# The detoxification of gold-mill tailings with hydrogen peroxide

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### SYNOPSIS
Hydrogen peroxide is gaining acceptance as a reagent for the treatment of mining effluents containing cyanide. In this paper some of the chemical and environmental aspects of treatment with hydrogen peroxide are discussed, and one way of improving the economics of the process is described. This is known as selective detoxification, which involves the oxidation of the less stable (cyanide) complexes while not affecting the more stable complexes, which contribute very little to the concentration of free cyanide or to the toxicity of the treated water.

### SAMEVATTING
Waterstofperoksied word al hoe meer aanvaar as 'n reagens vir die behandeling van mynuitvloeisels wat sianied bevat. Sommige van die chemiese en omgewingsaspekte van behandeling met waterstofperoksied word in hierdie referaat bespreek en een manier om die ekonomie van die proses te verbeter word beskryf. Dit staan bekend as selektiewe ontgifting en behels die oksidasie van die minder stabiele (sianied) komplekse sonder om die meer stabiele komplekse wat baie min tot die konsentrasie van vry sianied, of tot die giftigheid van die behandelde water bydra, te beïnvloed.
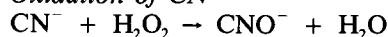
## Introduction

The detoxification plant supplied by Degussa for use at the gold mine of Ok Tedi Mining Ltd in Papua New Guinea represents the first large-scale application of hydrogen peroxide for the detoxification of tailings from a cyanidation plant. A detailed description of the treatment was given in an earlier publication[1]. The treatment plant at Ok Tedi has now been in operation for over two years, during which more than 20 million cubic metres of high-solids pulp have been treated continuously with hydrogen peroxide at an average rate of over 1000 m$^3$/h.

The experience gained during this period has led to a better understanding of the chemistry involved in the treatment of gold-mill tailings and this, in turn, has been utilized to develop a cost-cutting modification to the process, which is termed here *selective detoxification*.
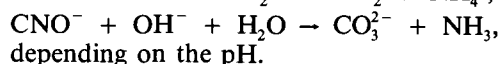
## Detoxification with Hydrogen Peroxide

The main advantage of hydrogen peroxide in the treatment of waste water is that it is a 'clean' chemical, in the sense that no substances are introduced with the oxidizing agent that might impair the quality of the water. The reaction between cyanide and hydrogen peroxide takes place in a single step, without the formation of toxic intermediates. The product of the reaction is cyanate, which subsequently hydrolyses slowly to give ammonium and carbonate ions:

*Oxidation of CN$^-$*
$$CN^- + H_2O_2 \rightarrow CNO^- + H_2O$$

*Hydrolysis of CNO$^-$*
$$CNO^- + 2 H^+ + H_2O \rightarrow CO_2 + NH_4^+, \text{ or}$$
$$CNO^- + OH^- + H_2O \rightarrow CO_3^{2-} + NH_3,$$
depending on the pH.

Although ammonia (NH$_3$) is toxic to fish at concentrations[2] above about 1 p.p.m., it is almost entirely present in the far less toxic cationic (ammonium) form at the natural pH of open waterways.

If excess hydrogen peroxide is present in treated waste water, it rapidly decomposes to water and oxygen, and therefore presents no environmental threat:

$$2 H_2O_2 \rightarrow 2 H_2O + O_2.$$
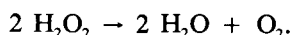
In addition, it does not contribute to the salt content of the water, unlike most of the other chemicals used in the treatment of cyanide.

Hydrogen peroxide can be shipped safely at high concentrations (up to 70 per cent by mass) and stored for long periods without appreciable loss of activity, which makes it an ideal choice for remote locations and for emergency detoxification units where low capital costs and quick start-up are essential requirements.

