



An amperometric instrument for the determination of cyanide on gold plants

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Synopsis

A method is described for the determination of cyanide in gold slurries, based on amperometry. The measured current is proportional to the concentration of cyanide, and is not affected by pH or by the concentration of oxygen in solution. It is also unaffected by other ions that may be present in gold-leaching solutions, including sulphide, thiocyanate, and thiosulphate. The current depends on the temperature, and an activation energy of 17,9 kJ/mol was determined. Since the current is controlled by the mass transfer of cyanide to the anode, it depends on the conditions of agitation.

In tests on an operational gold plant, slurry was pumped directly from the top of the leaching tank, through the measuring cell, and back into the tank. The results indicate that the instrument is a promising alternative to the instruments currently available. The readings from the instrument remained in calibration for at least two days, showing that the instrument would need to be re-calibrated by the operating staff at regular periods.

Introduction

Cyanide is measured by titration on most plants that treat gold-bearing ores. The sampling and filtration procedures are slow, and the endpoint is difficult to detect. As a result, control of the treatment process by the manual titration method is relatively inefficient, and the concentrations of cyanide can display large variations with time.

The efficient control of cyanide has substantial financial implications. Brandt *et al.*¹ reduced the consumption of cyanide at the Afrikaander Leases gold plant by over 30 per cent by controlling the addition of cyanide with CYCAD. The soluble gold losses were reduced by half, from 0,022 to 0,011 g/m³. They calculated that the costs were also reduced: by 30 per cent from 0,77 to 0,55 rands per tonne of ore. In 1989, the members of the Chamber of Mines spent R97,2 million on cyanide. A reduction in the consumption of cyanide of 30 per cent would have amounted to a saving for the industry of R29,1 million in the costs of reagents for that year. Other savings can be realized from the lower losses of soluble gold.

The aim of the work described here was the development of an instrument for the purposes of automatic process control. This paper discusses the experimentation undertaken in the development of an instrument for the determination of free cyanide in process slurries. The instrument was tested on a plant, and these results are also presented.

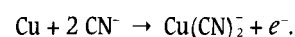
Cyanides in leaching solutions occur as free cyanide (CN⁻) and as metal-cyanide complexes of varying stability. It is the concentration of free cyanide in solution that needs to be determined, since it is this species that is available for reaction with the gold.

Pohlandt *et al.*² reviewed 92 different methods for the analysis of cyanide and metal-cyanide complexes. Many of these methods are subject to interferences from the other ions present in the leaching solution and are therefore not suitable for the determination of free cyanide in process streams. Moreover, most methods call for sample preparation, such as filtration of the slurry, which may result in a significant delay between the sampling and the reporting of the result.

A method that does not suffer from sampling delays is measurement by use of the Kegold electrode, developed at Mintek³. The method is based on the measurement of the potential of a silver button in contact with the solution. This potential is the mixed potential due to the corrosion of silver by oxygen in a solution containing cyanides. The measurement is affected by the concentrations of cyanide and oxygen. The dependence of the measurement on the concentration of oxygen makes control of the cyanide concentration difficult. In addition, the long-term stability of the instrument is poor, primarily owing to the formation of oxide films on the surface of the silver.

Methods of cyanide analysis based on amperometry have been proposed by Baker and Morrison⁴, McCloskey⁵, and Miller *et al.*⁶. The anodes are made of gold and silver. These methods were designed for small samples of clear solution containing low concentrations of cyanide. Pilhar *et al.*⁷ used a silver anode to detect nanograms of cyanide in samples of 10 µl. They used a flow-through cell with the silver wire mounted centrally. The current was found to be a linear function of the concentration of free cyanide in solution from 0,5 µg/l to 1 g/l. Of the thirty ions tested for interference, sulphide, iodide, and thiocyanate were the only ions to interfere seriously⁴⁻⁷, but these can be removed by precipitation with lead.

