CYANIDE DETOXIFICATION OF CYANIDATION TAILS AND PROCESS STREAMS

By

Danielle Hewitt, Paul Breuer & Coby Jeffery

CSIRO Minerals Down Under National Research Flagship, Australia

Presenter and Corresponding Author

Danielle Hewitt
danielle.hewitt@csiro.au

ABSTRACT

Cyanide detoxification by chemical means (sulfite, hydrogen peroxide or Caro's acid) has typically been adopted by the gold industry to meet the International Cyanide Management Institute (ICMI) code and/or regulatory compliance for discharge into tailings storage facilities (TSF) or the discharge of excess water from the mining operation. The treatment of process streams or TSF return water is also often required as residual cyanide in reclaimed/recycled water can impact on upstream processes. This paper presents and discusses results from a number of different evaluations that have been conducted to reduce the cyanide concentration in cyanidation tails and process streams by chemical means. Pre-oxidation before cyanidation and the ore mineralogy were both found to potentially have a significant impact on reagent requirements in the treatment of cyanidation tails. The solution speciation provided important insights into the reagent consumption, which becomes very high in targeting residual weak acid dissociable (WAD) cyanide concentrations below 1 mg L^{-1}. Preliminary evaluations of polishing and alternative processes for reducing the WAD cyanide showed potential to achieve these low concentrations and reduce the treatment costs.

INTRODUCTION

This paper presents and discusses results for several evaluations conducted to destroy the cyanide in cyanidation tails and other process streams using sulfite (with copper as a catalyst), Caro's acid or hydrogen peroxide. Evaluations have included target weak acid dissociable (WAD) cyanide concentrations of less than 50 mg L^{-1} down to as low as 0.2 mg L^{-1}. Parallel investigations with tails slurry and filtered solution have also been conducted in some cases to establish the impact the solids have on the cyanide destruction processes. The measurement of solution speciation has also been used to provide important insights into the reagent consumption.

Commercially sulfite or Caro's acid are commonly employed to treat cyanidation tails from gold plants to achieve regulatory requirements and the International Cyanide Management Institute (ICMI) Code compliance of less than 50 mg L^{-1} WAD cyanide for the discharge of cyanidation tails into a tailings storage facility (TSF). Hydrogen peroxide, which is less effective on slurries, is often used to treat the return water from the TSF to lower cyanide levels that would otherwise impact plant performance. Detailed descriptions of these processes[1, 2] and the chemistries involved[3, 4] can be found in the literature. A summary of the important features for each of these processes is outlined below.

Sulfite Process

There are two patented sulfite processes utilising sulfur dioxide[5, 6], of which the INCO process is more commonly adopted and used for the treatment of slurries. The sulfur dioxide dissolves into solution forming sulfite at the pH's typically adopted in the destruction process:

$$SO_2 + H_2O \rightarrow SO_3^{2-} + 2H^+ \tag{1}$$

The sulfite ion is the reactant in the process and thus sodium sulfite (Na_2SO_3) or sodium metabisulfite ($Na_2S_2O_5$) can also be used as a source of sulfite. The process is based upon conversion of cyanide (including cyanides weakly complexed with metal ions) to cyanate using sulfite and air with copper as the catalyst (copper not added if it is already present in the cyanide solution) at a controlled pH. The overall reaction is:

$$CN^- + SO_3^{2-} + O_2 \xrightarrow{Cu} OCN^- + SO_4^{2-} \tag{2}$$

The reaction is normally carried out at a pH of 8.0 to 9.0, with lime normally required for pH control. The lime (or other alkali) requirement to control pH depends on the choice of reactant (Na_2SO_3 < SMBS < SO_2). The reaction rate is extremely fast and is limited by the transfer of oxygen. Typical reaction times in order to achieve the required oxygen mass transfer vary from about 30 minutes to 2 hours. Iron complexed cyanides are reduced to the ferrous state and precipitated with copper, nickel or zinc as insoluble metal-iron-cyanide complexes. Residual metals liberated from the WAD cyanide complexes are precipitated as their hydroxides. The process does not preferentially attack thiocyanate, with generally less than 10% oxidised in the process[1]. Inefficiency in the process results from the direct oxidation of sulfite rather than cyanide:

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-} \tag{3}$$

The sulfite process and reaction chemistry is not straight forward as indicated by the difficulties experienced in the early 1980's when this process was first being implemented[7]. The experience and learning's gained by INCO at the time provided knowledge of the process and equipment limitations which guided future testwork, process design and engineering of the cyanide destruction reactor. However, little of the fundamental understanding of the reaction chemistry was made publicly available. Recent fundamental studies by the authors[3, 4] found:

1.   Upsets to the process (for example the loss of sulfite or oxygen addition) which result in the presence of free cyanide in the reactor will stop the oxidation of cyanide. The addition of copper sulfate is required to complex free cyanide ions to restart the detox process.
2.   In a continuous stirred tank reactor (CSTR) or series of CSTR's, the dissolved oxygen (DO) concentration provides an indicator to the residual oxygen capacity available in the process;

zero DO in the last reactor indicates insufficient oxygen addition for the rate of cyanide and sulfite addition.

3.   The addition of hydrogen peroxide to the sulfite process is not beneficial and is not recommended as sulfite is preferential oxidised by the peroxide over cyanide.

