Laboratory investigation of Hydrogen Cyanide (HCN) gas formation from cemented paste fill (CPF) samples

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Abstract

The potential environmental impact of using cyanide-bearing tailing in the cemented paste fill (CPF) has been investigated. A series of laboratory tests were conducted to determine the total and WAD cyanide content in tailings, and CPF samples. In addition, a chemical analysis of water which could have been exposed to CPF during underground mining operations has been undertaken. In all cases the liberated HCN has been monitored. This study showed that, the total and WAD cyanide content increased with cement content in the CPF mixes. However, the values measured did not exceed recommended maximum level for acceptable environmental impact.

Keywords: cyanide-bearing tailing; cemented paste fill; weak acid dissociable cyanide; hydrogen cyanide gas; underground mining

1. Introduction

The issue of cyanide contamination within mining backfill has been recently highlighted by Reichardi [1] . Although the mining industry only accounts for 15% of global cyanide consumption, the gold mining industry is under scrutiny from both regulators and the society at large. Therefore, the mining industry has to demonstrate that the potential migration of cyanide (and its degradation products) from emplaced backfill will not have an unaccepted impact on worker health and safety or the environment either during mine life or after closure [1].

Currently no literature is available to indicate the level of hydrogen cyanide (HCN) gas emission from cemented past fill (CPF) using cyanide bearing tailings. This paper presents a laboratory investigation of HCN gas liberated from cemented paste fill samples when mixing with water which could have been exposed to the CPF during underground mining operations.

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2. Cemented paste fill operation in Australian underground mines

One of the main functions of fill materials in mines is to provide stability to the resulting voids. The use of different fill types and their specific functions and engineering requirements is related to the mining methods, mining strategies and mining sequences used [2]. The three main types of fill are rockfill, hydraulic fill and paste fill. The fill material can be either cemented or unconsolidated. Cemented rock fill (CRF) is generally described as any waste material greater than sand size that is used to backfill underground mines. Hydraulic fill consists of silty sands or sandy silts without clay fiction, which can be classified as ML or SM under the Unified Soil Classification System [3]. The clay fraction is removed through a process known as desliming, whereby the entire fill material is circulated through hydrocyclones and the fine fraction is removed and then sent to the tailings dam. The remaining hydraulic fill fraction is reticulated in the form of slurry through pipelines to underground voids [3]. Paste fill is a non-segregation slurry, which means that it has negligible excess water when stationary and remains essentially as a homogeneous single phase product [4]. Usually paste fill contains some binder in order to eliminate the risk of subsequent liquefaction and remobilization, even if fill is not exposed by future mining of adjacent stopes [5].

In the recent years, the application of cemented paste fill in the underground mines has increased significantly. Extensive research and development work has been carried for optimization of CPF systems. Most of the research has been mainly focused on the geotechnical, rheological properties and also to lower the operational cost. Table 1 shows a number of Australian mines that are currently using and planning to use CPF.

Table 1. Mines in Australia with CPF application.

Company	**Mine**	**State**	**Commodity**
BHP Billliton	Cannington	Queensland	Pb, Zn, Ag
Xstrata	Mt Isa	Queensland	Pb, Zn, Ag
Newcrest	Cracow	Queensland	Au
Barrick	Osborne	Queensland	Cu, Ag
Gold Fields	Argo	Western Australia	Au
Gold Fields	Agnew	Western Australia	Au
Barrick	Plutonic	Western Australia	Au
Barrick	Darlot	Western Australia	Au
Barrick	Kanowna Belle	Western Australia	Au
Lanfranchi JV	Lanfranchi	Western Australia	Ni
Barrick	Raleigh	Western Australia	Au
Barrick	Henty	Tasmania	Au

3. Cyanide in cemented paste fill (CPF)

Cyanide has been used for more than 100 years for extracting gold. The liberation of gold is achieved by a series of process such as, combination, flotation, thickening, roasting, biological oxidation, cyanidation, carbon-in-pulp, carbon-in-leach, leaching, elution, electro winning, smelting and refining. Cyanide is used in the leach stage, and is typically added at a rate of 0.5 kg sodium cyanide (NaCN) per tone of ore. The National Pollutant Inventory (NPI) [6] suggest that, when used in gold process, cyanide may:

- be carried through the system in a dissolved form to be re-used in the recycle circuits or through tailings storage facilities return waters;
- seep from tailings storage facilities (TSFs) as a ground emission;
- convert to various degradation products such as thiocyanate and cyanate;
- react with metals such as copper, iron and cobalt;
- decompose to form ammonia a bicarbonate and
- be released in gaseous form, as hydrogen cyanide (HCN).

