

The removal of cyanide from aqueous solution by the use of ferrous sulphate

by M. D. Adams*

SYNOPSIS

The treatment of gold-plant tailings with ferrous sulphate to remove the cyanide is currently in use on several gold plants. In some cases there is scope for optimizing the process. The present work provides a detailed study of the reaction between cyanide and ferrous sulphate. Optimal conditions for the removal of total cyanide require a pH of 5,5 to 6,5 and an Fe:CN molar ratio of 0,5. Ferrocyanide ion is shown to be unstable in aqueous acidic solution, with rapid oxidation to ferricyanide, $(\text{Fe}(\text{CN})_6^-)$, and formation of $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ at pH values below 4. The precipitate from the reaction between cyanide and ferrous sulphate consists mainly of insoluble Prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, and is shown to be unstable in the presence of alkaline solution, since it decomposes rapidly at pH values above 7 to form ferrocyanide, $(\text{Fe}(\text{CN})_6^-)$, in solution and various insoluble iron oxides.

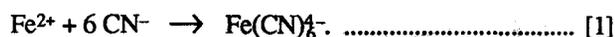
SAMEVATTING

Verskeie goudmyne behandel tans goudaanleguiskotte met ferrosulfaat om sianied te verwyder. Daar bestaan in sommige gevalle 'n behoefte aan prosesoptimering. Die huidige werk behels 'n uitvoerige studie van die reaksie tussen sianied en ferrosulfaat. Die optimale toestande vir die verwydering van die totale sianied, vereis 'n pH van 5,5 tot 6,5 en 'n molêre verhouding van Fe:CN van 0,5. Daar word getoon dat die ferrosianiedioon onstabiel is in 'n waterige suuroplossing, met vinnige oksidasie tot ferrisianied, $(\text{Fe}(\text{CN})_6^-)$, en die vorming van $\text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$ by pH-waardes onder 4. Die presipitaat van die reaksie tussen sianied en ferrosulfaat bestaan hoofsaaklik uit onoplosbare berlynsblou, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, en daar word getoon dat dit onstabiel is in die teenwoordigheid van 'n alkaliese oplossing aangesien dit by pH-waardes bo 7 vinnig ontbind om ferrosianied, $(\text{Fe}(\text{CN})_6^-)$, in oplossing en verskeie onoplosbare ysteroksiede te vorm.

INTRODUCTION

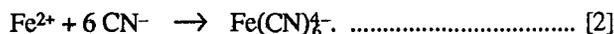
The treatment of toxic industrial-waste streams is becoming increasingly important internationally, and much attention is being focused on the disposal of cyanide wastes from gold plants.

At present, the main area of concern is the detoxification of gold-plant tailings prior to their use as backfilling in mined-out stopes. Most mines currently using the backfill procedure are treating the gold-plant tailings with ferrous sulphate. The ferrous ions in solution react with free cyanide to form the ferrocyanide complex in solution:

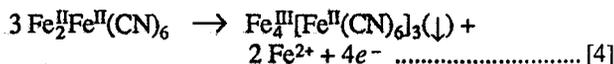


A drawback of the process depicted in equation [1] is that ferrocyanide is known to be unstable under conditions of high temperature, low pH, and ultraviolet light¹⁻³. In a backfilling operation, the solution is drained and re-used, resulting in a build-up of ferrocyanide. Moreover, it is possible that some of the solution may escape and contaminate the natural ground water.

When an excess of ferrous sulphate is added to a cyanide-containing solution, the cyanide can be immobilized as an insoluble precipitate, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, known as Prussian blue. Various patents have been taken out that relate to this process⁴⁻⁷, including the addition of insoluble ferrous sulphide⁵ and the co-addition of iron and copper⁷. The reaction proceeds as follows:



The insoluble white ferrous ferrocyanide product rapidly absorbs oxygen from the air and turns deep blue, with the formation of ferric ferrocyanide⁸. The vivid blue colour of these compounds is due to a charge-transfer transition between the $\text{Fe}^{\text{II}}(\text{CN})_6^-$ and the Fe^{III} ions⁹. The following redox couple could account for the reaction:



However, the reaction is not likely to be simple since there is a range of Prussian blue products depending on the solution conditions. One such compound is the so-called 'soluble Prussian blue', $\text{MFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ ($\text{M} = \text{K}$ or Na), which forms a colloidal solution with water¹. Moreover, the precipitation and oxidation of ferrous hydroxides are reactions that are also likely to play a role.

The aim of the present work is to elucidate the optimum conditions for the removal of cyanide from solution by the use of ferrous sulphate, and to demonstrate the regimes of stability of the soluble and insoluble complexes that are formed during the reaction.

EXPERIMENTAL PROCEDURE

All the chemicals used were of A.R. grade, and the solu-

* Mintek, Private Bag X3015, Randburg, 2125 Transvaal.
© The South African Institute of Mining and Metallurgy, 1992. SA ISSN 0038-223X/3.00 + 0.00. Paper received 5th November, 1990.

tions were made up with deionized water.

In the precipitation experiments, 500 ml of solution containing 0,5 g of NaCN (0,02 M) was placed in a magnetically stirred beaker, and the pH value was adjusted by the use of H_2SO_4 or NaOH. To this was added 500 ml of a freshly made-up solution containing 1,419 g of $FeSO_4 \cdot 7H_2O$ (0,01 M). The Fe:CN ratio was changed by varying the mass of ferrous sulphate used. The Fe:CN molar ratios vary by approximately 0,1 around the nominal value 0,5. As these values are still in excess of the stoichiometric value of 0,17 for complexation as $Fe(CN)_6^{4-}$, the overall trends still hold. The pH value of the ferrous sulphate solution was not adjusted.

Before and during the experiments carried out on the effect of oxygen, both solutions were purged with either oxygen or nitrogen gas for 10 minutes before being mixed.

Prior to the experiments with pulp tailings, 0,5 g of NaCN was added to 1 litre of the tailings. $FeSO_4 \cdot 7H_2O$ (1,419 g) was dissolved in the minimum amount (10 ml) of water. This was added to the tailings at the start of the experiment.

Samples of solution were filtered and contacted with Dowex 50-S8 cation-exchange resin so that excess Fe^{2+} could be removed and further reaction prevented. The pH value of the sample was then adjusted to about 11 with NaOH, to stabilize both the $Fe(CN)_6^{4-}$ and the CN^- in solution. The samples were immediately analysed for $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, and CN^- by use of ion chromatography³. Aluminium foil was used to protect the experimental apparatus and sample containers from light at all times.

