FMC Corporation
Hydrogen Peroxide Division
1735 Market Street
Philadelphia, PA 19103
Phone: 1-800-442-6236 Visit our web site at **http://www.fmcchemicals.com/division_hydrogenperoxide.asp**

Hydrogen Peroxide and Caro's Acid Powerful Oxidants for Cyanide Destruction

Abstract

A brief review of the use of peroxygens to destroy free CN-, WAD (weakly acid dissociable) CN- and tightly complexed cyanides will be followed by a case history on the use of Caro's acid (peroxymonosulfuric acid) to treat cyanide in a tailings slurry at a large North American Gold mine. Peroxygens such as hydrogen peroxide and peroxymonosulfuric acid (Caro's acid) will destroy cyanides. The choice of peroxygen depends on the type of cyanide and the nature of the substrate. Free cyanide and some WAD cyanides are destroyed with catalyzed hydrogen peroxide. For highly complexed cyanides, an advanced oxidation process such as UV H202 is required. For treating free and WAD CN- in slurries containing high concentrations of heavy metals such as gold mine tailings, Caro's acid is most effective. Caro's acid (peroxymonosulf uric acid) was used to successfully treat a 6,500 GPM gold mining tailings slurry. Using an on-site FMC generator, Caro's acid reduced the CN concentration from 40 ppm to below the target level of 20 ppm. At increased Caro's acid levels, CN- levels as low as 4 ppm were achieved. The raw material costs for the detoxification were reduced over 60% with Caro's acid compared to using H202 alone. In addition to the considerable savings in chemical raw material costs, the detoxification time with Caro's acid was much less compared to H202.

Peroxygens and Cyanide Destruction

Free CN-, weakly complexed cyanides and highly complexed cyanides can be destroyed with hydrogen peroxide or Caro's acid. The peroxygen and specific conditions to be used depends on the type of cyanide and substrate to be treated. For solutions containing free and weakly acid dissociable CN-, H202 catalyzed with a soluble copper salt is the preferred treatment. A vanadium, *tungsten or* silver salt may be substituted for the copper salt.

$$H_2O_2 + CN^- \xrightarrow[\text{pH 9-11}]{Cu^{++}} CNO^- + H_2O$$

Where the use of copper as a catalyst may be objection able, citric acid can be substituted [1]. For tightly bound complexes such as ferrocyanides, the Fe-CN bond must first be broken before the CN- can be attacked. This can be accomplished by using UV to dissociate the Fe-CN- bond and H202 to destroy the free CN- (2].

$$Fe(CN)6^{-4} \xrightarrow{UV} Fe{+}{+} + 6\ CN^-$$

$$CN^- + H_2O_2 \longrightarrow CNO^- + H_2O$$

The Bureau of Mines developed a process for removing cyanides and heavy metals. H202 and sodium thiosulfate are used to convert free CN- and WAD CN- to thiocyanate (SCN-) . Ferrocyanide is removed by adding steryldimethylbenzyl ammonium chloride. other heavy metals are removed by precipitation with ferric sulfate (3). Slurries such as tailings from gold mining operations usually contain heavy metals which can lead to excessive decomposition of H202 when used to treat free CN- and WAD CN-. This reduces the amount of the H202 for cyanide destruction. In these cases, the use of Caro's acid is preferred since (1) Caro's acid is less sensitive to decomposition from heavy metals than H202- (2) Caro's acid reacts substantially faster than H202 with cyanides thereby minimizing the metal induced peroxygen decomposition reaction.

$$H_2SO_5 + CN^- \xrightarrow{\text{Fast}} H_2SO_4 + CNO^-$$

Ammonium, potassium or sodium persulfate will also destroy cyanides but react much slower compared to Caro's acid.

$$Na_2S_2O_8 + CN^- + H_2O \text{ -------------> } CNO^- + 2\ NaHSO_4$$

The cyanate (CNO-) formed from the reaction of cyanides with peroxygens hydrolyzes as follows:

$$CNO^- + 2\ H_2O \text{ ---------------> } NH_4^+ + CO_2$$

In addition to its use in gold mines, the focus of this paper, Caro's acid is applicable to destroying cyanides in a range of waste discharges, including electroplating operations, iron and steel operations, organic chemicals, and plastics.

Preparation and Properties of Caro's Acid

Caro's acid is formed as follows:

H2SO4 + H202 ---------- > H2SO5 + H20

Caro's acid can be prepared from concentrated hydrogen peroxide and concentrated sulfuric acid. Caro's acid yield will drop if dilute H202 and acid are used in its preparation. The exothermic nature of the reaction is primarily due to the heat of dilution of the, sulfuric acid. The temperature rise of 500C-600C that results, intensifies the inherent instability of Caro's acid. For this reason, it is generated and consumed immediately at the point of use.

For laboratory use, small quantities of Caro's acid may be prepared by slowly adding H202 to concentrated sulfuric acid contained in a inert container e.g., glass, surrounded by an ice bath. Prepared in this way, the Caro's acid can be stored under refrigeration for several days.

Caro's acid also may be prepared by adding sulfuric acid to aqueous slurries of sodium, ammonium or potassium persulfate (4).