An amperometric method for the determination of cyanide in gold slurries was tested^{8,9} in 1991. The method is based on the measurement of the anodic dissolution current of copper due to the reaction



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The rate of this reaction at the potential chosen for operation is controlled by the mass transfer of cyanide ions to the electrode surface. The rate of reaction, and hence the current, is directly proportional to the concentration of cyanide if the flow conditions remain constant. A range of metals, including silver and gold, and semiconductors, such as copper sulphide, might also serve as appropriate electrodes. The chemical reactions involved in the operation of the instrument was investigated, and a South African patent was filed^{8,9}.

The requirements for successful design are that there should be no interference either by process variables or by other chemical species in solution, and that there should be no delay associated with sample preparation, so that effective process control is possible. In the present work, the sampling method was adapted so as to eliminate the need for filtration. As the cell is placed directly in a leaching tank or slurry pipeline, a direct, immediate, and continuous response is obtained.

Experimental

A three-electrode cell was used in this work. The electrodes consisted of a copper anode, a stainless-steel cathode, and a calomel reference electrode. A BASS CV27 potentiostat was used, and the output was sampled by use of an A/D card controlled by an IBM-compatible computer at a frequency of 1 Hz and averaged every 200 seconds. During the plant tests, a chart recorder was used to record the data.

The laboratory experiments were conducted in a 10-litre vessel agitated by a Heidolph overhead stirrer. The apparatus is shown in Figure 1. The samples were milled solids collected from a dump site in Roodepoort. The pH value was adjusted with either lime or sodium hydroxide.

An instrument employing amperometry (Figure 2) was tested at an operational gold plant. Slurry was pumped from the top of the leaching tank in the gold circuit, through the measurement cell, and back into the tank. The measurement cell, which contains the three electrodes, is robust. The cell is designed to ensure that no settling of solids occurs, and the hydrodynamic characteristics of the cell ensure that the conditions of flow are constant.

For comparison, the concentration of cyanide in solution was determined by titration with silver nitrate. Potassium iodide was used as the indicator according to the method of Vogel¹⁰. The concentrations of cyanide determined by the plant operator were obtained for comparison with those measured by the instrument.

The oxygen concentration and the temperature were determined by use of a Schott-Gerate oxygen meter.

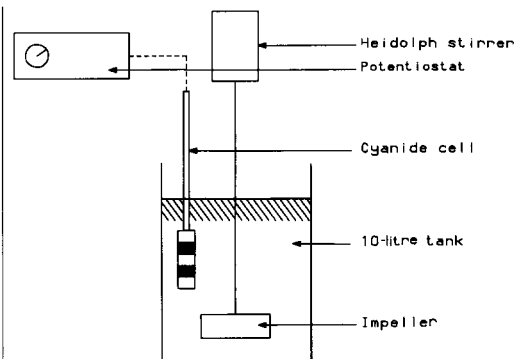


Figure 1—Schematic diagram of the laboratory apparatus

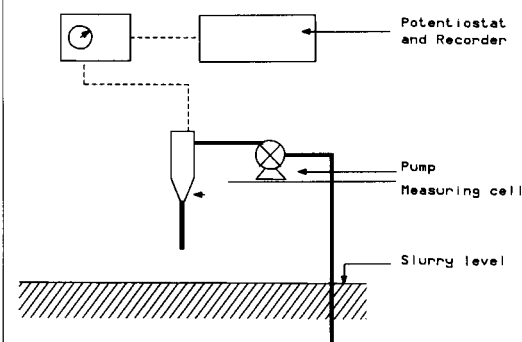


Figure 2—Schematic diagram of the plant apparatus

Results

The current due to the anodic dissolution of copper is affected by the concentration of free cyanide in solution, by the conditions of agitation in the vicinity of the anode, and by the temperature⁸. In addition, the current may be affected by the other chemical species present in the leaching solution. The effects of these parameters were quantified in laboratory experiments.

