

# The chemical behaviour of cyanide in the extraction of gold. 1. Kinetics of cyanide loss in the presence and absence of activated carbon

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## SYNOPSIS

The kinetics of cyanide loss were found to be first order under any given set of conditions, allowing rate constants to be easily determined. At room temperature and in the absence of activated carbon, some cyanide is lost by hydrolysis to hydrogen cyanide, but this does not occur to any significant extent at pH values higher than about 10. A higher rate of hydrolysis occurs when air agitation is used.

When activated carbon is present, an additional carbon-catalysed oxidation reaction is responsible for a fairly high loss of cyanide. The evidence indicates a reaction mechanism that consumes oxygen and produces cyanate ion. Some of the cyanate thus produced decomposes to form a mixture of ammonia, carbonate, and urea, depending on the solution conditions. Additional cyanide is lost as a result of the adsorption of sodium cyanide by the activated carbon.

At high temperatures, an additional hydrolysis reaction, which involves the formation of ammonium formate as an intermediate, occurs and is responsible for a high loss of cyanide, leading ultimately to the formation of ammonia, hydrogen, and carbon dioxide. The presence of activated carbon has no effect on the rate of this reaction.

## SAMEVATTING

Daar is gevind dat die kinetika van sianiedverlies onder enige gegewe omstandighede van die eerste orde is wat dit moontlik maak om die tempokonstantes maklik te bepaal. By kamertemperatuur en in die aanwesigheid van geaktiveerde koolstof, gaan van die sianied deur hidrolise verlore aan waterstofsianied, maar dit vind nie in enige beduidende mate by pH-waardes bo ongeveer 10 plaas nie. 'n Hoër hidrolisetyempo kom voor wanneer lugroering gebruik word.

Wanneer daar geaktiveerde koolstof aanwesig is, is 'n bykomende koolstofgekataliseerde oksidasiereaksie verantwoordelik vir 'n betreklik hoë sianiedverlies. Daar is aanduidings van 'n reaksiemechanisme wat suurstof verbruik en 'n sianaat ion produseer. Van die sianaat aldus geproduseer, ontbind om 'n mengsel van ammoniak, karbonaat en ureum te vorm, afhangende van die oplostoestande. Verdere sianied gaan verlore as gevolg van die adsorpsie van natriumsianied deur die geaktiveerde koolstof.

By hoë temperature vind daar 'n bykomende hidrolisereaksie plaas wat die vorming van ammoniumformiaat as 'n tussenstof behels, vir 'n hoë sianiedverlies verantwoordelik is, en uiteindelik tot die vorming van ammoniak, waterstof en koolstofdoksied lei. Die aanwesigheid van geaktiveerde koolstof het geen uitwerking op die tempo van hierdie reaksie nie.

## INTRODUCTION

A knowledge of the chemical behaviour and stability of the cyanide ion in aqueous solution is of particular importance to the gold-processing industry in terms of process control and the detoxification of tailings solutions. However, the mechanisms involved in the reaction of the cyanide ion in aqueous solution can be complex, particularly in the presence of activated carbon. The present work was undertaken in an effort to clarify the kinetics and mechanisms of cyanide loss under various conditions.

Two general types of reaction have been proposed for the loss of cyanide from aqueous solution, viz hydrolytic and oxidative reactions.

At low pH values, the well-known hydrolysis of cyanide occurs as follows:



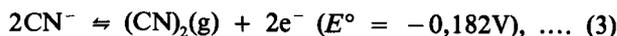
The hydrogen cyanide thus formed will volatilize to some extent<sup>1</sup>. At high pH values, another hydrolysis reaction has been postulated<sup>2-6</sup> to occur, particularly at high

temperatures:

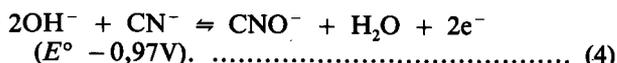


It is reported<sup>1</sup> that reaction (2) occurs very slowly at ambient temperatures, resulting in the gradual decomposition of cyanide in alkaline solutions. Additional hydrolytic reactions have been reported<sup>7,8</sup> to result in various ill-defined polymeric forms of hydrogen cyanide and cyanogen. As these reactions are not important in gold-plant solutions, the species involved are not dealt with in any detail in this paper.