Caro's Acid Process

Caro's acid (H_2SO_5), also known as oxone monopersulfate and peroxymonosulfuric acid, is a strong oxidising agent (E^o = 1.85 $V^{[8]}$) and has recently been applied at a number of mining operations for cyanide detoxification, particularly for pulps post cyanidation. Caro's acid is produced from concentrated hydrogen peroxide and concentrated sulfuric acid (0.33 - 0.66 mole ratio of peroxide/sulfuric) in an exothermic reaction:

$$H_2O_2 + H_2SO_4 \rightarrow H_2SO_5 + H_2O \tag{4}$$

The "hot" process yields 25 - 45% Caro's acid, whilst a "cold" process yields 70 - 80%[1]. Due to its instability, Caro's acid is produced on-site and used immediately for cyanide detoxification with only minimal or no storage. The reaction of Caro's acid with cyanide (and WAD cyanides) does not require a catalyst such as copper as the reaction is rapid and typically complete within a few minutes.

$$H_2SO_5 + CN^- \rightarrow OCN^- + H_2SO_4 \tag{5}$$

Further oxidation of cyanate by Caro's acid is slow at pH 10, but increases in rate with decreasing pH[1]. Thus, avoiding a significant decrease in the pH is important to assure cyanide destruction without the need to add excess Caro's acid. Some cyanate oxidation also occurs even at the higher pH's due to the localised low pH upon the addition of Caro's acid and the extremely fast reaction kinetics[3]. As shown by reaction 6 this can have a significant impact on reagent consumption.

$$3H_2SO_5 + 2OCN^- + H_2O \rightarrow N_2 + 2HCO_3^- + 3H_2SO_4 \tag{6}$$
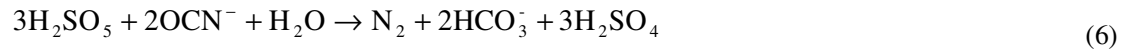
Caro's acid will also react to some extent with thiocyanate[9], where the reagent consumption can be high as a result of the reaction stoichiometry:

$$4H_2SO_5 + SCN^- + H_2O \rightarrow OCN^- + 5H_2SO_4 \tag{7}$$
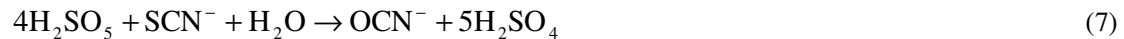
Recent fundamental investigations by the authors[4] found:

1.   Free cyanide and thiosulfate (Reaction 8) are preferentially oxidised prior to the oxidation of copper cyanide and thiocyanate which occur in parallel.

2.   The control of pH is important since at low pH, HCN forms which is not readily oxidised and the rate of cyanate oxidation increases.

$$4H_2SO_5 + S_2O_3^{2-} + H_2O \rightarrow SO_4^{2-} + 5H_2SO_4 \tag{8}$$

Hydrogen Peroxide Process

DuPont and Degussa separately developed and patented several versions of the hydrogen peroxide process for treating cyanide tailings solutions[10-14]. The process has limited application for pulps due to the high reagent consumption resulting from the reactions of peroxide with solids in the pulp. The process is based upon oxidation of WAD cyanides to cyanate using hydrogen peroxide in the presence of a soluble copper catalyst (not added if already present) to increase the reaction rate. The overall reaction being:

$$CN^- + H_2O_2 \xrightarrow{Cu} OCN^- + H_2O \tag{9}$$

Reaction periods typically range from about 30 minutes to 3 hours depending upon the copper to cyanide ratio, the untreated and treated cyanide levels, and the quantity of hydrogen peroxide used. The process operates over a wide range of pH values, with the fastest rate reported to be pH 10[1].

The optimal pH for metals removal after cyanide destruction is about 9.0 to 9.5. Iron cyanides are precipitated as for the sulfite process. Similarly, the process does not oxidise thiocyanate to any appreciable extent. Excess hydrogen peroxide added for cyanide oxidation will decompose to yield oxygen and water, which is an advantage when the concentration of total dissolved salts is of concern in the treated water.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{10}$$

Recent fundamental investigations by the authors[4] found that the solution composition (especially metal ions) and pH have a significant impact on the reaction chemistry. In particular, the inception of precipitation results in the catalysed decomposition of peroxide which dramatically increases the peroxide stoichiometry required to reduce the residual cyanide concentration below the point where precipitation commences.

DETOX OF CYANIDATION TAILS FOR DISCHARGE TO TSF

Many operations are required to treat carbon-in-leach (CIL) tails before discharge into the TSF. For ICMI compliance the discharge into the TSF requires reduction in the WAD cyanide concentration to less than 50 mg L^{-1}, though regulations for the site may require a lower discharge WAD cyanide concentration. The test work presented in this section was targeted at meeting the ICMI compliance of less than 50 mg L^{-1}. WAD cyanide measurements were completed at CSIRO using the Picric acid method and confirmed by the WA ChemCentre using the American Public Health Association (APHA) Standard Method 4500 CN.

Sulfite Detox

Cyanide destruction was investigated for CIL tails generated from a cyanide leach (with a three hour pre-oxidation stage) of two ore samples (Samples A and B). A summary of the tails solution speciation is provided in Table 1 (note that the measured "free" or available cyanide is presented as mg L^{-1} NaCN where as the WAD cyanide is presented as mg L^{-1} CN^-). Most notable are the significant concentrations of thiosulfate and thiocyanate due to the presence of a small quantity of reactive sulfides in these ore samples.

Table 1: CIL tails solution compositions before sulfite detox.

Sample	CIL tails soln conc. (mg L^{-1})					WAD CN (mg L^{-1})	
	NaCN	Cu	OCN^-	SCN^-	$S_2O_3^{2-}$	Calc.*	Picric
A	644	29	225	263	416	377	308
B	671	148	518	476	565	538	544

* NaCN + 3 x Cu

As the copper concentration for the Sample A leach tails was less than 50 mg L^{-1} (Table 1), solid copper sulfate was added to increase the copper concentration to ~50 mg L^{-1} before the detox tests were conducted (this is the typically recommended Cu concentration required for effective detox).

Results of the cyanide destruction investigations conducted on the CIL tails with the sulfite process are presented graphically in Figure 1 and Figure 2. Both pulp and solution detox investigations were conducted with sodium metabisulfite (SMBS) used as the reactant with the pH maintained at 9 by controlled NaOH addition. The critical WAD CN line shown in both figures is the WAD cyanide concentration above which free cyanide is present and thus the detox process stops because the SMBS addition rate is insufficient[3]. The result for data points shown above this line is only a transient average WAD cyanide value of the detox discharge as the free cyanide concentration was still increasing with time; if copper sulfate was not added to restart the detox process (and the SMBS addition rate increased), the WAD cyanide level would approach some value below that of the cyanidation tail feed to the process (a lower value than the feed because some detox occurs on the addition of sulfite despite free cyanide being present[3]). The percentage of stoichiometry SMBS addition for pulp detox to achieve the target of less than 50 mg L^{-1} WAD cyanide for Samples A and B is 240 and 290%, respectively.