During the experiments designed to demonstrate the stability of the Prussian blue precipitate, the pH value was adjusted to the required value after 2 hours. Samples were taken periodically, and were pretreated and analysed as described above. The pH value of the solution was maintained at the required level.

To characterize the precipitate, a large batch was made up as follows: the masses and volumes were quadrupled, and the precipitate was filtered after 2 hours at the required pH value. The precipitate was washed with deionized water prior to being dried in a vacuum desiccator for 24 hours.

For the experiments carried out to demonstrate the stability of ferrocyanide ion, 250 ml solutions of $K_4Fe(CN)_6$ (0,001 M) were made up and placed in round-bottomed flasks with reflux condensers. One solution was exposed to sunlight, and one was kept covered. Ultraviolet-visible spectra were recorded with a Beckman Acta MIV spectrophotometer, and the $Fe(CN)_6^{3-}$ concentration was monitored by measurement of the absorbance at 420 nm, where $Fe(CN)_6^{4-}$ does not absorb. Free cyanide was measured periodically by ion chromatography. X-ray diffractograms of Prussian blue precipitates were obtained by use of $Cu K\alpha$ radiation with a Philips PW1050/25 X-ray diffractometer. Vacuum-dried samples of precipitate for infrared spectrophotometry were pulverized for 5 minutes in a Spex 5100 mixer/mill, and 6 mg were then shaken manually with 200 mg of dry KBr. Spectra were obtained with a Perkin-Elmer 1725X Fourier Transform Infrared Spectrophotometer used in conjunction with a diffuse reflectance (DRIFT) accessory.

RESULTS AND DISCUSSION

Reaction of $FeSO_4$ with CN^-

In the only previous comprehensive study¹⁰ of the reaction between $FeSO_4$ and CN^- , oxygen was excluded from the reaction vessel, which meant that the reactions of relevance were those shown in equations [2] and [3]. In the presence of oxygen, as was the case in the present experiments, the white ferrous ferrocyanide precipitate turned blue almost instantaneously via reactions [4] and [5].

Effect of Fe:CN- Ratio

The stoichiometry of reactions [2] to [5] demands an Fe:CN- molar ratio of 0,39. The effect of variations in the Fe:CN- ratio on the resultant solution species is shown in Fig. 1. Theoretically, complete conversion to $Fe(CN)_6^{4-}$ is achieved at an Fe:CN- molar ratio of 0,17, and this is borne out in Fig. 1. At an Fe:CN- molar ratio of 0,10, there is insufficient Fe^{2+} to complex with all the CN^- and, at Fe:CN- ratios of 0,5 and higher, blue precipitates were obtained, and no cyanide-containing species were detected in solution after 6 hours.

Detailed results are shown in Table I, where the pH value at $t = 0$ refers to the 500 ml NaCN solution before it was mixed with the $FeSO_4$ solution. The value of Fe_T at $t = 0$ refers to the total iron concentration in the 500 ml of $FeSO_4$ solution before it was mixed with the NaCN solution, but corrected to a total volume of 1 litre. It is interesting to note that the pH value of the $FeSO_4$ solution prior to the mixing varied between 3,6 and 5,0, depending on the $FeSO_4$ concentration. These low pH values are a result of the hydrolysis of Fe^{2+} in aqueous solution. The steady decrease in pH after the two solutions had been mixed is probably due to the slow oxidation of $Fe(II)$ to hydrated $Fe(III)$ oxides, a process that involves further hydrolysis and the liberation of protons. At Fe:CN- molar ratios of 0,5 and higher, no

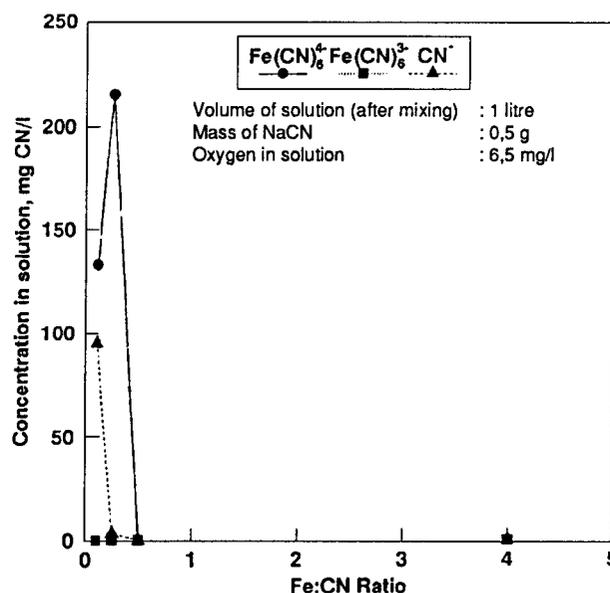


Fig. 1—Effect of Fe:CN ratio on solution species after 6 hours of reaction

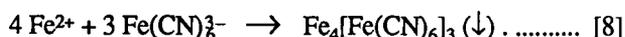
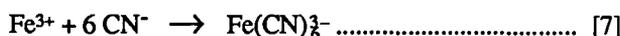
TABLE I
Effect of Fe:CN⁻ molar ratio on the reaction of cyanide with ferrous sulphate

Conditions: Volume of solution (after mixing) 1 litre
Mass of NaCN 0,5 g
Oxygen in solution 6,5 mg/l

Fe:CN ⁻	Time min	pH	Precipitate	Concentration in solution			
				mg/l		mg/l (expressed as CN ⁻)	
				Fe _T	Fe(CN) ₆ ⁴⁻	Fe(CN) ₆ ³⁻	CN ⁻
0,1	0	10,5	None	48	NA	NA	265
	5	10,4	None		134	ND	113
	30	10,4	None		134	ND	109
	360	10,4	None	51	133	ND	95
0,25	0	10,5	None	162	NA	NA	265
	5	6,4	None		211	ND	15,4
	30	6,4	None		225	ND	10,4
	360	6,4	None	118	215	ND	3,4
0,5	0	10,5	None	218	NA	NA	265
	5	6,3	Brown/ turquoise		ND	ND	1,58
	30	6,1	Blue		ND	ND	0,76
	360	5,2	Blue	0	ND	ND	ND
4	0	10,5	Brown/ turquoise	1116	NA	NA	265
	5	5,0	Turquoise		ND	ND	1,49
	30	4,7	Turquoise		ND	ND	ND
	360	3,3	Blue	822	ND	ND	ND

ND Not detected NA Not analysed

Fe(CN)₆⁴⁻ or Fe(CN)₆³⁻ species were detected in solution even after only 5 minutes of reaction, at which time about 1,5 mg/l of free cyanide was detected. The cyanide level may be reduced to below the detection limit (0,02 mg/l) by an increase in either the reaction time or the Fe:CN⁻ ratio. In each case where a precipitate formed, an instantaneous colour change (brown, followed by blue-green) was noted, followed by the familiar bright blue of Prussian blue. These colours suggest that a portion of the Fe²⁺ precipitates as Fe(OH)₂ on contact with the alkaline cyanide solution, followed by rapid oxidation to Fe₂O₃·n H₂O. Reactions such as the following may also occur to some extent:



Exact identification of the form in which the iron initially precipitates is difficult, owing to the short time-span during which the precipitate exists before being converted to Prussian blue. Moreover, the chemistry of the iron (III) oxides is complex, with the existence of a range of possible hydrated Fe₂O₃·n H₂O species of varying colour.