The second general type of reaction, viz oxidative reaction, is also responsible for the loss of cyanide from aqueous solution. Cyanide is fairly easily oxidized to cyanate or cyanogen. In alkaline solutions, these reactions are<sup>9</sup>



and



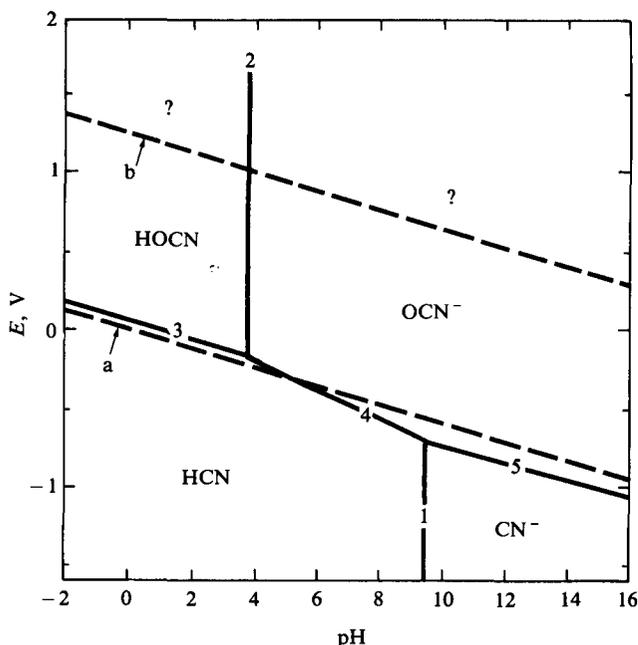
All  $E^\circ$  values refer to standard reduction potentials versus

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the standard hydrogen electrode (SHE), even though the reactions to which they refer may, for convenience sake, be written as oxidation reactions.

A diagram of potential versus pH for CN-H<sub>2</sub>O at 25 °C is shown in Fig. 1, together with the associated thermodynamic functions represented by the curves. It is clear that the oxidation of cyanide to cyanate is thermodynamically favourable at room temperature. However, the kinetics of this reaction are exceedingly slow in the absence of any catalyst, which is why cyanide can be used economically in large-scale hydrometallurgical processes.



**Reactions**

- a  $2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{OH}^- + \text{H}_2$   $E = -0,0591 \text{ pH} - 0,0295 \log p_{\text{H}_2}$
- b  $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$   $E = -1,228 - 0,0591 \text{ pH} + 0,0147 \log p_{\text{O}_2}$
- 1  $\text{HCN}_{(\text{aq})} \rightleftharpoons \text{CN}^- + \text{H}^+$   $\log \frac{[\text{CN}^-]}{[\text{HCN}]} = -9,39 + \text{pH}$
- 2  $\text{HOCN}_{(\text{aq})} \rightleftharpoons \text{OCN}^- + \text{H}^+$   $\log \frac{[\text{OCN}^-]}{[\text{HOCN}]} = -3,89 + \text{pH}$
- 3  $\text{HOCN}_{(\text{aq})} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HCN}_{(\text{aq})} + \text{H}_2\text{O}$   
 $E = 0,021 - 0,0591 \text{ pH} + 0,0295 \log \frac{[\text{HOCN}]}{[\text{HCN}]}$
- 4  $\text{OCN}^- + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HCN}_{(\text{aq})} + \text{H}_2\text{O}$   
 $E = 0,136 - 0,0885 \text{ pH} + 0,0295 \log \frac{[\text{OCN}^-]}{[\text{HCN}]}$
- 5  $\text{OCN}^- + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{CN}^- + \text{H}_2\text{O}$   
 $E = 0,141 - 0,0591 \text{ pH} + 0,0295 \log \frac{[\text{OCN}^-]}{[\text{CN}^-]}$
- ? Reaction not identified by Bard<sup>9</sup>

**Fig. 1—Homogeneous equilibrium diagram of potential versus pH for the CN-H<sub>2</sub>O system at 25 °C (after Bard<sup>9</sup>)**

**EXPERIMENTAL PROCEDURE**

The sodium cyanide, sodium hydroxide, and potassium cyanate were of A.R. grade, and were supplied by SAAR-Chem and Merck. All the other chemicals were of A.R.

grade. Oxygen of commercial purity and high-purity nitrogen were used, and 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.

In the experiments conducted at ambient temperature, 500 ml of a 0,5 g/l solution of sodium cyanide was employed, of which the natural pH value was 10,2. The pH values of the solution were 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. The 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. For the adsorption experiments, 5,0 g of activated carbon was contacted in a rolling bottle with 50 ml of solution for 24 hours. Various concentrations of NaCN and NaOH were employed, and the ionic strength was kept constant at 0,2 mol/kg (adjusted with NaCl).

In the experiments conducted at higher temperatures, 300 ml of solution containing 0,2 M sodium cyanide and 0,2 M sodium hydroxide were employed. 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 Vogel<sup>10</sup>. 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. Cyanate was determined by ion chromatography. The cyanide content of some of the samples was also checked in this manner, and a good correlation between the two methods was noted, even at cyanate concentrations as high as 0,1 M. The carbons were analysed for nitrogen by use of a Heraeus elemental analyser and a Leco nitrogen analyser.

