

The chemical behaviour of cyanide in the extraction of gold. 2. Mechanisms of cyanide loss in the carbon-in-pulp process

by M.D. ADAMS*

SYNOPSIS

Most of the cyanide lost in carbon-in-pulp plants is due to the reaction of cyanide with base metals and sulphides during leaching. Some cyanide is also lost in the adsorption tanks as a result of oxidative and adsorption reactions with the activated carbon. The high rates of cyanide loss in the elution and electrowinning stages are attributable to hydrolytic decomposition and anodic oxidation, respectively. However, the relative amount of cyanide lost during these two stages is small for a given amount of ore treated.

SAMEVATTING

Die grootste sianiedverlies in koolstof-in-pulpaanlegte is toe te skryf aan die reaksie van sianied met onedelmetale en sulfiede tydens loging. Van die sianied gaan ook in die adsorpsietanks verlore as gevolg van oksidatiewe en adsorpsieaksies met die geaktiveerde koolstof. Die hoë tempo van sianiedverlies tydens die eluëer- en elektro-ekstraksiestadium is onderskeidelik toe te skryf aan hidrolitiese ontbinding en anodiese oksidasie. Die betrokke hoeveelheid sianied wat tydens hierdie twee stadiums verlore gaan, is egter klein vir 'n gegewe hoeveelheid erts wat behandel word.

Introduction

Since the turn of the century, cyanide has generally been used as the lixiviant for gold. The chemical behaviour and stability of the cyanide ion in aqueous solution have been largely neglected until now, despite the fact that cyanide is lost in varying amounts in the different stages at gold-processing plants. Moreover, the stability of the cyanide in large volumes of tailing solutions is an issue of increasing environmental concern.

Part 1 of this series¹ examined the chemical behaviour and stability of the cyanide ion in aqueous solution in some detail. The conditions studied were selected as being directly applicable to the carbon-in-pulp (CIP) process, and it is the aim of the present work to elucidate the main areas and mechanisms of the cyanide loss that occurs in CIP circuits.

A typical flowsheet of a CIP plant for the recovery of gold and silver is shown in Fig. 1. The spent solution of caustic cyanide after the gold has been recovered by elution and electrowinning is often recycled to the leaching stage. Concentrations of cyanide at the start of the leaching stage are typically about 0,5 g of sodium cyanide per litre of pulp, while those in the elution stage are typically about 0,2 M. The concentrations and conditions used in this study were chosen to closely approximate those in the CIP process.

Experimental Procedure

The sodium cyanide and sodium hydroxide were of A.R. grade, and were supplied by SAARChem and Merck. All the other chemicals were also of A.R. grade. Oxygen of commercial purity and high-purity nitrogen were used. All the solutions were made up with deionized

water. The activated carbon used was Le Carbone G210, which was purified by continual washing with cold deionized water.

The experiments conducted at ambient temperature used 500 ml of a 0,5 g/l solution of sodium cyanide at a natural pH value of 10,2. The pH of the solution was adjusted with sodium hydroxide or sulphuric acid. The solution was stirred with a magnetic or overhead stirrer, and the required amount of activated carbon was added. The pH value was measured by use of a Knick pH-meter, and the solution potential was measured with a Labion Model 15 potentiometer, which uses a platinum electrode in conjunction with a saturated calomel reference electrode. Dissolved oxygen was measured with a YSI dissolved-oxygen meter model 54A, which was calibrated with atmosphere-equilibrated deionized water, and corrected for altitude and ambient temperature. When different temperatures were used, a thermostatically controlled water-bath was employed in which the variation in temperature did not exceed 0,01°C.

The experiments conducted at higher temperatures used 300 ml of solution containing 0,2 M sodium cyanide and 0,2 M sodium hydroxide. The solution was refluxed in a round-bottomed flask with a water-cooled condenser.

Cyanide was determined titrimetrically with a silver nitrate solution, as described by Vogel³. Iodide ion (as KI) was used as the indicator, and aqueous ammonia was introduced to solubilize the silver cyanide that formed. The end-point is indicated by a golden-yellow turbidity. The cyanide content of some of the samples was also checked by ion chromatography.