For both samples, a greater than stoichiometric SMBS requirement for WAD cyanide detox (Reaction 2) was required for both the pulp and solution investigations. This is attributed to

competing reactions, such as the direct oxidation of sulfite by oxygen (Reaction 3) and oxidation of thiosulfate (potentially via a similar reaction mechanism to cyanide). Most notable from the results is that the reagent addition required to detox the pulp compared to the solution is significantly greater and may be due to the solids catalysing the oxidation of sulfite to sulfate by oxygen.
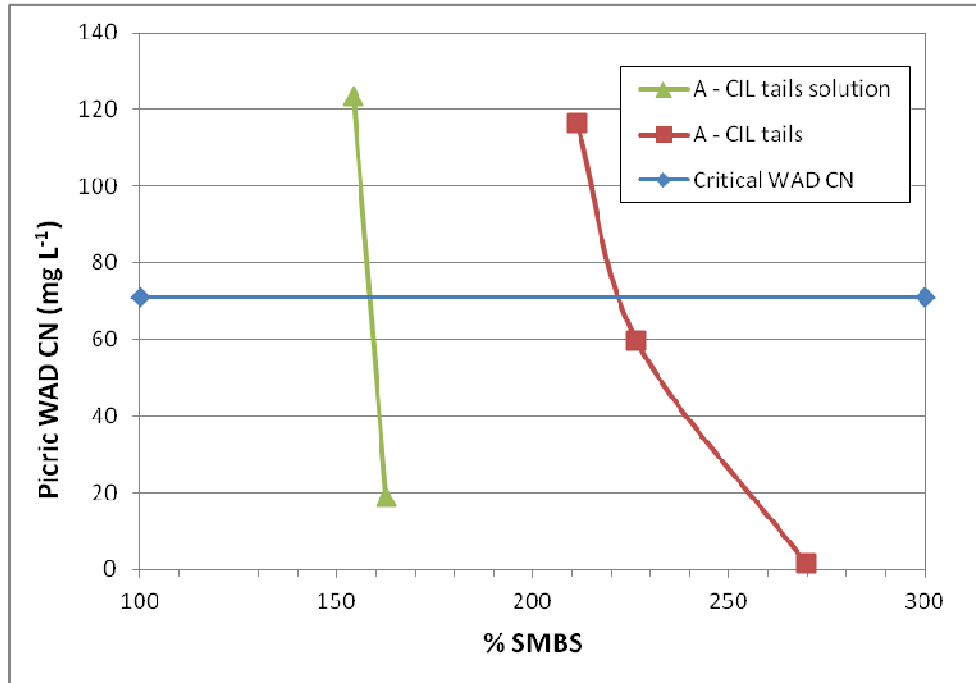

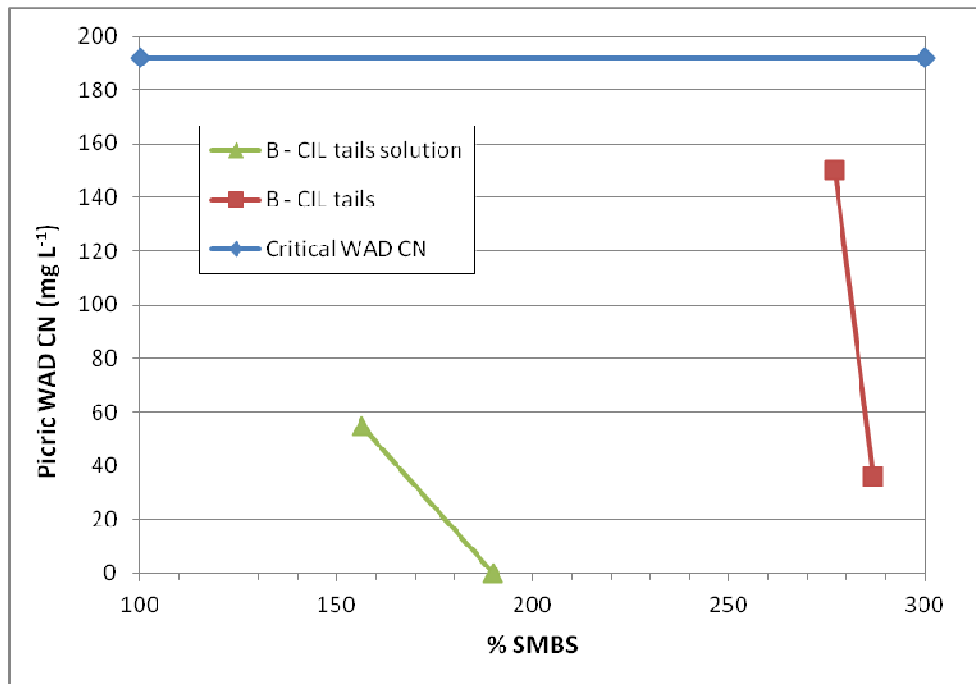**Figure 1: Residual WAD cyanide after sulfite detox (using SMBS) of Sample A tails at pH 9.**

Figure 2: Residual WAD cyanide after sulfite detox (using SMBS) of Sample B tails at pH 9.