H2SO4
Na2S208 + H20 ------------- > NaHS04 + NaHSO5

Caro's acid solutions are clear, colorless and have an oily consistency. Caro's acid possesses the properties of an oxidizer and strong acid. A typical solution prepared from 70% H202 and 93% sulfuric acid at a 2.5/1 mole ratio of H2SO4 /H202 will contain 25% Caro's acid, 47 % sulfuric acid, 3% hydrogen peroxide and 25% water. Caro's acid once formed and diluted only slowly hydroyzes back to sulfuric acid and H202.In addition to detoxifying cyanides, Caro's acid can destroy phenols, alcohols, aldehydes and ketones.

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Gold Mining Case Study

Overview of Gold Mine Milling Operation

In a typical gold mining milling operation, ore is dry crushed followed by wet grinding. The aqueous slurry is sent to a series of leach tanks where sodium cyanide, a lixiviate is added along with lime and air. After the gold solution is drawn off in a counter-current decantation process, the tailings containing residual cyanide is sent to a tailings pond for disposal (see Figure 1).

If the tailings require treatment to reduce residual cyanide concentrations, the detoxification agent is usually added to the tailings prior to discharge to the tailings pond. Alternatively the detoxification agent can be added directly to the pond.

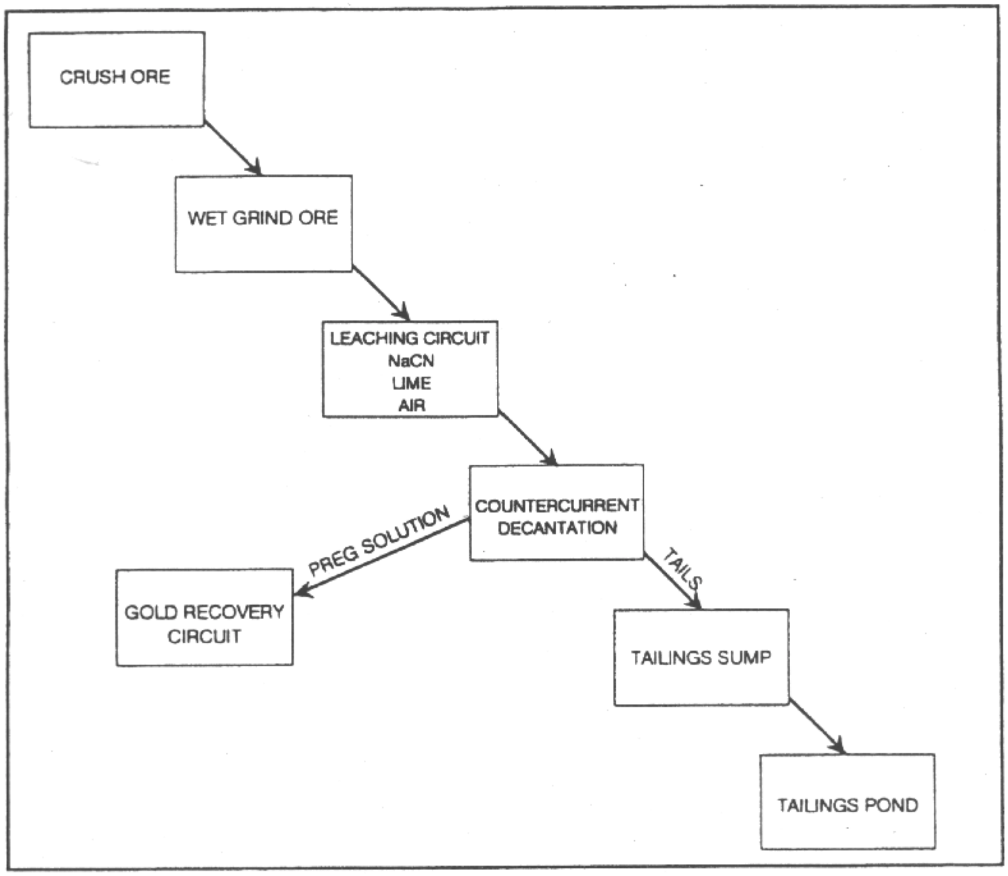

FIGURE 1 - GOLD MINE MILLING OPERATION

Cyanide Detoxification Background

A large North American gold mine processing 6,500 GPM tailings containing WAD CN- residuals of 40-50 ppm had been using ferrous sulfate to complex the CN- and reduce the hazard to wildlife in their tailings pond. These techniques did not prove entirely effective however and the mine staff switched from ferrous sulfate to H202 in the Spring of 1992. Hydrogen peroxide reduced the cyanide levels to 25 ppm, the target level.

As part of the mine's continuous improvement program, the staff's next goal was to reduce detoxification costs and improve the detoxification kinetics. With H202, a portion of the CN- detoxification is completed within the 20 minute travel time to the pond from the tailings sump through HDPE lines to the tailings pond.. The remainder of the detoxification is completed in the pond after several more minutes. Ideally, the entire detoxification should be completed before the treated tailings enter the pond. In this way, wildfowl landing on the pond in the vicinity of the tailings discharge lines would not be subject to high cyanide levels.