The behaviour of cyanide within TSFs is extremely complex and has not been accurately modeled to date [6]. The current Australia water quality trigger values for free cyanide in freshwater and marine water are 7μg/L and 4μg/L, respectively. A water quality benchmark for the protection of wildlife of 50 mg WAD-CN/L within the tailing dams is recommended by the mining industry [7].

The tailings from TSFs, dry or wet, are used with a combination of cementatious materials (usually ordinary portland cement) and water to mix a CPF. Fresh water, hypersaline water or a blended fresh and hypersaline water is used as mixing water. The mix designs vary from site to site depending upon the geotechnical, reheological requirements and the local availability of tailings and mixing water. Initial test results conducted at Western Australian School of Mines (WASM) show that a CPF sample made with cyanide-bearing tailings contains WAD cyanide ranging from <1 to <5 mg/kg. This WAD cyanide is highly unstable and can emit volatile HCN when sufficient hydrogen ion occurs in the CPF.

4. Experimental methodology

Gold tailings and mine water from Agnew gold mine and mine cement from Cockburn Cement Limited were used for this experiment. The laboratory program consisted of two stages. Firstly, a physical, chemical and mineralogical characterization of the tailings, binder and mixing water was undertaken. The second stage consisted of CPF mixing, determination of total and WAD cyanide content in the CPF and monitoring of the liberated HCN gas from the CPF samples.

4.1 Physical and chemical analysis of tailings, mine water and cement

The mineralogical composition of the tailings was determined by the XRD method. The XRD scan pattern is shown in Figure 1. The intensity of the peaks in an XRD pattern depends upon the crystallinity as well as the concentration of the phase. The quantitative phase analysis results is given in Table 2. The mineralogical analysis shows that the Agnew gold tailings are mainly composed of Hornblende, Anorthite, Quartz, Chlorite, Dolomite, Talc Biotite Mica, and Gypsum. Figure 2 shows the particle size distribution curves (PSD) of Agnew tailings. A chemical analysis result of Agnew mine water is presented in Table 3 and the chemical composition of Cockburn Mine cement is shown in Table 4.