The effect of solids on the oxidation of sulfite was investigated in a batch reactor using a solution containing sulfite and cyanide (no copper), where the presence of free cyanide ions stops the direct oxidation of sulfite by oxygen[4]. The measured DO in the solution containing sulfite and cyanide was ~8 mg L^{-1} with air sparging. The sulfite concentration was monitored for 60 minutes and did not

decrease appreciably during this time (Figure 3). When washed leach tail solids were added to this solution at 60 minutes, the DO concentration dropped very quickly to zero. Air sparging was replaced by oxygen sparging with still no measurable DO. The sulfite concentration also decreased rapidly in the presence of the solids as show in Figure 3, with all the sulfite oxidised within 30 minutes of the solids being added. The DO concentration sharply increased once the sulfite was all oxidised. This clearly indicates the solids catalyse the oxidation of sulfite by oxygen which results in the greater reagent requirement for cyanide detox of the pulp by sulfite. This undesirable oxidation of sulfite in the continuous detox process may be reduced by minimising the DO concentration in the reactor, though measurable DO must be maintained to assure the process does not become oxygen limited.
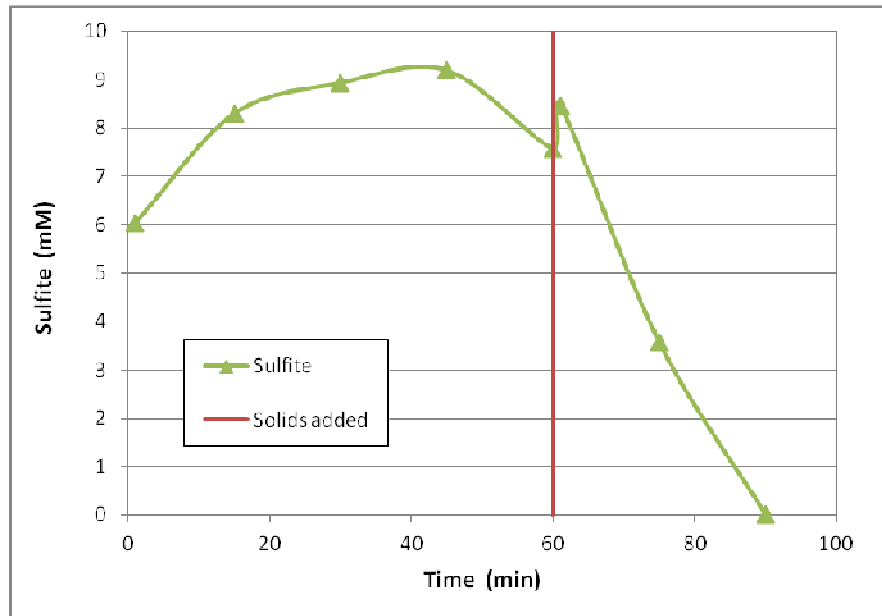

Figure 3: Catalysis of sulfite oxidation by leach tail solids.

Caro's Acid Detox

CIL tails were generated from two cyanide leaches of an ore sample where one leach was run with a three hour pre-oxidation stage and the other without. A summary of the tails solution speciation is provided in Table 2. Most notable is the higher thiosulfate and thiocyanate concentrations with pre-oxidation compared to without. Not presented here are that the pre-oxidation reduced the cyanide consumption and the soluble copper and iron, but had higher lime consumption.

Table 2: CIL tails solution compositions before Caro's acid detox.

Leach conditions	CIL tails soln conc. (mg L^{-1})				WAD CN (mg L^{-1})	
	NaCN	OCN^-	SCN^-	$S_2O_3^{2-}$	Calc.*	Picric
CIL	476	552	572	117	370	362
CIL with pre-ox	350	485	827	290	286	339

* NaCN + 3 x Cu

Figure 4 shows the residual WAD cyanide as a function of Caro's acid addition expressed as the percentage of stoichiometry in the treatment of both tails solution and pulp. Two notable observations are made from this figure:

1. Higher thiosulfate and thiocyanate generated in pre-oxidation requires more Caro's acid addition as a result of Reactions 7 and 8.
2. The presence of solids has a significant effect on the WAD cyanide destruction with higher residual WAD cyanide compared with the same Caro's addition rate to filtered CIL tails solution.

Thus, in this case, significantly more Caro's acid is required to achieve the less than 50 mg L^{-1} WAD cyanide target when treating the CIL tails pulp; linear extrapolation of the single pulp test results for the tails with and without pre-oxidation (based on that of the solution detox data) suggests a Caro's

acid addition of around 320 and 250%, respectively, is potentially required. It is thought that mineral surfaces are likely responsible for the decomposition/oxidation of Caro's acid (similar to the solids catalysed oxidation of sulfite described above), thus resulting in the increased reagent requirement for treating the pulp compared to solution.
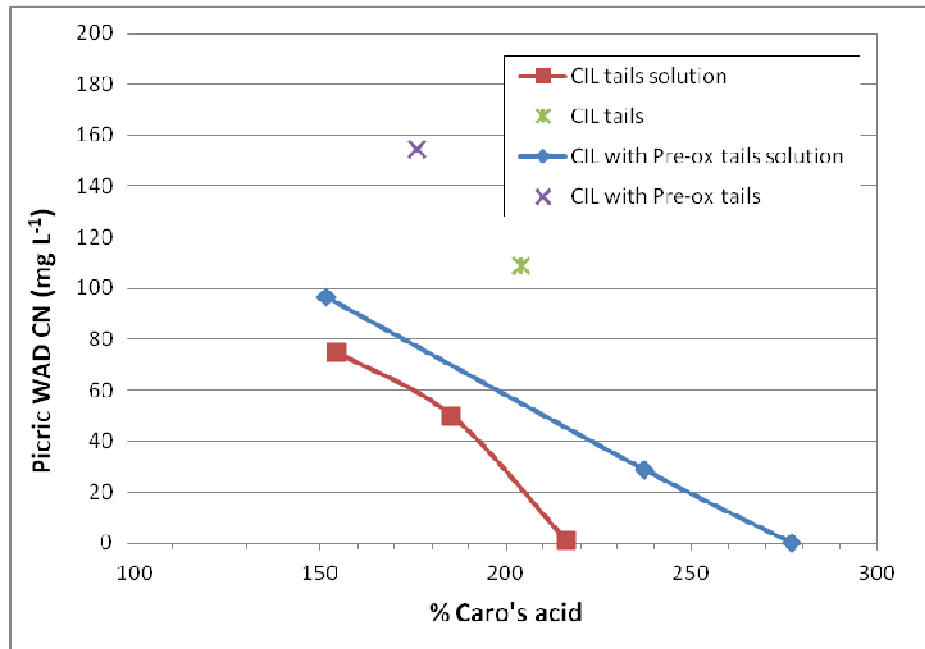

Figure 4: Residual WAD cyanide after Caro's acid destruction of cyanidation tails (with and without pre-oxidation) at pH 9.