Hydrogen peroxide is capable of oxidizing both free cyanide and weakly bound complex cyanides, including the following species, which are normally measured as 'weak acid dissociable' or 'easily liberatable' cyanide by standard analytical methods[3,4]:

$$CN^-, HCN, Cd(CN)_4^{2-}, Zn (CN)_4^{2-}, Cu(CN)_2^-,$$
$$Cu(CN)_3^{2-}, Cu(CN)_4^{3-}.$$
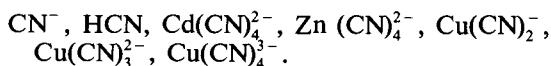
By contrast, the following species are too stable to be oxidized by hydrogen peroxide:
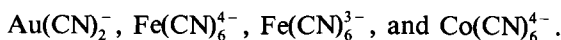
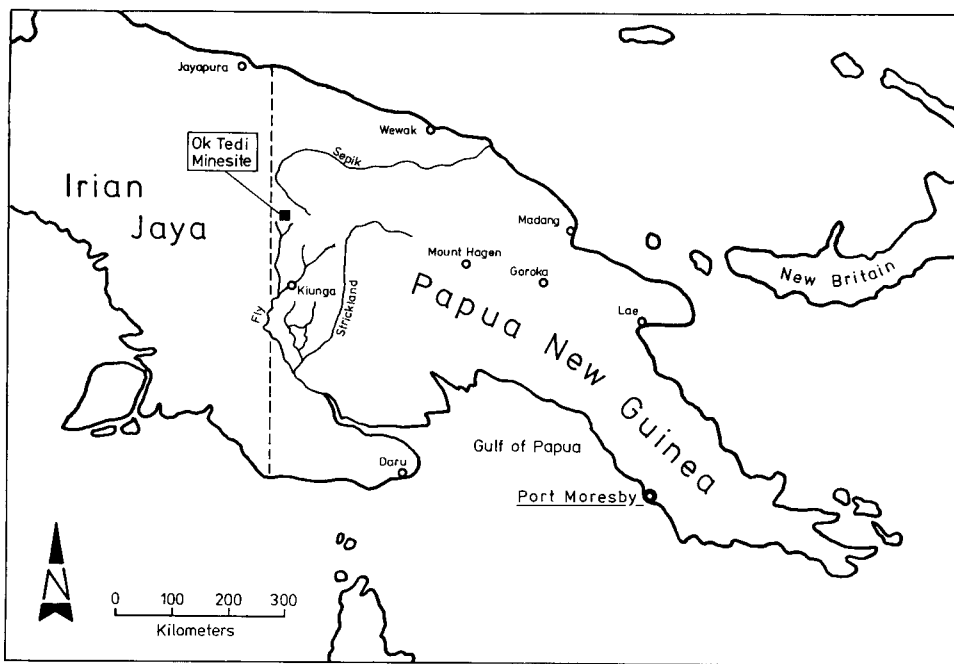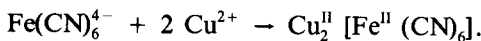$$Au(CN)_2^-, Fe(CN)_6^{4-}, Fe(CN)_6^{3-}, \text{ and } Co(CN)_6^{4-}.$$

Fig. 1—Map showing the location of the Ok Tedi Mine

Ferrocyanide is not oxidized to ferricyanide by hydrogen peroxide in alkaline solution, thus permitting its subsequent removal by precipitation with, for example, copper ions:

$$Fe(CN)_6^{4-} + 2\ Cu^{2+} \rightarrow Cu_2^{II}\ [Fe^{II}\ (CN)_6].$$

Hydrogen peroxide was chosen on the basis of these advantages for the treatment of the tailings from the Ok Tedi Mine.

### The Ok Tedi Mine

The Ok Tedi Mine is situated near the centre of the island of New Guinea, in an area of extremely high rainfall (Fig. 1). About 22,5 kt of ore are treated daily with sodium cyanide in the carbon-in-pulp process, giving rise to a tailings flow of about $1400\ m^3/h$ at 45 per cent solids. After treatment with hydrogen peroxide and cycloning, the slime fraction is discharged to the Ok Mani river (Fig. 2). About 15 km further downstream, the Ok Mani joins the Ok Tedi, where further dilution takes place.

