

Chapter 14

Cyanide Degradation and Detoxification in a Heap Leach

Adrian Smith

14.1 INTRODUCTION

From the time the last recoverable gold is extracted from ore on a heap leach, the ore - now spent ore - changes from being the resource, indeed the *raison d'etre* of the operator, to a potential liability. The spent ore contains process chemicals and constituents leached from the ore both in the interstitial pore water in the heap and on the surfaces of spent ore. If these chemical species were released to the environment, it could have a potential impact on the quality of both surface water and groundwater resources.

Accordingly, the spent ore must be left in a condition where it does not present a potential environmental liability. This can be accomplished either on a decommissioned pad or, if the heap leach is operated as a load/unload scheme, in a waste facility. In general, the residual cyanide level in the spent ore is the perceived controlling factor when determining whether the leached material is suitable for abandonment. Regulatory authorities set permit conditions for heap leach abandonment in terms of residual cyanide levels, for example, Smith and Struhsacker (1987).

This chapter discusses cyanide degradation and methods for detoxifying a heap leach in order to meet regulatory limits/permit conditions for abandonment. Cyanide degradation and detoxification by "natural" processes are described initially, based on the chemistry and geochemistry discussed in Chapter 13. This leads to a review of chemical treatment processes for detoxification of spent ore. The advantages and apparent disadvantages are then appraised.

14.2 NATURAL DEGRADATION AND DETOXIFICATION

For the purposes of discussion, "natural" detoxification processes can be divided into two alternatives:

- Passive abandonment (the so-called "do nothing" option); and
- Water.

In the first alternative, the spent ore is merely left on the leach pad to age; the second alternative involves the flushing of the spent ore with water.

14.2.1 Passive Abandonment

The degradation of cyanide, a time-dependent process, is well established and has been described in Chapter 13. It is not unreasonable, therefore, to leave the spent ore on the pad exposed to the forces of nature so that natural degradation can take place. In areas or climates where cyanide degradation is enhanced, for example high temperatures and altitudes as in Smith et al. (1985), this could be an appropriate strategy.

However, the time dependency of the process means that the control of the detoxification is out of the operator's hands. The operator is forced to monitor the system and collect any runoff or seepage from the spent ore which fails to meet regulatory discharge criteria, then wait until the heap leach can be decommissioned. Both the time/monitoring requirement and the possibility of handling/treating large volumes of non-dischargeable runoff can be financial and practical disincentives to natural degradation.

The effectiveness of natural degradation of cyanide has been evaluated and documented by Engelhardt (1985). While the method of cyanide degradation was not determined, this study bears more detailed description due to the careful quantification and monitoring made of the heap system during the evaluation. A precis of Engelhardt's work is given below; further details can be sought in the original text.

The heap was constructed in cells 150 x 125 ft (46 x 38 meters). The ore was stacked to 15 ft (4.5 m) in height. During the six months of operation, 11 cells were constructed containing a total of 84,000 tons of ore.

Sampling began three months after leaching stopped. The 11 sections of the heap area were sampled separately using 1.5 inch (37 mm) diameter pipe driven vertically through the heap to the pad. The specimens obtained by this method were then split into two-ft (0.6 m) depth intervals and shipped for analysis.

Water-soluble cyanide was recovered from the core samples using laboratory-agitated leaching with distilled water. This solution was analyzed for both free cyanide and total cyanide to determine the degradation rate in the inactive heap. A total of five sets of samples containing 356 individual samples were analyzed.

The initial samples indicated that 11.5 percent of the cyanide which had been applied to the heaps still remained. This cyanide, approximately 12,000 lb (5,450 kg), was present in the entrained solution. The final samples, taken after 18 months, indicated that 85 percent of the cyanide present at the end of leaching had been naturally degraded. This residual cyanide represented over two percent of the total cyanide initially applied. Although none of the samples tested was below one mg per kilogram, natural degradation of the cyanide is documented in this inactive heap. The data indicate destruction of cyanide approximates a first order chemical reaction, proportional to the concentration of the cyanide as illustrated on Figure 14.1. At the observed rate of degradation, it would take approximately four years to attain one mg of cyanide per kilogram of leachate.