Results and Discussion

The conditions pertaining to each of the unit operations of the CIP process were simulated, and the results are presented sequentially through the CIP process. The

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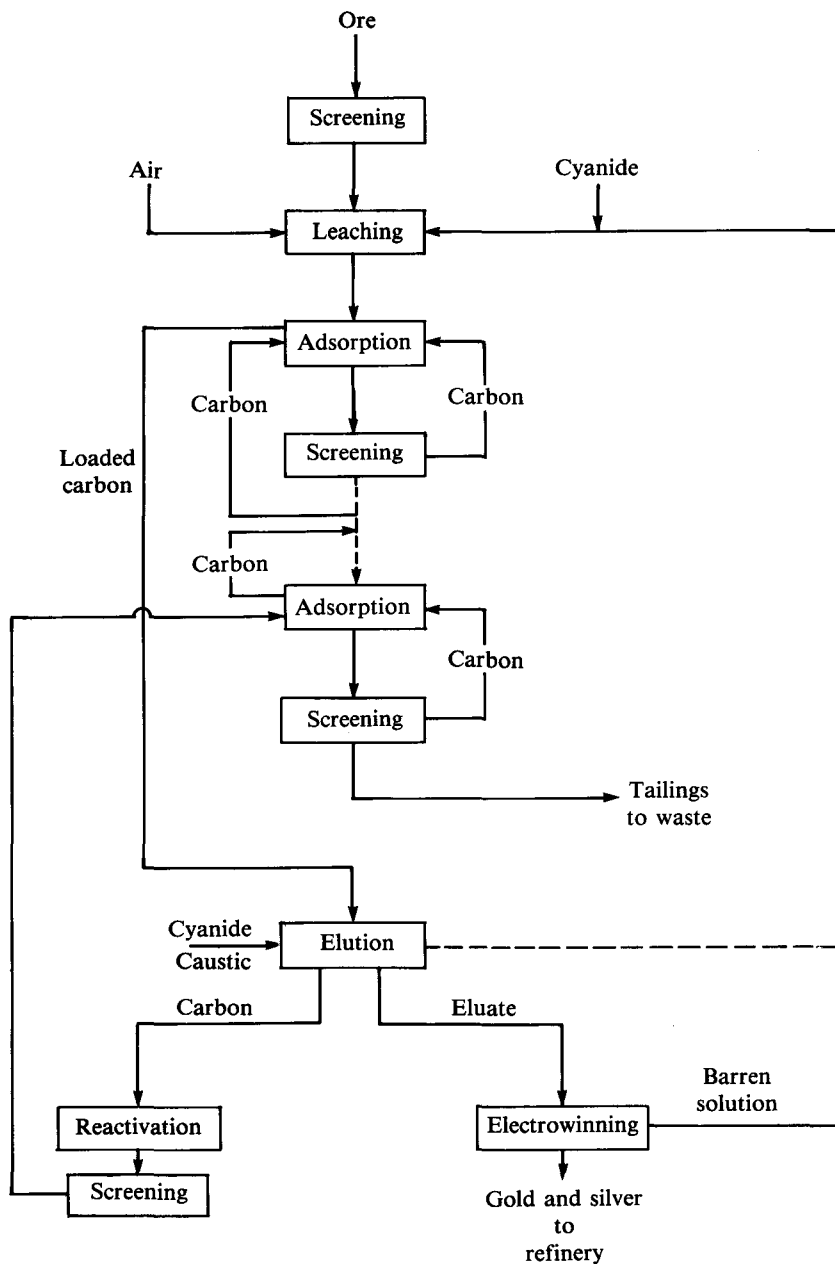


Fig. 1—Typical flowsheet of a CIP plant for the recovery of gold and silver (after McDougall and Fleming²)

reaction rates and mechanisms are discussed in relation to the most important cyanide decomposition reactions that occur for each unit operation.

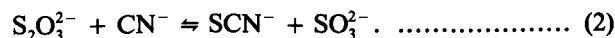
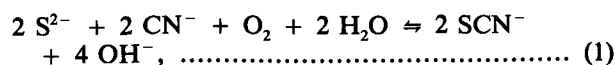
Stability of Cyanide during Leaching

The potential versus pH diagram for the Au-H₂O-CN system is shown in Fig. 2. A comparison with the diagram for the CN-H₂O system (Part 1 of this series, Fig. 1) shows that, under the conditions that are appropriate for the leaching of gold, cyanide is thermodynamically unstable, while cyanate is the more stable species. The kinetics of the oxidation of cyanide to cyanate are evidently extremely slow at room temperature under normal conditions^{1,5}.

Cyanide is consumed in the leaching stage via the formation of metal-ion complexes such as Au(CN)₂⁻, Fe(CN)₆⁴⁻, and Co(CN)₆³⁻. In ores that contain a large amount of iron or cobalt, six cyanide ions are consumed

for every metal atom. This is unavoidable, and contributes to the loss of cyanide in the leaching stage.

