate is controlled by the cyanide diffusion rate only. In this case a change in the corrosion current goes along with a change in the gold

concentration, but because it is not a direct proportionality, it is concluded that the rate is not controlled only by the rate of cyanide diffusion either.

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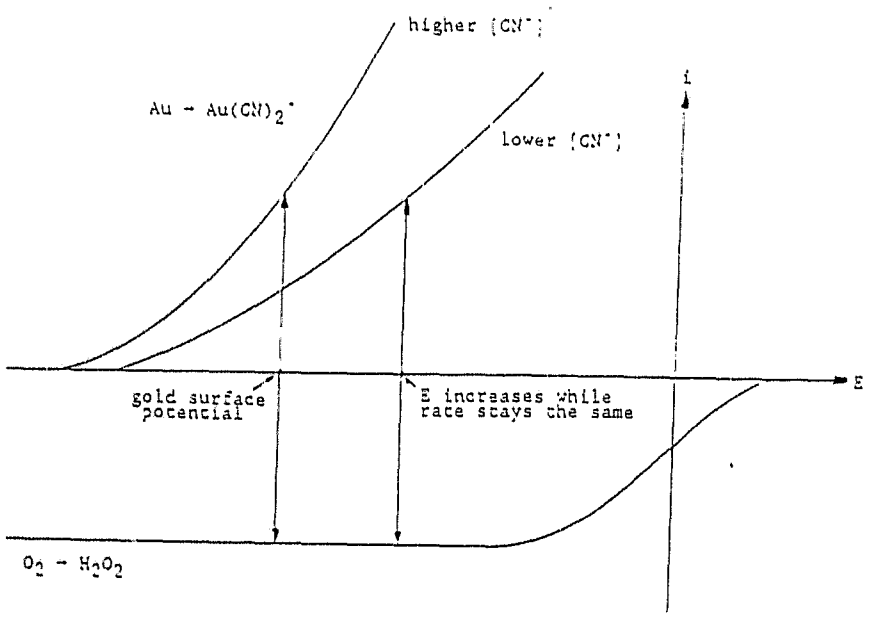

Figure 6.1: The appropriate polarization curves for the dissolution of gold when the rate is controlled by the rate of oxygen diffusion.

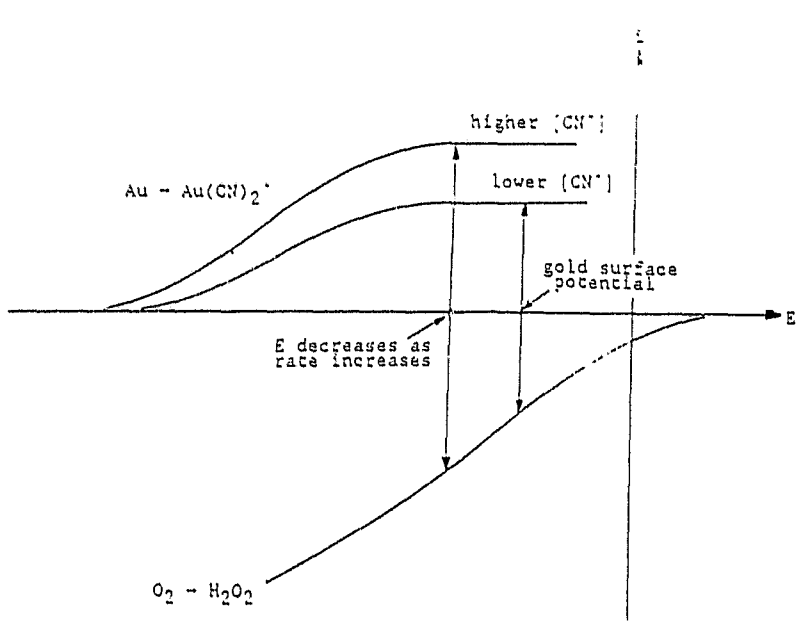

Figure 6.2: The appropriate polarization curves for the dissolution of gold when the rate is controlled by the rate of cyanide diffusion.

surface potential, given that the oxygen reduction curve stays unchanged. Although the Tafel equation does not describe the anodic curve up to the corrosion potential, it is possible to describe the maximum anodic current in terms of the potential at which the cathodic reaction takes place. Therefore, if the cathodic polarization curve follows the Tafel relationship and the cathodic curve does not change during the experiment, an electrochemical model seems to be a possibility.