**RESULTS AND DISCUSSION**

The experimental conditions selected were designed to simulate the various stages of a typical carbon-in-pulp (CIP) process. In this paper, the fundamental chemistry involved in the loss of cyanide will be discussed. In the second paper<sup>11</sup> in this series, these fundamental findings will be related to the practical situation in gold-processing plants. Recent work by Hoecker and Muir<sup>12</sup> presents a superficial study of some of the aspects investigated in detail in the present study. A comprehensive review of methods for the destruction of cyanide can also be found in that paper<sup>12</sup>.

The results of a typical experiment, plotted in semi-logarithmic form, are shown in Fig. 2. This linear relationship was found to be representative of the kinetics of cyanide loss under all the conditions studied. This suggests that a first-order rate law adequately describes

the kinetics of cyanide loss for all the reactions that occur. Hence,

$$-\frac{d[\text{CN}^-]}{dt} = k_1[\text{CN}^-], \dots\dots\dots (5)$$

where  $k_1$  is the first-order rate constant. Equation (5) can be integrated and rearranged in the normal manner to yield

$$\ln[\text{CN}^-]_t = \ln[\text{CN}^-]_0 - k_1 t, \dots\dots\dots (6)$$

which is the form in which Fig. 2 is plotted. This provides a useful predictive tool by which the cyanide concentration can be determined at any time, provided that the value of the rate constant  $k_1$  under the relevant conditions is known.

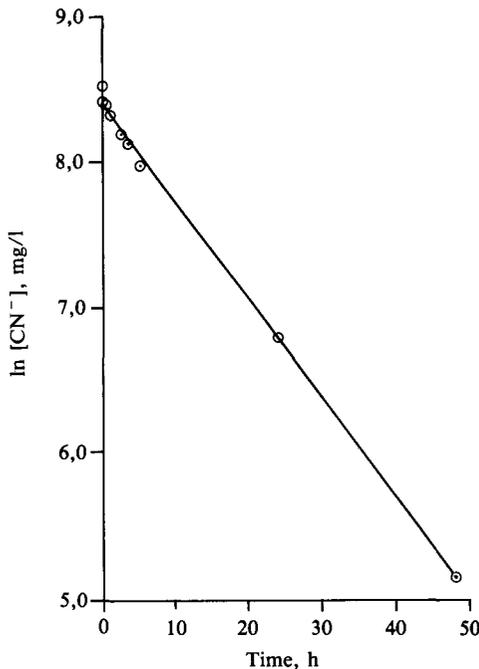


Fig. 2—Rate of cyanide loss for an aqueous solution at 95 °C in the presence of 89 g of activated carbon per litre

Several experiments were carried out in which the chemical and physical parameters were varied, and values for  $k_1$  were generated under various conditions. In view of the different reactions that have been postulated as occurring at high and low temperatures, the results are divided here into two main sections, corresponding to conditions of ambient and high temperature.

**Effect of Activated Carbon on the Stability of Cyanide at Ambient Temperature**

Activated carbon has been used for the removal of cyanide from aqueous solution for some years<sup>4,13-17</sup>, and reportedly acts as a catalyst for the oxidation of cyanide to cyanate. A comparison of the reduction potentials for reactions (3) and (4) (i.e. -0,182 and -0,97 V, respectively) and the reduction potentials of typical activated carbons<sup>18</sup> (+0,40 V to +0,08 V) shows that the oxidation of cyanide by carbon is thermodynamically favourable for both mechanisms. At this stage, it is not possible to determine whether the oxidation of cyanide to

cyanate proceeds directly—reaction (4)—or via a cyanogen intermediate—reaction (3).

**Effect of Carbon Concentration**

The presence of activated carbon in the cyanide solution has a marked effect on the rate of cyanide loss, as shown in Fig. 3. Some cyanide is lost even when no carbon is present, but the rate is very slow. This loss is ascribed to the evolution of some hydrogen cyanide via reaction (1), and evidence for this mechanism is presented later in this paper.

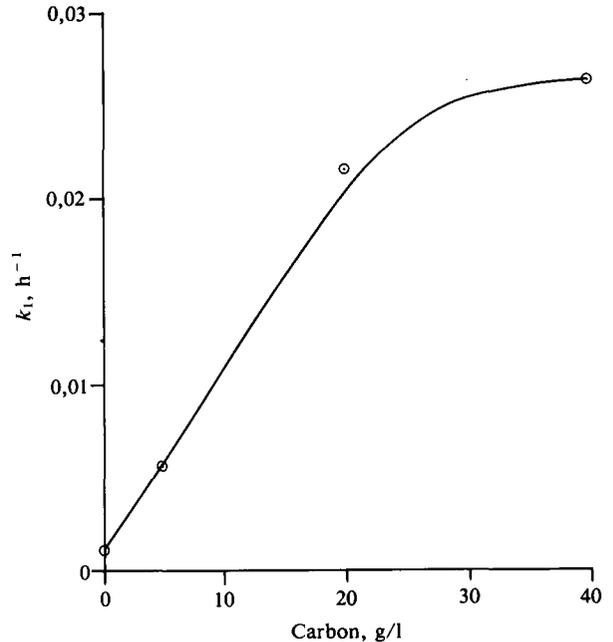
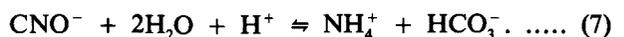