Beckenn¹¹ suggests that an Fe:CN⁻ ratio of 16 should be used for the effective removal of cyanide, but the results illustrated in Fig. 1 indicate that this would be an unneces-

sary excess, resulting in a high consumption of reagent.

For the remainder of the present testwork, an Fe:CN⁻ ratio of 0,5 was used.

Effect of pH

In this set of experiments, the pH of the cyanide solution was varied between 4 and 13, while that of the ferrous sulphate solution remained unadjusted. The concentration of solution species was measured as a function of equilibrium pH, and is shown in Fig. 2. Details of the results, including the initial pH values of the solutions, are listed in Table II.

It should be noted that no precipitates were formed when the FeSO₄ solution was added to cyanide solutions that had initial pH values of 4 or 7, and that only a small amount of precipitate was obtained from the cyanide solution with an initial pH value of 8,5. Analysis of these solutions yielded a value of about 50 mg/l (as CN) for both Fe(CN)₆⁴⁻ and free CN⁻, and the concentrations of these species dropped over the 6-hour period (Table II).

Fig. 2 also indicates that a significant amount of ferrocyanide forms in solution at final pH values of greater than approximately 6,5. This is due to the decomposition of Prussian blue under alkaline conditions, and is discussed in more detail later in this paper.

The optimum equilibrium pH range for the precipitation of Prussian blue is between 5,5 and 6,5 and, under these conditions, it is possible to achieve very low levels of cyanide species in solution after 5 minutes. Lower pH values result in incomplete precipitation, whereas higher pH values result in the decomposition of the Prussian blue product. In the present work, the optimum pH value was attained by the mixing of the FeSO₄ and CN⁻ solutions without any prior adjustment of the pH value of the cyanide solution (natural pH value of 10,5). The presence of lime and other soluble species in tailings may necessitate some adjustment of the pH value when this method is applied to plant tailings.

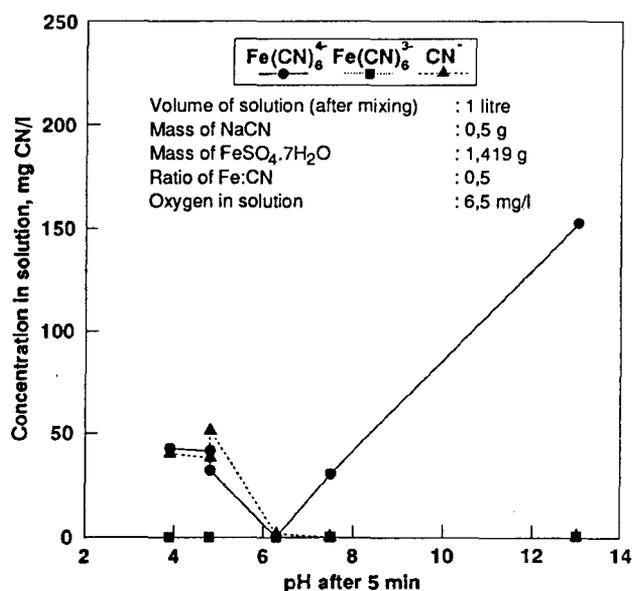


Fig. 2—Effect of pH on solution species after 5 minutes of reaction

TABLE II
Effect of pH on the reaction of cyanide with ferrous sulphate

Conditions: Volume of solution (after mixing) 1 litre
Mass of NaCN 0,5 g
Mass of FeSO₄·7H₂O 1,419 g
Ratio of Fe:CN 0,5
Oxygen in solution 6,5 mg/l

pH	Time min	Precipitate	Concentration in solution			
			mg/l	mg/l (expressed as CN)		
			Fe _T	Fe(CN) ₆ ⁴⁻	Fe(CN) ₆ ³⁻	CN ⁻
4,0	0	None	225	NA	NA	194
3,9	5	None		42,5	ND	40
3,9	30	None		25,0	ND	60
3,9	360	None	237	23,0	ND	ND
7,0	0	None	229	NA	NA	288
4,8	5	None (pale blue solns)		41,4	ND	38
4,7	30			72,5	ND	9
4,1	360		242	17	ND	5,2
8,5	0	None	236	NA	NA	323
4,8	5	Brown/turquoise		32	ND	51
4,2	30	Blue		33,8	ND	24
3,6	360	Blue	193	24	ND	4,5
9,5	0	None	243	NA	NA	267
5,2	5	Brown/turquoise		2,3	ND	49
4,2	30	Blue		5,8	ND	40
3,4	360	Blue		1,7	ND	ND
10,5	0	None	218	NA	NA	315
6,3	5	Brown/turquoise		ND	ND	1,58
6,1	30	Blue		ND	ND	0,76
5,2	360	Blue	0	ND	ND	ND
11,5	0	None	230	NA	NA	249
7,5	5	Brown/green		30,3	ND	ND
6,8	30	Turquoise		7,0	ND	ND
6,7	360	Turquoise	30	20,4	ND	ND
13,0	0	None	232	NA	NA	250
13,0	5	Green/brown		98	ND	ND
13,0	30	Blue/brown		88	ND	ND
12,9	360	Brown	85	63	ND	ND

ND Not detected NA Not analysed

Effect of Oxygen

The precipitation reaction, equations [2] to [5], involves the oxidation of Fe^{II} to Fe^{III}, and it is therefore useful to determine the effect of oxygen on the precipitation reaction. Much discrepancy exists¹² in the literature regarding the mechanism involved in the oxidation of ferrous ion by oxygen; however, the kinetics are both pH and [O₂] dependent¹².

In the present work, the cyanide solution was saturated by the bubbling of either oxygen or nitrogen for 15 minutes prior to contact with the FeSO₄ solution. Bubbling was continued throughout the reaction. The results are shown in Table III.

