

# Appendix 5

## Report on Cyanide Destruction for the Dargues Reef Project

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## Cyanide Destruction for the Dargues Reef Project

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Commercial in Confidence



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## EXECUTIVE SUMMARY

### CYANIDE DESTRUCTION FOR THE DARGUES REEF PROJECT

Danielle Hewitt

Cyanide destruction evaluations using sulfite and oxygen were conducted for the Dargues Reef project. Evaluations conducted on a carbon-in-leach (CIL) tails slurry sample using sodium metabisulfite (SMBS) showed that 140% of stoichiometry addition of sulfite is required to achieve less than 50 mg L<sup>-1</sup> weak acid dissociable (WAD) cyanide in the discharge from a single continuous stirred tank reactor. In comparison, 130% of stoichiometry addition of sulfite is required to achieve the same target for the treatment of the tails filtrate. The greater than stoichiometric sulfite requirements are attributed to competing reactions, such as the direct oxidation of sulfite to sulfate by oxygen as well as the oxidation of thiosulfate, with the presence of solids in the tails believed to further catalyse the direct sulfite oxidation reaction.

Under optimum conditions, some residual sulfite is typically present in the discharge which will continue to react with the metal complexed cyanide remaining in solution upon ingress of oxygen, reducing the residual WAD cyanide concentration of the discharge further. Thus, samples analysed after a period of time typically produce a lower result to an analysis conducted immediately. This may also explain why WAD cyanide readings for the process discharge are often higher than at the tailings storage facility discharge spigot.

The alkali requirement was found to be proportional to SMBS addition at ~0.9 mol OH<sup>-</sup> / mol SO<sub>3</sub><sup>2-</sup>.

Soluble arsenic and mercury were found to not be precipitated during cyanide destruction.

Thiocyanate is not destroyed or precipitated to any appreciable extent.

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## 1 INTRODUCTION

CSIRO was requested by Jonathan Childs and Steven Hoban (Independent Metallurgical Operations Pty Ltd) to evaluate the sulfite/oxygen cyanide destruction process for a carbon-in-leach (CIL) tail slurry sample as part of the Dargues Reef project. The objective was to determine the destruction reagent requirements to meet the International Cyanide Management Institute (ICMI) cyanide code compliance of less than 50 mg L<sup>-1</sup> weak acid dissociable (WAD) cyanide in the discharge to the tailings storage facility (TSF). Destruction evaluations were also to be conducted on the filtered solution to establish the impact of solids on the cyanide destruction process.

## 2 EXPERIMENTAL

### 2.1 Sample preparation for the destruction testwork

The samples received by CSIRO incorporated a CIL tails slurry sample (61% solids) and 3.1 kg of clarified liquor. The analysis results for the clarified solution are presented in Table 1. Note that the copper value in Table 1 attained by high performance liquid chromatography (HPLC) is lower based on the WAD to Free cyanide difference and in comparison to the ICP-OES values for the filtrate testwork (Table 3). During transportation and storage of the slurry sample, the free cyanide would have continued to react with copper containing mineral present in the solids. Thus, when the slurry was recombined with the clarified liquor, a higher copper concentration was measured in the resulting filtrate.

Table 1. Analysis results (mg L<sup>-1</sup>) of clarified liquor from the CIL tails.

Free cyanide (as NaCN)	WAD CN <sup>-</sup>	Total CN <sup>-</sup>	OCN <sup>-</sup>	SCN <sup>-</sup>	Cu	Fe	Ni	S <sup>2-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	SO <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>
680	1021	1234	195	763	424	123	0.2	0.0	141	0.0	144

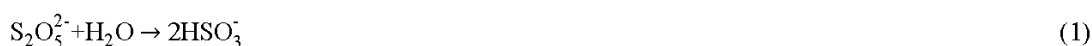
The clarified liquor was added back to the slurry sample and repulped to give 46% solids. A portion of this slurry was pressure filtered to obtain approximately 3 L sample of CIL tails filtrate which was used for the filtrate cyanide destruction investigations. The filtered solids were also retained.

After the completion of the CIL tails filtrate investigation, the untreated CIL tails filtrate and filtered solids were added back to the slurry sample to give 41% solids which was used for the slurry evaluations.