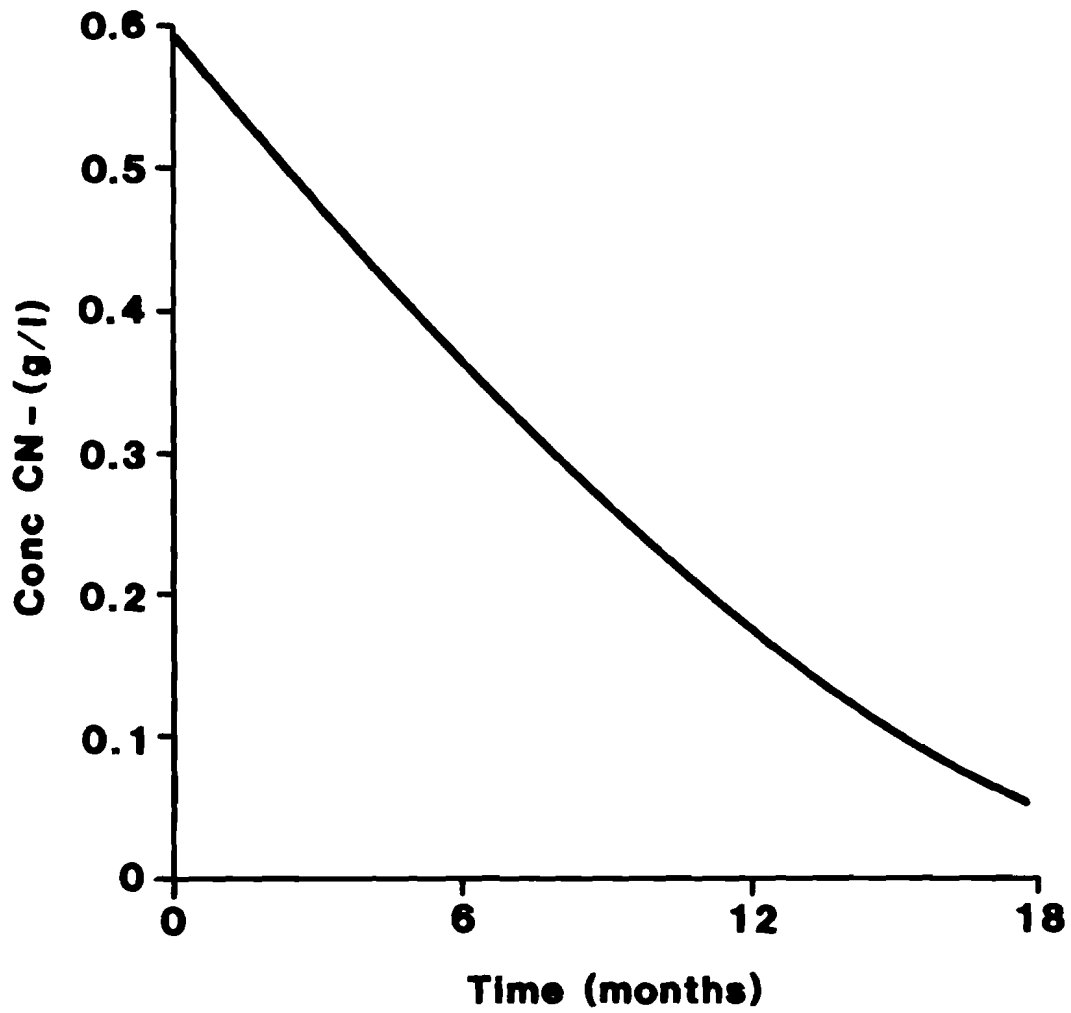


FIGURE 14.1

**Concentration of Cyanide in moisture in Abandoned Heap.
(from Englehardt, 1985)**

This degradation and its nature, as described by Engelhardt, is essentially consistent with data developed with other works; for example, data by Hendrix (1985) on cyanide decay in vat leached tailings, and degradation in effluents by Schmidt et al. (1981).

14.2.2 Water Leaching

The natural detoxification process is comparatively slow, but can be enhanced by "speeding up" the forces of nature. The most expedient method of achieving such acceleration, without resorting to chemical treatment, is cycling rainwater or similar water through the spent ore.