The concentrations of cyanide that have to be met by Ok Tedi Mining Ltd were originally 3,5 p.p.b. of free cyanide (24 h average) and 52 p.p.b. maximum. The point of measurement was chosen to be Ningerum, which lies some 60 km downstream of the Ok Mani–Ok Tedi confluence, because of the importance of fish as a food source for the local inhabitants of Ningerum and the surrounding area. These criteria were changed at the beginning of 1986 to 30 p.p.b. of free cyanide (24 h average) and 70 p.p.b. (peak).

At the time Ok Tedi went into production, there was no method for the analysis of such a low concentration of free cyanide. Thus, in order to ensure that the limit would not be exceeded due to the formation of free cyanide by the dissociation of weakly complexed cyanide on dilution in the Ok Tedi river, the Company decided that the concentration of easily liberatable cyanide should be reduced by treatment with hydrogen peroxide to less than 1 p.p.m. (which is equivalent to 1 mg of free cyanide

per litre of tailings filtrate).

Table I shows the typical composition of the tailings before and after treatment with hydrogen peroxide during this initial period of operation of the detoxification plant.

After about eight months of operation, during which the consumption of hydrogen peroxide was close to the design figure, a progressive change in the composition
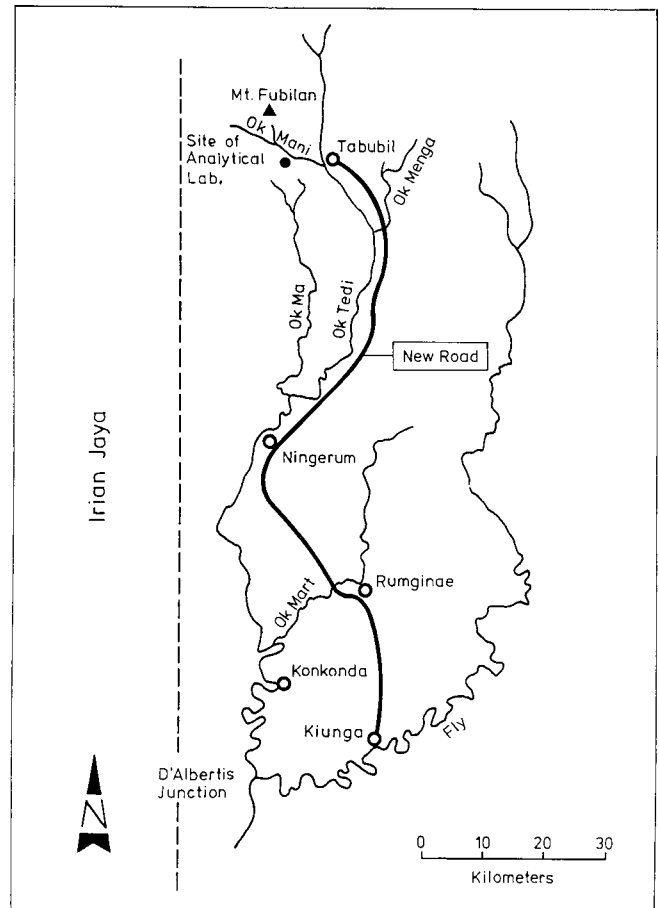


Fig. 2—Map showing the Ok Tedi river system

## TABLE I
### EFFECT OF TREATMENT WITH HYDROGEN PEROXIDE

| Parameter | Before treatment with $H_2O_2$ | After treatment with $H_2O_2$ |
|---|---|---|
| Flow of tailings, $m^3/h$ | 1100 | 1100 |
| Solids, % | 45 | 45 |
| pH* | 10,5 to 11,0 | 10,2 to 10,8 |
| CN†, mg/l | 50 to 100 | Undetected |
| Easily-lib. CN‡, mg/l | 90 to 200 | < 0,5 |
| Total cyanide§, mg/l | 110 to 300 | 1 to 10 |
| Dissolved metals**, mg/l | | |
| Cu | 50 to 100 | < 0,5 |
| Zn | 10 to 30 | < 0,1 |
| Fe | 1 to 3 | 1 to 3 |

\* A slight reduction in pH (0,2 to 0,3) takes place during the detoxification reaction

† Argentometric, 10 ml sample, 0,01 N AgNO$_3$ solution, rhodanine indicator

‡ Colorimetric determination with test kit from E. Merck, based on the pyridine–barbituric acid methods[5]

§ Distillation of HCN according to the German DIN standard method[4]

\*\* Metals determined by atomic-absorption spectroscopy

of the mill feed took place, which led to an increase in the consumption of cyanide and a corresponding increase in the consumption of hydrogen peroxide.