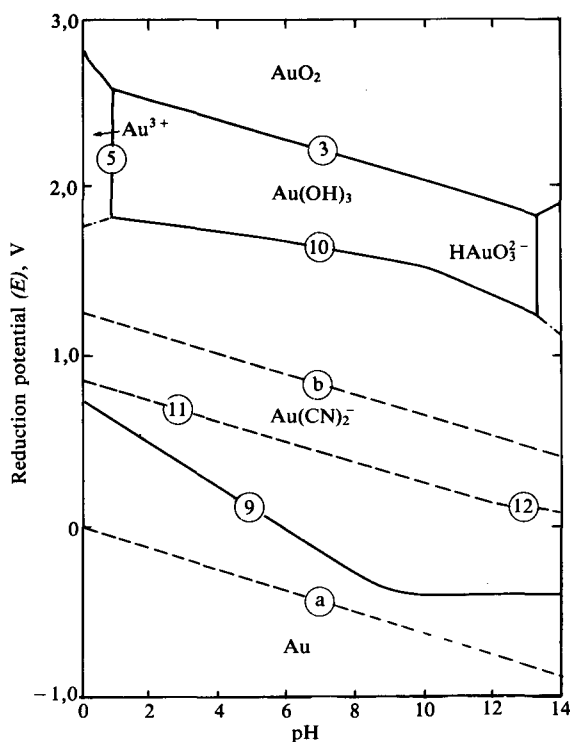
When sulphur-bearing minerals are present, further losses of cyanide are encountered as a result of the following reactions:



These side reactions are the main cause of cyanide loss during the leaching of gold.

Under typical leaching conditions, only a slight loss of cyanide due to its hydrolysis to hydrogen cyanide can be expected, and no measurable oxidation of cyanide to cyanate occurs¹.

When conditions other than those normally employed during leaching are prevalent, an increase in the consump-



Reactions:

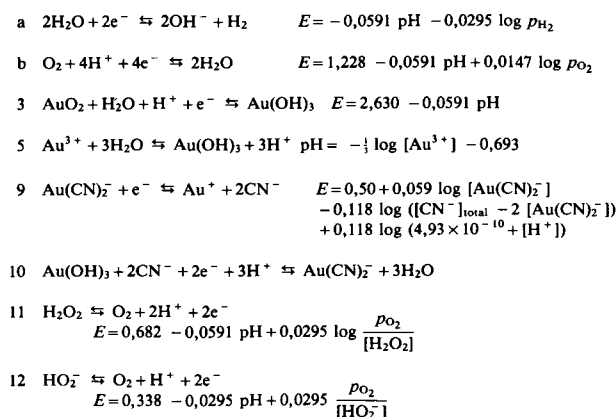


Fig. 2—Homogeneous equilibrium diagram of potential versus pH for the Au-H₂O-CN system at 25°C (after Finkelstein⁴)

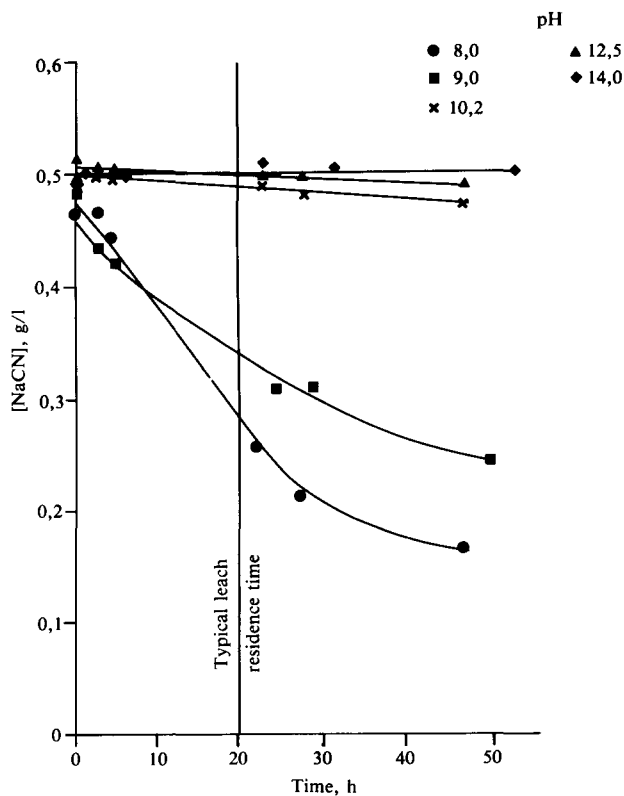
tion of cyanide can be expected. Changes in the pH of the pulp have a marked effect, as is shown in Fig. 3. When the pH is lowered below the pK_a of cyanide (9,39), a large loss of cyanide can be expected during a normal leaching period of 20 hours.