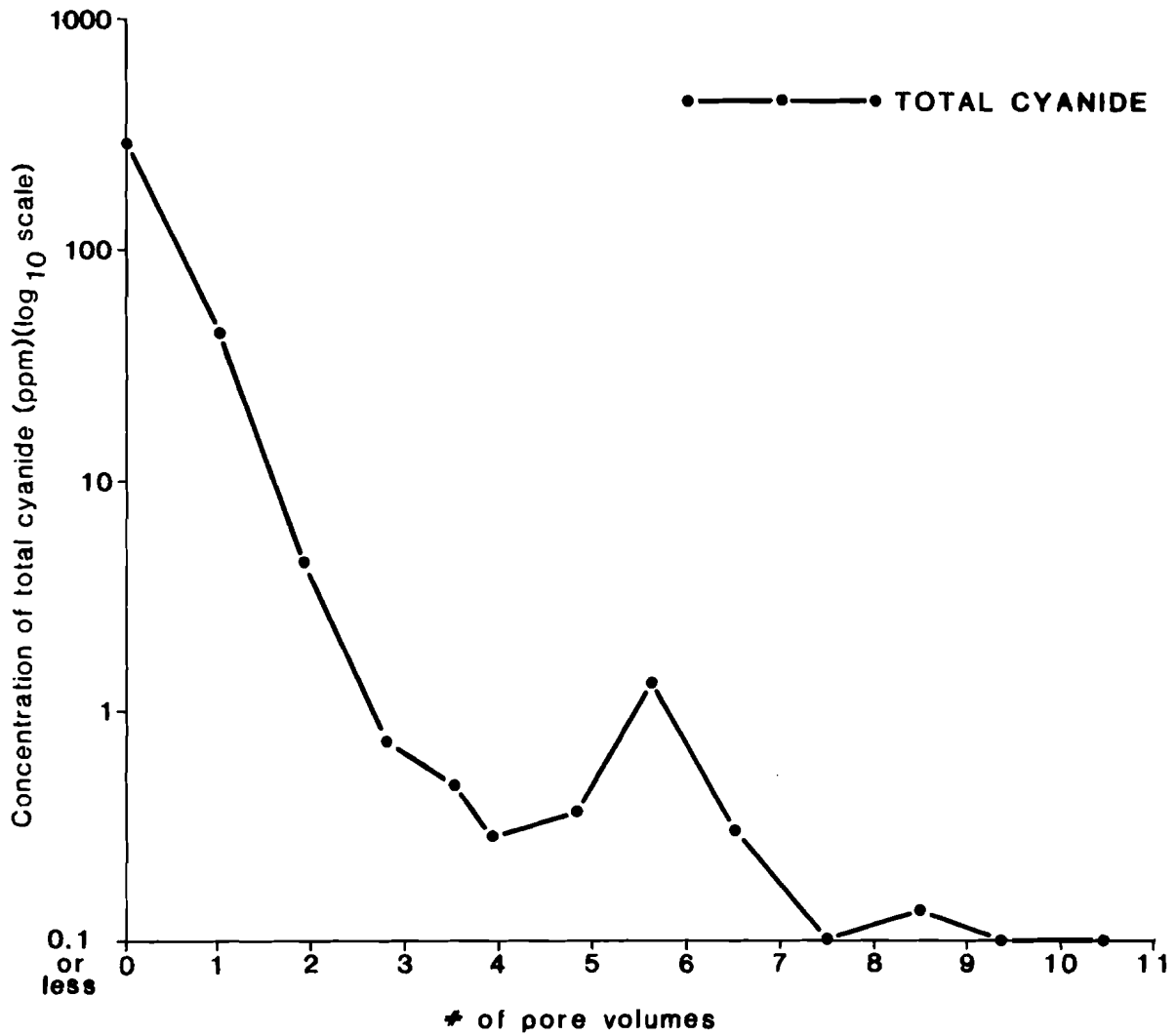
Rainwater normally has a pH value less than seven, meaning it is neutral to acidic, although the pH value is regionally variable. For example, a rainfall pH of 4 to 4.5 is not uncommon on the east coast of the United States while values approaching pH of 5 to 5.5 are more typical in the arid, southwestern states of Arizona and New Mexico. Although rainwater has a low neutralization capacity, when compared with the buffering capacity of the pore water in typical spent ore (pH \pm 10.5), circulation of rainwater through the spent ore can depress the pH enough to convert free cyanide to hydrogen cyanide, which is then lost to the atmosphere by volatilization (Huiatt, et al., 1982).

Data on cyanide degradation by water leaching have been developed by Wharf Resources, Lead, South Dakota. Their data were reported by Smith and Brown (1986), and serve as an illustration of the process as discussed below.