The presence of excess oxygen resulted in the occurrence of both Fe(CN)₆⁴⁻ and Fe(CN)₆³⁻ in solution, and suggests

that under these conditions Fe²⁺ and/or Fe(OH)₂ are oxidized to form hydrated ferric oxides prior to reaction with CN⁻, thus reducing the Fe²⁺:CN⁻ ratio. This is borne out by the observed colour changes.

The presence of nitrogen resulted in a lower oxygen concentration in the solution, and no ferricyanide was detected. However, these results highlight another effect: the slower rate of oxidation leads to the presence of a substantial amount of Fe(CN)₆⁴⁻ in the solution after 6 hours, which may possibly be attributed to the higher solubility of Fe^{II}Fe^{III}(CN)₆ compared with that of Fe^{III}₄[Fe^{II}(CN)₆]₃. Even in this case, however, there was also some pre-oxidation of divalent iron prior to the reaction with the CN⁻, as evidenced by the colour changes (Table III).

Effect of Pulp

In an effort to determine the effect of pulp solids on the reaction, the ferrous sulphate method was applied to a sample of pulp tailings from a mine. Two tests were carried out, the first with no pH adjustment and the second with the pH value adjusted to 6 immediately after the addition of the FeSO₄. The samples of plant solution produced chromatograms that contained many additional peaks, and it could not be established whether these were due to cyanide-containing species. The results are shown in Table IV.

In both cases, satisfactory levels of total cyanide were attained. It should be noted that the initial level of free cyanide was artificially high because the samples had been spiked with NaCN. The low concentrations of Fe(CN)₆⁴⁻ at pH values of 7,2 and 8,5 are somewhat surprising (Fig. 2). This effect could possibly be due to the presence of very insoluble complex precipitates of Fe(CN)₆⁴⁻ with various base metals. Since copper was the only base metal detected in the tailings apart from iron, and since the concentration of the Cu(CN)₃⁻ was found to drop steadily (Table IV), these results are consistent with the formation of the highly insoluble Cu₂Fe(CN)₆ in addition to the precipitation of Prussian blue.

Nature and Stability of the Soluble Complexes

The results in the previous section show that ferricyanide is not formed to any significant extent under the conditions pertinent to the precipitation of Prussian blue, and that ferrocyanide is the main soluble complex that is formed.

The potential-pH diagram for the Fe-CN-H₂O system is shown in Fig. 3. The Fe(CN)₆⁴⁻ species is thermodynamically unstable with respect to oxidation within the region of stability of water, which is shown bounded by the broken lines in Fig. 3. The ion is clearly also unstable with respect to changes in pH. This is exemplified by the results of a species-distribution calculation, obtained by means of the Haltafall¹⁴ computer program. The results are illustrated in Fig. 4, together with the relevant chemical equilibria and stability constants used. The ferrocyanide ion is thermodynamically unstable in acidic solutions, with the following reactions illustrating acid attack:

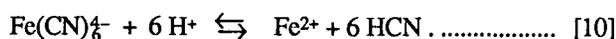


TABLE III
Effect of oxygen on the reaction of cyanide with ferrous sulphate

Conditions: Volume of solution (after mixing) 1 litre
Mass of NaCN 0,5 g
Mass of FeSO₄·7H₂O 1,419 g
Ratio of Fe:CN 0,5

Gas bubbling	[O ₂] mg/l	Time min	pH	Precipitate	Concentration in solution			
					mg/l	mg/l (expressed as CN)		
					Fe _T	Fe(CN) ₆ ⁴⁻	Fe(CN) ₆ ³⁻	CN ⁻
O ₂	>20	0	10,5	None	232	NA	NA	NA
		5	4,8	Brown/green		10,0	6,3	ND
		30	4,2	Brown/green		20,0	0,7	ND
		360	3,9	Blue		0	22,2	8,8
None	6,5	0	10,5	None	218	NA	NA	315
		5	6,3	Brown/turquoise		ND	ND	1,58
		30	6,1	Blue		ND	ND	0,76
		360	5,2	Blue		0	ND	ND
N ₂	2,0	0	10,5	None	236	NA	NA	NA
		5	6,1	Brown/turquoise		7,5	ND	5,8
		30	5,2	Blue		1,0	ND	5,1
		360	4,6	Blue		0	31,7	ND

ND Not detected NA Not analysed



Williams⁸ reports that these reactions, as well as the oxidation of ferrocyanide to ferricyanide, occur relatively rapidly in acidic solutions, particularly after exposure to light or heat. In alkaline solutions, ferrocyanide also becomes unstable⁸, owing to the decomposition of the complex and the precipitation of Fe₂O₃·nH₂O. It is also evident from Fig. 4 that the region of stability of ferrocyanide diminishes in size with a decrease in the ferrocyanide concentration.

The stability of ferrocyanide under the conditions of interest was investigated with the use of quantitative visible spectrophotometry for the determination of Fe(CN)₆³⁻ in solution, and ion chromatography for the determination of CN⁻.

Fig. 5 shows that a significant amount of the Fe(CN)₆⁴⁻ in K₄Fe(CN)₆ solution is oxidized to Fe(CN)₆³⁻, particularly in solutions with a pH value of 4. A complicating factor is the precipitation of Prussian blue from these solutions. The pH 4 solutions appeared somewhat green in colour; the pH 1 solutions contained a fine blue precipitate; the pH 7 solutions remained yellow in colour. The maximum in Fe(CN)₆³⁻ concentration at a pH value of 4 can thus be explained by the observation that an increasing amount of Prussian blue was formed in more acidic solutions, thus removing the Fe(CN)₆³⁻ ion from solution, probably in the form of soluble Prussian blue, KFe^{III}[Fe^{II}(CN)₆], which forms a colloidal blue solution. The effect of sunlight is somewhat variable, and further experiments would be required to quantify and characterize the chemistry involved.

No free cyanide could be detected in these solutions;

however, preliminary work¹⁸ suggests that reactions [9] and [10] also occur to some extent.

Nature and Stability of the Precipitates

To fully understand and optimize the reaction between FeSO₄ and CN⁻, it is necessary to characterize the precipitates formed. Moreover, it is essential to establish the stability of the precipitates under various conditions pertinent to backfill operations.