Temperature also has an effect on the loss of cyanide, as is shown in Fig. 4, and more cyanide will be lost as hydrogen cyanide on a hot day. The effect of air agitation over the typical 20-hour residence time is small, as shown in Fig. 5.

Stability of Cyanide in the Carbon Adsorption Stage

It was shown in the previous paper¹ that activated carbon acts as a catalyst for the oxidation of cyanide to cyanate. Moreover, evidence was cited for the adsorption, to some extent, of cyanide onto activated carbon. A relatively high loss of cyanide can therefore be expected in the adsorption tanks.

The typical residence time in an adsorption tank is



Conditions

Volume of solution 500 ml
O₂ in solution 6,5 mg/l

Fig. 3—Effect of pH on the stability of cyanide at 20°C

about 1 hour. Thus, for a six-stage adsorption circuit, the cyanide will be in contact with the activated carbon for about 6 hours. The effect of the concentration of carbon on the rate of cyanide loss is shown in Fig. 6. For a typical carbon concentration of about 25 g/l, the loss of cyanide is about 20 per cent over a 6-hour contact period. However, one-third of the cyanide can be lost if the concentration of carbon is increased to 40 g/l.

An even greater effect is evident when the pH value of the pulp drops, as shown in Fig. 7. The lowering of pH has been proposed⁶ as a means of improving the adsorption of gold onto carbon and, at the same time, achieving a low concentration of cyanide in the tailings. In a carbon-in-leach (CIL) situation, this would have to be carried out in the final adsorption stage only, since a certain nominal concentration of cyanide is required to achieve efficient leaching. The economic feasibility of destroying the cyanide and enhancing the adsorption of gold onto carbon by this technique has not been established.

Stability of Cyanide during Carbon Elution

The odour of ammonia that exudes from the elution column in a CIP circuit is well known to operators, and sodium cyanide is sometimes added to the eluate in a Zadra process to replenish cyanide lost as a result of decomposition. Operators at several plants in the USA, Canada, and Australia⁷ have reasoned that the presence of cyanide is not necessarily critical to the elution step in all cases, and therefore no longer use a caustic cyanide eluant but, for example, employ caustic soda alone.