The experimental results showed that the leaching rate is influenced by the rate of both oxygen and cyanide diffusion. One can therefore accept that neither the anodic nor the cathodic polarization curve flattens off before the potential at which the reaction takes place. This suggests that the polarization curves most probably have the following form as shown in figure 6.3.

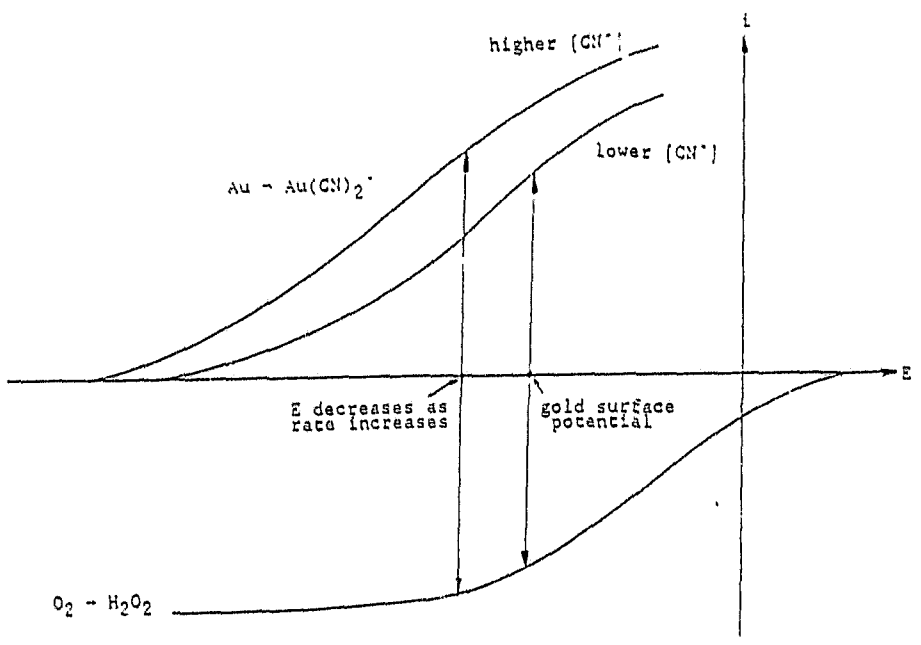

Figure 6.3: The appropriate polarization curves for the dissolution of gold when the rate is influenced by both the cyanide and the oxygen concentration.

surface potential, given that the oxygen reduction curve stays unchanged. Although the Tafel equation does not describe the anodic curve up to the corrosion potential, it is possible to describe the maximum anodic current in terms of the potential at which the cathodic reaction takes place. Therefore, if the cathodic polarization curve follows the Tafel relationship and the cathodic curve does not change during the experiment, an electrochemical model seems to be a possibility.

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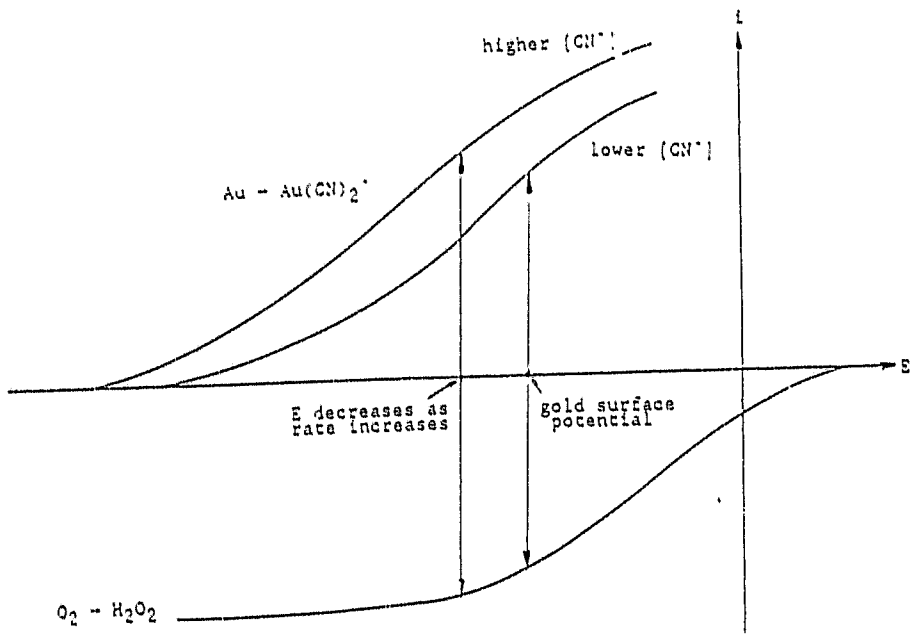