The reason for the increased consumption was traced to the presence of unexpectedly large amounts of cyanide-soluble copper minerals, which occurred in certain parts of the orebody. This problem was subsequently mitigated by selective mining, but it was evident that high levels of dissolved copper resulted in a high consumption of oxidizing agent, and ways were sought to combat this.

One possible answer was selective detoxification, by which is meant the oxidation of the less stable (cyanide) complexes while leaving the more stable complexes, which contribute very little to the concentration of free cyanide or to the toxicity of the treated water.
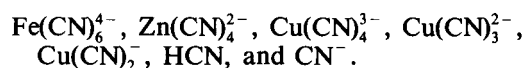
### Selective Detoxification

The concept of selective detoxification of cyanide complexes is not entirely new, since complex iron cyanides are normally left untouched by oxidative treatment with hydrogen peroxide or chlorine. In this case, however, the intention was to control the addition of hydrogen peroxide in such a way as to leave not only the ferrocyanide but also some of the copper complex $Cu(CN)_2^-$ unoxidized.

In order to be able to evaluate the results of selective detoxification, it was necessary to develop a method for the measurement of free cyanide in river water down to 5 p.p.b. and below. This was undertaken by Ok Tedi Mining Ltd. Degussa undertook the investigation of the theoretical background to permit the prediction of free cyanide levels on the basis of measurements of total cyanide and total copper.

### Theoretical Background

The important cyanide species present in Ok Tedi tailings are the following:

$Fe(CN)_6^{4-}$, $Zn(CN)_4^{2-}$, $Cu(CN)_4^{3-}$, $Cu(CN)_3^{2-}$, $Cu(CN)_2^-$, HCN, and $CN^-$.
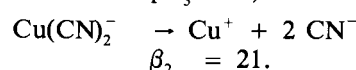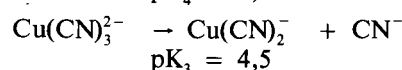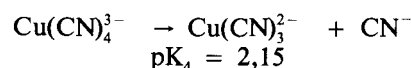
Of these, the ferrocyanide remains untouched by the detoxification reaction, although some may be removed from the river water by precipitation with divalent metal cations.

The formation of free cyanide by photolytic decomposition of any remaining ferrocyanide ions was not expected to be a major problem in Ok Tedi's case, because the river water is too turbid to allow much penetration of sunlight and the concentrations of dissolved iron are very small (typically 3 to 5 p.p.m. in the tailings filtrate).

Complex zinc cyanide is attacked quickly by hydrogen peroxide owing to the weakness of the complex, and is detoxified as rapidly as the free cyanide.

A large proportion of the cyanide in solution in untreated tailings is bound to copper. These copper complexes must be considered in more detail in order to explain the concept of selective detoxification more clearly. Three cyanocuprate complexes are known, which exist in equilibrium with each other and with $CN^-$:

$$Cu(CN)_4^{3-} \rightarrow Cu(CN)_3^{2-} + CN^-$$
$$pK_4 = 2,15$$

$$Cu(CN)_3^{2-} \rightarrow Cu(CN)_2^- + CN^-$$
$$pK_3 = 4,5$$

$$Cu(CN)_2^- \rightarrow Cu^+ + 2 CN^-$$
$$\beta_2 = 21.$$

The values of the dissociation constants quoted[6] above are higher than some others that have appeared in the literature. These higher values were chosen for use in the calculations in order to provide an extra safety margin.