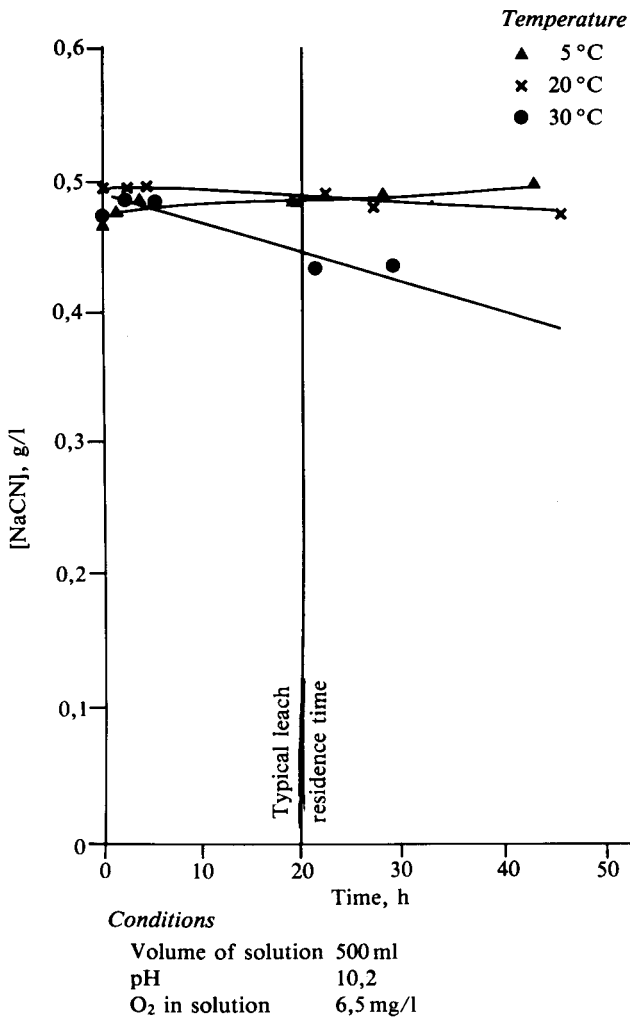


Fig. 4—Effect of temperature on the stability of cyanide

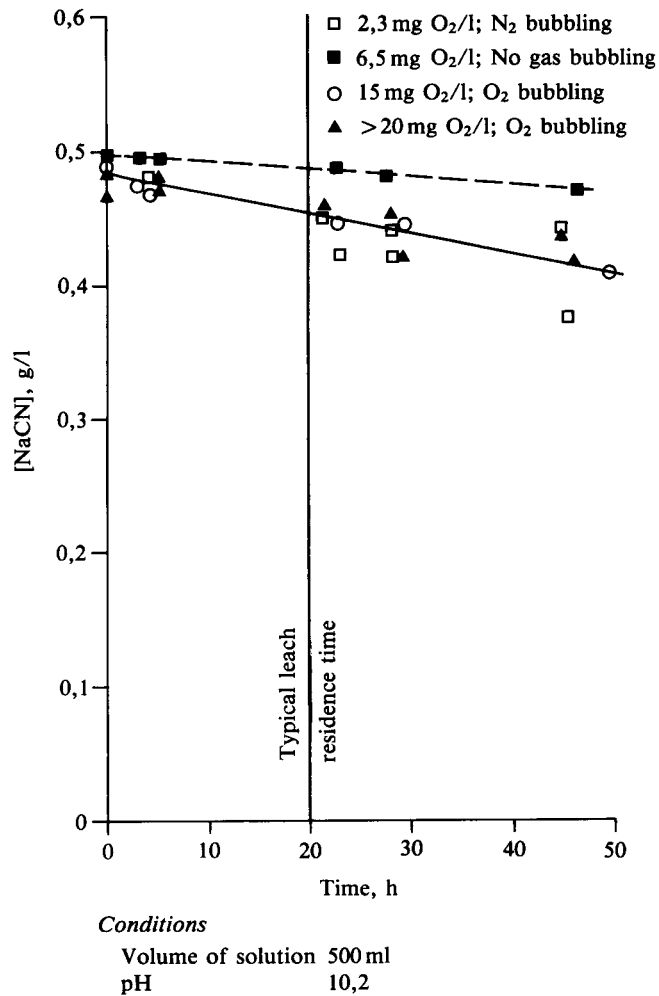


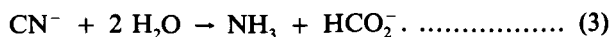
Fig. 5—Effect of the concentration of oxygen on the stability of cyanide at 20°C

The actual extent of the decomposition of cyanide that is inherent in various elution procedures has not, as yet, been firmly established. Fig. 8 shows the results for the loss of cyanide in the pre-treatment stage of an elution process developed by Anglo American Research Laboratories and known as the AARL process. A significant loss of cyanide is evident after 30 minutes of pre-treatment, particularly at higher temperatures. (At 130°C, 80 to 90 per cent of the cyanide has decomposed.) In fact, several processes have been reported^{9,10} for the destruction of cyanide in aqueous waste solutions by thermal decomposition techniques.

The experiments used here differ from those used earlier in this work, in that the elution conditions were simulated. A typical solution was chosen, composed of 0,2 M sodium cyanide and 0,2 M sodium hydroxide, and having a solution volume of 300 ml and a carbon concentration of 89 g/l. These conditions are exactly the same as those used in previous work on the kinetics of the elution of gold from activated carbon¹¹, and they afford an easy comparison between the decomposition of cyanide and the elution of gold under the same conditions.

In the preceding paper¹, it was shown that the loss of cyanide at 95°C, in both the presence and the absence of activated carbon, is due to the hydrolysis of cyanide

to ammonium formate:



The instability of formate at higher temperatures results in the following overall reaction:



Fig. 9 shows the dramatic effect of an increase in temperature from 72 to 95°C. At 95°C, about 93 per cent of the cyanide decomposed in 50 hours (the typical time taken for a Zadra elution at 95°C), whereas less than 30 per cent was lost at 72°C over the same time period. Even if the actual residence time of the eluant in the column is taken to be half this in total, a loss of about 85 per cent of the cyanide can be expected. The use of a pressurized elution vessel will result in an even greater loss of cyanide (Fig. 8).

The presence of activated carbon had little effect on the loss of cyanide at 95°C, except in the initial stages, whereas at 72°C a marked increase in the loss of cyanide was evident with activated carbon.