The effect of the cyanide concentration on the measured current is shown in Figure 3. The agitation in the laboratory tank was kept constant by an overhead stirrer. Figure 3 shows that the measured response is proportional to the concentration. Previously, this result was obtained by use of a rotating-disk electrode and pumping of the solution through the cell⁸.

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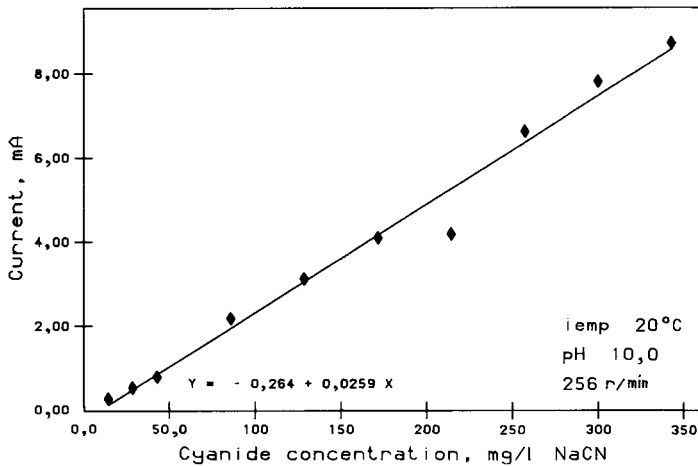


Figure 3—The effect of the cyanide concentration on current (10-litre stirred tank, 50 per cent solids)

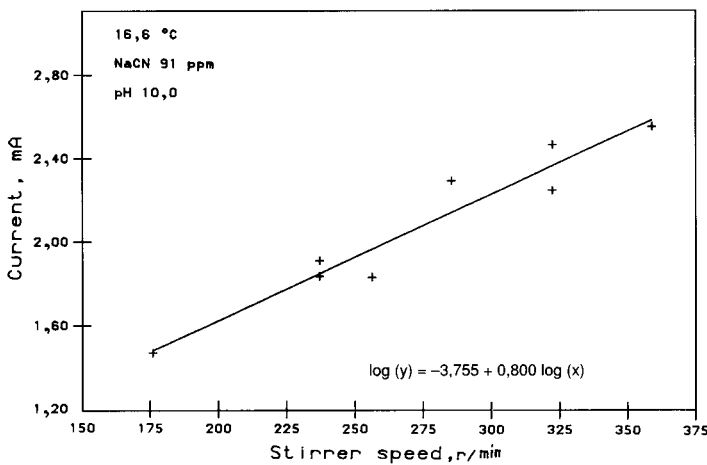


Figure 4—The effect of impeller rotational speed on current (10-litre stirred tank, 50 per cent solids)

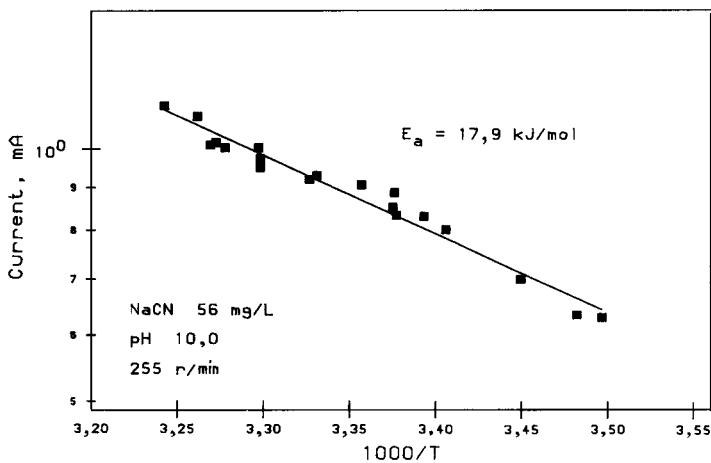


Figure 5—The effect of temperature on current (10-litre stirred tank, 50 per cent solids)

The laboratory apparatus illustrated in Figure 1 was set up at the top of the second tank in the leaching circuit of an operational plant, and slurry sampled from the tank was transferred immediately to the 10-litre tank. In this experiment, the concentration of cyanide was changed by the addition of either copper sulphate or sodium cyanide. The results obtained were similar to those obtained in the laboratory with slurry made up from dump material. The current was found to be proportional to the concentration of cyanide in solution, suggesting that the measurement was not adversely affected by slurries of different compositions.