Figure 6.3: The appropriate polarization curves for the dissolution of gold when the rate is influenced by both the cyanide and the oxygen concentration.

The effect that thallium had on the leaching rate, also supports the possibility that the polarization ourves had the form as shown in figure 6.3. It is proposed that the thallium increased the anodic current at a specific potential and that *this* resulted in a higher leaching rate becanse the cathodic curve had the form as shown in figure 6.3. If this is the case, the polarization curves can probably still be desoribed by means of an equation which relates the overpotential to the current density. That means that an electrochemical model might still be a possibility.

The obvious problems are, however, to predict the relationship between the overpotential and corrosion current on the gold surfaces in the ore, for both the anodic and the cathodic reactions. A further problem is to measure the surface potential of the gold in the ore accurately. This will be discussed further in section 6.2.

6.2 The gold electrode potential

In the leach experiments, a pure gold and a gold-silver alloy electrode were used to measure the gold surface potential. The reason why a 90% gold, 10% silver alloy electrode was also used, is because in South African ores, gold is usually found as an alloy with silver. It is difficult to say how well these potential measurements approximate the actual surface potential of the gold in the ore. These electrode potentials do not account for any galvanic interaction which might exist between the gold and the minerals in the ore. Furthermore, the laminar sub-layer around an ore particle is quite different from that around the symmetrical electrode.

In section 5.1.4 the changes observed in the gold and the gold-silver electrode potentials were discussed. It appears as if the changes in the potential only reflected changes in the physical condition of the electrode surface and this places a question-mark over the significance of these potential measurements. According to the literature, the gold surface becomes passive at potentials higher than -0.6 V (vs. S.C.E). This means that both the gold and the gold-silver electrode were passive in all the measurements. However, from the results ob-

tained in experiment 26, it was concluded that the gold in the ore was active in all the experiments. Hence, it appears as if the measured gold electrode potential did not give a true account of the surface potential of the gold in the ore.

It has already been said in section 5.1.4, that the sharp decrease in the electrode potential after ± 2 hours seemed to be the result of the formation of a film on the electrode surface. The fact that the potential decreased as a result of this film that was formed, indicates that the film probably formed a diffusion barrier for oxygen diffusion to the surface. No attempts were made to identify the substance that formed the layer on the gold electrodes. Thus the conclusion reached in this discussion also indicates that the measured gold surface potential was not related to the leaching rate.

The solution redox potential was also measured in the leach experiments, but as has been said before, no theoretical ground exists on which the solution redox potential can be taken as an approximation for the gold surface potential. The only possible way to approximate the gold surface potential, seems to be by using a gold electrode. More experimentation is needed though, to construct an electrode that will not passivate and which gives more reproducible results in potential measurements in pulps.

In the next section the significance of the redox potential is discussed.

6.3 Modelling, by using the Pt redox potential

In section 3.2 it was explained why the redox potential could have been used as an approximation for the mineral surface potential in the modelling of the leaching kinetics of base metal sulfides. In the case of the dissolution of base metal sulfides, the oxidizing agent (Fe^{+++}) forms part of a reversible redox system with a large exchange current at equilibrium. The oxidization of gold differs considerably from the oxidization of the base metal sulfides because the oxidizing agent (O_2) forms part of a non-reversible redox system. Therefore, the platinum redox potential cannot be used as an approxi-

mation for the gold surface potential.