Characterization of Precipitates

There are several types of Prussian blue that are formed under various conditions, and the colloidal variations would

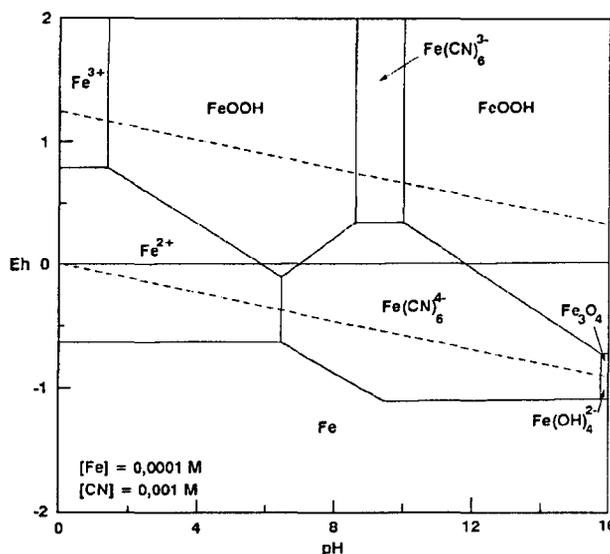
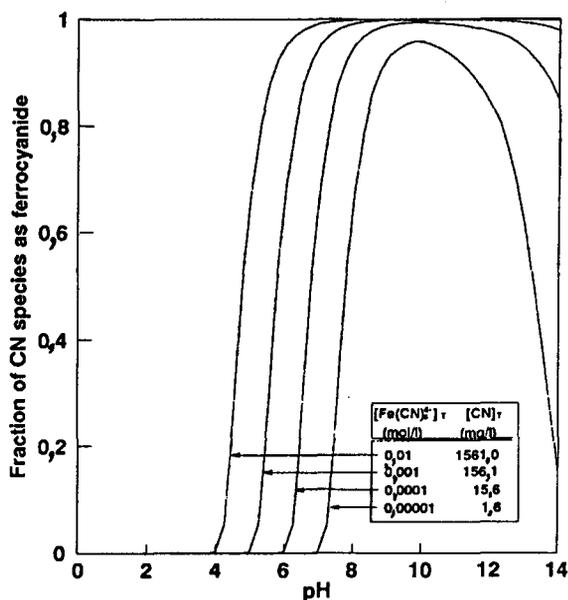


Fig. 3—Potential-pH diagram for the Fe-CN-H₂O system at 25°C (after Ciminelli¹³)



Equilibrium	Stability constant β_n	Solubility product K_{50}	Ref.
$\text{Fe}^{2+} + 6 \text{CN}^- \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	$1,000 \times 10^{36}$		15
$\text{Fe}^{2+} + 5 \text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{CN})_5\text{H}_2\text{O}^{3-}$	$5,000 \times 10^{27}$		16
$\text{Fe}(\text{CN})_6^{4-} + \text{H}^+ \rightleftharpoons \text{HFe}(\text{CN})_6^{3-}$	$1,995 \times 10^4$		17
$\text{Fe}(\text{CN})_6^{4-} + 2 \text{H}^+ \rightleftharpoons \text{H}_2\text{Fe}(\text{CN})_6^{2-}$	$7,943 \times 10^6$		17
$\text{Fe}^{2+} + \text{OH}^- \rightleftharpoons \text{FeOH}^+$	$1,995 \times 10^{-10}$		15
$\text{Fe}^{2+} + 2 \text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_2$	$1,585 \times 10^{-21}$		15
$\text{Fe}^{2+} + 3 \text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_3$	$1,000 \times 10^{-31}$		15
$\text{Fe}^{2+} + 4 \text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_4^{2-}$	$1,000 \times 10^{-46}$		15
$\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$	$9,886 \times 10^{-15}$		17
$\text{H}^+ + \text{CN}^- \rightleftharpoons \text{HCN}$	$1,622 \times 10^9$		17
$\text{Fe}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Fe}^{2+} + 2 \text{OH}^-$		$1,112 \times 10^{13}$	15

Fig. 4—Effect of pH on the stability of ferrocyanide in aqueous solution

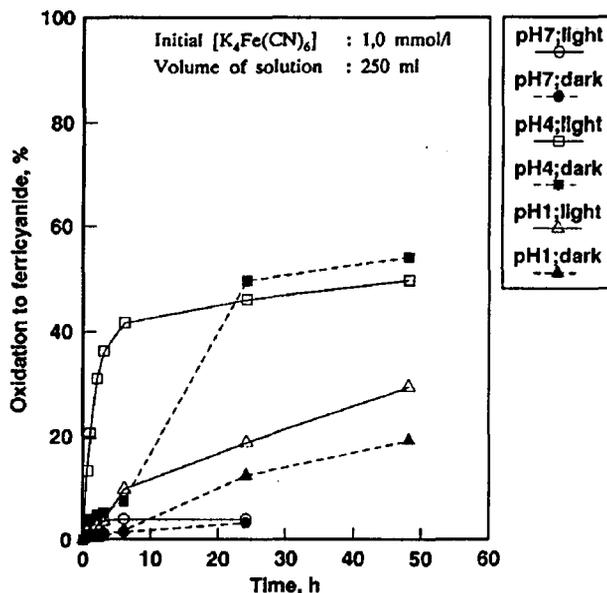


Fig. 5—Effect of pH on the rate of oxidation of ferrocyanide in aqueous solution

not be acceptable as an immobilized form of cyanide. Elemental analyses of the precipitate obtained under optimal conditions (Fe:CN 0,5; pH value 5,5 to 6,5) are shown in Table V, together with the theoretical elemental ratios of possible products.

The exact identification of the precipitate is not possible on the basis of the elemental analyses alone; however, the low concentration of sodium in the precipitate suggests that it is more compatible with $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ than with $\text{NaFe}[\text{Fe}(\text{CN})_6]$. The presence of 4,4 per cent oxygen over and above that associated with water is probably due to a small amount of iron oxide. The lack of a mass balance probably arises from the nitrogen analyses, which were carried out with an instrument designed for the analysis of alloys.

The characteristic bands¹⁹ common to both insoluble and soluble Prussian blue were evident in the infrared spectrum of the precipitate, and in particular in the very strong $\nu(\text{CN})$

TABLE IV
Removal of cyanide from pulp tailings by Prussian blue precipitation using FeSO_4

Conditions: Volume of slurry 1 litre
Mass of NaCN 0,5 g
Mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 1,419 g

pH of pulp	Time min	Concentration, mg/l (expressed as CN)					
		CN^-	$\text{Fe}(\text{CN})_6^{4-}$	$\text{Fe}(\text{CN})_6^{3-}$	$\text{Cu}(\text{CN})_3^-$	SCN^-	CNO^-
10,5	0	741	9,4	ND	14,6	ND	ND
-	5	2,7	4,7	1,2	8,6	ND	ND
8,5	30	2,0	2,7	1,2	6,0	ND	ND
7,2	360	0,4	ND	ND	ND	ND	ND
10,5	0	741	9,4	ND	14,6	ND	ND
6	5	2,0	5,2	2,2	12,7	ND	ND
6	30	0,5	4,2	ND	ND	ND	ND
6	360	2,5	ND	ND	ND	ND	ND

ND Not detected

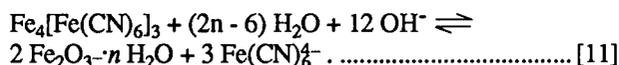
band at 2084 cm⁻¹. The X-ray-diffraction peaks of the precipitate were close to those reported²⁰ for pure Fe₄[Fe(CN)₆]₃.