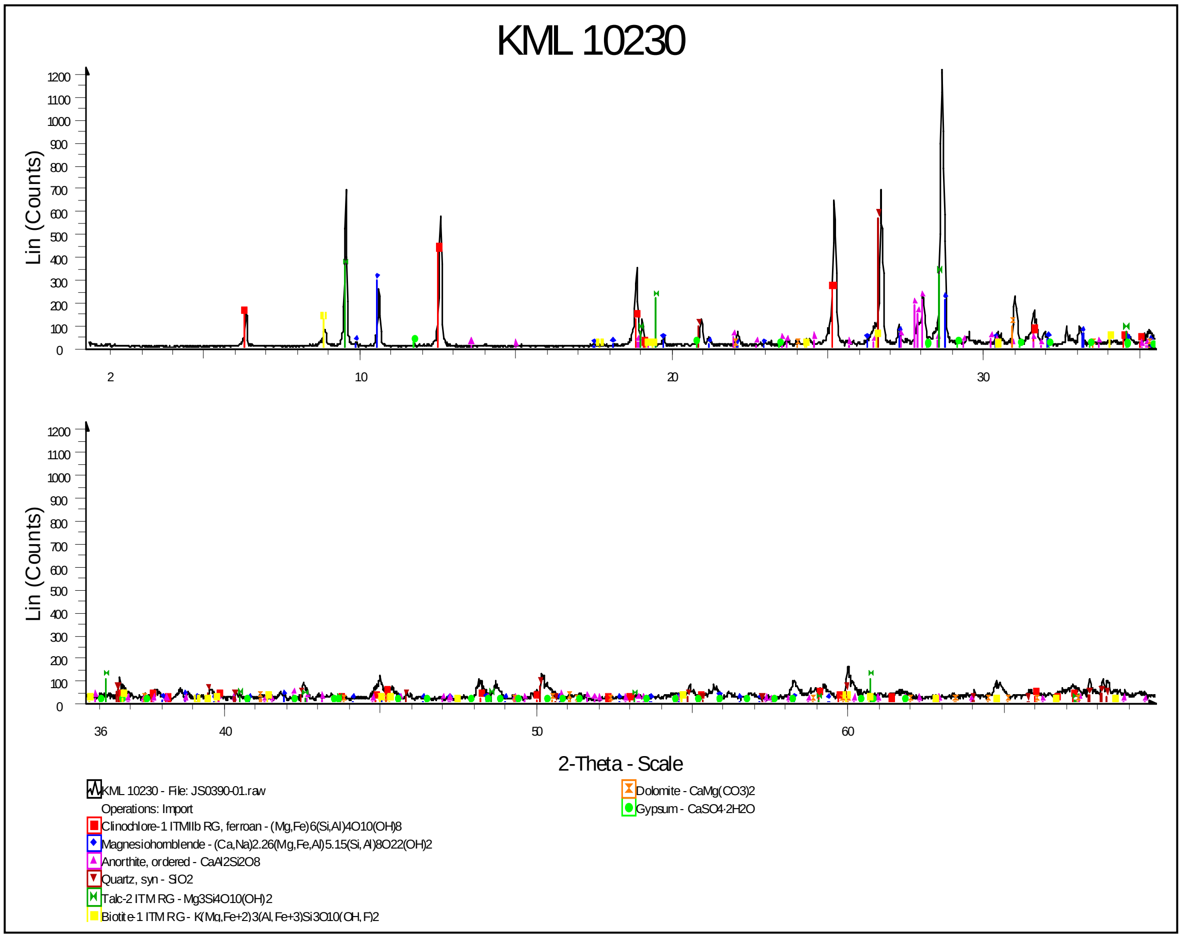

Figure 1. XRD analysis pattern of the Agnew Mine tailings.

Table 2. Quantitative phase analysis results.

Mineral	**Phase**	**Weight %**
Chlorite	$(Mg,Fe)_6(Si,Al)4O10(OH)_8$	14
Amphibole (hornblende)	$(Ca,Na)_2.26(Mg,Fe,Al)_5.15(Si,Al)_8O22(OH)_2$	38
Calcic plagioclase felspar (anorthite)	$CaAl2Si_2O_8$	17
Quartz	SiO_2	14
Talc	$Mg_3Si_4O10(OH)_2$	5
Dolomite	$CaMg(CO_3)_2$	9
Mica (biotite)	$K(Mg,Fe^{+2})_3(Al,Fe^{+3})Si_3O_{10}(OH,F)_2$	2
Gypsum	$CaSO_4 \cdot 2H_2O$	1