The solution redox potential was, however, still measured in the hope that this potential would provide a way to describe the solution parameter in the rate expression. The form of the proposed rate expression in which the redox potential was used, is the same as that previously given in section 3.2 (equation 27). The only difference is that the potential term in the expression is now the solution redox potential.

$$\text{Rate} = -k_1\left([Au]_s - [Au]_s^{\infty}\right)\exp\left(k_2 E_{redox}\right) \quad \ldots[30]$$

Equation 30 is now of course not derivable from the Tafel equation anymore. The reason why it was decided to use the potential in an exponential term, was because the relationship between a concentration of a species and a potential is usually of an exponential form (eg. the Nernst equation).

6.3.1 Fits obtained when using redox potential

A computer program was used to fit this rate expression to the experimental data. The constants, k_1 and k_2, were optimized simultaneously to obtain the minimum sum of squared differences between the experimental values and the model predicted values. The rate expression was integrated numerically by means of the Gauss Quadrature procedure. The integration was done from time zero, where the gold concentration was known in both the solid and the liquid fraction of the pulp. The optimization was done with a simplex method as proposed by Nelder and Mead(1965). Interpolation between the redox potential measurements was done by quadratic interpolation. A listing of the computer program is given in appendix B.

The expression was fitted simultaneously to the first three experiments, which were done with pulp from Vaal Reef, while forcing the constants to be the same. The leaching curves predicted by the rate expression are compared with the experimental data in figure 6.4. The predicted values and experimental data are given in appendix C. As can be seen, the fits are exceptionally good.

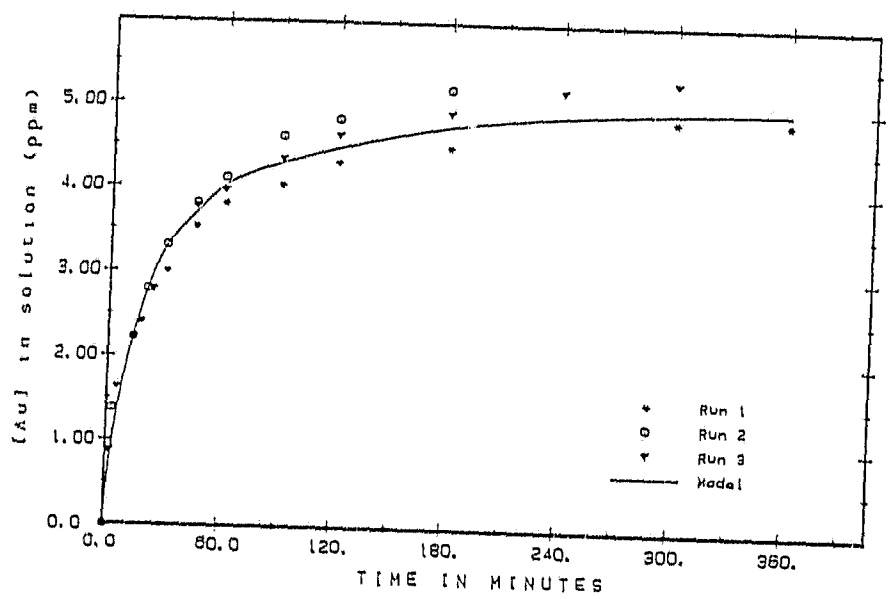

*Figure 6.4: Model prediction of leaching kinetics vs. the experimental results of experiments nos. 1, 2 and 3 (k_1 = 1.242*10^{-4} and k_2 = -0.040933).*

The model was also fitted to the experimental data of experiments 8, 9 and 12. The constants were first determined individually for each run. The optimum constants were then also determined, while forcing them to be the same for all three experiments. Only the results of experiment 8 are shown in figure 6.5. The other results, as well as the numerical data, are given in appendix C. Figure 6.5 shows that even when the constants were forced to be the same, the fits were still reasonably good.

The model was also fitted to the experiments 4 and 5, in which oxygen was used as aeration medium. Figure 6.6 shows the fit for experiment 4. The numerical data and fits for other experiments are also given in appendix C. As can be seen in figure 6.6 a reasonable fit was again obtained.