The effect of the agitation conditions on the measured current was investigated by varying the rotational speed of the tank impeller was varied. These results are shown in Figure 4. Since the dissolution of the copper anode is controlled by mass transfer, agitation has a strong influence on the measured current. This current was proportional to the 0,8th power of the rotational speed of the impeller. Theoretical analysis suggests¹¹ that the measured current should be proportional to the 0,6th power of the rotational speed of the impeller.

The effect of temperature on the measured current is shown in Figure 5 for temperatures between 13 and 36°C, and is described by the Arrhenius equation, with an activation energy of 17,9 kJ/mol. The value of this activation energy lies in the region expected for a reaction controlled by mass transfer. An instrument designed for plant operation would require temperature compensation.

Dissolved oxygen is present in the leaching solution. The potential of the anode was chosen so that the current due to oxygen reduction at the anode would be negligible⁸. That the oxygen concentration had no effect on the measured current is shown in Figure 6.

The effect of the pH value of the leaching solution is shown in Figure 7. Changes in pH up to pH 12 had no effect on the current. Above pH 12, the current decreased, possibly owing to the formation of a film of oxides or hydroxides on the surface of the copper. The operating potential of the anode was chosen so that, at pH 10, the formation of such films would not be favoured thermodynamically. As most leaching plants operate at below pH 12, this result is not expected to limit the value of this instrument.

Changes in pulp density affect the mass transfer, and hence the anode current. The effect of the solids concentration in the slurry on the measured current is shown in Figure 8. The current decreased with an increase in pulp density. As the pulp density on operational plants is generally maintained to within 5 per cent of a setpoint of 50 per cent solids, it is believed that the effect of pulp density will not affect the operation of this instrument.

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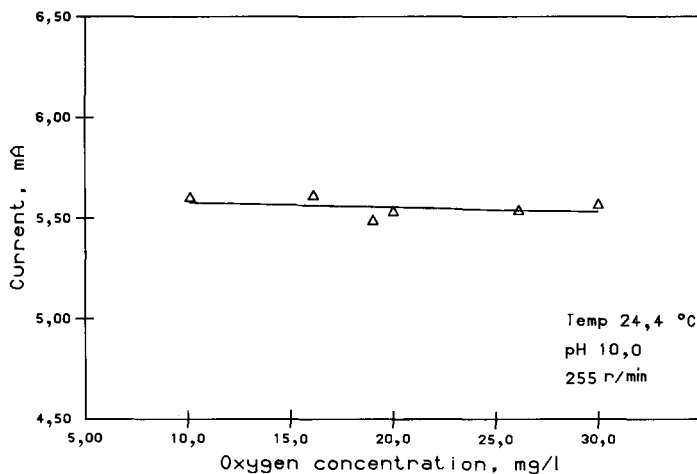


Figure 6—The effect of oxygen concentration on current (10-litre stirred tank, 50 per cent solids)

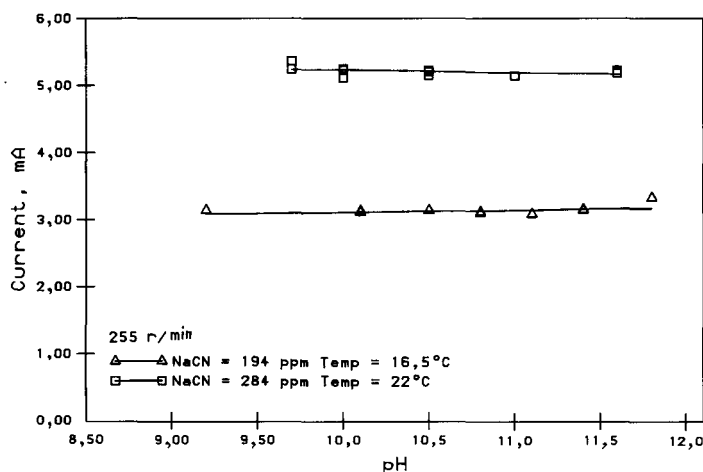


Figure 7—The effect of solution pH on current (10-litre stirred tank, clear solution, 5 g/l HBO_3 , 1 g/l KCl)