One further equation must be considered, which describes the pH-dependent equilibrium between HCN and $CN^-$:

$$HCN + OH^- \rightarrow CN^- + H_2O$$
$$pK = 9,36.$$
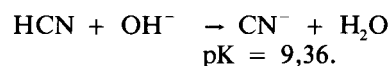
The value of the dissociation constant is that given by Broderius[7].

A computer program was developed by Degussa, which uses these equations to predict equilibrium concentrations of $CN^-$, HCN, and the three complexes for given total concentrations of cyanide and copper, and for given pH values. A typical result is shown in Fig. 3, in which the distribution of cyanide among the various forms is shown for a total copper concentration of $10^{-3}$ mol/l and a pH of 10.

At a CN/Cu mole ratio (called Q in Fig. 3) of 2 : 1 (and below), the cyanide in solution is present entirely as $Cu(CN)_2^-$ at the concentrations and pH values shown in Fig. 3. This is due to the extremely low dissociation constant for this complex $(10^{-21})$. As the CN concentration rises (the total copper concentration is considered to be constant in this example at $10^{-3}$ mol/l), the proportion of cyanide in the $Cu(CN)_2^-$ form drops quickly, while the proportion present as $Cu(CN)_3^{2-}$ rises, and reaches a maximum at a CN/Cu ratio of about 3 : 1. The $Cu(CN)_4^{3-}$ complex increases steadily in importance through the CN/Cu range shown (2 to 5), as does the proportion of free cyanide, both as $CN^-$ and as HCN.

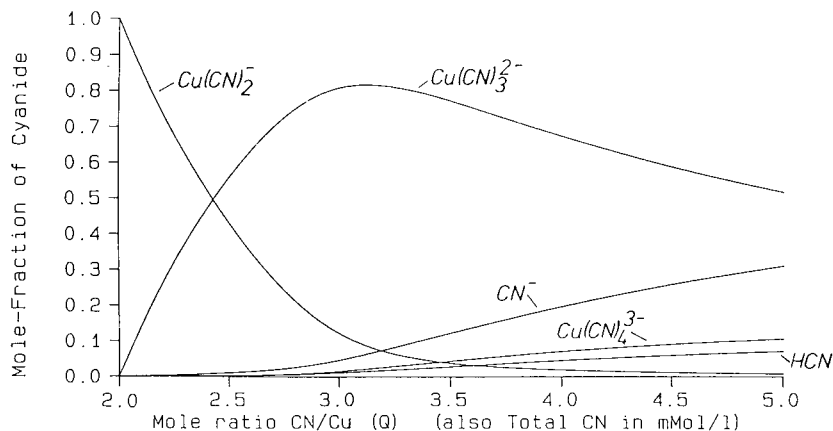The line at Q = 5 in Fig. 3 indicates a situation that

Fig. 3—Calculated distribution of cyanide among the copper complexes as a function of mole ratio CN/Cu

may represent actual tailings before treatment, with total cyanide and copper concentrations of 130 and 63,5 p.p.m. respectively. The predicted distribution of cyanide among the complexes is that shown in Table II.

TABLE II

PREDICTED DISTRIBUTION OF CYANIDE AT pH 10 BASED ON THE DATA PRESENTED IN FIG. 3

| Form of cyanide | Concentration p.p.m. | % of total cyanide |
|---|---|---|
| HCN | 9,0 | 6,9 |
| $CN^-$ | 40,0 | 30,8 |
| $Cu(CN)_4^{3-}$ | 12,9 | 9,9 |
| $Cu(CN)_3^{2-}$ | 67,2 | 51,7 |
| $Cu(CN)_2^-$ | 0,9 | 0,7 |
| Total CN | 130,0 | 100,0 |
| Total Cu | 63,5 | – |

Looking at Fig. 3 again, we can simulate the early stages of the detoxification reaction by moving down the x-axis. As cyanide is removed by oxidation, the distribution of the remaining cyanide among the various ions changes continuously, until at Q = 2 only $Cu(CN)_2^-$ is left. (It has been assumed for the purpose of this discussion that the system is in equilibrium at all times. This is, of course, not true during the detoxification reaction itself, but the system rapidly re-attains equilibrium if the addition of oxidizing agent is stopped.)

