Cyanide Decay and Metal Speciation in Decant Ponds of Carbon-in-Leach Tailings Storage Facilities – A Case Study at Gold Fields Ghana Limited, Tarkwa Mine (GFGL)

M. A. Sackey[1], G. K. Anornu[1], J. S. Y, Kuma[2], B. K. Kortatsi[3]

[1]*Department of Civil Engineering, KNUST, Kumasi*
[2]*UMat –P.O. Box 237, Tarkwa Ghana;*
[3]*CSIR-Water Research Institute, P. O. Box M32, Accra, Ghana*

Abstract The environmental fate of cyanide in gold processing tailing dams has raised concerns over the last two decades especially the presence of residual cyanide and metals which may lead to chronic groundwater contamination. Results from the TSFs at Gold Fields Ghana Limited (GFGL) Tarkwa Mine TSFs show that WAD and total cyanides for the two dams increased significantly with increase in depth of decant which is inversely proportional to pH of decant pond. Significantly, metal concentrations (Na, Fe, Cu and Mn) increased proportionally with depth in the decant pond and consistent metals identified in ore geochemistry and underdrainage sump.

Keywords Cyanide Decay, Geochemical, Total Dissove Solids (TDS), Weak Acid Dissociable (WAD), Tailings Storage Facility (TSF)

Introduction

Cyanide concentrations in the decant ponds vary with depth, season and temperature varies with respect to depth of burial and distance from the discharge point. Total cyanide is independent of depth although constraints like time lag may affect it, but that cannot be said about Weak Acid Dissociable (WAD) and free cyanide. The possibility that cyanide salt and complexes occur at depth is high and under anaerobic conditions in non-sterilized soil mediums it is converted to nitrates with the potential to migrate into the groundwater system. Free cyanide concentrations decay with increased depth of burial and this makes migration into the groundwater system difficult. Metals and other trace element concentrations may vary with depth due to association with cyanide. This study is to assess the decay and concentration of cyanide and metals at depth variations in the two tailings dams at GFGL and the associated impact on the immediate environment.

Study Area

The study area is the operating tailings dams of GFGL. It is located in the Western Region of Ghana at latitude 5°15′N and longitude 2°00′W. Tarkwaian formation in the concession is mined as ore and geological tests on the ore proves that there is no potential for acid generation due to high level of neutralizing minerals present in the rocks (Arthur *et al.* 2004). Gold is extracted from crushed ore using the cyanidation technique via a Carbon in Leach (CIL) plant and a heap leach facility. This generates on the average 900,000 m^3 of tailings every month and is deposited in two clay lined TSF's (TSF 1 and TSF 2). The TSF site is generally underlain by Huni Sandstone with the south western boundary of the site by a ridge of Tarkwa Phyllite. In addition more recent Quaternary deposits formed by the fluvial system in the area overlie these.

Methodology

Sampling of the two TSF was carried out in three areas comprising the two supernatant ponds (decants), three underdrainage sumps which collects seepages from the network of underdrainage pipes, slurry from spigotting points along the discharge pipeline. Profile depth sampling was carried out in the decant ponds on the TSF 1 and 2 respectively. Sampling regimes started from July 2010 to July 2011. Sampling locations were selected at random and accessed by a canoe. The depth sampler was used at 1.0 m interval and the contents emptied into a dark (500 mL) and 1000 mL sterilized sample bottles. A total of eighty-nine samples were taken at thirteen locations in the TSFs.

Results and Discussion

Cyanide Decay with Depth

According to Botz *et al.* (1999), cyanidation of tailings disposed in a surface impoundment experiences a loss of cyanide due to natural degradation, frequently reducing the cyanide concentration to very low levels. Quantifying cyanide losses in terms of pond geometry, local weather conditions and feed solution chemistry has been largely empirical though in many cases mining operations rely on surface impoundments to reduce cyanide to below an internally regulated concentration or an effluent limitation. Cyanide, depending on the form and concentration tends to react readily with many other chemical elements and molecules to form, as a minimum, hundreds of different compounds (Flynn and Haslem 1995). Several of these compounds break down and are generally less toxic than the original cyanide. However, these compounds are known to be toxic to aquatic organisms, and persist in the environment for significant periods of time. In addition, there is evidence that some forms of these compounds can be accumulated in plant tissues (Eisler 1991) and may be chronically toxic to aquatic life; in fishes, micro vertebrates and invertebrates (Heming 1989). WAD and total cyanide levels at two monitoring locations in the decant ponds of TSF1 and TSF 2 increased significantly over depth of pond water (Fig. 1).