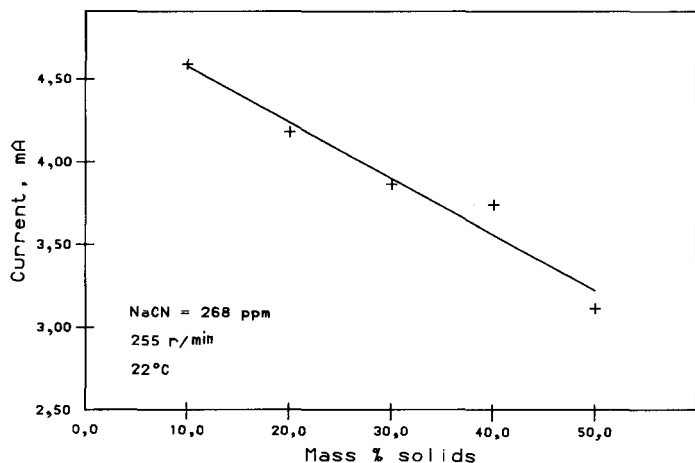


Figure 8—The effect of solids density on current (10-litre stirred tank)

For this technique to be used in an operating environment, the measured current must be free of interference from other ions in solution. The composition of a typical leaching solution in a Witwatersrand plant is shown in Table I.

The effect of other ions found in the leaching solution on the current is shown in Table II and Figure 9. These ions were added progressively to the solution, so that the final solution giving the results presented in Figure 9 contained all the species listed. Similarly, the species that are grouped together in Table II were added progressively to the solution. These ions were added in quantities exceeding the values found in typical leaching solutions. These results show that the measured current was not affected by any of the ions tested.

Results on an Operational Plant

The instrument illustrated in Figure 2 was installed at the top of the second tank of the leaching circuit in the plant. Slurry from the tank was pumped to a measurement cell, and returned to the tank. The instrument operated at the gold plant for two weeks, and data were obtained for an uninterrupted period of one week.

The concentration of cyanide in the tank was determined by titration, and the calibration curve for May 27th is illustrated in Figure 10. The calibration was re-examined by a comparison of the measured current with cyanide titrations at regular periods during the week of operation. The calibration remained accurate for the first two days of operation but, by the end of the week, there was significant deviation between the results of 27th May and the titrations conducted on 2nd June.

It should be noted that, although these results form straight-line plots, the lines do not have a zero intercept as expected. The value of the intercept changed during the period of operation, perhaps as the result of a layer of material on the surface of the anode, or as the result of changes in other parameters, such as the pulp density. However, there did not seem to be a correlation between changes in the operating conditions, such as in lime concentration or pulp density, during this period that would explain this drift in the calibration.

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Table I

Composition of a leaching solution in a typical Witwatersrand gold plant (after Davidson et al.¹²)

Elements present	Concentration mg/l	Anions present	Concentration mg/l
Pb	5,4	Ca	590
Ag	0,69	Ba	3
Cu	7	Na	310
Al	2	K	45
SO	<1	Si	20
Fe	1	SCN ⁻	90
Zn	15	S ₂ O ₃ ²⁻	4
Pb	<1	SO ₄ ²⁻	1680
Hg	0,01	Cl ⁻	240
Al	<1	Free CN ⁻	92