It was decided to evaluate Caro's acid (peroxymonosulfuric acid), a cyanide detoxification agent known to possess fast cyanide detoxification kinetics and high detoxification efficiency.

Cn Detoxification Process Description

For the trial, an FMC Caro's acid generator was supplied which consisted of two components: (1) a feed skid containing the chemical feed pumps, a programmable logic controller and a water deluge system, (2) a reactor which was located over the tailings sump remote to the feed skid (see Figure 2).

Tank trucks of hydrogen peroxide and sulfuric acid served as temporary storage vessels during the trial. The process described is continuous. Sulfuric acid and hydrogen peroxide are pumped from the feed skid at a tightly controlled rate and ratio Of H2SO4/H202 to the CA reactor. The Caro's acid is then metered into the tailings stream where rapid oxidation of cyanide takes place. After the Caro's acid is mixed with the tailings slurry, it travels about one mile (20 minutes) prior to release to the tailings pond.

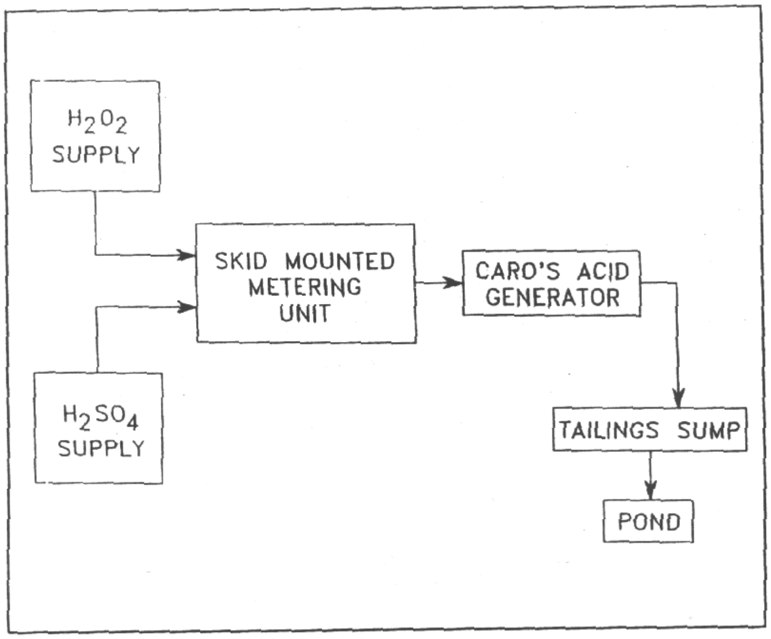

FIGURE 2 - SCHEMATIC FOR CARO'S ACID DETOXIFICATION OF CYANIDE IN GOLD MINE TAILINGS SLURRY

Safety Considerations

Safe operation of the process was of paramount importance and was insured by the following steps.

1. Several safety features were built into the generator itself to maximize safe operation. These included separation of the mixer-reactor from the feed skid/control unit, and a programmable logic controller (PLC) to monitor and control the chemical feed rates. The PLC also controlled alarms and emergency shutdowns. Also, design features eliminated the possibility of Caro's acid back-flowing into the feed system.

2. A Hazardous operation study was conducted on the Caro's acid generator and the proposed test area.

3. Bags of soda ash were provided to clean up any spills of sulfuric acid that might occur.

Cyanide Nomenclature

The term "WAD CN" as used in this paper, is the sum of true WAD (weakly acid dissociable) CN- plus free CN-. True WAD CN- are weakly acid dissociable complexes of CN-, e.g., the copper and nickel complexes. True WAD CN- and free CN are specifically designated as such.

Experixental

Outline of Test Plan

Several runs were made on mill tailings slurry at initial WAD CN- levels of 40-50 ppm and 100-120 ppm. Mole ratios of H2SO4 to H202 for Caro's acid generation were either 2.0/1 or 2.5/1. Mole ratios of CA/CN- were between 0.7/1 and 2.9/1.

Analytical

Sampling

Samples of feed slurry were taken at the head of the line and samples of treated slurry were "taken as the slurry entered' the tailings pond.

Analytical Methods

WAD CN- (free + WAD) was determined by the picric acid method and free cyanide by the silver nitrate titrimetric method using Rhodanine indicator. As a cross check, WAD CN and free CN- were also determined by the LaChat Micro-Distillation method. The methods generally were in good agreement.

Results and Discussion

1.Release Of HCN

The atmospheric HCN detectors at the tailings treatment site registered non-detectable levels of HCK during most of the plant trial never exceeding 2 ppm HCN. The 2 ppm HCN maximum level was well within the 5 ppm limit at which point an alarm would be sounded. The low atmospheric HCN levels are attributed to the very rapid reaction of the Caro's acid with the cyanide.