The UNEP Baia Mare report (Moran 2002) indicates that elevated total cyanide concentrations were detected for hundreds of kilometers downstream, for up to four weeks after the Baia Mare spill. The report stated total cyanide in the Tisza River did not decompose quickly as expected or from studies carried out to date.

WAD and total cyanides for the two sampling location increased significantly with increase in depth of decant which is inversely proportional to pH of decant pond. pH of samples ranged from 9.5 to 10.0 for both sampling locations. According to Lighthall *et al.* (1987), the rate of natural degradation is a function of cyanide type and concentration, pH, temperature, bacteria, sunlight, aeration and pond conditions, such as area, depth, turbidity, turbulence and retention time. At sampling location PBM (TSF1), alkalinity increased from 9.8 to 9.9 over a depth of 5 m of decant pond and total cyanide increased proportionally from 0.36 mg/L to 1.11 mg/L. A similar trend was documented for WAD cyanide concentrations. Higher decant pond depth (10 m) monitored at location PAM (TSF2) with alkalinity increasing from 9.4 at 1 m to 10.0 at 7 m and declined to 9.9 at 10 m; returned elevated Total (from 0.1 mg/L to 0.28 mg/L) and Wad (0.01 to 0.17 mg/L) cyanides with increase in depth. Toxicity cyanide calculated from the difference in Total and WAD cyanide ranges from 0.04 to 0.16 mg/L and there is clear indication from

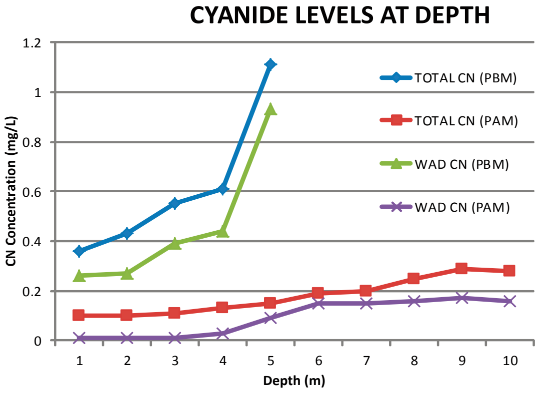

Fig. 1 *Total and WAD Cyanide Levels at Depth*

the sampling regime that cyanide concentrations increase with increase in depth which could be attributed to dissociation of cyanide metal complexes. Many aspects of the geochemical behavior and toxicity of complex mixtures such as tailings are poorly known. For example, mining literature frequently states that cyanide naturally breaks down quickly in the presence of sunlight, into relatively harmless, non-toxic substances (Botz *et al.* 1999).

Practically, there is a restriction on the depth of light penetration in the tailings decant pond due to high turbidity. According to Moran (2002), studies conducted over the last twenty years by various authors represent useful discussion on the presence and toxicity of cyanide forms on the environment. A report sponsored by the Mining and Cyanide Manufacturing Industries states: "Since cyanide oxidizes when exposed to air or other oxidants, it decomposes and does not persist. While it is a deadly poison when ingested in a sufficiently high dose, it does not give rise to chronic health or environmental problems when present in low concentrations" (Logsdon *et al.* 1999). This statement is misleading and presents a falsely benign picture.

Metals, Trace Elements, Physicals and Anions Concentration

According to Clarke *et al.* (1987), cyanide species may be considered to act chronically on the environment in three distinct ways. The first is to produce a direct and ongoing minor acute poisoning, resulting in chronic symptoms, including anomalies in the nervous system of many of the higher organisms. The second is by the formation as well as the action of its compound thiocyanate in interfering with certain common metabolic pathways. Lastly, because cyanide (and thiocyanate) is capable of complexing metals contained in natural water supplies, organisms using this water could either be subjected to toxic doses of certain metals or deficiencies of others. The surplus could arise from metals being retained in solution in assimilable complexes (*e.g.* Cu), while deficiencies in naturally occurring trace metals could result from the retention of these in non-assimilable complexes (*e.g.* Fe, Cu, Mn, Mg). Variation of average pH with depth in the decant ponds is insignificant and pond ranges from 10.0 at 1 m to 9.9 at depth of 8 m as shown in Table 1. Average conductivity values increased with depth implying elevated Total Dissolved Solids (TDS) as a result of metal-complex dissociation which releases metals into solution corresponding to WAD and total cyanide speciation levels at depth.