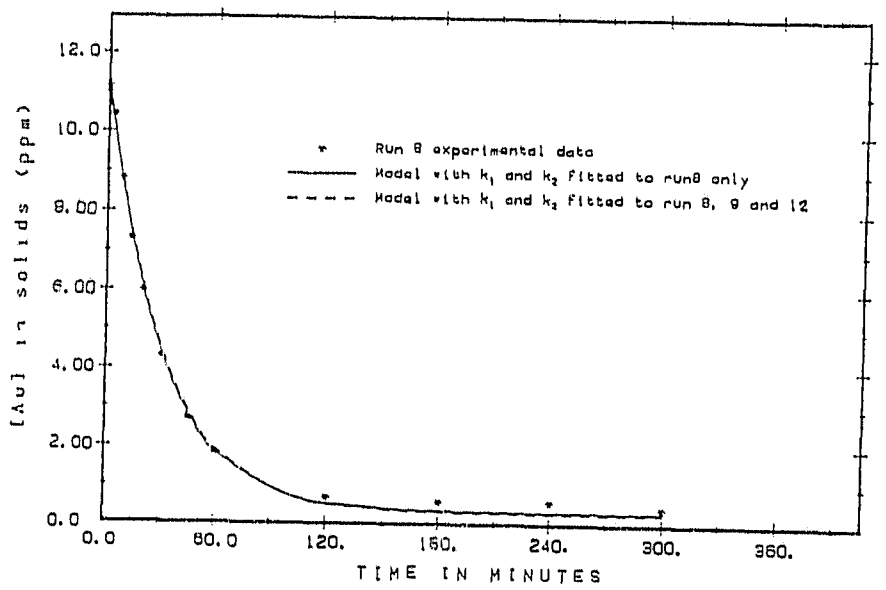

Figure 6.5: Model prediction of leaching kinetics vs. the experimental results of experiment no. 8.
Fitted to run 8 only: $k_1 = 4.612*10^{-2}$ *and* $k_2 = +0.0023231$
Fitted to 8,9 and 12 simult.: $k_1 = 6.027*10^{-2}$ *and* $k_2 = +0.0043686$

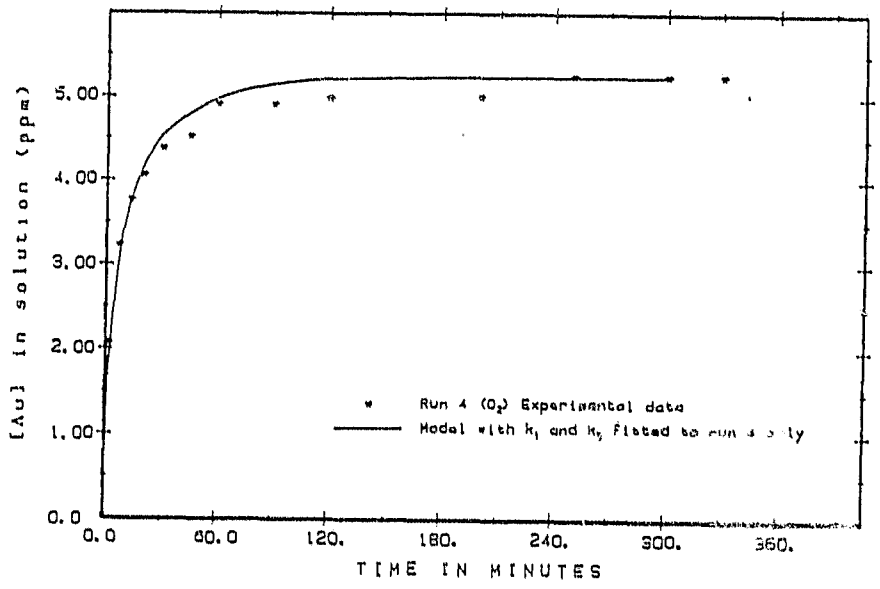

Figure 6.6: Model prediction of leaching kinetics vs. the experimental results of experiment no. 4 ($k_1 = 7.031*10^{-4}$ *and* $k_2 = -0.047321$).

A sensitivity analysis was conducted on the two constants. The sensitivity analysis performed on the fitted constants for experiment 8 is discussed here. Figure 6.7 shows the changes in the sum of squared differences with changes in k_1 and k_2 in the form of a contour plot. As can be seen from this contour plot, there appears to be a correlation between them, which means that they were compensating for each other.