DETOX OF TSF RETURN WATER AND PROCESS STREAMS

Return water from the TSF is often further treated to lower cyanide levels that would otherwise impact plant performance (e.g. flotation). The effectiveness of Caro's acid, sulfite (using SMBS with pH control using NaOH) and hydrogen peroxide were all assessed to further detox a solution recovered after SMBS pulp detox to less than 50 mg L^{-1} WAD cyanide and targeting less than 1 mg L^{-1} Total cyanide (WAD cyanide, which is less than or equal to the Total cyanide was used as the initial measure). Figure 5 shows the residual WAD cyanide in the detox solution after treatment with the various reagents investigated. Clearly hydrogen peroxide requires much greater reagent addition to achieve very low residual WAD cyanide concentrations than Caro's acid or the sulfite process (as SMBS in this case). The 260% stoichiometric addition of Caro's acid was more than sufficient to achieve less than 1 mg L^{-1} residual WAD cyanide, whilst 200% stoichiometric addition of SMBS reduced the WAD cyanide to 2 mg L^{-1} based on the Picric acid determination. Subsequent analysis of these two detox solutions by the ChemCentre by APHA 4500 CN indicated that for both the Caro's acid and sulfite treatments, the WAD cyanide was less than 0.1 mg L^{-1}. The residual Total cyanide (APHA 4500-CN) for both solutions was ~0.4 mg L^{-1}.

In a separate evaluation, the efficiency of hydrogen peroxide detox was investigated on three cyanide solutions of varying WAD cyanide concentration. Hydrogen peroxide was initially looked at in this instance due to the much simpler implementation of such a treatment process. Figure 6 shows that the hydrogen peroxide initially had high reagent efficiency with a noticeable decrease in the WAD cyanide levels at lower percentage additions. The point at which the hydrogen peroxide efficiency slowed closely correlated with the start of copper precipitation from solution which catalyses hydrogen peroxide decomposition[4]; this also explains the poor utilisation of hydrogen peroxide in Figure 5. Notably, the log scale indicates a 250 - 300% of stoichiometry hydrogen peroxide addition yields an order of magnitude decrease in the WAD cyanide concentration. Clearly the simpler and cheaper installation of a hydrogen peroxide treatment has to be considered against the much higher reagent requirement.
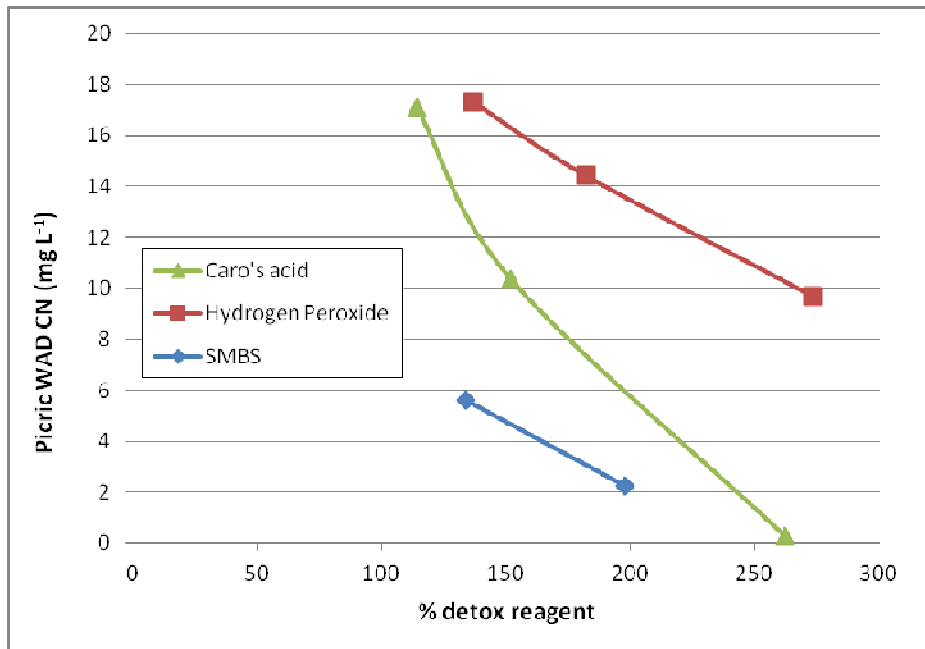
Figure 5: Residual WAD cyanide after further detox at pH 9 of recovered solution from an initial pulp detox with SMBS (initial WAD cyanide was 36 mg L^{-1}).
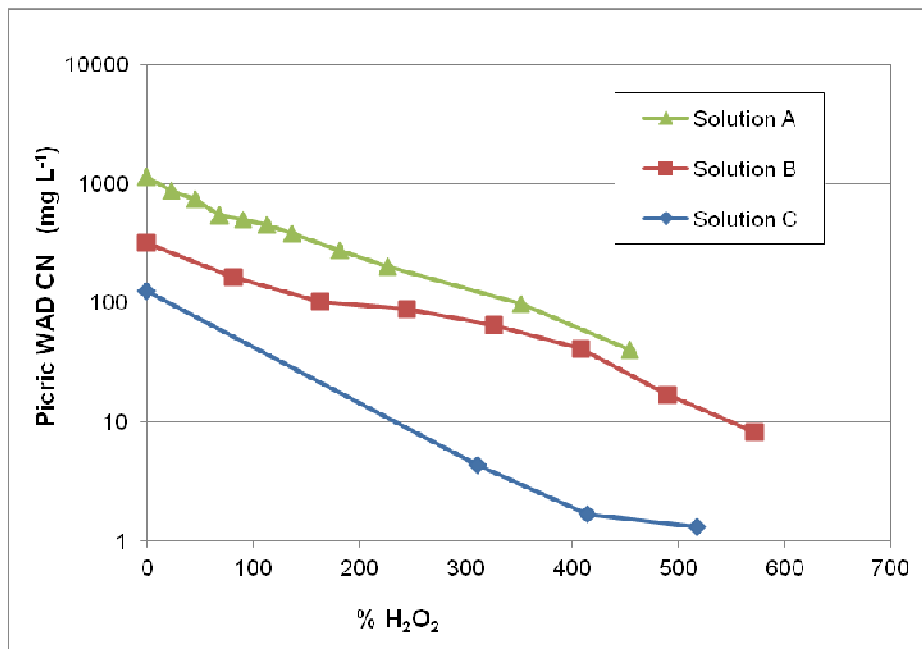

Figure 6: Residual WAD cyanide after hydrogen peroxide detox of three cyanide process solutions (pH monitored but not controlled).