In analyzing the concentration of metals and trace elements in the decant pond of the tailings dams, reference was made to chemical and mineralogical characterization carried out on the tailings and whole ore samples (Anon 2011). Averaged multi-element analysis of decant pond at various depths shows variations with concentrations in the supernatant pond and tailings slurry at the spigoting points and significant metal/trace metals are Ca, Mg, Fe, Cu, Na, Mn and K (Table 2). Significant elements identified conform to both ore and tailings chemistry and geochemistry respectively.

Averaged Na, Mn, Ca, Fe, Cu and Mg concentrations increased significantly with increase in depth whiles K decreased (Figs. 2 and 3). Comparing the concentration of these elements in the decant pond to levels in the su-

Depth (m)	pH	EC (µS/cm)	TDS (mg/L)	NH_3 (mg/L)	SO_4 (mg/L)	PO_4 (mg/L)	Cl (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)
1	10.0	1112	744	0.14	33.40	0.62	26.22	171.44	128.22
2	10.0	1112	743	0.11	33.80	0.71	25.78	169.28	131.07
3	10.1	1154	776	0.13	36.60	0.56	26.74	167.22	134.94
4	10.0	1153	776	0.07	34.80	0.58	26.32	176.22	129.49
5	10.1	1154	779	0.06	34.80	0.67	22.75	221.70	116.63
6	10.1	1167	787	0.15	34.80	0.62	25.80	160.40	133.17
7	10.1	1170	788	0.10	37.67	0.66	27.80	177.63	141.87
8	9.9	1169	759	0.16	36.50	0.77	22.00	216.65	115.08

Table 1 *Mean Physical and Anion Levels in Decant Pond of TSF 1 and 2*

Depth m	Ca mg/l	Mg mg/l	Fe mg/l	Cu mg/l	Ni mg/l	Mn mg/l	Pb mg/l	Zn mg/l	Na mg/l	K mg/l	Ag mg/l	As mg/l
1	10.4	0.40	1.66	0.67	0.02	0.48	0.09	0.03	177.6	23.34	0.01	0.03
2	10.8	0.40	1.50	0.70	0.03	0.41	0.11	0.03	178.2	24.66	0.02	0.03
3	10.7	0.39	1.91	0.81	<0.02	0.57	0.17	0.02	180.4	20.84	0.02	0.03
4	10.6	0.43	1.92	0.79	<0.02	0.55	0.27	0.02	180.9	19.00	0.01	0.03
5	10.3	0.41	2.16	0.84	<0.02	0.72	0.10	0.02	183.3	20.75	0.01	0.03
6	10.0	0.43	2.15	0.83	<0.02	0.73	0.15	0.02	184.3	20.68	0.01	0.03
7	11.3	0.53	2.37	0.83	<0.02	0.86	0.16	0.02	184.2	20.73	0.02	0.03
8	13.3	0.68	2.50	1.01	<0.02	1.29	0.17	0.06	185.5	22.12	0.01	0.04
SP	10.3	0.14	0.58	0.19	0.02	1.13	0.02	0.09	169.0	20.09	0.02	0.04
T1	12.5	0.15	0.75	0.96	0.03	1.25	0.02	0.01	210.8	15.07	0.02	0.04
T2	11.4	0.12	0.90	0.92	0.03	1.30	0.02	0.03	211.8	19.61	0.02	0.03

Note; SP = Supernatant Pond, T1 = Tailings Slurry from TSF 1, T2 = Tailings Slurry from TSF 2

Table 2 *Mean Metal and Trace Metal Concentrations in Decant Pond of TSF 1 and 2, Supernatant Ponds and Underdrainages for TSF1 and TSF2*

Mineral SQ-XRD	Chemical Formula	WT (%)
Quartz	SiO_2	87.96
Albite	$Na(AlSi_3O_8)$	4.74
Talc	$Mg_3(Si_4O_{10})(OH)_2$	2.65
Hematite	Fe_2O_3	2.57
Clinochlore/Chlorite	$Mg_2Al_3(Si_3Al)O_{10}(O)_e$	1.34
Annite	$KFe_3AlSi_3O_{10}(OH)_2$	0.74

Table 3 *Ore Geochemistry at GFGL*

pernatant pond (supernatant tower), which was 22 m deep at the time of sampling and at the same level as the underdrainage channels. Metals identified in the decant pond, underdrainage sump and tailings slurry were Na and Mg with trace elements being Fe, Cu, Mn, As, Ni, Zn and Cr, whiles alkali metals identified were Ca and K. The average concentrations of Na, Mg, Mn, Fe, Ca, Cu and K increase with depth whiles Zn, As, Ni and Cr increased at 7 m (Figs. 2 and 3) The tailings geochemistry indicated that silica was dominant as well as the presence of Ca, Mg, Fe, Cu, Na, Mn and K. Significant metals and trace elements identified in the in the decant pond were consistent with that of ore geochemistry (Table 3), tailings and in the underdrainage system.