Fig. 3—Effect of the concentration of activated carbon on the rate of cyanide loss at 20 °C (pH = 10,2)

The cyanate concentration was monitored also so that the relative amount of cyanide lost via oxidation to cyanate in the presence of activated carbon could be determined. The final solution was found to contain more cyanate (2,40 mmol/l) than cyanide (2,15 mmol/l), which confirms that catalytic oxidation of cyanide to cyanate is the primary mechanism for the loss of cyanide in the presence of activated carbon. However, this scheme is unable to account for all the cyanide lost, since the total cyanide and cyanate present in the final solution is only about half that of the initial cyanide content (8,05 mmol/l).

The normal hydrolysis reaction by which hydrogen cyanide is formed—equation (1)—accounts for a loss of about 5 per cent. In addition, it is well known<sup>2,19</sup> that the cyanate ion is decomposed slowly by water, and that ammonium carbonate and some urea are formed:



and



A simple experiment was performed to quantify the above reactions under the conditions of interest. The results presented in Table I show the decomposition of cyanate in aqueous solution over a 48-hour period under

conditions that were similar to those of the previous experiment. The fact that a higher rate of cyanate loss occurred in the presence of activated carbon suggests that the carbon acts as a catalyst for the decomposition of cyanate. The nitrogen analyses given in Table I indicate that some cyanate is also adsorbed onto the carbon. The high background of nitrogen prevents any quantitative conclusions from being made regarding the relative importance of the reactions. A simple calculation shows that the amount of cyanate that is lost is insufficient to account for the remainder of the cyanide loss: on the basis of the kinetic results given in Table I, one would predict that 0,80 mmol/l of cyanide originally present in the experiment would be lost in this manner.

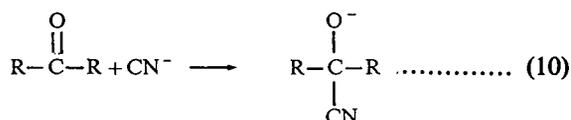
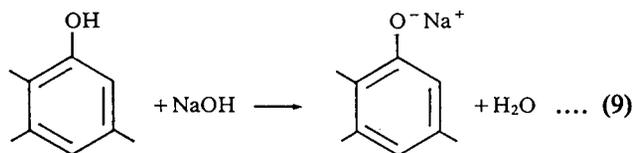
TABLE I  
DECOMPOSITION OF CYANATE AT 20 °C  
WITH NO CYANIDE PRESENT

Conditions:  
Volume of solution 500 ml  
Temperature 20 °C ± 2 °C  
Cyanate present as KCNO

pH of solution	Time h	[CNO <sup>-</sup> ] in solution* mmol/l		[N] on carbon† mmol/g
		Activated carbon present (25 g/l)	No activated carbon present	
7,0	0	8,00	8,00	0,029
	24	7,54	8,04	
	48	7,04	7,92	
10,2	0	8,00		0,021
	24	7,56		
	48	7,22		

\* Determined by ion chromatography  
† Background (0,093 mmol/g) subtracted

Previous work<sup>20</sup> suggested that both cyanide and hydroxide are adsorbed onto the surface of activated carbon to some extent, while hydroxide reacts with phenolic-type groups—reaction (9)—and cyanide reacts with surface carbonyl-type groups—reaction (10):



As confirmation of this result, a series of tests was undertaken in which solutions of NaOH and NaOH/NaCN of constant ionic strength (adjusted with NaCl) were contacted with activated carbon for a period of 24 hours. These results are presented in Tables II and III respectively. For solutions of sodium hydroxide, a stoichiometric amount of Na<sup>+</sup> and OH<sup>-</sup> was found to have

entered the carbon, and their reaction with phenolic groups is most likely. For solutions of sodium cyanide at a pH of 12, an increase in the nitrogen content was observed with an increasing concentration of cyanide. An almost stoichiometric increase in the concentration of sodium was also observed once the adsorption of the sodium associated with hydroxide had been corrected for. The amount of cyanide that was lost from the solution is larger than this stoichiometric amount, and this occurred undoubtedly as a result of the oxidation and hydrolytic reactions discussed above. The capacity of G210 activated carbon to adsorb cyanide is less than that to adsorb hydroxide, and this indicates a preponderance of phenolic groups over carbonyl groups under the postulated mechanism.