Each morning, prior to the commencement of the cyanide destruction testwork, the pH of the feed was measured, and if necessary, adjusted to pH 10.9 using Marvelime. The WAD cyanide concentration in the feed was also measured using an OI Analytical cyanide analyser (USEPA OIA-1677) and if necessary, adjusted to 38.5 mM (1000 mg L<sup>-1</sup>) using solid sodium cyanide. These set-points were determined from the analysis of the clarified liquor received by CSIRO (Table 1).

### 2.2 Cyanide destruction: CIL tails filtrate

Continuous cyanide destruction experiments using 200 g L<sup>-1</sup> sodium metabisulfite (SMBS) as the source of sulfite (Equation 1) and industrial oxygen were carried out in a single 90 mL continuous stirred tank reactor (CSTR) set atop a magnetic stirrer plate. To start the destruction process, sufficient copper sulfate pentahydrate was added to complex the free cyanide in the feed to the CSTR (estimated by potentiometric silver nitrate titration); due to the high level of copper in the feed (~550 mg L<sup>-1</sup>) constant addition was not required to sustain the reaction. Industrial oxygen was sparged into the reactor to maintain a measurable dissolved oxygen (DO) concentration and the pH of the reactor was controlled to a pH of 9 with 5 M sodium hydroxide using a computer controlled dosing device. All experiments were undertaken at room temperature and atmospheric pressure.



Prior to commencing the destruction testwork, the concentration of sulfite in the SMBS feed was confirmed by potentiometric iodine back-titration against sodium thiosulfate. This value was used to calculate the pump rate of the SMBS feed (used to control percentage of stoichiometry addition rate) with the pump rate of the cyanide feed kept constant to yield an approximate 30 min residence time.

Testwork commenced at a sulfite:WAD cyanide mole ratio of 2.0 (200% of stoichiometry addition of sulfite) with discharge samples taken every 30 min, filtered by vacuum filtration and analysed for WAD cyanide using an OI Analytical cyanide analyser (USEPA OIA-1677) which enabled real-time tracking of the destruction process. After three residence times, a sample of the discharge ( $\approx 50$  mL) was taken and analysed for the following:

- Cu, Ni, Fe, Zn, As, Ag, and Au by ICP-OES. To ensure metal stability during storage prior to analysis, subsamples were diluted into a  $500 \text{ mg L}^{-1}$  sodium cyanide matrix.
- Hg by CVAAS. To ensure metal stability during storage prior to analysis, subsamples were diluted into a  $500 \text{ mg L}^{-1}$  sodium cyanide matrix.
- WAD and Total cyanide using the OI Analytical cyanide analyser (USEPA OIA-1677 and ASTM D 7511-09e2 methods, respectively).
- Cyanate, thiocyanate and thiosulfate by established high performance liquid chromatography (HPLC) methods developed by CSIRO for determining the cyanide speciation. The presence of sulfite in the discharge was also monitored.

The sulfite:WAD cyanide ratio was then reduced by a factor of 0.5, followed by a further reduction by a factor of 0.25, with both destruction tests and sampling repeated as outlined above.

### 2.3 Cyanide destruction: CIL tails slurry

To establish the impact of solids on cyanide destruction, reagent requirements for the cyanide destruction of the CIL tails slurry was also investigated. Testwork was undertaken in accordance with the method described for the filtrate investigation with the exception of using a 500 mL CSTR with agitation provided by an overhead agitator fitted with a Rushton impeller. Samples were also centrifuged and then syringe filtered to remove any unsettled fines ( $0.45 \mu\text{m}$ ).

Prior to commencing the destruction testwork, samples of the feed were taken for % solids (dried at  $60^\circ\text{C}$ ) and slurry density measurements. The concentration of sulfite in the SMBS feed was also confirmed by potentiometric iodine back-titration against sodium thiosulfate. These values were then used to calculate the pump rate of the SMBS feed (used to control percentage of stoichiometry addition rate) with the pump rate of the slurry feed kept constant to yield an approximate 30 min residence time. To initiate the destruction process, the CSTR was filled with a mixture of filtrate cyanide destruction tails and water.

### 3 RESULTS AND DISCUSSION

All percentage sulfite addition rates quoted in the following section are as percentages of WAD cyanide stoichiometry.