2. Effect Of Feed CA/CN- Mole Ratio

How the dosage level of Caro's acid relative to the WAD CN- in the feed affects CN- detox is examined in this section. Figure 3 shows that a CA/CN- mole ratio of 1/1 is sufficient to control effluent at 12-16 ppm WAD CN-, which is well below the 25 ppm target level. Figure 3 also indicates a refractory lower level of WAD CN- which will not yield even to CA/CN- ratios of greater than 2.5. This lower level is about 4 ppm WAD CN- for the tailings tested. Results with other tailings slurries may result in lower or higher final WAD CN- levels and will depend in large part on the type of WAD CN- that are present.

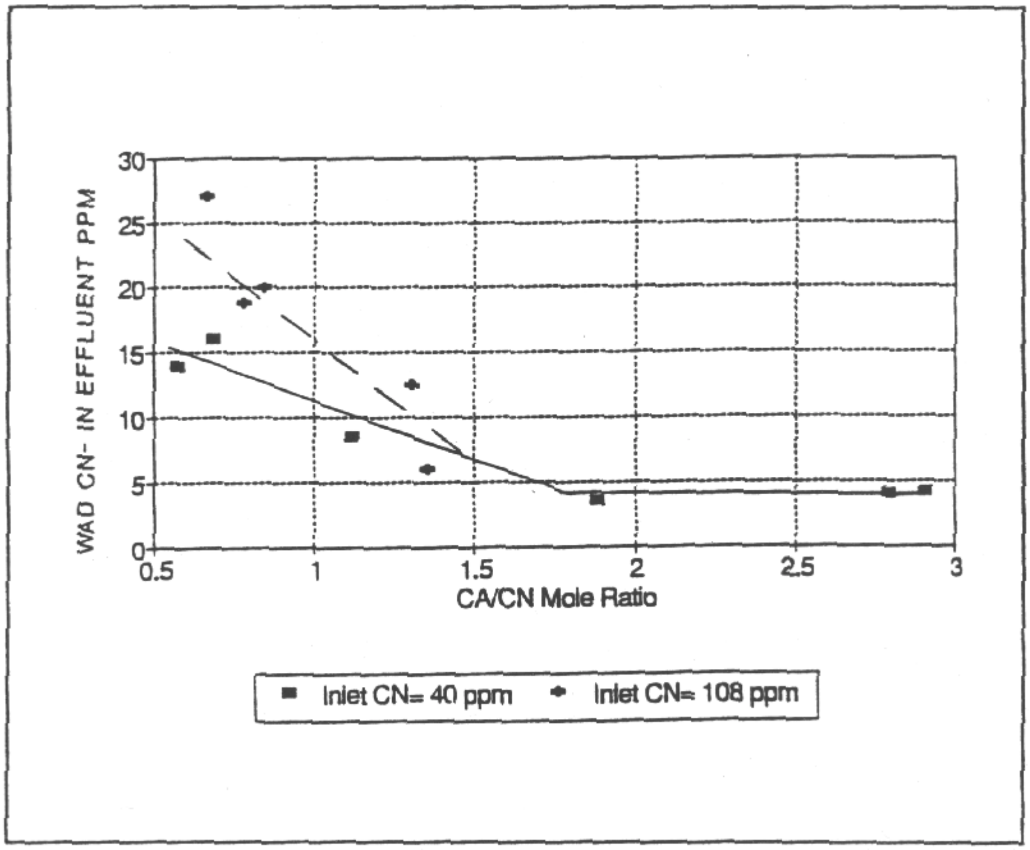

FIGURE 3 - CONCENTRATION OF WAD CN^- IN EFFLUENT VS CA/CN^- MOLE RATIO

3. Effect Of Operating Parameters On Effluent pH

Figure 4 shows the relation of effluent pH to CA/ CN mole ratios for 40 ppm and 108 ppm, inlet WAD CN-. At a CA/CN mole ratio of 1/1 and a H_2SO_4/H_202 mole ratio of 2.5/1, effluent pH will be 8.8 and 6.6 for inlet WAD CN- levels of 40 and 108 ppm respectively. At 108 pp* inlet WAD CN-, an increase of about 0.6 pH units occurs by decreasing the H_2SO_4/H_2O_2 mole ratio from 2.5 to 2.0. The effect of lowering the H_2SO_4/H_2O_2 mole ratio was too small to be measured under plant conditions at 40 ppm inlet WAD CN-. Lowering the R_2SO_4/H_2O_2 mole ratio however, raises the adiabatic mix temperature. This may not be desirable since the higher temperature can lead to greater instability of the Caro's acid.