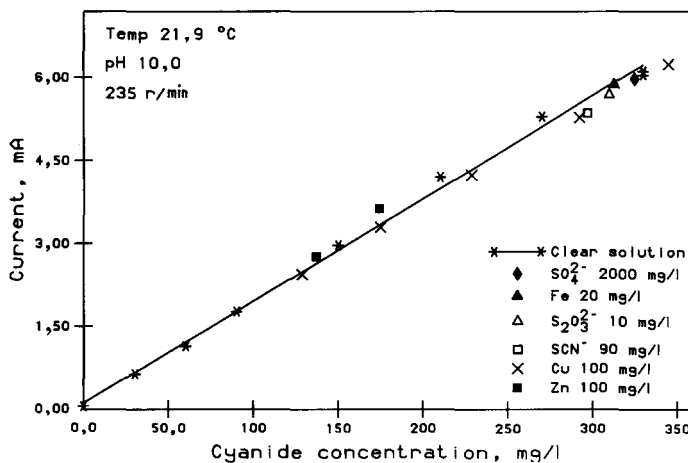


Figure 9—The effect of other ions in solution on the current (10-litre tank, clear solution, 5 g/l HBO₂, 1 g/l KCl)

Table II

Effect of ions in solution

Ion	Concentration mg/l	Current without addition, mA	Current with addition, mA
Cl ⁻	1000	9,8	9,8
ClO ₄ ⁻	20	9,7	9,6
Acetate	20	9,4	9,1
CO ₃ ²⁻	20	9,2	9,0
Dichro	20	9,2	9,0
Chloro	40	9,1	8,8
Bromate	20	8,9	8,6
SO ₄ ²⁻	50	8,2	8,3
SCN ⁻	20	8,2	8,3
Cu ₂ S ₂	10 g/l	8,0	7,6
O ₂	40	15,4	17,0

The calibration curve of 27th May (and 28th) shown in Figure 10, was used in the calculation of the cyanide concentration from the current as measured by the instrument. These concentrations were compared with the experimenter's and the plant operator's determination of cyanide for a seven-day period, from 27th May to 2nd June. These results are shown in Figure 11. The instrumental reading is the line with the legend 'Cyanide meter', while the experimenter's titrations are represented by circles with the legend 'Titration', and the plant operator's data are the crosses with the legend 'Plant data'. A complete set of operator's data for this period was not available.

The comparison between the instrumental readings and the titrated values suggests that the instrument is suitable for the monitoring of cyanide concentrations.

By the seventh day, 2nd June, there was a difference of 18 to 40 per cent between the instrumental reading and the titration values. Clearly, this indicates that the instrument requires re-calibration before the seventh day. However, even on the seventh day, the changes in cyanide concentrations resulted in proportional changes in the readings of the instrument (Figure 10). A control instrument based on this measured value would still change the cyanide concentration correctly, but the setpoint would have effectively drifted to a higher value. For example, the control system would maintain the concentration at 260 ppm, rather than at the required value of 200 ppm.

These results demonstrate the successful operation of the instrument on the plant.

Discussion

The results reported here show that amperometry is a potentially suitable technique for the determination of cyanide on a gold plant. The current due to the dissolution of a copper anode is proportional to the concentration of cyanide in solution. It is not affected by the concentration of oxygen, or by the pH value.

A proportional response to the concentration of cyanide is an advantage in an operational environment since only one measurement is required for calibration of the instrument.

The current has an Arrhenius type of dependence on the temperature. This means that the instrument requires temperature compensation.