Despite the increase in the rate of cyanide loss with an increase in temperature, the actual amount of cyanide consumed in the elution stage for a given amount of ore

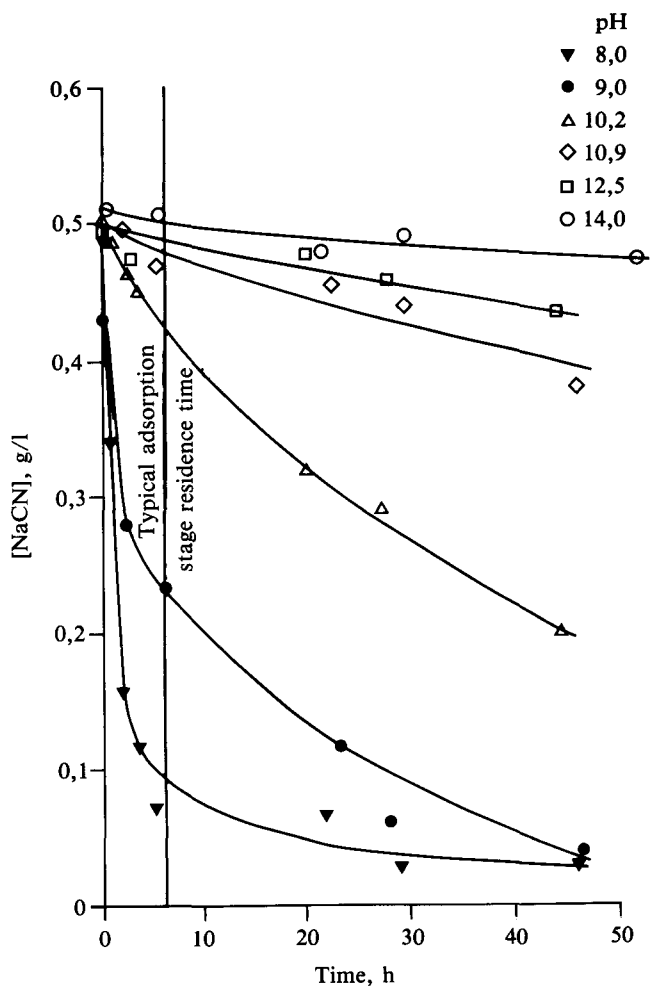
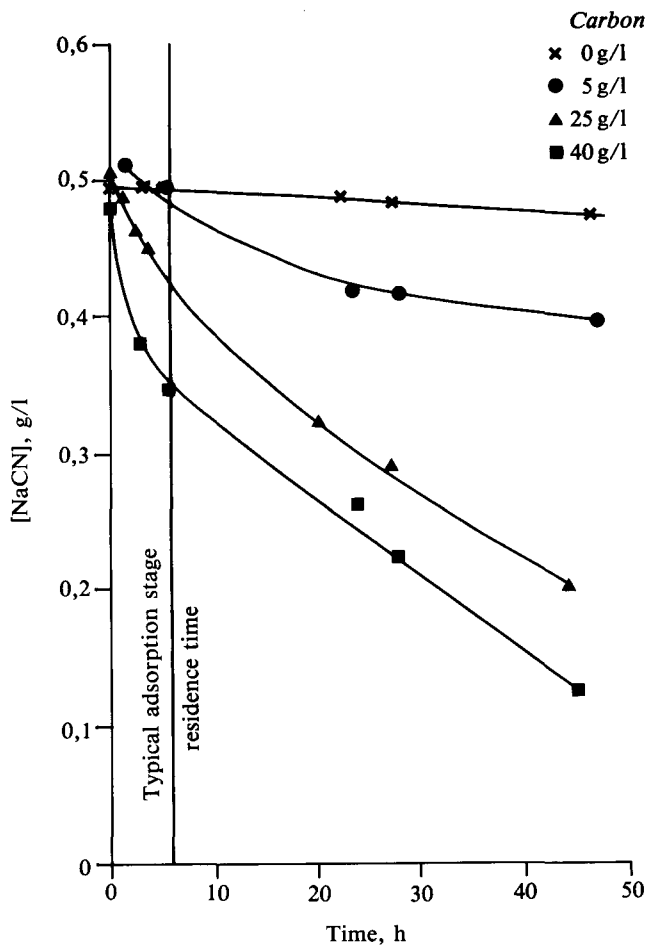


Fig. 6—Effect of the concentration of activated carbon on the stability of cyanide at 20°C

Fig. 7—Effect of pH on the stability of cyanide in the presence of activated carbon (25 g/l) at 20°C

treated is less than that consumed during the leaching and adsorption stages. This occurs because much larger volumes of solution are involved in the latter case. The experience gained by operators on CIP plants has been used to predict that the amount of cyanide consumed in the elution stage can be expected to be roughly 10 to 20 per cent of the amount consumed during leaching.