#### 3.1 Cyanide destruction: CIL tails filtrate

A summary of the three cyanide destruction evaluations conducted on the CIL tails filtrate is presented graphically in Figure 1. These results indicate that a 130% stoichiometric addition is sufficient to achieve less than 50 mg L<sup>-1</sup> WAD CN<sup>-</sup> in the discharge. The greater than stoichiometric sulfite requirement for WAD cyanide destruction (Reaction 2) is attributed to competing reactions, such as the direct oxidation of sulfite (Reaction 3) and the oxidation of thiosulfate (potentially via a similar reaction mechanism to cyanide).

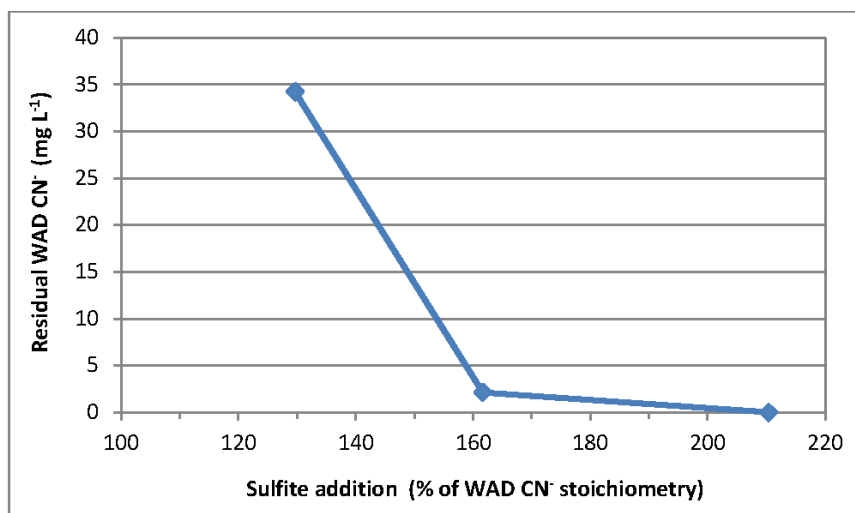
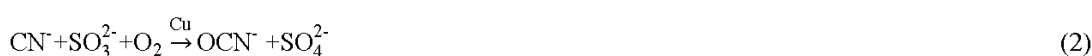


Figure 1. Residual WAD cyanide in the CSTR discharge after cyanide destruction of the CIL tails filtrate using SMBS and industrial oxygen at pH 9 (WAD CN<sup>-</sup> in the destruction feed was ~1000 mg L<sup>-1</sup>).

Detailed results of the filtrate cyanide destruction investigations are provided in Tables 2, 3 and 4. Also included in these tables are the results for a second sub-sample (labelled “Further reaction”) which was taken from filtered discharge and that had been left to stand in capped vials for several days and from which further precipitation of metals (green in colour) was observed, suggestive of further cyanide destruction. Although measurable DO was maintained in the CSTR during the destruction process, the presence of a small concentration of sulfite (estimated to only be ~1% of the feed) was detected in the discharge for two of the tests (data was unavailable for the third test). This is not surprising due to the dispersion and potential of short-circuiting within a CSTR. This sulfite, in combination with oxygen in the sample and/or the vial headspace, was therefore available to continue to react with residual WAD cyanide in the sample. Sample analysis confirmed this with the results presented in Table 2 clearly showing a reduction in WAD cyanide levels between the “Discharge” and “Further reaction” samples, with the loss of metals (particularly copper) confirmed by ICP-OES

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measurements (Table 3). Images of the precipitate formed during cyanide destruction of the CIL tails discharge are shown in Figure 2.

Table 2. Results from cyanide destruction of CIL tails filtrate using SMBS and industrial oxygen at pH 9.

Sulfite addition (%)	Residence time (min)	Reagent requirement (g L <sup>-1</sup> of filtrate)		WAD CN <sup>-</sup> (mg L <sup>-1</sup> )		Total CN <sup>-</sup> (mg L <sup>-1</sup> )	
		SMBS	NaOH	Discharge	Further reaction	Discharge	Further reaction
Feed	-	-	-	990	-	1195	-
210	30.1	7.61	3.41	0.02	0.04	0.3	0.4
162	30.6	5.85	2.24	2.1	0.1	3.4	0.5
130	30.8	4.69	1.84	34	21	34	22

Table 3. Metal profiles from cyanide destruction of CIL tails filtrate using SMBS and industrial oxygen at pH 9.