Conclusion and Recommendations

It has been reported in the literature that free cyanide in nature, breaks down completely to CO_2 or nitrated compounds, which is not often the case as demonstrated in this study. Compounds of metals do form and resist decomposition in natural environments for long periods of time. Cyanide compounds assumed to be "destroyed" or "not-present" are in fact present and continually emit harmfµL/toxic components.

Both WAD and total cyanide concentrations increase significantly with increase in depth in the decant pond and consistent in both TSF 1 and 2. Total cyanide ranged from 0.1 mg/L to 1.11 mg/L whiles WAD cyanide concentrations ranged from 0.01 mg/L to 0.93 mg/L.

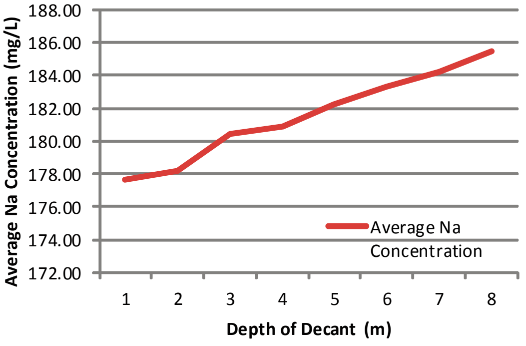

Fig. 2 *Na Concentrations with Depth*

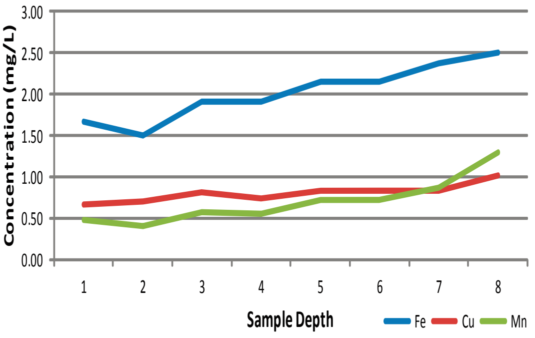

Fig. 3 *Mg Concentrations with Depth*

pH in the decant pond, tailings slurry and underdrainage supernatant tower remains alkaline with values ranging from 9.4 to 10.6. Comparing this to the natural pH of groundwater (4.5 to 5.6) in the study area, an unsaturated interface is created which could lead to water movement from the facility into aquifers.

Ore and tailings geochemistry indicates that silica is dominant and the presence of Ca, Mg, Fe, Cu, Na, Mn and K in the tailings dam. Significant metals and trace elements from laboratory analysis is consistent in the four components of the study; ore, tailings slurry, decant pond and in the underdrainage system. Average metal concentrations increased in depth of decant pond. Significant increased in average concentrations of Ni, Zn, Cr and As were recorded at depths exceeding 7 m in the decant pond was recorded whiles Ag concentrations decreased over the same depth of decant pond. It can be concluded from the study that Ag complexes at depth due to reduced concentration at high depths of the decant pond

References

Botz MM, Mudder TI (1999) Modeling of cyanide degradation in tailings impoundments, SME Annual Meeting, March 1–3, 1999, Denver, Colorado.

Clarke MC, Linkson PB (1987) The Toxicity and Degradation of Cyanide in Mine Tailings. Mining and Environment, A Professional Approach, National Conference, Brisbane. Pp 87 -93.

Eisler R (1991) Cyanide Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review: Contaminant Hazard Review report 23, U. S. Dept. Interior, Fish and Wildlife Service, Pp. 55.

Flynn, C. M. and S. M. Haslem 1995, Cyanide Chemistry—Precious Metals Processing and Waste Treatment: U. S. Bur. Of Mines Information Circular 9429.

Heming, TA, Blumhagen K A (1989) Factors Influencing Thiocyanate Toxicity in Rainbow Trout Salmo gairdneri: Bull. Environ. Contam. Toxicol. V. 43, P363–369.

Logsdon MJ, Hagelstein K, Mudder TI (1999) The Management of Cyanide in Gold Extraction: International Council on Metals and the Environment, Ottawa, Canada.

Lighthall PC, Bruce IG, McLeod HN (1987) Tailings Management for Cyanide Leach Gold Plant. Klohn Leonoff Ltd, Richmond, British Columbia.

Moran RE (2002) De-Coding Cyanide, An Assessment of Gaps in Cyanide Regulation at Mines. A Submission to the European Union and the United Nations Environmental Programme.