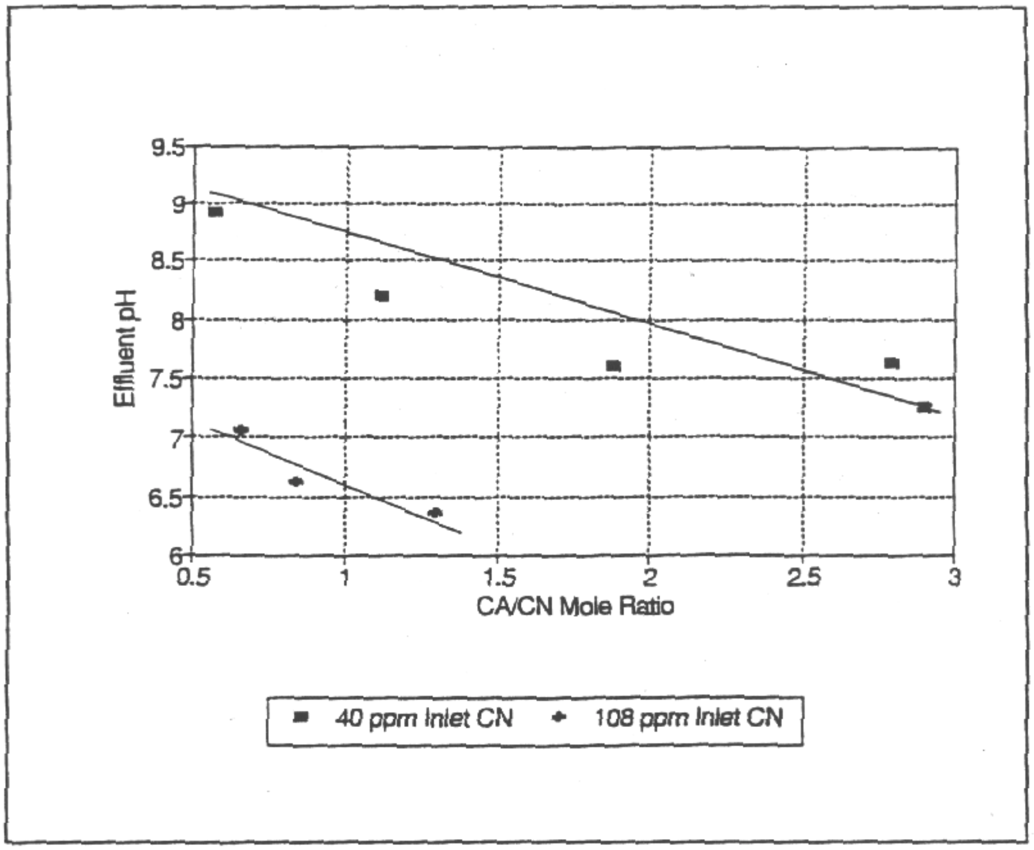

FIGURE 4 - EFFLUENT pH VS CA/CN^- MOLE RATIO

4. Free CN- And True WAD CN- Destruction

Data on the relative ease of destruction of free and true WAD CN- is shown in Figures 5-6. It is more difficult to destroy true WAD CN- than free CN-. For example, Figures 5 and 6 indicate that at an inlet CA/CN- mole ratio of 1.0, about 90-95% of the free CN-, but only 20-40% of the WAD CN would be destroyed. However, by increasing the mole ratio of CA/CN- to 1.8/1, the amount of true WAD CN- destroyed increases to 90%.