TABLE II  
ADSORPTION OF NaOH ONTO A TYPICAL ACTIVATED CARBON

Conditions:  
Ionic strength 0,2 m (adjusted with NaCl)  
Mass of carbon 5,0 g  
Volume of solution 50 ml  
Contact time 24 h  
Temperature 20 °C ± 2 °C

Equilibrium hydroxide concentration in solution* mmol/l	Equilibrium concentration on carbon mmol/g	
	Sodium	Hydroxide†
1,3 × 10 <sup>-4</sup>	0,118	0,097
22,2	0,293	0,263
63,2	0,321	0,338
154,0	0,348	0,400

\* Determined by titration  
† Determined by difference

TABLE III  
ADSORPTION OF NaCN ONTO A TYPICAL ACTIVATED CARBON

Conditions:  
Ionic strength 0,2 m (adjusted with NaCl)  
Mass of carbon 5,0 g  
Volume of solution 50 ml  
Contact time 24 h  
Temperature 20 °C ± 2 °C  
pH of solution 12,0 (adjusted with NaOH)

Equilibrium cyanide concentration in solution* mmol/l	Equilibrium concentration on carbon mmol/g		
	Sodium†	Nitrogen‡	Cyanide§
9,86	0,050	0,061	0,086
49,3	0,165	0,173	0,238
98,6	0,169	0,164	0,358
187,3	0,209	0,184	0,467

\* Determined by argentometric titration  
† Corrected for NaOH adsorption (Table III)  
‡ Background (0,173 mmol/g) subtracted  
§ Determined by difference (these figures include the amount of cyanide lost to the hydrolysis and oxidation reactions (1) to (4))

The carbon used in the first experiment was therefore analysed for nitrogen, both before and after it had been contacted with the cyanide solution. The amount of adsorbed cyanide could now be included in the mass balance and, given the uncertainty caused by the high background

of 0,13 per cent nitrogen, effectively accounts for the remainder of the cyanide that is lost. In the light of these results, a detailed account can now be given of the relative importance of the various reactions that occur under these conditions. Table IV presents these results, and shows that there is a reasonable mass balance provided that all the reactions are taken into account. The adsorption of NaOH and NaCN onto the activated carbon (Tables II and III respectively) appears to have reached limiting values, which probably correspond to a limitation in the amount of functional groups present. Thus, whereas the adsorption reaction, equation (10), plays a significant role under the present conditions (Table IV), its relative importance may be reduced at higher concentrations of cyanide. Moreover, it is not necessary to invoke the formation of cyanogen to account for some of the loss; however, cyanogen may be formed as an intermediate in the oxidation of cyanide to cyanate.

TABLE IV  
MECHANISMS OF CYANIDE LOSS FROM AQUEOUS SOLUTION  
IN THE PRESENCE OF ACTIVATED CARBON

Conditions:  
Mass of carbon 12,5 g  
Volume of solution 500 ml  
Temperature 20 °C ± 2 °C  
pH of solution 10,2

Reaction mechanism	Reaction no.	Concentration mmol/l	
		0 hours	48 hours
CN <sup>-</sup> present in solution*		8,04	2,15
CNO <sup>-</sup> formed in solution*	(4)	0,00	2,40
HCN evolved†	(1)	-	0,45
CNO <sup>-</sup> lost‡	(7)	-	0,80
CN <sup>-</sup> adsorbed§	(10)	-	1,96
Total		8,04	7,76

\* Determined by ion chromatography

† Corresponds to the loss occurring when no carbon is present

‡ Calculated from the results shown in Table I

§ Determined from nitrogen analyses of the carbon

### Effect of pH

As could be predicted from equation (1) and the pK<sub>a</sub> value of cyanide (9,39), pH has a marked effect on the stability of cyanide. Fig. 4 shows that, in the absence of activated carbon, much higher rates of cyanide loss are observed at pH values below the pK<sub>a</sub> value. Only a slight amount of cyanide is lost at the natural pH of cyanide solutions (about 10,2). No cyanate could be detected in these solutions, which indicates that the hydrolysis of cyanide to hydrogen cyanide—reaction (1)—is responsible for the cyanide loss even at high pH values. (For example, at a pH value of 10,2, it can be calculated from the pK<sub>a</sub> value that 4,5 per cent of the cyanide will be present in solution in the form of hydrogen cyanide.)