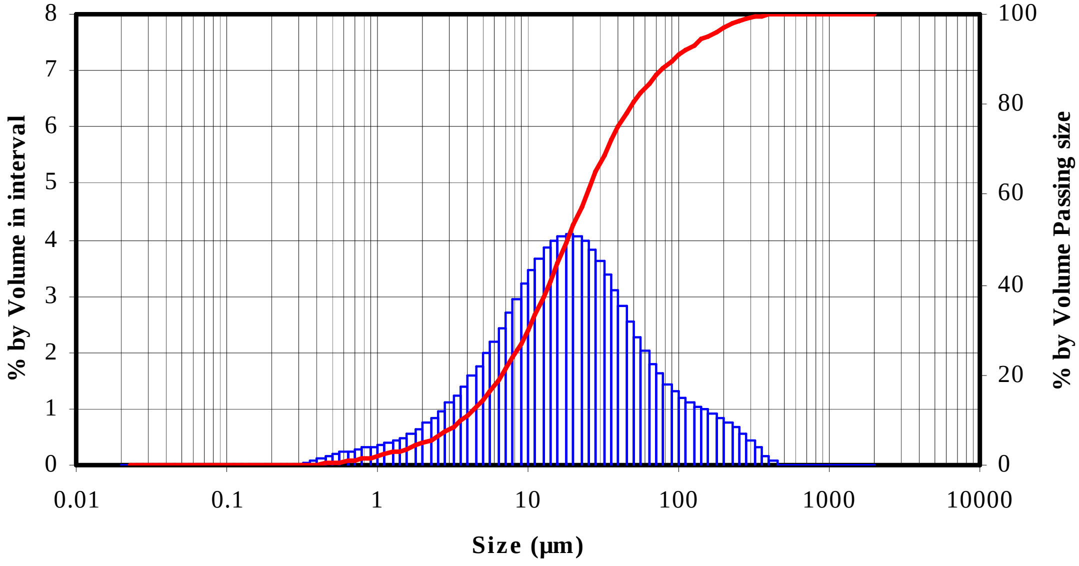

Figure 2. Particle size distribution (PSD) curve of the Agnew Mine tailings.

Table 3. Chemical analysis result of Agnew mine water.

pH	pH Units	7.1
Conductivity @25˚C	mS/cm	11,000
TDS (Calculated)	mg/L	6,400
Soluble Iron, Fe	mg/L	<0.04
Sodium, Na	mg/L	930
Postassium, k	mg/L	89
Calcium, Ca	mg/L	510
Magnesium, Mg	mg/L	600
Chloride, CL	mg/L	3,200
Carbonate, CO_3	mg/L	<1
Bicarbonate, HCO_3	mg/L	100
Sulphate, SO_4	mg/L	1,500
Nitrate, NO_3	mg/L	120
Cation/Anion balance	%	-2.8
Sum of Ions (Calculated)	mg/L	7,032

Table 4. Chemical composition of Cockburn mine cement.

Parameter	**Method**	**Units**	**Typical**	**Range**
SiO_2	XRF	%	26.5	25.5 - 27.5
Al_2O_3	XRF	%	10.3	9.5 - 11.0
Fe_2O_3	XRF	%	1.1	0.9 - 1.3
CaO	XRF	%	51.0	49.0 -53.0
MgO	XRF	%	4.5	4.0 - 5.0
SO_3	Gravimetric	%	2.4	2.0 - 2.8
Chloride	ASTMC114	%	0.02	0.01 - 0.03
Na_2O equivalent	ASTMC114	%	0.5	0.4 - 0.6

CPF mixing, determination of total and WAD cyanide content and liberated HCN gas

The CPF was mixed in the WASM geomechanic laboratory using Agnew Mine tailings and mine water as well as Cockburn mine cement. In addition, a water reducing polymer admixture (Meyco Minefill R01) was also added in the mix. Four cement dosages such as 3%. 4%, 5% and 6% were used in four batches. The mix was designed with a solid density between 69% and 70%. The detailed mix design is shown in Table 5.

Table 5. Detailed mix design for the paste fill samples.

Mix ID	**Cement (%)**	**Tailings (%)**	**Cement (g)**	**Moisture content of tailings (%)**	**Tailings (kg)**	**Meyco Minefill R01 (g)**	**Water addition (g)**
AG 1	3	97.0	300.0	12	10.864	1.1	3120.6
AG 2	4	96.0	400.0	12	10.752	1.5	3339.3
AG 3	5	95.0	500.0	12	10.640	1.8	3350.9
AG 4	6	94.0	600.0	12	10.528	2.2	3362.6

Determination of total cyanide, WAD cyanide and monitored liberated HCN gas from the CPF samples were conducted by SGS Australia Pty Ltd., environmental services laboratory. A summary of the testing standard is given in Table 6. The test was conducted by reacting the crushed CPF samples with mine water. The liberated HCN was collected in a caustic solution and analysed by the standard pyridine-barbituric acid procedure. Pictures of the distillation system for water/solid and HCN liberation are given in Figures 3 and 4, respectively.