Stability of Cyanide in the Electrowinning Stage

An eluate from the elution of a loaded sample of carbon from Mintek's pilot plant at Kloof Gold Mine was used in this experiment. This plant solution was chosen so that the effect of actual electrowinning conditions on the stability of cyanide could be determined, the gold, silver, and base metal contents of the solution being sufficient for electrowinning to occur.

The eluate consisted of the first three bed volumes of an eluate from an AARL type of process. The pre-treatment involved a 30-minute pre-soak of the loaded carbon in a solution comprising 2 per cent sodium hydroxide, 2 per cent sodium cyanide, 6 per cent ethanol, and 0,5 per cent methanol, followed by elution with

deionized water.

The electrowinning cell had an electrolyte capacity of about 20 litres. The electrodes consisted of two titanium cathodes and three stainless-steel anodes, all of which were 240 mm by 190 mm in size. The cell was filled with electrolyte, and raised to a temperature of 50°C. Electrolysis was then applied to the cell at a voltage of 7 V and a current of 19 A. The concentration of cyanide in the cell, as well as a control sample of the eluate kept at 50°C with no current passing through, are shown in Fig. 10.

About 58 per cent of the cyanide had been lost from the solution in the electrowinning cell after 5 hours. In contrast, none of the cyanide in the control experiment was lost over the same period. (It had been found previously that 5 hours was a sufficient period in which to electrowin more than 95 per cent of the gold, and represents the typical electrowinning period for these conditions.)

This also has ramifications for the Zadra type of elution, and shows that a substantial loss of cyanide occurs due to hydrolysis, and due to catalytic oxidation in the elution column and anodic oxidation in the electrowin-

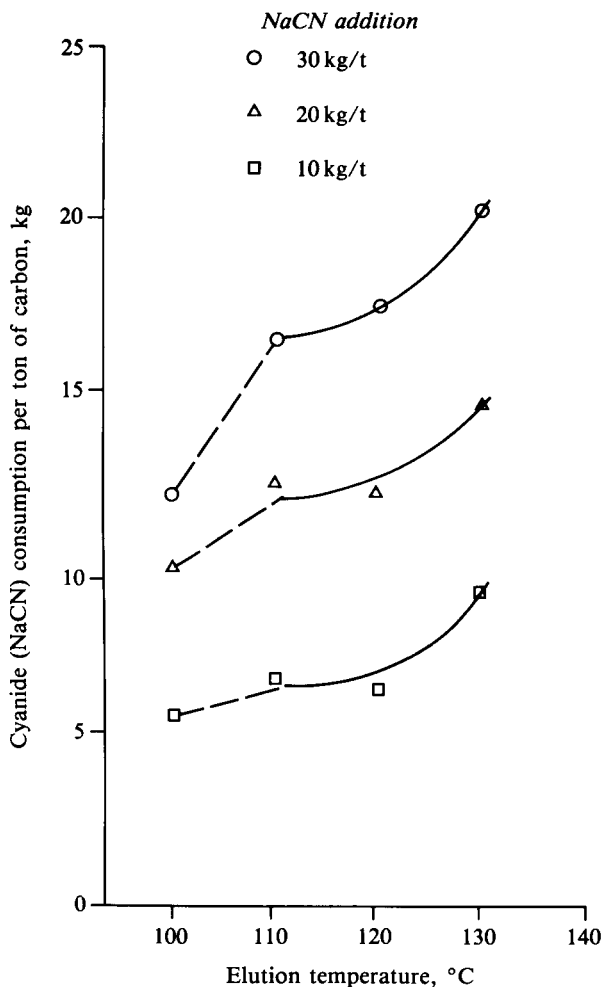


Fig. 8—Effect of elution temperature on the consumption of cyanide at various concentrations in the presence of 20 g/t sodium hydroxide (after Davidson and Schmidt⁶)

ning cell.

Conclusions

The major loss of cyanide in a typical CIP plant occurs as a result of reactions with base metals and sulphides during leaching. No significant losses occur due to oxidation or hydrolysis during leaching. A further loss is encountered in the adsorption circuit, where about 20 per cent of the cyanide entering the circuit is lost under typical operating conditions. This is due to the carbon-catalysed oxidation of cyanide to cyanate and other compounds, as well as to the adsorption of cyanide onto the carbon. A higher rate of cyanide loss can be achieved by the lowering of the pH value of the pulp. This would result in both improved gold-adsorption efficiencies and lower concentrations of cyanide in the tailings.