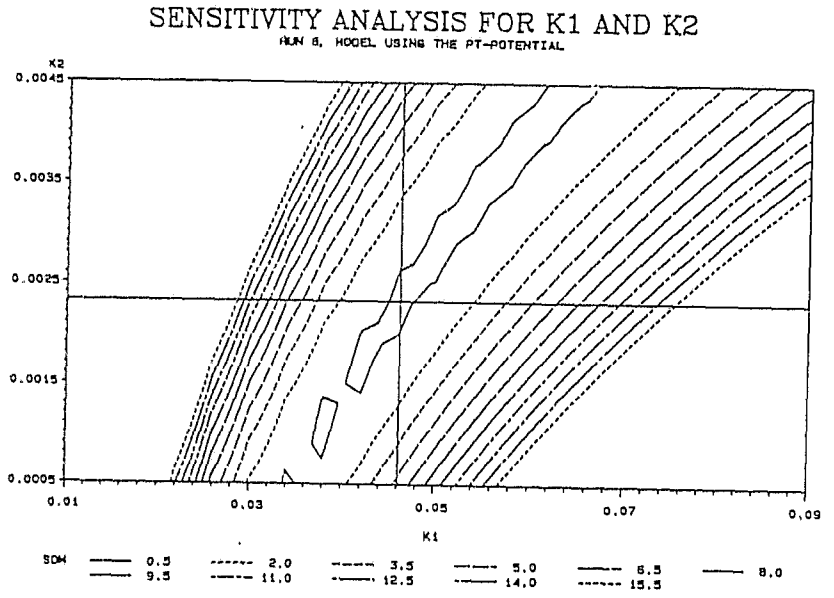

Figure 6.7: A sensitivity analysis for the constants k_1 and k_2.

Hence, to conclude this section: The rate expression in which the redox potential is used, was successfully fitted to the experimental results. Although this expression has the same form as an electrochemical rate expression, it must be emphasized that because the redox potential is used in it, the expression is not fundamentally based. In the next chapter the significance of the fact that the redox potential can be used to model the leaching kinetics of gold, is taken into consideration. The question that needs to be answered is which ions in solution determine and set the measured solution redox potential.

7 THE PLATINUM REDOX POTENTIAL

7.1 Possible explanations

The potential which was measured in the solution could result from one of two possibilities. On the one hand it could be a potential set by one or more of a number of redox couples present in the solution. On the other hand the potential could be a mixed potential of two redox couples present in the solution. The latter seems to be the more probable mechanism involved in setting the potential. A few reasons are stated below:

1. The potential is affected by the oxygen concentration. The O_2/OH^- couple is almost totally non-reversible, which means that if the potential was set by this couple only, one would not have been able to measure a stable potential. From this it was concluded that the O_2/OH^- couple did not set the potential on its own, but that it was perhaps one of the two couples involved in the redox reaction which set the potential.

2. The potential is affected by the cyanide concentration. The CN^-/CNO^- couple is also essentially non-reversible. Hence, this couple cannot set the potential on its own either.

The possibility that the potential was set by the redox reaction between CN^- and O_2, was also considered. Cyanide is not thermodynamically stable in the presence of oxygen in an alkaline solution. It is, however, known that because of the non-reversibility of the CN^-/CNO^- couple, the oxidation of CN^- takes place at a very slow rate. The corrosion current is therefore very small. The mixed potential at which this redox reaction will take place is set by the polarization curves of the two couples as shown in figure 7.1. There are a few reasons why it is very unlikely that this mixed potential was measured with the Pt electrode in this project.

1. First of all, the corrosion current is very small, which again means that this mixed potential is not very stable. The potential measured in this project was, however, fairly stable.

2. Because the CN^- was present in great excess, the cyanide concentration did not change much during the experiments. The oxygen concentration also stayed more or less the *same*. However, the redox potential changed by more or less 60 mV during the experiments. Hence, the change in $[CN^-]$ was too small to account for the relatively large changes in the redox potential.