Table 6. Summary of standard for determination of cyanide content and liberated HCN.

Test parameters	**Standard method**
Total Cyanide	PEI-021
Weak Acid Dissociable Cyanide	PEI-026
pH (1:5)	AN-101
Liberated Hydrogen Cyanide	APHA 4500-CN.E

Figure 3. Distillation system for water and solids.

Figure 4. Distillation system for HCN liberation.

5. Results and discussion

Table 7 shows the total and WAD cyanide in the tailings and CPF samples. A graphical presentation of total and WAD cyanide in CPF sample with different cement dosage is shown in Figure 5. The data from Table 7 shows that Agnew tailings contain 19 mg/kg of total cyanide and 1 mg/kg of WAD cyanide. In the CPF samples, the measured total cyanide content ranged from 33 mg/kg to 38 mg/kg and WAD cyanide ranging from 1 mg/kg to 2 mg/kg. The pH (1:5) value ranged from 11.7 to 12.1. The measured total and WAD cyanide content in the CPF samples is higher than the cyanide content in the tailings samples. The difference may be a contribution from the mixing water, the additive and type of cement. A further study is required to investigate those factors.

Table 7. Total and WAD cyanide content in tailings and CPF samples.

Parameter	**Units**	**Tailings**	**CPF AG-1**	**CPF AG-2**	**CPF AG-3**	**CPF AG-4**
Total Cyanide	mg/kg	19.0	33.0	37.0	34.0	38.0
WAD cyanide	mg/kg	1.0	1.5	1.8	2.1	2.0
pH (1:5)	pH units	NA	11.7	11.9	12.0	12.1

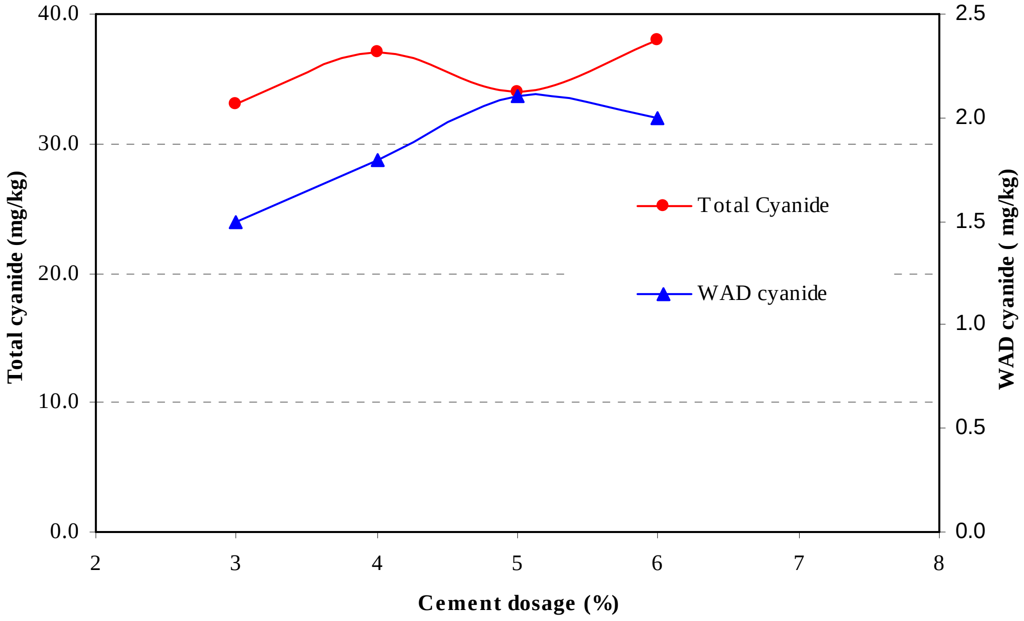

Figure 5. Total and WAD cyanide content in CPF samples with different cement dosage.

The HCN liberated less than 0.1 mg/kg in all crushed CPF samples regardless of the cement dosage. The result of monitored liberated HCN is shown in Table 8. Generally, CPF in the underground mines is consolidated (cemented) and the permeability is low compared to other types of fill. Therefore, the amount of liberated HNC will be lower than that of crushed CPF samples monitored in the laboratory.