DETOX TO 0.2 MG L-1 WAD CYANIDE

As referred to in the introduction, regulations for some sites may require a much lower WAD cyanide concentration at the TSF discharge than 50 mg L^{-1} or for discharge of excess water off the mine site. In this section we outline evaluations conducted targeting WAD cyanide levels of less

than 0.2 mg L^{-1} for a cyanidation tail (oxide ore) where initial tests were conducted with filtered solution to establish the reagent requirements in the absence of the solids; results above clearly demonstrate that the solids can have a significant impact on the quantity of reagents required to treat cyanidation tails and which could be significantly greater for lower target WAD cyanide concentrations. Unless stated otherwise, WAD cyanide measurements were completed at CSIRO using the Picric acid method tailored for very low WAD cyanide concentrations and confirmed by the WA ChemCentre using the APHA Standard Method 4500 CN.

Caro's Acid Detox

Cyanidation tails solution for the investigations was obtained by filtering the pulp post cyanidation. A summary of the tails solution speciation is provided in Table 3. The low thiosulfate and thiocyanate concentrations are indicative of an oxide ore.

Table 3: Cyanidation tails solution composition before detox testwork.

Concentrations (mg L^{-1})				WAD CN (mg L^{-1})	
NaCN	OCN$^-$	SCN$^-$	S$_2$O$_3$$^{2-}$	Calc.*	Picric
234	12	74	24	418	476

* NaCN + 3 x Cu

Figure 7 shows the residual WAD cyanide in the final detox solutions as a function of Caro's acid addition expressed as the percentage of stoichiometry. These results clearly indicate a ~300% stoichiometric addition of Caro's acid is sufficient to achieve less than 1 mg L^{-1} WAD cyanide after detox. However, at higher dosages the residual WAD cyanide becomes difficult to destroy with a treatment of 700% stoichiometry unable to achieve the targeted 0.2 mg L^{-1} WAD cyanide.
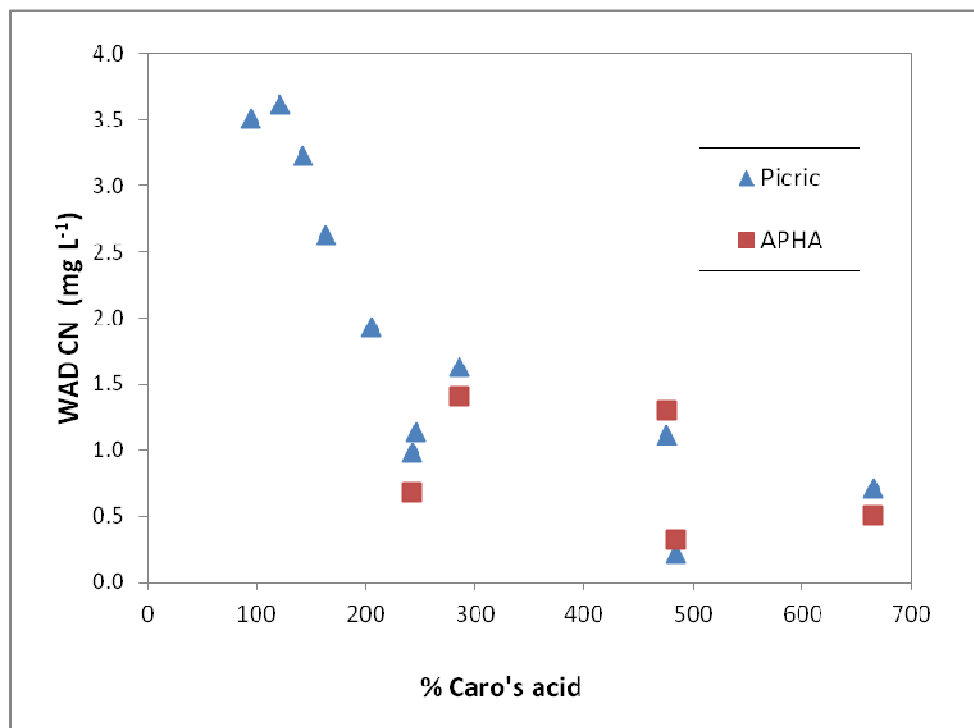

Figure 7: Residual WAD cyanide after Caro's acid detox of cyanidation tails solution at pH 9.

A summary of the change in solution speciation with percentage of stoichiometry Caro's acid addition is provided in Table 4. Clearly, the thiosulfate is readily destroyed by the Caro's acid (Reaction 8); thiocyanate also reacts with Caro's acid (Reaction 7) and is progressively destroyed with increasing additions. At the lower percentage Caro's acid additions significant cyanate concentrations are generated according to Reaction 5, however, as the quantity of Caro's acid added increases the generated cyanate is also destroyed (Reaction 6). It is believed the variability

in the data at higher Caro's acid additions is largely related to the reaction of Caro's acid with cyanate due to variability in localised pH and bulk pH control.

Table 4: Change in speciation (mg L^{-1}) with % stoichiometry of Caro's acid addition.