If the detoxification is continued by the addition of larger amounts of oxidizing agent, the $Cu(CN)_2^-$ ion is also broken down, and $Cu(OH)_2$ precipitates. If the addition of hydrogen peroxide is stopped at any time after $Cu(OH)_2$ starts to precipitate, $Cu(CN)_2^-$ is the only species of those listed in Table II that remains in solution with a significant concentration. The concentration of dissolved copper can thus be reduced to the required level by the addition of an appropriate amount of hydrogen peroxide. Calculations show that the concentration of free cyanide ($CN^-$ + HCN) is well below 1 p.p.m. in this case, once the detoxification has been carried through to this stage.

Before we move from theory to practice, answers must be given to four important questions.

## Toxicity of $Cu(CN)_2^-$

Broderius[8,9] reported a 48 h $LC_{50}$ value of 9000 p.p.b. for $Cu(CN)_2^-$, which, by use of published factors of safety, implies a safe annual median concentration of 450 p.p.b. and a safe annual 95 percentile of 1800 p.p.b. In practice, a lower limit applies to Ok Tedi in that the concentration of dissolved copper must not exceed 50 p.p.b. at Ningerum.

## Precipitation of CuCN

Copper(I) cyanide is highly insoluble, and it is important to consider the possibility that it may precipitate in the course of selective detoxification. Toxic effects of copper cyanide towards benthic organisms have not been studied as far as we are aware, but they cannot be ruled out. Analysis of the solid component of treated tailings has, however, shown that copper cyanide does not precipitate significantly under the detoxification conditions described here.

## Natural Degradation of Cyanide

The calculations described earlier do not take into account such reactions as the loss of hydrogen cyanide to the atmosphere, bacterial attack on cyanide, and precipitation and adsorption of cyanide compounds, all of which tend to reduce the concentration of free cyanide under natural conditions.

## Process Control

Selective detoxification of the kind described here can be carried out reliably on a continuous basis only if the process is under close control and surveillance. Degussa's process-control method[1] can be used to control complete or selective detoxification automatically according to requirements, but regular checks on the actual concentration of free cyanide in the river water are still necessary. In order to be able to measure free cyanide at very low concentrations (less than 5 p.p.b.) in river water, Ok Tedi Mining Ltd successfully developed an analytical method based on the hydrogen cyanide diffusion method described by Broderius[10].

In addition, a transportable analytical laboratory has been installed on the bank of the Ok Mani river (Fig. 2). The dilution of the mine effluent at this point in the river system is much lower than at Ningerum (approximately 14 times compared with approximately 500 times at mean

daily flow levels), thus enabling a wider range of analytical methods to be used.