When activated carbon is present, a similar effect is obtained, as shown in Fig. 4. However, in that case, the curve is displaced towards higher values of  $k_1$ . The curves obtained in the presence of activated carbon and in its absence are roughly parallel, which indicates a similar pH dependence. The higher rates obtained when

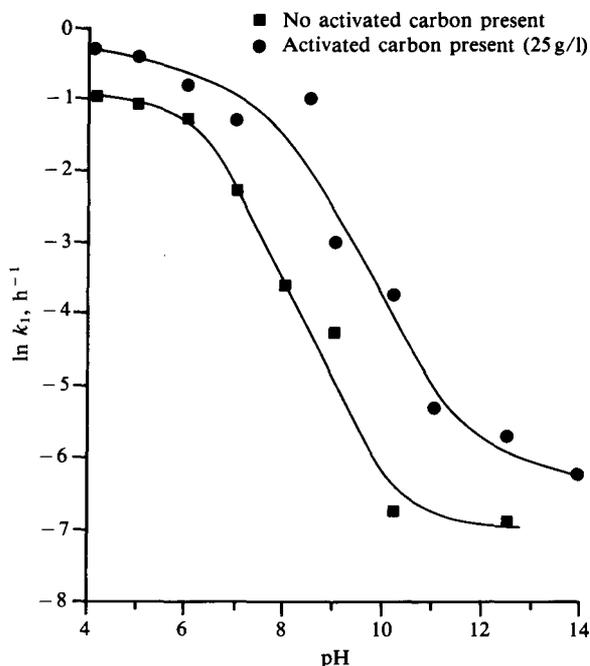


Fig. 4—Effect of pH on the rate of cyanide loss at 20 °C

carbon is present are due simply to the additional reactions that occur in the presence of activated carbon, as discussed earlier.

### Effect of Oxygen Concentration

Experiments were conducted in which oxygen or nitrogen was bubbled through the solution at different rates, resulting in different oxygen levels in solution. The results are shown in Table V. The bubbling of both oxygen and nitrogen resulted in an increase in the loss of cyanide, indicating that the effect is a physical, not a chemical one (i.e. at high flowrates of oxygen or nitrogen gas, hydrogen cyanide is more effectively displaced from the solution). Moreover, in the absence of activated carbon, the concentration of oxygen in the solution has no effect *per se* on the rate of cyanide loss.

TABLE V  
EFFECT OF OXYGEN CONCENTRATION ON THE LOSS OF CYANIDE  
FROM AQUEOUS SOLUTION AT 20 °C

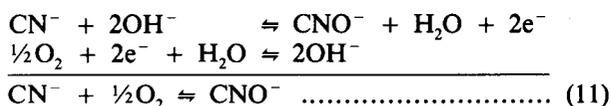
Conditions:  
Volume of solution 500 ml  
Initial cyanide in solution 0,01 M  
pH 10,2

Gas bubbling	Oxygen in solution mg/l	$k_1, h^{-1}$	
		Activated carbon present (25 g/l)	No activated carbon present
None	6,5	0,0214	0,00104
N <sub>2</sub>	2,5	0,0473 (0,0051)*	0,00267
O <sub>2</sub>	>20	0,0512 (0,0222)*	0,00252

\* The figures in parentheses refer to  $k_1$  values after 20 hours (two rate constants were required to describe the data in these instances)

However, when activated carbon is present, the presence of oxygen in the solution results in a greater loss of cyanide than does the presence of nitrogen (Table V). This suggests that molecular oxygen acts as the oxidant for

the oxidation of cyanide to cyanate in the presence of activated carbon:



This rate drops after 20 hours for the bubbling of both nitrogen and oxygen, but the drop is far more significant when nitrogen is bubbled through, suggesting that the oxygen that is adsorbed onto the carbon surface takes several hours to be purged out. The drop in the value of  $k_1$ , even with the bubbling of oxygen, suggests that the catalytic activity of the carbon decreases slowly.

**Effect of Cyanate Ions**

The presence of cyanate ions has a negligible effect on the rate constant within the limits of experimental error. The results given in Table VI show this to be the case both in the presence and the absence of activated carbon.

TABLE VI  
EFFECT OF CYANATE ON THE RATE OF CYANIDE LOSS AT 20 °C

Conditions:  
Volume of solution 500 ml  
Initial cyanide in solution 0,01 M  
pH 10,2  
O<sub>2</sub> in solution 6,5 mg/l

Condition	$k_1, \text{h}^{-1}$	
	Activated carbon present (25 g/l)	No activated carbon present
No cyanate added	0,0214	0,00104
0,1 M KCNO	0,0159	0,00333

This result is not unexpected, since reaction (11) was shown earlier to be first-order kinetically controlled, and therefore independent of the concentration of the products.

It should be noted that, in this experiment, the concentration of cyanate remained essentially constant over a period of 48 hours.

**Effect of Activated Carbon on the Stability of Cyanide Under High Temperature Conditions**

The thermal decomposition of cyanide has been proposed<sup>21</sup> as a process option for the detoxification of cyanide solutions. Moreover, the stability of cyanide at high temperatures is of interest in the elution of gold from activated carbon. This aspect will be discussed in more detail in the second paper in this series<sup>11</sup>.