Wharf degradation testing resulted in data on both total and weak acid dissociable cyanide (Method "C", ASTM) with respect to pore volumes of discharged effluent. From an initial total cyanide value of 133 ppm CN in the spent ore pore fluid, the total cyanide levels were reduced to below one ppm before three pore volumes of water had passed through the material. As shown on Figure 14.2, the vertical scale for cyanide concentration is logarithmic.

It is worth noting the apparent "spike" in total cyanide level at about 5.5 pore volumes. This may be due to diffusion back into the leach water of cyanide held in the matrix of the ore. This delayed response could lengthen the time taken to reach the acceptable regulatory level for detoxification. The delayed response phenomenon is not an issue confined only to natural spent ore leaching and can occur in chemically treated spent ore. This is because diffusion is a physico-chemical effect related to the properties of the spent ore independent of the detoxification method.

Perhaps the major potential concern with water leaching for spent ore detoxification is the possibility of generating large volumes of partially contaminated wash solutions. These solutions may be unacceptable for discharge to the environment and/or unamenable to further treatment. Should this be the case, chemical treatment for detoxification becomes more attractive.



NOTE:

All weak acid dissociable levels measured are below 0.1 ppm CN.

FIGURE 14.2

**SEMI-LOGARITHMIC PLOT OF CYANIDE CONCENTRATION
VS
NUMBER OF PORE VOLUMES FOR WATER LEACHING**

14.3 CHEMICAL TREATMENT

The objectives of chemical detoxification of cyanide in spent ore are to achieve low levels of residual cyanides in the effluents from the heap leach and to satisfy the following operational considerations:

- Destroy cyanide rapidly;
- Minimize effluent volumes;
- Generate no metastable cyanide compounds or derivatives; and
- Limit buildup of adverse process chemicals or their degradation/reaction products in the effluent.

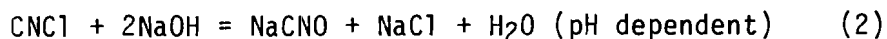
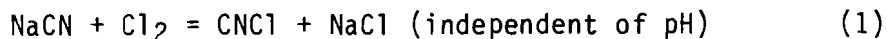
The potential for the various chemical detoxification processes to achieve these objectives is discussed in Section 14.4, after each of the principal processes currently in case or under consideration has been described. Based on a review by Scott (1985), the following chemical treatment methods are available:

- Alkaline chlorination;
- Sulfur dioxide - air oxidation;
- Hydrogen peroxide oxidation;
- Biological processes;
- Acidification; and
- Iron sulfide process.

Variants of these and other processes are described in Huiatt et al. (1982). The first three processes are the most widely used in industry and will be discussed individually.

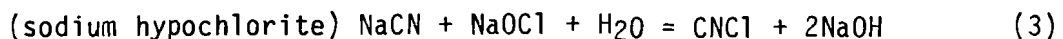
14.3.1 Alkaline Chlorination

Cyanide can be oxidized by the use of chlorine or hypochlorate, generally under alkaline conditions. The reactions of cyanide and cyanide-bearing components with chlorine gas are described by Ingles and Scott (1981). In summary, the principal reactions are:

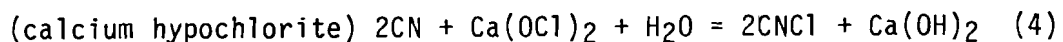


The product of the second reaction, which is most rapid between pH 10 and 11, is cyanate, which will react slowly by a two-stage process with chlorine to form sodium bicarbonate, sodium chloride and nitrogen (White, 1972).

If hypochlorite is used instead of chlorine gas, the reactions would be modified to:



or



An example of the alkaline chlorination approach to cyanide destruction at the Stibnite Property, Idaho is described by Stotts (1985).

The mine operating permit requires that the free cyanide remaining in the processed ore must be reduced to an environmentally safe level of a 0.2 mg/l prior to disposal. Cyanide destruction is accomplished in the 10-day cycle following leaching, i.e., two days for draining, six days for alkaline chlorination treatment, and two days for final draining.

For cost saving, alkaline calcium/chlorine hypochlorite is prepared at the site. Chlorine is consumed at a rate of 4,000 lbs (1,800 kg) per day. Lime is added at the rate of 8,000 lbs (3,600 kg) per day. The resulting solution has a chlorine concentration of approximately 1,000 ppm free chlorine.