Sulfite addition (%)	Sample	Cu (mg L <sup>-1</sup> )	Ni (mg L <sup>-1</sup> )	Fe (mg L <sup>-1</sup> )	Zn (mg L <sup>-1</sup> )	As (mg L <sup>-1</sup> )	Ag (mg L <sup>-1</sup> )	Au (mg L <sup>-1</sup> )	Hg (mg L <sup>-1</sup> )
Feed	-	549	0.46	139	7.89	2.92	0.92	0.73	2.53
210	Discharge	16.2	<0.2	0.87	0.57	1.41	<0.2	0.31	2.15
162	Discharge	15.4	<0.2	1.00	0.46	1.55	0.21	0.28	2.15
130	Discharge	93.1	<0.2	0.68	0.97	1.67	0.35	0.30	2.12
	Further reaction	38.8	<0.2	0.13	0.66	0.67	<0.2	0.29	2.10

Table 4. Anions measured in the discharge from cyanide destruction of CIL tails filtrate using SMBS and industrial oxygen at pH 9.

Sulfite addition (%)	OCN <sup>-</sup> (mg L <sup>-1</sup> )	SCN <sup>-</sup> (mg L <sup>-1</sup> )	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	SO <sub>3</sub> <sup>2-</sup> (mg L <sup>-1</sup> )
Initial	227	777	145	0
210	1713	775	5	data unavailable
162	1600	782	10	53
130	1582	755	10	41

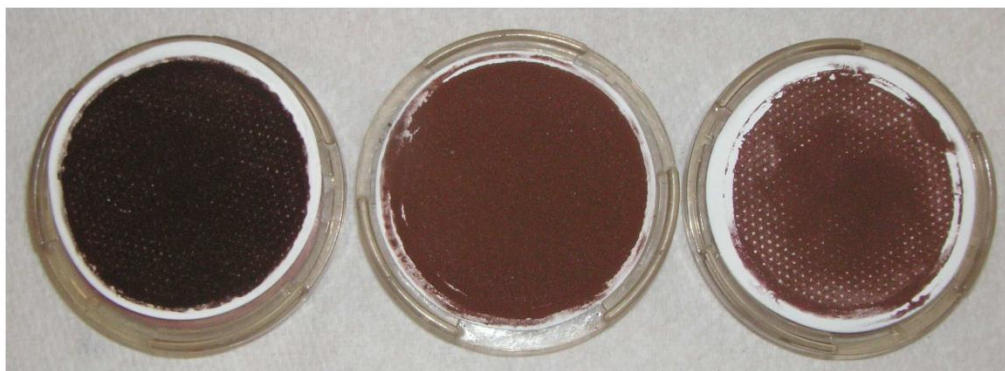


Figure 2. Precipitates formed during cyanide destruction of the CIL tails filtrate (Left: 210%; Centre: 162%; Right 130%).

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Notable additional observations from the filtrate results are:

- Alkali requirement is proportional to SMBS addition (at ~0.9 mol OH<sup>-</sup> / mol SO<sub>3</sub><sup>2-</sup>).
- All metals other than arsenic and mercury are significantly precipitated as a result of cyanide destruction.
- Cyanide oxidation produces cyanate.
- Thiocyanate is not destroyed, but thiosulfate is.

### 3.2 Cyanide destruction: CIL tails slurry

Due to the limited amount of slurry sample provided, only two short test runs were able to be conducted. Detailed results from the slurry cyanide destruction investigations are provided in Tables 5, 6 and 7. Also included in these tables are the results for a second sub-sample (labelled “Further reaction”) which was taken from filtered discharge and that had been left to stand in capped vials for several days and from which further precipitation of metals (green in colour) was observed, suggestive of further cyanide destruction (as observed for the filtrate tests).