Table 8. Liberated HCN from crushed CPF samples

Parameter	**Units**	**CPF AG-1**	**CPF AG-2**	**CPF AG-3**	**CPF AG-4**
Liberated Hydrogen Cyanide	mg/kg	<0.1	<0.1	<0.1	<0.1

Furthermore, the liberation of HCN is highly depending on the pH value of the groundwater. Figure 6 shows the potential of HCN liberation as a function of pH [8]. Table 9 shows the average pH level of groundwater at some Australian underground mines [9]. The data shows that the pH level ranged from 2.8 to 8.3. Although a possibility exists for HCN liberation, the amount shown in Table 8 appears to be insignificant.

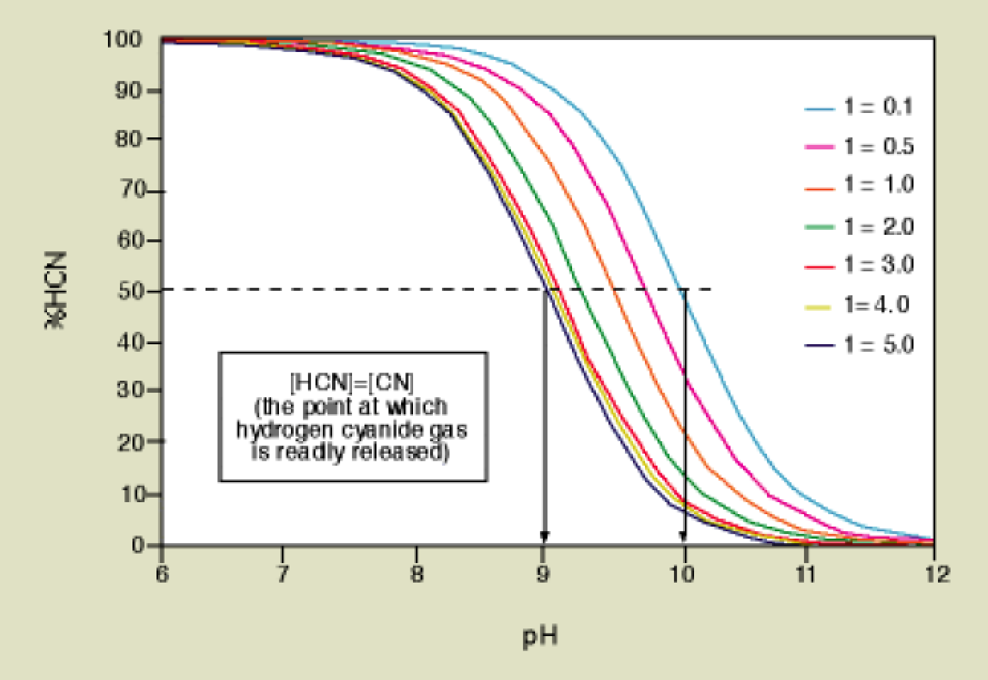

Figure 6. HCN liberation as a function of pH.

Table 9. Average pH level of groundwater at some Australian underground mines.

Mine	pH Units
Argo	6.2
Cannington	7.8
Darlot Aquifer 1	7.3
Darlot Aquifer 2	6.9
Enterprise	7.5
Gunpowder	2.8
Kanowna Belle Aquifer 1	7.3
Kanowna Belle Aquifer 2	7.3
Kundana	7.0
Leinster Nickel Aquifer 1	8.3
Leinster Nickel Aquifer 2	7.2
Olympic Dam Aquifer 1	7.4
Olympic Dam Aquifer 2	7.0
Raleigh	7.3
Telfer	6.5
Waroonga	7.2

6. Summary

The nature of HCN gas liberation from CPF is very complex because the material consists of the tailings from TSFs, mixing water which may be contaminated with cyanide and the chemical reaction with cement and additives. This study shows that, the total and WAD cyanide content increased with cement content in the CPF mixes. However, the values measured for the Agnew Mine did not exceed recommended maximum level [10].

7. Acknowledgements

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