The solution is sprayed on the heaps, about 30,000 tons per heap, using the same sprinkler system used in the leaching cycle. After the solution percolates through the heap, it is collected in the chlorine pond where it is recycled through the neutralization system.

14.3.2 Sulfur Dioxide-Air Oxidation

Sulphur dioxide-air oxidation is a relatively new process patented by the International Nickel Company. It is commonly known as the INCO process for cyanide destruction. The cyanide is oxidized under high pH conditions at ambient temperature with a combination of sulphur dioxide and air. Lime is added to stabilize the system pH, in the presence of copper, which acts as a catalyst. The process is described in detail by Devuyst et al. (1985).

The process is said to oxidize cyanide and metal cyanide complexes and will react with iron-cyanide complexes, which are not amenable to treatment by alkaline chlorination. Residual total cyanide levels in the range of 0.05 mg/l to 1 mg/l have been obtained using the process and, due to solubility controls and the high pH range of 9-10 at which the process operates, most residual metal levels (including iron) will be low.

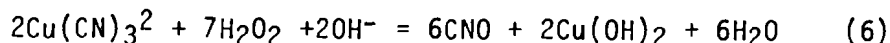
It is claimed that the INCO process can be more efficient, less reagent intensive, and more economical than the alkaline chlorination process with certain specific gold mine effluents. This may be true, in certain cases, with detoxifying effluents and pore water from spent ore after heap leaching.

14.3.3 Hydrogen Peroxide Oxidation

There are a number of variants on the use of the hydrogen peroxide oxidation; details are given in Griffiths (1988) and Huiatt, et al. (1982). The basic oxidation chemistry is:

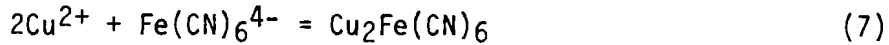


where cyanate is the principal product. This process is carried out in alkaline solution, in the presence of a copper catalyst. Metals, such as copper, will be precipitated during the process, for example, Griffiths (1988) cites:



where copper hydroxide is essentially insoluble at high pH conditions. As noted in Chapter 13, cyanate generated in equation (5) will be hydrolyzed to ammonia and carbonate, the former eventually oxidizing to nitrate.

Griffiths (1988) notes also that iron-cyanide complexes can be removed from the system by the addition of copper, in the form of divalent copper ions, as copper ferrocyanide:



However, this can only be done as a second step to the hydrogen peroxide oxidation process. This process has been developed extensively by Degussa Corporation, and is sometimes known as the Degussa Hydrogen Peroxide process. Degussa has refined the process to allow for the removal of metals in solution as other complex, organic forms using a proprietary reagent TMT 15 (a sodium trimercaptotriazine). This enhances the efficiency of the treatment process.

An alternative to the Degussa process is the "Kastone" process. This process converts hydrogen cyanide, via a two-stage reaction at an elevated temperature, to a glycolic and amide, cyanate and ammonia. A proprietary solution containing + 40 percent hydrogen peroxide, catalyst and stabilizers, is used in conjunction with formaldehyde. The solution is manufactured by DuPont.

The Degussa process has been used at the OK Tedi Mine, in Papua-New Guinea, to treat cyanide-bearing effluents. Knorre and Griffiths (1985) note removal of cyanide, zinc and copper ions by the process as follows:

Free cyanide:	initial:	50-100 mg/l	final:	< 0.02 mg/l
Total cyanide:	initial:	110-300 mg/l	final:	1-10 mg/l
Copper:	initial:	50-100 mg/l	final:	< 0.5 mg/l
Zinc:	initial:	10-30 mg/l	final:	< 0.1 mg/l

Percentage removal varies from 91 percent to over 99 percent for total and free cyanide. Iron, Fe and/or Fe-CN, however, were not removed in the process.

Consumption of hydrogen peroxide in the detoxification process varies depending on spent ore composition and the composition of the remaining interstitial pore water. A typical range for consumption might be 0.4 to 1 litre of 70 percent hydrogen peroxide per cubic metre of waste (Knorre & Griffiths, 1985).

14.4 DETOXIFICATION PROCESSES: ADVANTAGES AND DISADVANTAGES

This section will attempt to give some perspective on the apparent advantages of the various detoxification processes, particularly the chemical treatment methods. Advocates of a particular process could claim that such a discussion is arbitrary, as it may not completely describe all apparent benefits or flaws of any one process. However, the author believes, in this case, that such a risk is warranted in order to provide the reader with at least the basis for a comparison among the various processes.