**Effect of Temperature**

Table VII gives the details of rate constants, calculated from decomposition data at various temperatures both in the presence of activated carbon and in its absence. The results for the percentage loss of cyanide after 30 minutes and 24 hours are also given. It is evident that the loss of cyanide is enhanced in the presence of activated carbon at lower temperatures and in the initial stages of reaction. At 95,3 °C, activated carbon has a negligible effect on the  $k_1$  value, which indicates that the hydrolytic decomposition reaction—reaction (2)—is more im-

portant than oxidation to cyanate—reaction (4)—at high temperatures.

TABLE VII  
KINETIC DATA FOR THE DECOMPOSITION OF CYANIDE AT VARIOUS TEMPERATURES

Conditions:  
Volume of solution 300 ml  
Initial cyanide in solution 0,2 M (as NaCN)  
pH 13,3

Temperature °C	Loss of cyanide, %				$k_1, \text{h}^{-1}$	
	After 30 min		After 24 h		No carbon	89 g/l carbon
	No carbon	84 g/l carbon	No carbon	89 g/l carbon		
95,3	5,7	8,3	84,5	82,9	0,0790	0,0714
81,0	0,0	8,5	32,2	48,7	0,0185	0,0240
72,0	1,1	6,6	20,2	30,0	0,0113	0,0121
50,0	0,0	0,0	2,2	7,9	0,0008	0,0033
23,0	0,9	4,8	0,0	6,5	—	—

— Not measurable

An activation energy of 74,9 kJ/mol can be calculated from the results by use of the Arrhenius equation:

$$\ln k_1 = \ln A - \frac{E_a}{RT}, \dots\dots\dots (12)$$

where  $k_1$  is the rate constant,  $A$  a constant,  $E_a$  the activation energy,  $R$  the gas constant, and  $T$  the temperature. This is comparable with the activation energy of 92,3 kJ/mol determined by Mishra and Joshi<sup>22</sup> for the decomposition of cyanide at temperatures in the range 100 to 180 °C under conditions of high pressure.

**Effect of pH**

The effect of pH on  $k_1$  is shown in Table VIII. Unlike the situation at 20 °C (Fig. 4), where a decrease in pH results in an increase in  $k_1$ , at 95 °C  $k_1$  remains essentially constant over a pH range of 10 to 14, both in the presence and in the absence of activated carbon. As the  $pK_1$  values of formate (3,74) and ammonium (9,27) both fall in a region outside this range in pH, reaction (2) would not be expected to display any significant pH effects. Similarly, activated carbon would not be expected to have any major influence. Once again, the results are consistent, and reaction (2) dominates under these conditions.

TABLE VIII  
EFFECT OF pH ON THE RATE OF CYANIDE DECOMPOSITION AT 95 °C

Conditions:  
Volume of solution 300 ml  
Initial cyanide in solution 0,2 M (as NaCN)

pH	$k_1, \text{h}^{-1}$	
	Activated carbon present (89 g/l)	No activated carbon present
10,0	0,0841	0,0695
11,5	0,0950	0,0719
13,3	0,0715	0,0790
14,0	0,0714	0,0785

The results that are presented in Table IX show the concentrations of cyanide and cyanate in solutions at 95°C. Although, in one instance, some cyanate was detected in the presence of activated carbon, its concentration relative to that of the cyanide is insignificant. (This does not, however, rule out the possibility that cyanate is an intermediate in the decomposition reaction—a mechanism that is exceedingly difficult to prove or disprove experimentally owing to the short half-life of the intermediate reaction products.)

TABLE IX  
ANALYSIS OF SOLUTIONS FOR CYANIDE AND CYANATE AT 95 °C

Condition	Time, h	Concentration, mol/l	
		CN <sup>-</sup>	CNO <sup>-</sup>
No carbon present	0	0,208	<0,0002
	5,8	0,178	<0,0002
	46,2	0,007	<0,0002
Carbon present (89 g/l)	0	0,189	<0,0002
	6,1	0,105	0,0040
	46,5	0,002	<0,0002

#### Effect of Oxygen Concentration

The results given in Table X show that the bubbling of oxygen or nitrogen through the vessel at 95 °C, both in the presence of activated carbon and in its absence, has an insignificant effect on  $k_1$ . This is again consistent with the hydrolysis of cyanide to ammonia and formate—reaction (2)—which is predominant at 95 °C, and is inconsistent with the other mechanisms discussed for the low-temperature reactions.