## Results

Selective detoxification has been practised at Ok Tedi for over a year with encouraging results. The measured concentrations of free cyanide in the Ok Tedi at Ningerum are consistently below the predicted levels, as expected from the losses of free cyanide via natural degradation during the 12-hour transit time between the Ok Mani and Ningerum. Fig. 4 demonstrates the extent to which selective detoxification has assisted the operations of Ok Tedi Mining Ltd. In spite of a marked trend of increasing copper concentrations in the pulp being treated, the concentrations of free cyanide in the river at Ningerum have been maintained at acceptable levels without incurring high reagent consumptions. As the analytical and process-control procedures have become more finely tuned, the consumption of hydrogen peroxide has even been reduced. The curve shows a period of increased hydrogen peroxide consumption around January 1986,
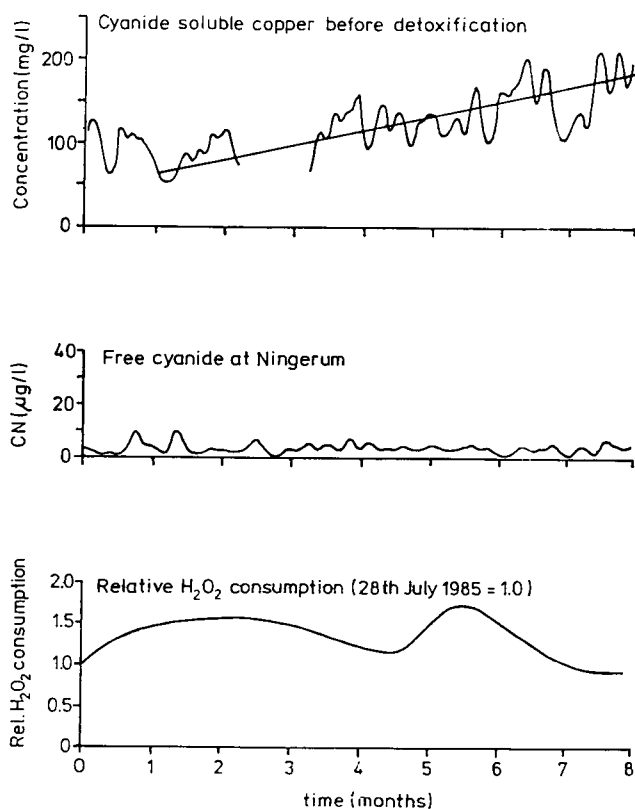
which was the result of overdosing due to incorrect cyanide measurements. (There was sulphide interference with the measurements, which were made with an ion-selective electrode at the Ok Mani laboratory.)

## Conclusions

By the use of selective detoxification, it has proved possible to make major savings in the running costs of the detoxification plant of Ok Tedi Mining Ltd. The consumption of oxidizing agent has been reduced from 1,5 to approximately 1,0 kg per cubic metre of tailings (45 per cent solids), despite increasing levels of copper and cyanide in the solution being treated. This saving has been effected without exceeding the strict government limitation on free cyanide in the Ok Tedi river, and without any observed negative effect on the aquatic life.

In the case of most mines, we expect that complete detoxification of the waste water will continue to be the standard procedure. Selective detoxification will not be appropriate where the composition of the tailings and the geographical situation are radically different from those at Ok Tedi. However, the example presented here shows the flexibility of hydrogen peroxide as a detoxifying agent for gold-mill wastes, and the advantage of effective process control.

## References

1. KNORRE, H., and GRIFFITHS, A. Cyanide detoxification with hydrogen peroxide using the Degussa Process. *Proceedings of the Conference on Cyanide and the Environment.* Van Zyl, D. (ed.). Tucson, Colorado State University, 1985. vol. 2, p. 519.
2. MEINCK, F., STOOF, H., and KOHLSCHÜTTER, H. *Industrie-Abwässer.* Stuttgart, Gustav Fischer Verlag, 1968.
3. *ASTM standard test method for cyanides in water.* D 2036-81, 1982.
4. *German standard methods for the analysis of water, waste water and sludge. Determination of cyanide.* DIN 38 405, Part 13, 1981.
5. *'Microquant' cyanide test set.* Nr. 14798, E. Merck, Darmstadt, West Germany.
6. ROTHBAUM, H.P. *J. Electrochem. Soc.,* vol. 104. 1957. p. 682.
7. BRODERIUS, S.J. Quoted in ref. 9.
8. *Cyanide: An overview and analysis of the literature on chemistry, fate, toxicity and detection in surface waters.* Towson (U.S.A.), Ecological Analysts, Inc. 1979.
9. DOUDOROFF, P., LEDUC, G., and SCHNEIDER, C.R. Acute toxicity to fish of solutions containing complex metal cyanides in relation to concentrations of molecular hydrocyanic acid. *Trans. Am. Fish. Soc.,* vol. 95. 1966. p. 6–22.
10. BRODERIUS, S.J. Determination of molecular hydrocyanic acid in water and studies of the chemistry and toxicity of fish of metal cyanide complexes. Ph.D. Dissertation, Oregon State University (U.S.A.), 1973.

**Fig. 4—Operational data for the Ok Tedi detoxification plant from 28th July, 1985, to 1st April, 1986**