The benefits or otherwise of the natural processes have already been mentioned in Section 14.2. In summary, the passive abandonment and rainwater leaching approach have the advantages and disadvantages outlined in Table 14.1.

TABLE 14.1

ADVANTAGES AND DISADVANTAGES OF PASSIVE ABANDONMENT AND WATER
LEACHING APPROACHES TO CYANIDE DETOXIFICATION

	ADVANTAGES	DISADVANTAGES
a) Passive abandonment	<ul style="list-style-type: none"> - no cost in process reagents or operating costs - no chemical addition - no induced chemical reactions to form reaction products which could be toxic 	<ul style="list-style-type: none"> - lack of control of the process and hence unpredictability of operation - formation of large volumes of contaminated solution during major precipitation events - non-dischargeable contaminated solutions (small volumes) - excessive time dependency - no certainty of meeting regulatory compliance
b) Water leaching	<ul style="list-style-type: none"> - as for a), except there are some operating costs for pumping 	<ul style="list-style-type: none"> - as for a), except there is some control of the rate of detoxification

For chemical treatment options, Ritcey and McNamara (1978), modified by Ingles and Scott (1981), listed the advantages and disadvantages of the use of alkaline chlorination to detoxify cyanide. In summary, they note the following principal benefits and disadvantages shown in Table 14.2.

TABLE 14.2

ADVANTAGES AND DISADVANTAGES OF CHEMICAL TREATMENT
OPTIONS FOR CYANIDE DESTRUCTION

a) Advantages:	Reactions complete and rapid; Toxic metals usually removed; Chlorine available in different forms; Nominally good, safe control; and Solution already alkaline prior to treatment.
b) Disadvantages:	Reagent costs high, particularly if complete cyanate oxidation is also required; Careful pH control needed to prevent formation of toxic cyanogen chloride; Iron cyanides not usually decomposed; Potential for residual chlorine in effluent; and Potential for formation of toxic chlorinated organic components.

While the process of alkaline chlorination has some obvious advantages, the disadvantages are significant, particularly in the current regulatory environment. Both the potential for cyanogen chloride formation and residual chloride levels are major health issues in themselves. In the longer term, the potential to form persistent, highly toxic chloro-organic compounds - currently an anathema to regulatory authorities - may present such an unknown liability that operators may not wish to risk being left with a future, non-quantifiable problem.

The INCO sulfur dioxide-air process would appear to have advantages over the alkaline chlorination process in terms of reagent requirements, efficiency, effectiveness, and overall costs (DeVuyst et al., 1985). Transportation, handling, and storage of liquid sulfur dioxide may present an issue in terms of permitting, but this should be no worse than similar issues with liquid chlorine. There will be potential to form sulfides, which could be left to react with acidic materials in future to form hydrogen sulfides, but this possibility may be somewhat remote. An accumulation of sulfates within any re-circulated detoxifying solution could lead to both discharge constraints and precipitation of calcium sulfate in the solution distribution system over time, the latter causing blockage of the system.

As with alkaline chlorination, there may be reactions with organic materials in the spent ore resulting in sulfo-organic compounds, which may be persistent and toxic. From a fundamental level, it appears that such an issue

should be no worse and, if anything, significantly better than with the chloro-organic compounds potentially produced by alkaline chlorination.

One potentially negative aspect of the sulfur dioxide-air process is the addition of copper as a catalyst to the process. Regulatory levels for copper discharge to the environment, particularly aquatic criteria and standards, are normally very low and addition of copper to the cyanide detoxification process could result in enhanced copper levels in the residual effluent.

At least superficially, the hydrogen peroxide oxidation process appears to have a number of environmental and practical advantages over the other two processes. These are:

- Nominally, there are no toxic reaction or transformation products formed in the reaction;
- There is no potential for build up of dissolved species in a circulated detoxifying solution; and
- Excess hydrogen peroxide readily degrades in ambient conditions to water and oxygen, hence it will have no material aquatic environmental impacts.

However, should discharge of copper in the detoxified effluent or runoff be an issue, the addition of copper in the process (equation 7) described by Griffiths (1988) may present a problem.