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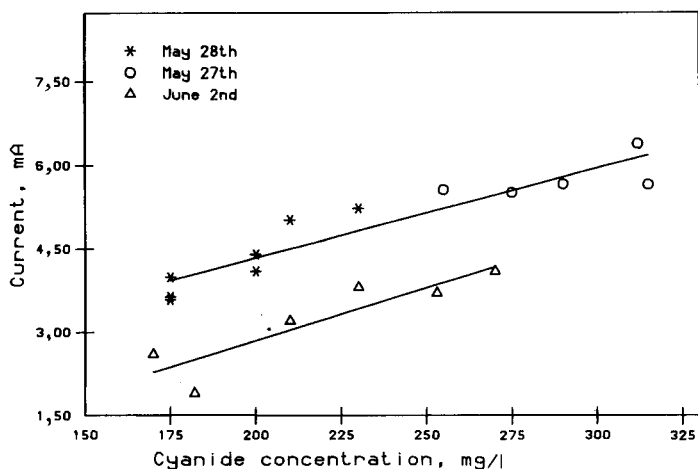
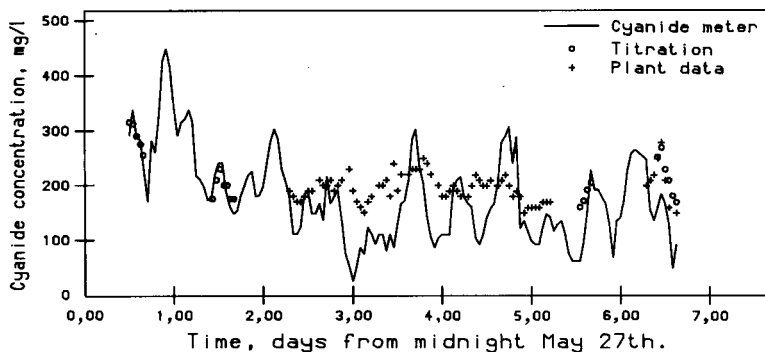


Figure 10—The calibration curve of 27th May and the subsequent examination of the calibration curve



$$i = 1.1066 + 0.0161637\text{NaCN}$$

Figure 11—Plant results for the week 27th May to 2nd June

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However, since the rate of reaction at the anode is controlled by mass transfer, the current is affected by the conditions of agitation in the vicinity of the anode. For successful implementation of this technique, the conditions of agitation must be constant. In this investigation, the conditions of agitation were controlled by pumping of the slurry through the measuring cell. This could also be achieved by agitation of the slurry in the measuring cell, or by the provision of an in-line cell with slurry from a constant head.

The measurement is not affected by the other ions typically found in gold-leaching solutions. Baker *et al.*⁴, McCloskey⁵, Miller *et al.*⁶, and Pihlar *et al.*⁷ found that, of over 30 ions tested, only sulphide, iodide, and thiocyanate resulted in any serious interference at a silver anode. However, the concentrations of these anions were a thousand times greater than the free cyanide concentration. In the work described here, the concentration of cyanide was usually higher than the concentrations of these anions. The anion concentrations tested in the present work were far greater than the concentrations found in typical gold-leaching solutions.

At present, the only cyanide instruments used on some plants are based on automatic titration systems. They require titration reagents, are difficult to run, and have not gained wide acceptance within the industry. The present work tested a new type of instrument based on a different analytical technique. Alternatively, an instrument could be constructed by the adaptation of the existing instrumentation to utilize the amperometric method. For example, the automatic titration system of the CYCAD system¹ could be replaced with the amperometric technique discussed here, which would greatly simplify the CYCAD system. The combined system would operate in clear solutions, so that the measured current would not be affected by changes in pulp density in the plant, and would not require titration reagents. In addition, the combined system would produce a continuous result, rather than the discrete sampling at present produced by the CYCAD system.

Conclusions

The results presented here indicate that a cyanide detection cell based on the amperometric technique is accurate under the operating conditions found on a gold plant. The measurement is not affected by changes in oxygen concentration, pH, or other ions present in the leaching solution, but is affected by the agitation in the tank, the solids concentration, and the temperature. Therefore, the conditions of agitation should be kept constant in the vicinity of the anode, and the instrument should include temperature compensation.

The operation of the instrument on a gold plant was very good. The instrument is robust and reliable, but would require re-calibration after a period of a week. This instrument is suitable for operation on South African gold mines as a process-control instrument. ♦