Much higher rates of cyanide loss occur in the elution and electrowinning stages, because of hydrolysis and anodic oxidation respectively. However, the total amount of cyanide lost in these stages is less than that lost during leaching and adsorption.

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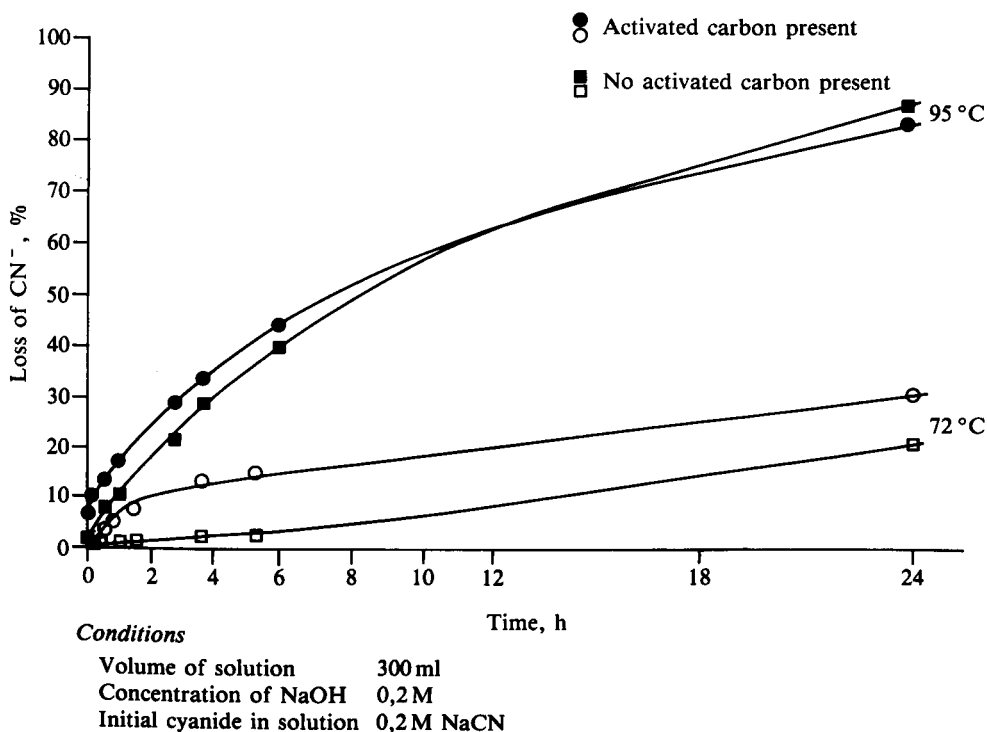


Fig. 9—Rate of decomposition of cyanide at high temperatures in the presence and absence of activated carbon (89 g/l)

Conditions

Volume of solution 300 ml
 Concentration of NaOH 0,2 M
 Initial cyanide in solution 0,2 M NaCN

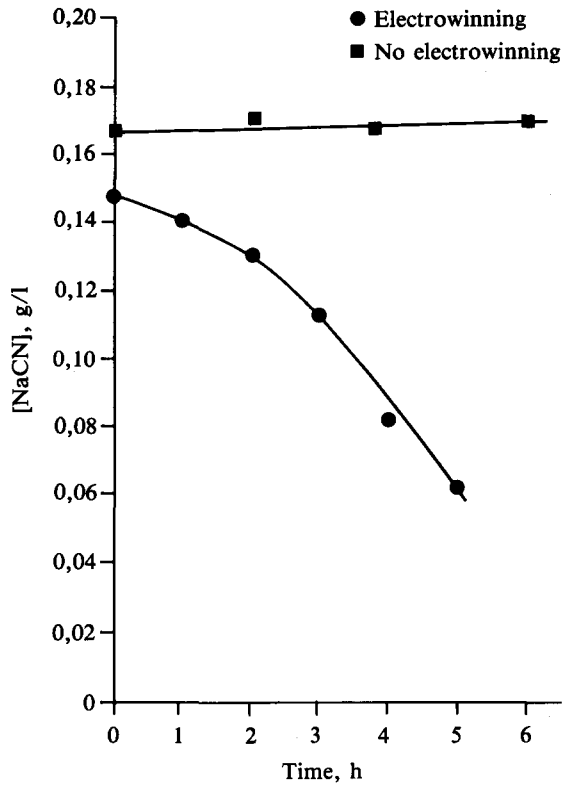


Fig. 10—Rate of oxidation of cyanide in a typical gold-electrowinning cell

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