In summary, advantages and disadvantages vary with each process. All processes are vulnerable to the presence of material in the spent ore which can react with the oxidizing agent used to detoxify the cyanide, causing increased reagent assumption and cost. The alkaline chlorination appears to present great potential environmental problems, although its simplicity makes the process attractive. It will be expensive to operate in terms of reagents.

The INCO sulfur dioxide-air and the Degussa hydrogen peroxide processes may be more technically efficient, though admittedly, descriptions of each effluent are by advocates of each system. Even allowing for natural enthusiasm, the data presented generally appear to support their findings. However, a recent study of the comparative effectiveness of the three processes on a carbonaceous gold-cyanide mill tailings showed that the hydrogen peroxide process was the least attractive, due to excessive reagent consumption.

Perhaps the final conclusion should be that there is not necessarily a universally superior detoxification process for cyanide-bearing spent ore. Each of the major processes currently in use has an application in a particular set of circumstances.

14.5 REFERENCES

- De Vuyst, E.A., B.R. Conard, and W. Hudson (1985). Commercial operation of INCO's SO₂-air cyanide removal process, *in* Cyanide and the environment, ed. D. van Zyl. Geotechnical Engineering Program: Colorado State University, pp. 469-498.

- Engelhardt, P.R. (1985). Long-term degradation of cyanide in an inactive heap leach, in Cyanide and the environment, ed. D. van Zyl. Geotechnical Engineering Program, Colorado State University, pp. 539-547.
- Griffiths, S.A. (1988). Detoxification of gold mill waste water with hydrogen peroxide: three case studies, Preprint 88-27, SME-AIME Annual Meeting, Phoenix, Arizona, January 1988.
- Hendrix, J.L. (1985). Investigation on the rate of cyanide in precious metal mill tailings impoundments. Quarterly Report, University of Nevada-Reno, Submitted to USBM November 4, 1985.
- Huiatt, J.L., J.E. Kerrigan, F.A. Olson, and G.L. Potter, eds. (1982). Cyanide from mineral processing, workshop: USBM, Salt Lake City, Utah, February 1982.
- Ingles, J.C. and J.S. Scott (1981). Overview of cyanide treatment methods, in Proc. seminar on cyanide in the gold mining industry: Environment Canada, Ottawa, Ontario, January 1981.
- Knorre, H. and S.A. Griffiths (1985). Cyanide detoxification with hydrogen peroxide using the Degussa process, in Cyanide and the environment (Ed. D. van Zyl). Geotechnical Engineering Program: Colorado State University, pp. 519-529.
- Ritcey, G.M. and V.M. McNamara (1978). Treatment of gold mill effluents for removal and recovery or destruction of cyanide, in Proc. 10th annual conference of Canadian mineral processes, pp. 152-196.
- Schmidt, J.W., L. Simoria, and E. Shannon (1981). Natural degradation of cyanides in gold milling effluents, in Proc. seminar on cyanide in the gold mining industry: Environment Canada, Ottawa, Ontario, January 1981.
- Scott, J.S. (1985). An overview of cyanide treatment methods for gold mill effluents, in Cyanide and the environment, ed. D. van Zyl. Colorado State University, Fort Collins, Geotech., Eng. Prog. v. 2 pp. 307-330.
- Smith, A. and A. Brown (1986). The potential for cyanide migration from Annie Creek Processing Facility, Report No. 1086/2 to Wharf Resources: Steffen Robertson and Kirsten, Lakewood, Colorado, November 1986.
- Smith, A. and D. Struhsacker (1987). Cyanide geochemistry in an abandoned heap leach system and regulations for cyanide detoxification, in Proc. 1st international conference on gold mining, Vancouver, Canada, Chapter 29, pp. 412-430.
- Smith, A., A.A. Dehrmann and R. Pullen (1985). The effects of cyanide-bearing, gold tailings disposal on water quality in the Witwatersrand, South Africa, in Cyanide and the environment (Ed. D. van Zyl), Geotechnical Engineering Program: Colorado State University, pp 221-230.
- Stotts, W.G. (1985). Handling cyanide at Superior Mining Company's stibnite heap leaching operation, in Cyanide and the environment, ed. D. van Zyl. Colorado State University, Fort Collins, Geotech. Eng. Prog., V. 1 pp. 231-247.

White, G.C. (1972). Handbook of chlorination: Van Nostrand Reinhold, New York, New York.