TABLE X  
EFFECT OF THE BUBBLING OF OXYGEN OR NITROGEN ON THE RATE OF CYANIDE DECOMPOSITION AT 95 °C

Conditions:  
Volume of solution 300 ml  
Initial cyanide in solution 0,2 M (as NaCN)  
pH 13,3

Condition	$k_1, h^{-1}$	
	Activated carbon present (89 g/l)	No activated carbon present
O <sub>2</sub> bubbling	0,0733	0,0696
No gas	0,0714	0,0790
N <sub>2</sub> bubbling	0,0563	0,0680

#### Effect of the Presence of Potassium Cyanate

The effect of potassium cyanate on the rate constant is shown in Table XI.

An excess of cyanate ions has a negligible effect on  $k_1$ , as was shown for a temperature of 20°C. The cyanate concentrations determined during the course of this experiment are presented in Table XII.

All the cyanate had decomposed—presumably to ammonia and carbon dioxide via reactions (7) and (8)—after 22 hours, in contrast to the situation at 20 °C, where effectively no cyanate loss was detected from a 0,1 mol/l solution of potassium cyanate after 48 hours both in the presence and in the absence of activated carbon.

TABLE XI  
EFFECT OF KCNO OR NH<sub>4</sub>CO<sub>2</sub> ON THE RATE OF CYANIDE DECOMPOSITION AT 95 °C

Conditions:  
Volume of solution 300 ml  
Initial cyanide in solution 0,2 M (as NaCN)  
pH 13,3

Condition	$k_1, h^{-1}$	
	Activated carbon present (89 g/l)	No activated carbon present
No additive	0,0714	0,0790
0,2 M KCNO added	0,0811	0,0947

TABLE XII  
CYANATE CONCENTRATIONS FOR THE EXPERIMENTS REPORTED IN TABLE VII

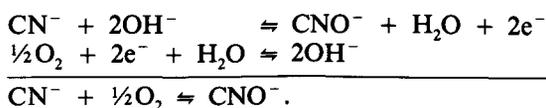
Conditions:  
Volume of solution 300 ml  
Initial cyanide in solution 0,2 M (as NaCN)  
pH 13,3

Time, h	[CNO <sup>-</sup> ], mg/l	
	Activated carbon present (89 g/l)	No activated carbon present
0	8560	8560
1	7813	7000
22	<10	<10
46,5	<10	<10

#### CONCLUSIONS

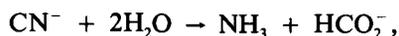
The kinetics of cyanide loss were found to be first order under any given set of conditions, allowing rate constants to be easily determined. At room temperature and in the absence of activated carbon, some cyanide is lost by hydrolysis to hydrogen cyanide, but this does not occur to any significant extent at pH values higher than about 10. A slightly higher rate of hydrolysis occurs at higher temperatures and when air agitation is used.

When activated carbon is present, an additional carbon-catalysed oxidation reaction is responsible for a fairly high loss of cyanide. The evidence indicates that a reaction mechanism occurs that consumes oxygen and produces cyanate ion:

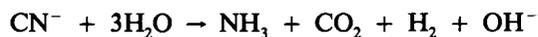


Some of the cyanate thus produced decomposes to form a mixture of ammonia, carbonate, and urea, depending on the conditions in the solution. Additional cyanide is lost as a result of the adsorption of sodium cyanide by the activated carbon.

At high temperatures, the following additional hydrolysis reaction, which involves the formation of ammonium formate as an intermediate, occurs:



and, because it leads ultimately to the formation of ammonia, hydrogen, and carbon dioxide, the reaction



is responsible for a high loss of cyanide. The presence of activated carbon has no effect on the rate of this reaction.

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## Code of practice: Painting systems\*

The South African Hot Dip Galvanizers Association is preparing a specification and code of practice for painting systems that are to be applied to newly galvanized steel. This is a means of introducing the modern-day painting of newly galvanized steel to all concerned, with the efficient cost-effective and predicted corrosion-free life to first maintenance of such paint systems.

These standards are being compiled under the directive of the South African Hot Dip Galvanizers Association, by the following interested paint members, after evaluation of the testwork undertaken by Eric Duligal & Associates:

Advanced Coatings (Pty) Ltd  
 AECI Paints (Pty) Ltd  
 Chemrite Coatings (Pty) Ltd  
 ICI (SA) Ltd  
 Ivory Industrials (Pty) Ltd  
 Plascon Evans Paints (Tvl) Ltd

Supacryl (Pty) Ltd  
 Union Carbide (Pty) Ltd.

The standards are expected to be available at cost towards the end of this year. The standards will meet the needs of manufacturers, contractors, engineers, and others involved in the design or installation of duplex systems. They are being compiled from work carried out by a paint co-ordinating committee drawn from the above companies. The scope will include mild, marine, industrial, and mining environments, and pipe linings and coatings for application to new hot-dip galvanized structural-steel sections, sheet steel, and steel pipes. Should these standards prove to be popular, they will be sent to the SABS for conversion into South African standards.

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\* Released by the South African Hot Dip Galvanizers Association, P.O. Box 77, Wits 2050.