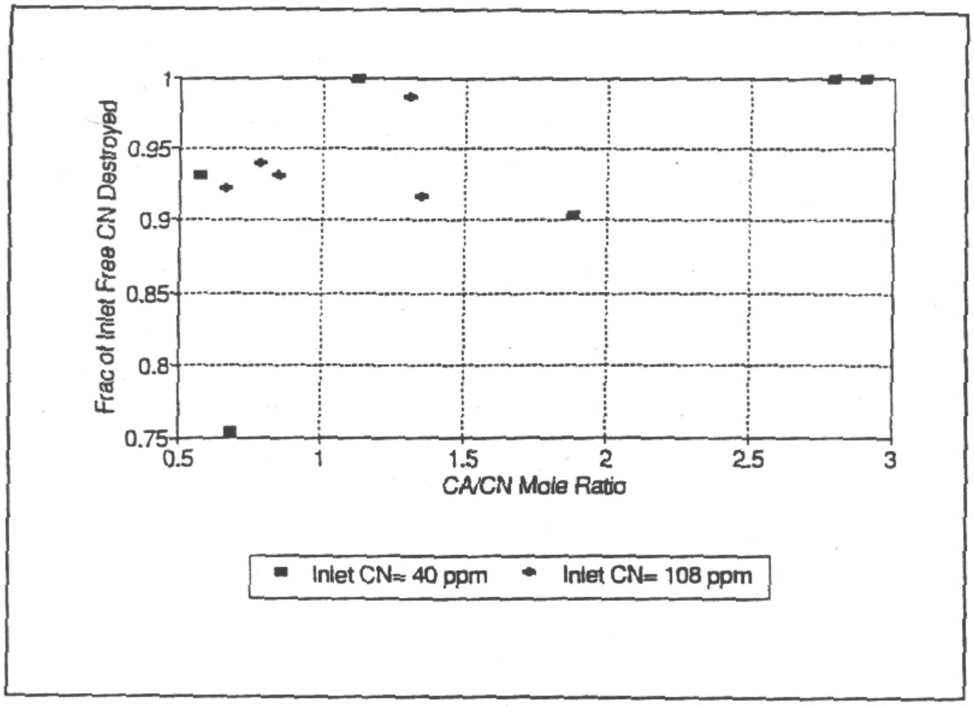

FIGURE 5 - FRACTION OF INLET FREE CN^- DESTROYED VS CA/CN^- MOLE RATIO

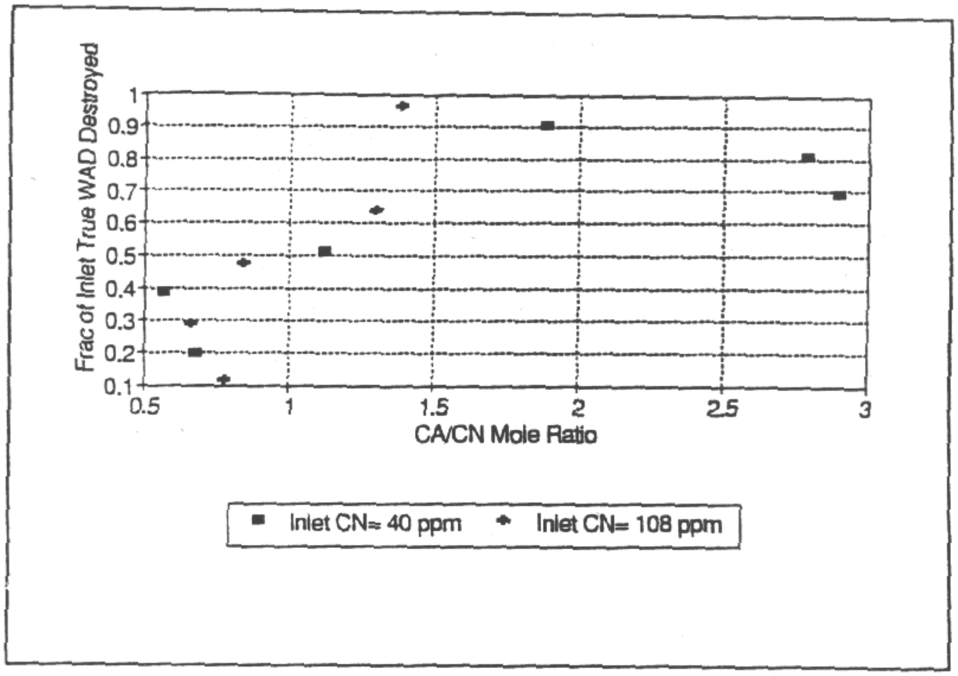

FIGURE 6 - FRACTION OF INLET TRUE WAD CN^- DESTROYED VS CA/CN^- MOLE RATIO

5. Economics

The raw material costs for Caro's acid is comprised of the cost of peroxide, sulfuric acid and added Cao (lime) for neutralization. An estimated raw material cost breakdown for the Caro's acid is as follows.:

	% of Total Cost	
	w/CaO	w/o CaO
H_2O_2	57	67
H_2SO_4	29	33
CaO	14	0

For this plant trial, extra lime was not needed but in less buffered tailings slurries, extra lime might be required during the addition of the Caro,'s acid. In addition, since most mines recycle a portion of their tailings pond back to the mill, some neutralization will be required either during or after Caro's acid treatment. If the neutralization is conducted only on that portion of water reclaimed, then neutralization costs will be less than if the entire tailings slurry is neutralized.

The raw material cost to destroy one pound of CN- is plotted, including CaO, cost for complete neutralization of the acid in Figure 7. Figure 7 shows that the cost per pound of CN- destroyed is independent of inlet CN level. Figure 8 shows $/lb of CN- cost, excluding CaO. Thus if CaO is not needed, then for a 20 ppm effluent CN- level, the cost without Cao is $1.30 vs $1.55/lb of destroyed CN- with CaO.

Raw material costs on a $/ton dry ore basis are shown in Figure 9. This basis will be dependent on the inlet CN loading and percent solids in the slurry. Figure 9 shows the total cost, including CaO for neutralization as a function of exit WAD CK for 40 and 108 ppm CN- inlet loadings. Obviously, the $/ton cost is higher for the higher inlet CN- concentration.

Finally, the $/T cost to achieve either 10 or 20 ppm CN in the effluent is plotted in Figure 10 over a range of inlet CN- concentrations. It costs about $0.10/ton in total raw material cost to bring inlet WAD CN- from 40 ppm down to 20 ppm. This compares to $0.32/ton using H202 alone. Thus Caro's acid has the potential to substantially reduce raw material costs for CN- detoxification.

The capital cost for a Caro's acid generator is < $200,000 The costs for the H202 and H2SO4 storage vessels are not included but would be significantly less than the investment in the Caro's acid unit.