% stoichiometry of Caro's acid	NaCN	OCN$^-$	SCN$^-$	S$_2$O$_3^{2-}$
CIL Tails	234	12	74	24
95	0	768	61	0
143	0	786	40	0
285	0	524	0	0
475	0	399	0	0
666	0	461	0	0

Additional batch tests were also conducted to investigate potential means by which the target WAD cyanide concentration could be achieved without excessive Caro's acid addition. The residual WAD cyanide in the final detox solutions from staged Caro's acid addition are shown in Table 5. The staged addition of Caro's acid resulted in a lower final WAD cyanide concentration compared with a single addition of Caro's acid. This may be due to the reduced low pH excursion with the smaller Caro's additions; as referred to in the introduction the detox efficiency is reduced at low pH as the Caro's acid will react more readily with the generated cyanate than cyanide. The staged addition of Caro's acid is potentially advantageous, particularly when using lime for neutralisation as lime acts slower than more soluble bases (like sodium hydroxide) to neutralise the added acid. From an industrial perspective, if the Caro's acid is added along with lime into a stirred tank, the tank contents will also act as a buffer and results better than those achieved in batch tests with lime may be expected. However, even with stage Caro's acid addition a greater than 400% of stoichiometry Caro's acid addition would be required to meet the targeted WAD cyanide concentration.

Table 5: Effect of staged Caro's acid addition on detox of cyanidation tails solution.

Test	Picric WAD CN (mg L^{-1})
242% Caro's	0.98
242% Caro's in steps (3)	0.65
485% Caro's	0.22
485% Caro's in steps (3)	0.15

Sulfite Detox

Sulfite detox investigations (sodium sulfite used as the reactant) were also completed on the same cyanidation solution detailed in Table 3. By using sodium sulfite in these tests, no pH control was required as the detox discharge was close to or at pH 9. Figure 8 shows the residual WAD cyanide in the final detox solutions as a function sulfite addition expressed as a percentage of stoichiometry. These results indicate that ~250% stoichiometric addition of sulfite in a single stirred tank reactor would be sufficient to achieve less than 1 mg L^{-1} WAD cyanide after detox. The reason for the scatter in the results at these low WAD cyanide concentrations is attributed to the fluctuations in the DO concentration which was difficult to control (the undesirable sulfite reactions being a function of DO concentration). A test conducted at 725% stoichiometric addition of sulfite to WAD cyanide did not achieve the target of less than 0.2 mg L^{-1} WAD cyanide, indicating a sharp tail off in the residual WAD cyanide concentration similar to that observed for Caro's acid. The slightly reduced requirements for the sulfite process compared to the Caro's acid system can be attributed to the competing reactions with other species; unlike Caro's acid which reacts with thiosulfate, thiocyanate and cyanate, only thiosulfate is destroyed in the sulfite system (Table 6).
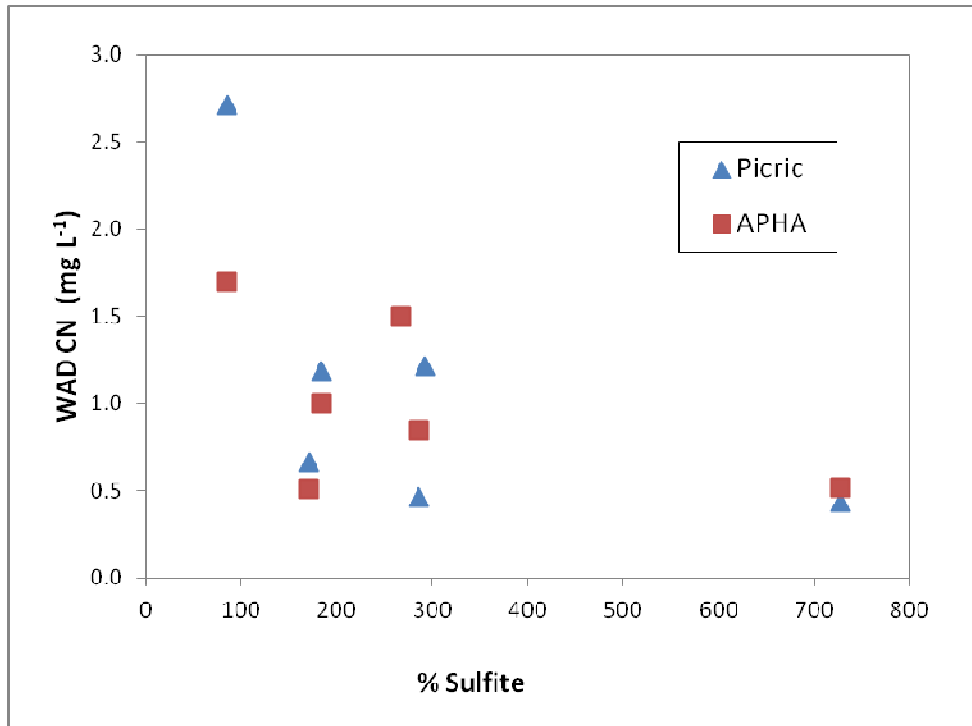
Figure 8: Residual WAD cyanide after sulfite detox of cyanidation tails solution at pH 9.

Table 6: Change in solution speciation (mg L^{-1}) of cyanidation tails solution with % sulfite addition.

% stoichiometry of sulfite	NaCN	OCN$^-$	SCN$^-$	S$_2$O$_3$$^{2-}$
CIL Tails solution	234	12	74	24
100	0	868	69	5
200	0	812	66	0
300	0	952	70	0

Additional tests were also conducted to investigate potential means by which the target WAD cyanide concentration could be achieved without excessive sulfite addition. The results of these tests are shown in Table 7 and indicate that the use of two CSTR's resulted in slightly better cyanide detox than in a single CSTR (same total oxygen addition as for the single CSTR), possibly due to improved reagent utilisation as a result of a very low DO in the first CSTR (partially this improvement can also be attributed to the slightly higher sulfite addition). Multiple CSTR's would appear to be beneficial, though achieving the target WAD cyanide concentration would still require significant reagent addition. The addition of ferrous sulfate (typically added to reduce the total cyanide in solution by forming insoluble iron cyanide double salts) was investigated subsequent to detox, but did not result in a lower residual WAD cyanide concentration. After sulfite detox; there was no residual iron and only some residual soluble copper, but there was a negligible decrease in the copper concentration with ferrous sulfate addition suggesting no formation of an iron double salt with the residual copper.