Most notable is that the reagent addition (sulfite % stoichiometry) required to detox the slurry is slightly higher in comparison to the filtrate. This indicates that the solids have a small impact on reagent requirements (potentially catalysing the direct oxidation of sulfite; Hewitt 2012), which results in a slightly higher percentage of stoichiometry addition of sulfite to gain the same level of destruction of the slurry in comparison to the filtrate (~145% stoichiometry for the slurry would give comparable residual WAD cyanide to the 130% stoichiometry result for the filtrate).

Table 5. Results from cyanide destruction of CIL tails slurry using SMBS and industrial oxygen at pH 9.

Sulfite addition (%)	Residence time (min)	Reagent requirement (g L <sup>-1</sup> of solution)*		WAD CN <sup>-</sup> (mg L <sup>-1</sup> )		Total CN <sup>-</sup> (mg L <sup>-1</sup> )	
		SMBS	NaOH	Discharge	Further reaction	Discharge	Further reaction
Feed	-	-	-	1076	-	1328	-
136	30.6	5.19	1.83	51	45	58	44
152	30.6	5.65	2.00	22	13	23	12

\*Calculations based on 41% solids measured for the slurry.

Table 6. Metal profiles from cyanide destruction of CIL tails slurry using SMBS and industrial oxygen at pH 9.

Sulfite addition (%)	Sample	Cu (mg L <sup>-1</sup> )	Ni (mg L <sup>-1</sup> )	Fe (mg L <sup>-1</sup> )	Zn (mg L <sup>-1</sup> )	As (mg L <sup>-1</sup> )	Ag (mg L <sup>-1</sup> )	Au (mg L <sup>-1</sup> )	Hg (mg L <sup>-1</sup> )
Feed	-	600	0.52	157	8.26	2.54	0.66	0.36	1.54
136	Discharge	120	0.20	2.82	0.35	1.07	<0.2	0.36	1.39
	Further reaction	99.2	0.22	0.12	0.29	0.71	<0.2	0.37	1.41
152	Discharge	57.3	0.24	0.24	0.39	0.83	<0.2	0.36	1.46
	Further reaction	30.7	0.23	0.16	0.38	0.80	<0.2	0.38	1.29

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Table 7. Anions measured in solution in discharge from cyanide destruction of the CIL tails slurry using SMBS and industrial oxygen at pH 9.

Sulfite addition (%)	OCN <sup>-</sup> (mg L <sup>-1</sup> )	SCN <sup>-</sup> (mg L <sup>-1</sup> )	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	SO <sub>3</sub> <sup>2-</sup> (mg L <sup>-1</sup> )
Initial	237	893	155	0
136	1739	857	17	63
152	1772	843	11	52

Other notable observations for the slurry evaluations are the same as observed for the filtrate.

## **4 CONCLUSIONS**

An assessment has been completed for the Dargues Reef project of the sulfite/oxygen process (SMBS used in this testwork) for the destruction of cyanide in the CIL tails. The evaluations conducted on the provided samples indicated that a 140% of stoichiometry addition of sulfite is required to achieve a WAD cyanide concentration of less than 50 mg L<sup>-1</sup> in the discharge using a single stirred tank reactor. A lower stoichiometry addition of sulfite of 130% was able to achieve the same target for the treatment of the CIL tails filtrate. This indicates that the solids have a small impact on reagent requirements, which results in a slightly higher percentage of stoichiometry addition of sulfite to gain the same level of destruction of the slurry in comparison to the filtrate. In both investigations, the greater than stoichiometric sulfite requirement is attributed to competing reactions, such as the direct oxidation of sulfite and oxidation of thiosulfate, with the presence of solids believed to catalyse the direct oxidation of sulfite to sulfate.

Although measurable DO was maintained during these investigations, sulfite was typically detected in the discharge filtrate samples (only at ~1% of that added), which continued to react with metal complexed cyanide, further reducing the WAD cyanide levels in each of the samples over time. The extent of residual sulfite is dependent on the mixing and any short circuiting between the reagent addition point and the outlet.

Other notable conclusions were:

- Alkali requirement is proportional to SMBS addition (at ~0.9 mol OH<sup>-</sup> / mol SO<sub>3</sub><sup>2-</sup>).
- Soluble arsenic and mercury were found to not be precipitated during cyanide destruction.
- Thiocyanate is not destroyed or precipitated to any appreciable extent.



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