Chemical Stability of Prussian Blue

It has been reported⁸ that Prussian blue decomposes when contacted with alkaline solution, and this should be taken into account in any process that places large amounts of Prussian blue underground.

A detailed investigation of this reaction is reported here. The precipitate obtained under optimal conditions was exposed to solutions of various pH values for several weeks, and both solid and solution phases were characterized by a variety of techniques. The solution compositions are shown in Fig. 6. Significant quantities of ferrocyanide were found in the solution at pH values of 7 and above, and the Fe(CN)₆⁴⁻ concentration increased with time. Free cyanide was analysed for but not detected in any of the solutions. In the case of the pH 13 solution, almost complete decomposition to Fe(CN)₆⁴⁻ occurred after 28 days. The presence of some Fe(CN)₆³⁻ in certain samples is inconsistent, and could be due to oxidation in the sample bottle itself. (There is no logical explanation for the large concentration of Fe(CN)₆³⁻ that formed after 7 days at a pH value of 7, most of which disappeared after 28 days.)

The precipitate itself appeared progressively more brown and less blue in colour as the pH value of the contacting solution was raised, which suggests that Fe₂O₃.n H₂O is the other product of the reaction:



Elemental analyses of the precipitates after 2 hours of contact with the various solutions are shown in Table VI.

The steady drop in carbon and nitrogen contents and the increase in iron and oxygen contents are consistent with the

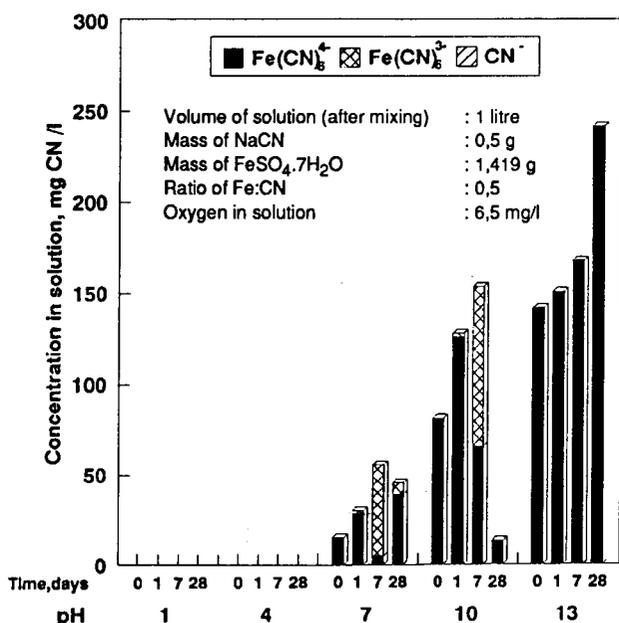


Fig. 6—Decomposition of Prussian blue with pH and time

disappearance of Prussian blue and the appearance of iron oxides. The results listed in Table VI also suggest that, in the presence of alkaline solutions, a small amount of the precipitate may contain co-precipitated soluble Prussian blue, as evidenced by the somewhat higher sodium contents of the precipitates under these conditions.

Infrared spectra of some of the precipitates after 2 hours of contact with the various solutions are shown in Fig. 7. The precipitates in contact with solutions having a pH value of 6 and less are not changed to any great extent. The precipitates in contact with solutions having pH values of 6 to 9 retain a very strong C≡N stretch at 2084 cm⁻¹; however, the three characteristic bands at 1140, 1056, and 996 cm⁻¹ begin to disappear. Between pH values of 10 and 13, the 2084 cm⁻¹ band begins to disappear, and the Prussian blue starts to decompose. The other bands introduced at high pH values can all possibly be attributed to various forms of Fe₂O₃.n H₂O.

X-ray diffractograms for the precipitates under different pH conditions are compared in Fig. 8. The precipitates in contact with solutions of pH 1 to 8 display only the X-ray-

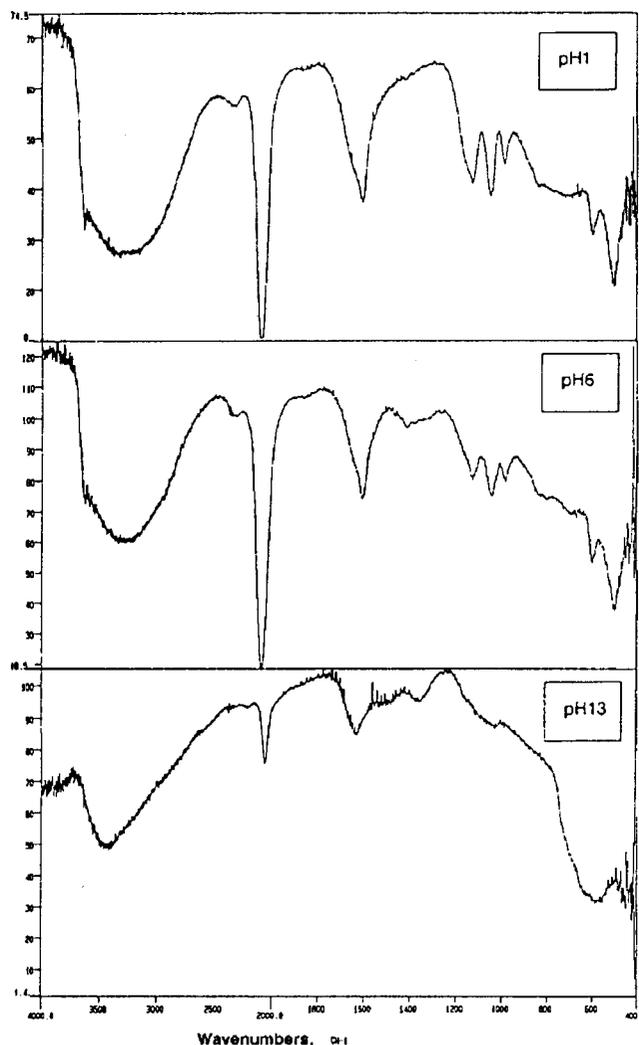


Fig. 7—Infrared spectra of Prussian blue precipitate after 2 hours of contact with solutions of varying pH value