Table 7: Results from additional sulfite detox investigations to improve detox efficiency.

Test	Picric WAD CN (mg L^{-1})
286% SO$_3$$^{2-}$	0.46
305% SO$_3$$^{2-}$ (two CSTR's)	0.26
728% SO$_3$$^{2-}$	0.43
728% SO$_3$$^{2-}$ + ferrous sulfate	0.56

Polishing Using Activated Carbon or Ion Exchange Resins

Given the high percentage of stoichiometry for Caro's acid or sulfite addition required to potentially achieve WAD cyanide concentrations as low as 0.2 mg L^{-1} in the treatment of cyanidation tails or process solutions, polishing and alternative methods were considered for the efficient reduction in WAD cyanide levels. Activated carbon and particularly strong base ion exchange (IX) resins are able to absorb metal cyanide species from solution; activated carbon readily adsorbs copper cyanide species when the cyanide to copper ratio is close to two[15]. The preliminary investigations outlined below trialled several polishing systems directly on cyanide solutions and post detox.

The results presented in Table 8 show that polishing using either activated carbon or strong base IX resin subsequent to detox successfully removes the metal cyanides and results in a significant reduction in the WAD cyanide concentration for both systems. The picric acid measurements indicate that a WAD concentration of less than 0.2 mg L^{-1} CN is achieved; however conformational measurements using the APHA method 4500-CN do not support this. It is suspected that there may be an interference with the 4500-CN measurement used in this case (method I used in this case where as all other samples sent for confirmation were analysed by method O and which were in agreement with the Picric acid results) but further investigations are required to confirm if there is an interference with the method used. It is also important to note that these measurements are near the detection limits and thus more prone to interferences.

Table 8: Results for detox solution polishing with activated carbon (20 g L^{-1}) or IX resin (10 g L^{-1}). Each contact stage was 1 hour with fresh adsorbent used for each stage.

Test	Metal concentrations (mg L^{-1})				WAD CN (mg L^{-1})	
	Cu	Ni	Fe	Zn	Picric	APHA
Detox solution	3.20	0.06	0.02	0.11	0.33	0.32
1st contact with carbon					0.13	
2nd contact with carbon	0.23	0.03	<0.02	0.04	0.01	0.27
1st contact with IX resin					0.02	
2nd contact with IX resin	0.28	0.07	<0.02	0.05	0.01	0.20

The second system investigated was to complex all the free cyanide in a solution by adding copper ions(solid CuCN added) to give a CN:Cu of ~2.2, followed by contact with a strong base IX resin to recover all the metal cyanides. The results in Table 9 show that the IX resin is very effective at recovering the copper cyanide, with the residual WAD cyanide concentration after two contacts less than 0.1 mg L^{-1}.

Table 9: Residual WAD cyanide concentrations in a cyanidation tails solution after CuCN addition and IX resin polishing (10 g L^{-1}).

Test	Cu (mg L^{-1})	Picric WAD CN (mg L^{-1})
Leach tail + CuCN	684	718
1st contact (4 hr) with IX resin	45.7	44.0
2nd contact (16 hr) with IX resin	0.64	0.06

Further testwork is required to determine if pulp treatment is as successful as the solution systems trialled above. It is however anticipated that both would perform well with both activated carbon and IX resins already used widely for metal cyanide recovery in pulp leaching circuits.

It is worth keeping in mind that due to the very low concentrations being measured here, the measurement techniques could be contributing to some of the variability observed in the results as measurements are close to the detection limits and thus more prone to interferences. Thus in order to establish cyanide detox compliance to very low concentrations a very good understanding of the measurement technique and interferences will be required.

CONCLUSIONS

Pulp detox evaluations of a CIL tail found that a 200 - 350% stoichiometric addition of sodium metabisulfite or Caro's acid was required to achieve detox to below 50 mg L^{-1} WAD cyanide. Significantly the reagent addition for filtered tails solution was lower by 70 - 100% of stoichiometry. The solids were shown to catalyse the oxidation of sulfite by oxygen which contributes largely to the higher than stoichiometry sodium metabisulfite addition; it is thought that the mineral surfaces are also likely responsible for the decomposition/oxidation of Caro's acid. Thiocyanate and thiosulfate generated in the leach (and cyanate generated during detox) also consume Caro's acid whereas thiosulfate only is destroyed in the sulfite system. Their concentrations in cyanidation leach tails will therefore also affect detox reagent requirements.

Detox evaluations conducted on recovered solution from a sodium metabisulfite pulp detox found that the hydrogen peroxide requirement would be a much greater percentage of stoichiometry compared to Caro's acid and sodium metabisulfite to achieve the targeted less than 1 mg L^{-1} Total cyanide. The poor utilisation of hydrogen peroxide is attributed to the copper precipitate catalysed decomposition of the reagent, however the simpler and cheaper installation of a hydrogen peroxide treatment plant for the treatment of TSF return water or process streams has to be considered against the much higher reagent requirement.

The pH and DO control are likely to be critical during detox to very low WAD cyanide levels with fluctuations in these parameters affecting the rate of undesirable side reactions, such as the reaction of cyanate with Caro's acid or the oxidation of sulfite to sulfate; 700% stoichiometric addition of sodium sulfite and Caro's acid was insufficient to achieve 0.2 mg L^{-1} WAD cyanide when treating solution tails alone. Reagent addition when treating pulp could be significantly higher! Preliminary evaluations of polishing with activated carbon or strong base ion exchange resins after detox, or complexation of the free cyanide in a leach tail using copper and subsequent contact with ion exchange resin, have been shown to be effective in removing metal cyanide complexes from solution and are seen as potential alternatives when low level detox is. Importantly, the accuracy, reproducibility and interferences of measurements at these very low concentrations could be significant and contribute to the variability observed in the results presented. required

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