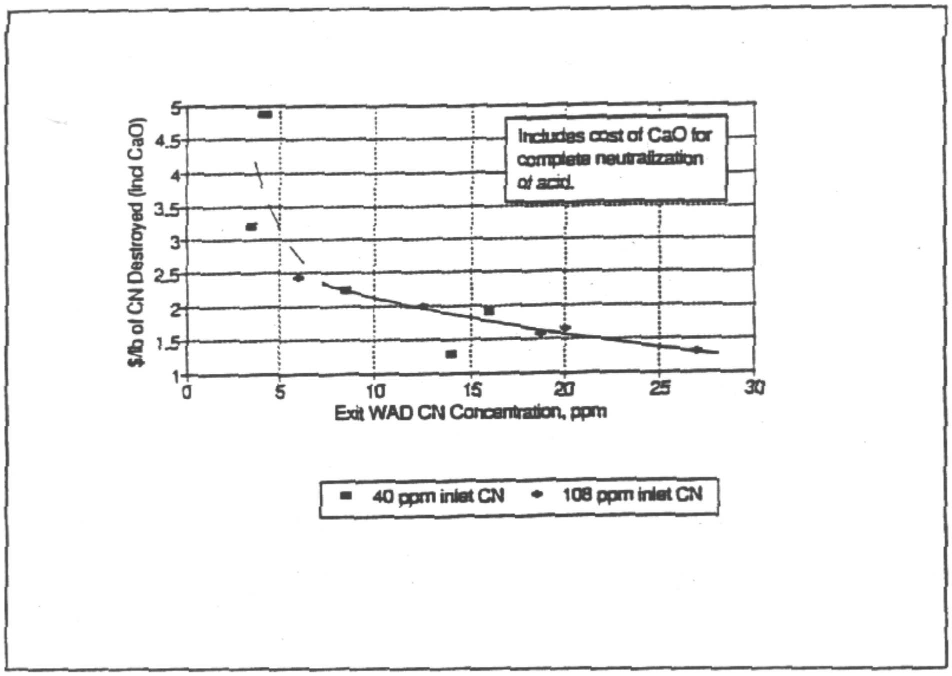

FIGURE 7 - COST OF CN^- DESTRUCTION VS CN^- EXIT CONC.

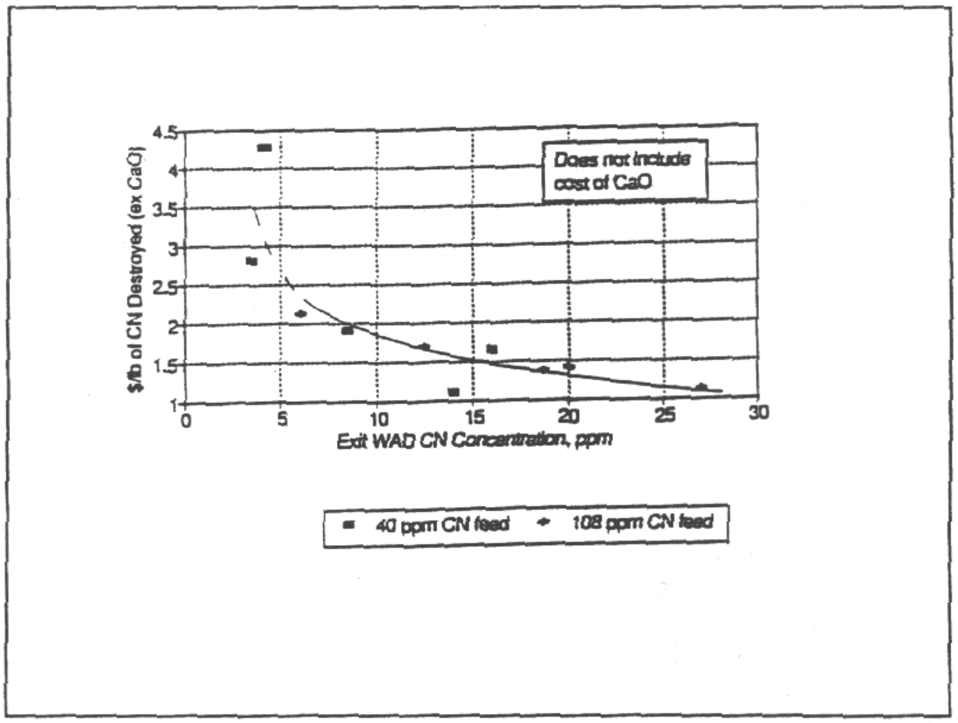

FIGURE 8 - COST OF CN^- DESTRUCTION VS CN^- EXIT CONC.