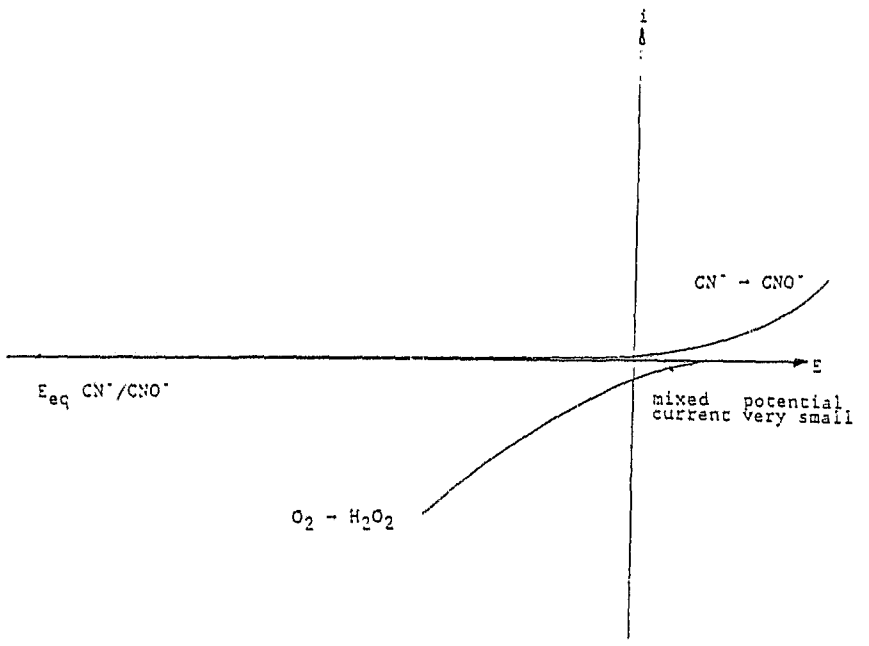

Figure 7.1: Mixed potential set by the redox reaction between CN^- and O_2.

Having eliminated both the O_2/OH^- and the CN^-/CNO^- couples, as well as the mixed couple between O_2 and CN^-, the only possibility which remains is that the measured redox potential was a mixed potential between the reduction of oxygen and the oxidation of impurities present in the solution. If this was the case, it would be almost impossible to explain exactly what set the measured redox potential. The presence of such a great number of ions in the leach solution

makes the system extremely complex. Impurities present at concentrations as low as 1 ppm can play a role.

By careful examination of the experimental results, it is possible to narrow the possibilities down slightly. The fact that the measured potential increased during the experiments indicates that the rate of the anodic reaction was probably controlled by the rate of diffusion of the impurities to the electrode. The concentration of the impurities decreased in the course of time and as a result, the maximum rate of diffusion of the specie decreased and the mixed potential increased as shown in figure 7.2.

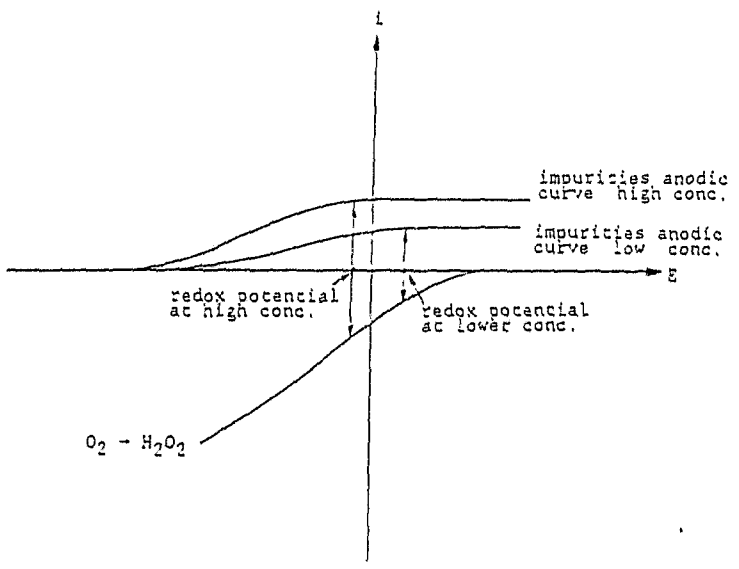

Figure 7.2: Probable explanation for the solution redox potential.

The fact that the redox potential changed much more rapidly and over a much greater interval in the experiments where potential measurements were only made in the liquid fraction of the pulp, tends to indicate that the relevant impurities dissolved from the solids during the experiments. Furthermore, because the cyanide concentration had an

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

PUBLISHER:
University of the Witwatersrand, Johannesburg
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