TABLE V
Elemental analyses of Prussian blue precipitate

Compound	Elemental analysis, %					
	Na	Fe	C	N	O	H ₂ O
Precipitate as analysed	0,016	34,6	14,5	6,0	4,4	24,1
Precipitate corrected to the anhydrous state	0,021	45,6	19,1	7,9	5,8	-
Fe ₄ [Fe(CN) ₆] ₃	0	45,5	25,2	29,3	0	-
NaFe[Fe(CN) ₆]	7,9	38,4	24,8	28,9	0	-
Fe ₂ O ₃	0	69,9	0	0	43,0	-
Fe(OH) ₂	0	62,1	0	0	35,6	-
FeO.OH	0	62,9	0	0	18,0	-

TABLE VI
Elemental analyses of Prussian blue precipitate after 2 hours of contact with solutions of varying pH value

Compound	pH of solution	Elemental analysis, %					
		Na	Fe	C	N	O	H ₂ O
Precipitate	1	0,003	30,7	16,5	8,8	2,4	
	4	0,006	33,3	14,5	9,3	3,2	
	6*	0,016	34,6	14,5	6,0	4,4	24,1
	7	0,63	42,5	9,4	7,2	6,1	
	8	0,68	49,3	8,9	3,6	11,7	22,2
	9	0,47	53,5	4,1	2,8	17,3	
	11	0,52	53,1	4,9	3,3	17,9	
	12	0,30	56,1	5,8	2,8	18,4	
	13	0,18	62,8	1,0	0,3	26,6	11,8
Fe ₄ [Fe(CN) ₆] ₃	-	0	45,5	25,2	29,3	0	-
NaFe[Fe(CN) ₆]	-	7,9	38,4	24,8	28,9	0	-
Fe ₂ O ₃	-	0	69,9	0	0	43,0	-
Fe(OH) ₂	-	0	62,1	0	0	35,6	-
FeO.OH	-	0	62,1	0	0	18,0	-

* Natural pH of the solution after precipitation

diffraction (XRD) peaks characteristic of Fe₄[Fe(CN)₆]₃. At higher pH values, these peaks drop in intensity, whereas peaks due to γ-Fe₂O₃ increase in intensity. The XRD technique is sensitive only to crystalline compounds, which means that the various forms of Fe₂O₃.n H₂O detected in the infrared spectra are probably amorphous.

CONCLUSIONS

Environmental regulations require that total cyanide in solution should be reduced to a specified level, and do not refer to cyanide in solids. Therefore, the ferrous sulphate method must be optimized for the formation of the Prussian blue precipitate, and not the soluble ferrocyanide complex. The optimal conditions for the removal of cyanide by reaction with FeSO₄ and the formation of Prussian blue are as follows:

pH 5,5 to 6,5
Fe:CN 0,5.

The bubbling of either oxygen or nitrogen was found to be detrimental to the removal of cyanide: oxygen bubbling results in the formation of both ferrocyanide and ferri-

cyanide in solution as a result of oxidation; nitrogen bubbling results in the formation of ferrocyanide in solution.

The ferrocyanide ion is unstable in acidic solution, and forms either the pentacyanide ferrous complex, Fe(CN)₅.H₂O³⁻, or undergoes rapid oxidation to ferricyanide, Fe(CN)₅²⁻. These reactions occur at pH values of less than 4.

The precipitate that forms in the reaction between excess FeSO₄ and CN⁻ was identified as comprising mainly insoluble Prussian blue, Fe₄[Fe(CN)₆]₃. The Prussian blue precipitate is stable over a pH range of 1 to 7, but is unstable in alkaline solution, decomposing rapidly to form Fe(CN)₅²⁻ in solution. It forms various insoluble iron oxides, Fe₂O₃.n H₂O (n = 1-3), at pH values above 7.

ACKNOWLEDGEMENT

The work described here was carried out in collaboration with the Chamber of Mines as part of its research programme, and is published by permission of the Chamber of Mines. The contribution to this work by O.L. Wellington, M.J. Hemmings, E.A. Jones, and K.T. Wintle is greatly appreciated.

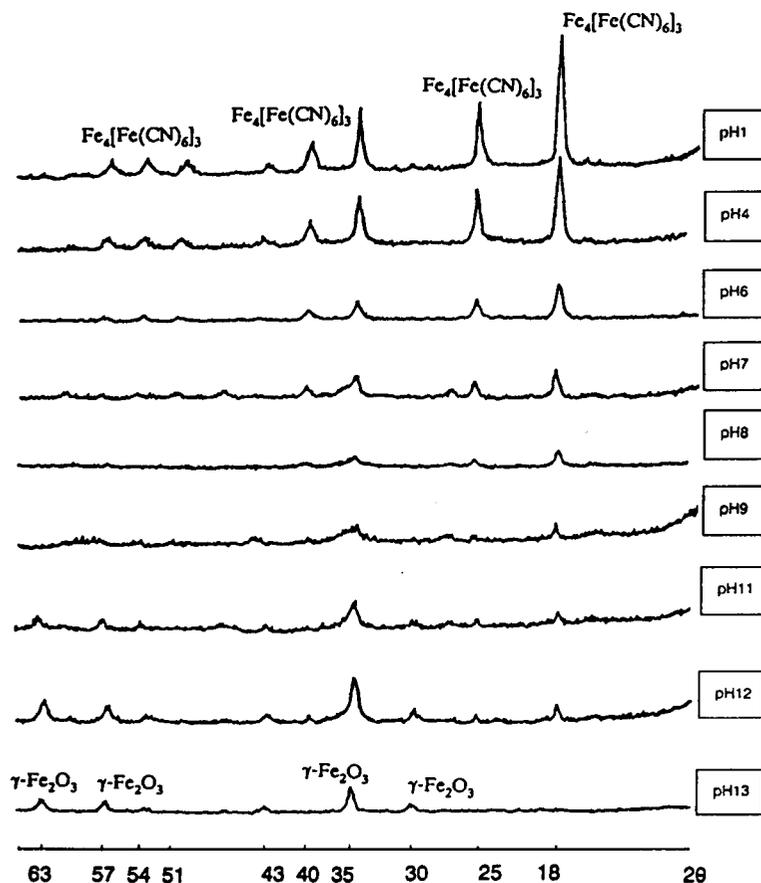


Fig. 8—X-ray diffractograms of Prussian blue precipitate after 2 hours of contact with solutions of varying pH value