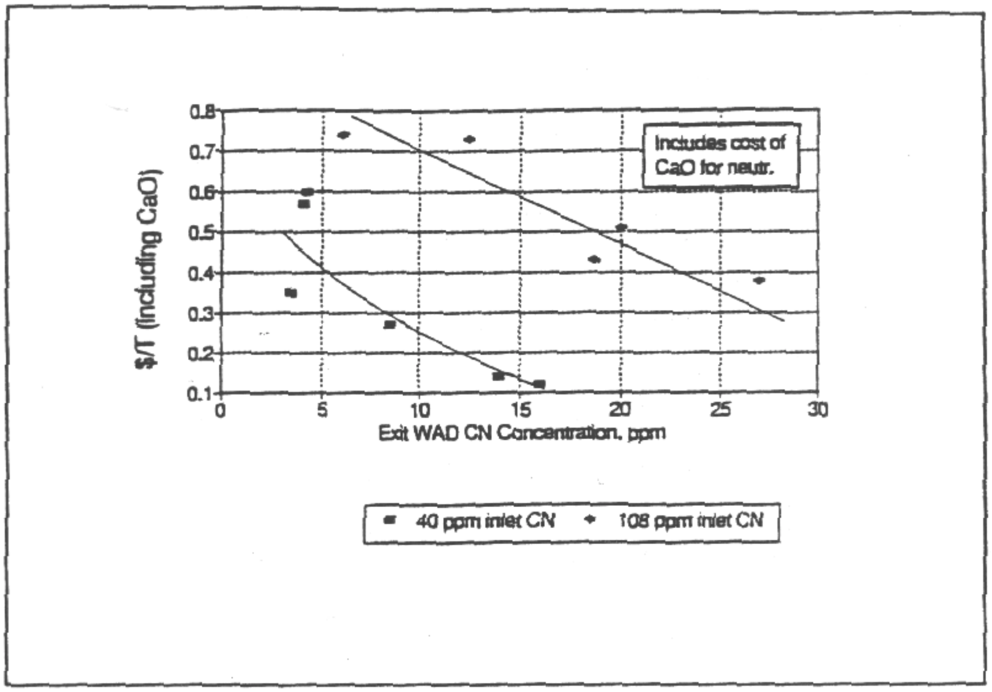

FIGURE 9 - COST OF CN⁻ DESTRUCTION VS CN⁻ EXIT CONC.

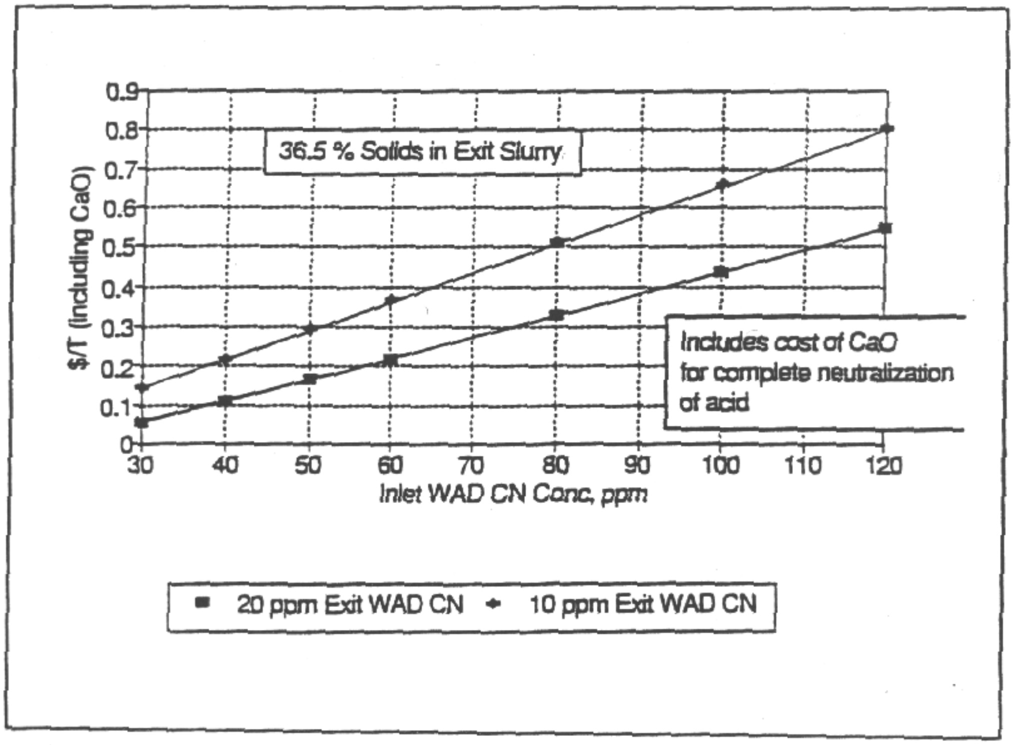

FIGURE 10 - $/TON COST OF CN⁻ DETOXIFICATION WITH CARO'S ACID VS INLET WAD CN⁻ CONCENTRATION

Conclusions

1. Carol's acid (peroxymonosulfuric acid) was successfully field tested as a cyanide detoxification agent.

2. Substantial raw material savings and shortened cyanide detoxification times compared to using H202 alone were realized.

3. Atmospheric HCN levels at the tailings treatment site were at 0-2 ppm over the course of the plant trial even though extra alkali was not added.

4. Using a 1/1 mole ratio of Carols acid/CN-, and a 2/1 or 2.5/1 mole ratio of H2SO4/H202, WAD CN- levels were reduced from 40 -108 ppm to below the target concentration of 20 ppm. By increasing the CA/CN- mole ratio to 1.5/1, WAD CN- levels were reduced to 4 ppm.

5. At a CA/CN- mole ratio of 1/1, the effluent pH dropped from an initial pH of 10.5 to a pH of 8.8 and 6.6 for feed WAD CN- levels of 40 and 108 ppm, respectively.

6. The raw material costs for the detoxification were reduced from $0.32/dry ton ore with H202 to $0.10/dry ton ore with Carols acid starting with a WAD CN- concentration of 40 ppm.

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