REFERENCES

- CHADWICK, B.M., and SHARPE, A.G. Transition metal cyanides and their complexes. *Advances in inorganic chemistry and radiochemistry*. Emeleus, H.J., and Sharpe, A.G. (eds.). New York, Academic Press, 1966. pp. 83–176.
- ZAIDI, S.A., and CAREY, J. Ultraviolet irradiation for removing iron cyanide from gold mill effluents. *Conference on cyanide and the environment*. Van Zyl, D. (ed.). Fort Collins, Colorado State University, 1984. pp. 363–377.
- POHLANDT, C. Chromatographic separation and determination of stable metal cyanide complexes in gold processing solutions. *S. Afr. J. Chem.*, vol 38, no. 3. 1985. pp. 110–114.
- WESTBROOK, C.W., PARCELL, T., CLAYTON, G.L., and KLOCK, B.V. Waste water process. *U.S. Patent* 4 211 646. 8th Jul. 1980.
- KENT, W.J., and BABCOCK, A.R. Process for the removal of cyanides from effluent. *U.S. Patent* 4 250 030, 10th Feb., 1981.
- NEVILLE, R.G. Method for the removal of free and complex cyanides from water. *U.S. Patent* 4 312 760. 26th Jan., 1982.
- GOODWIN, E. Process for the removal of cyanide and other impurities from solution. *S. Afr. Patent* 88/3302. 10th May, 1988.
- WILLIAMS, H.E. *Cyanogen compounds*. 2nd edn. London, Edward Arnold, 1948. pp. 170–200.
- ROBIN, M.B. The colour and electronic configurations of Prussian blue. *Inorg. Chem.*, vol. 1, no. 2. 1962. pp. 337–342.
- SZARAWARA, J., and POCIECHA, Z. Equilibria of the complexing of cyanides with ferrous sulphate. *Chem. Stosow.*, vol. 16, no. 1. 1972. pp. 79–100.
- BECKEN, W.E. Treatment of cyanide waste. *Electroplating and Metal Finishing*, Dec. 1972, pp. 20–21.
- VERBAAN, B., and CRUNDWELL, F.K. An electrochemical model for the leaching of a sphalerite concentrate. *Hydrometall.*, vol. 16. 1986. pp. 345–359.
- CIMINELLI, V.S.T. *Oxidation of pyrite in alkaline solutions and heterogeneous equilibria of sulphur- and arsenic-containing minerals in cyanide solutions*. Ph.D. Thesis, Pennsylvania State University, 1987. p. 170.
- INGRI, N., KAKOLOWICZ, W., SILLEN, L.G., and WARNQVIST, B. High-speed computers as a supplement to graphical methods. V. Håltafall, a general program for calculating the composition of equilibrium mixtures. *Talanta*, vol. 14. 1967. pp. 1261–1286.
- KRAGTEN, J. *Atlas of metal-ligand equilibria in aqueous solution*. Chichester, Ellis Horwood, 1978.
- BECK, M.T. Critical survey of stability constants of cyano complexes. *Pure & Appl. Chem.*, vol. 59, no. 12. 1987. pp. 1703–1720.
- SMITH, R.M., and MARTELL, A.E. *Critical stability constants. Vol 4: Inorganic Complexes*. New York, Plenum, 1976.
- HEMMINGS, M.J. Mintek, Randburg, personal communication, Feb. 1990.
- WILDE, R.E., GHOSH, S.N., and MARSHALL, B.J. The Prussian blues. *Inorg. Chem.*, vol. 9, no. 11. 1970. pp. 2512–2516.
- SMITH, J.V. (ed.). *X-ray powder diffraction file*. Philadelphia, American Society for Testing Materials, 1960. p. 1-0239.

GR Bozzoli Awards*

The Anglo American Corporation, Murray & Roberts, and Mr George Brown were recipients of the GR Bozzoli Awards for 1991.

These Awards, named after Professor G. R. Bozzoli, a highly respected past head of Electrical Engineering, Dean of the Engineering Faculty, and Vice-Chancellor of Wits University, are presented annually by the Faculty of Engineering at Wits to individuals and organizations for their outstanding contribution to engineering education.

ANGLO AMERICAN

Anglo American was nominated for its foresight in establishing the Cadet Scheme ten years ago. The Scheme was aimed at developing technologically trained black engineers and managers. The Scheme is now administered by the Engineering Faculty and sponsored by eleven engineering companies. It provides a pre-university year of academic upgrading and attention to problem-solving, language, and study skills, as well as practical experience in the work environment.

Anglo American's selfless concern for the future of engineering education in South Africa is also illustrated by the recent decision of the Chairman's Fund to finance an engineering stream of the College of Science at Wits University over the next five years at a cost of more than 2 million rands.

This will enable 60 students from disadvantaged educational backgrounds to spend two years of intensive preparation in gaining credit for first year.

MURRAY & ROBERTS

Murray & Roberts was nominated for the Bozzoli Award by the School of Mechanical Engineering and the Department of Civil Engineering in recognition of substantial support, including a new CAD facility for first-year mechanical-engineering students, an annual grant to support a member of the civil-engineering staff on overseas research study, and the provision of teaching equipment.

* Released by Lynne Hancock Communications, P.O. Box 3712, Honeydew, 2040 Transvaal.

MR GEORGE BROWN

Mr George Brown, former Electrical Service Manager in the Engineering Department of AECI, who retired from AECI recently, was nominated by the Department of Electrical Engineering for consistently promoting and influencing the cause of education at South African universities.

Since the 1960's, Mr Brown has played a leading role in strengthening the staff and computing facilities in the Department of Electrical Engineering at Wits, helping to establish an FRD programme in the field of process control, and serving on advisory committees investigating the structure and teaching of undergraduate programmes.

PROGRESS IN ENGINEERING

Professor Alan Kemp, Dean of the Engineering Faculty, told guests at the Awards ceremony that, in the past year, the Faculty had made good progress in its strategic priorities of improving the quality of education in terms of both students and staff, developing closer associations for mutual benefit with industry, and addressing the needs of educationally disadvantaged students.

He said: 'The average matriculation mark in higher-grade mathematics, science, and home language of admitted first-year students is now more than 70 per cent, probably the highest in any engineering faculty in South Africa.' It was important that pass rates reflected this improved quality of student, and attention was being given to the teaching process to counterbalance the negative effects of massive cuts in university subsidies by the State.

A first priority for private-sector funding is the establishment of scholarships, fellowships, and named chairs that can support full-time post-graduate students to act as part-time teaching assistants while undertaking their research and coursework. In addition, the Engineering Faculty at Wits had a proud record of developing, together with the private sector, more academic support schemes addressing the needs of more disadvantaged students than most faculties in South African universities.

Mr Paul Kruger, Managing Director of Sasol, was guest speaker at the presentation.