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A Study of Residual Cyanides and Potential Stabilities in Tailings Storage Facility of Gold Mining Operation

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Abstract

The study aimed to investigate residual cyanides and their potential stabilities in tailings from a gold processing plant deposited in the Tailings Storage Facility (TSF) of a gold mining site. For this purpose, several samples of tailings were taken from the recently abandoned TSF to a depth of 2.5 meters, representing 1 to 2 years old tailings. The samples were analyzed for pH, metals, residual cyanides, and Net Acid Generation Test (NAG test). The results showed that, in all samples, pH values were neutral to slightly alkaline. Fe concentrations were relatively high (22,800-35,000 mg/kg) indicating that Fe can readily react with free cyanide (CN^-) to form iron cyanide complexes (strong metal cyanide complexes). The residual cyanide concentration in tailings was found to be very low; free cyanide (CN_{Free}), weak acid dissociable cyanide (CN_{WAD}), strong acid dissociable cyanide (CN_{SAD}) and total cyanide (CN_T) were in the range of 0.16-0.64, 0.37-1.06, 1.96-3.89 and 2.33-4.95 mg/kg, respectively. Cyanides in the tailings were predominantly strong metal cyanide complexes being more stable to dissociate. Total cyanide (CN_T) concentration was quite low compared with Thailand's environmental regulations for soil quality standards and were environmentally insignificant. The NAG test for all samples revealed that NAG pH was in the range of 5.02-6.10 and NAG was in the range of 0.08-0.31 kg H_2SO_4 t^{-1} indicating all samples have low or non-acid forming potentials. The findings indicated a potential to form a high proportion of strong metal cyanide complexes in the tailings, which is difficult to dissociate and release high toxic cyanide to the environment.

Keywords: Cyanide; gold processing tailings; net acid generation test; natural cyanide attenuation; residual cyanides

Introduction

Cyanide is normally used in gold industry to extract elemental gold from ores in the extraction process. After extraction, residual cyanides are normally treated and discharged to a Tailings Storage Facility (TSF); however, any residual free cyanide may contaminate the environment if not properly treated and contained. Cyanide can exist in various forms and its toxicity relates to its stability to dissociation. Cyanide in gold mill effluents can be divided into four categories [1]: (1) free cyanide in the form of HCN and CN^-; (2) readily soluble cyanide (e.g. NaCN); (3) weak acid dissociable cyanide; and (4) strong acid dissociable cyanide. Free cyanide in the forms of HCN and CN^- are considered to be the most toxic form [2]. Free cyanide is very unstable at pH <9.24 at 25℃. The readily soluble cyanides can dissolve in water and dissociate into free cyanide ions and may react to form insoluble compounds such as CuCN. Weak acid dissociable cyanide is derived from the reaction of CN^- with transition metals (e.g. Cd, Zn, Ag, Cu, Ni, Hg) to form weak complexes; these are less toxic than free cyanide and can dissociate under weakly acidic pH conditions (4<pH<6); hence, unstable with decreasing pH [3]. Strong acid dissociable cyanide is a result of the reaction of CN^- ions with heavy metals (e.g. Co, Pt, Au, Pd, Fe). The resulting stable complexes are less toxic, dissociating only under strongly acidic pH conditions (pH<2) [3]. Most commonly occurring in the environment are iron cyanide complexes such as ferro-cyanide [$Fe(CN_6)^{4-}$] and ferric-cyanide [$Fe(CN_6)^{3-}$]. It was demonstrated that ferro-cyanide and ferric-cyanide complexes are quite stable in the dark but decompose very rapidly when exposed to daylight, when they are considered to be as toxic as free cyanide [4].

Although tailings may be contaminated with cyanide, natural cyanide attenuation processes reduce concentrations by volatilization, biodegradation (transformation of cyanides to less toxic forms), adsorption, precipitation and the effect of sunlight [2]. In order to determine the stabilities of residual cyanides in the TSF, an understanding of the fate of cyanide in tailings is important. The purpose of this study is therefore to determine tailings characteristics (including pH, metals, and residual cyanides) and Net Acid Generation potential in order to assess the stability of cyanide and cyanide complexes in releasing free cyanide to the environment, in tailings deposited in TSF over a period of time.

Materials and Methods

1) Tailings sampling

Tailing samples were collected from the abandoned TSF-1 of a gold mining operation in Phichit Province, northern Thailand. The TSF was closed on reaching its full capacity about 2 years ago; therefore, tailings discharged around 1–2 years before TSF closure was sampled. The sampling was carried out in February 2014. Using a hand auger for 2.5 m. sampling and a thin wall shelby tube for 0.2 m. sampling were used to collect samples from the outer perimeter of TSF inwards to the center of the pond. Five locations were drilled and 2 kg samples taken at depths of 0.2 and 2.5 m. interval as shown in Figure 1. There were a total of 10 samples. 1.5 kg of each sample was placed directly in zip-lock bags for metal analysis of metals and NAG test, while the remaining 0.5 kg sample was placed directly in amber glass bottles, sealed with parafilm and immediately stored in the dark at 4℃ for analysis of pH and residual cyanides.

2) Tailings characterization

Tailings samples were tested for pH according to US EPA Standard Method 9045. The samples were digested with HNO_3, $HClO_4$, HF, and HCl prior to ICP-ES analysis for metals including Ni, Cu, Zn, Co and Fe. APHA-AWWA-WEF (22nd edition 2012, 4500 CN^--E) which is a standard method for examination of water and waste water, was used for analysis of residual cyanides in the sample, including free cyanide (CN_{Free}), weak acid dissociable cyanide (CN_{WAD}) and total cyanide (CN_T). Strong acid dissociable cyanide (CN_{SAD}) can be determined by calculation of the difference between CN_T and CN_{WAD} [5] according to equation (1).

$$CN_{SAD} = CN_T - CN_{WAD} \qquad (1)$$

*CN_{Free} was detected and includes in CN_{WAD} or CN_{Free} was a subset unit of CN_{WAD}.

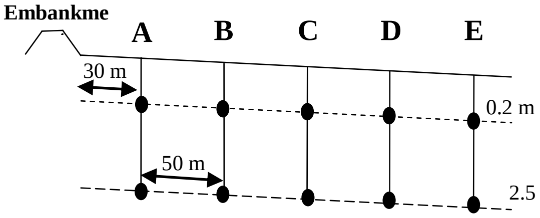

Figure 1 Sampling locations with transects

3) Net Acid Generation Test (NAG Test)

The samples were prepared by grinding to a particle size <75 µm. The NAG test was carried out by adding 250 ml of 15% H_2O_2 in 2.5 g of sample, mixing and then the sample was placed inside a fume hood for 24 hrs. After 24 hrs, the sample was boiled for 2 hrs to remove excess H_2O_2 and encourage release of inherent neutralizing capacity [6]. The sample was put aside to cool to room temperature. Sample solutions were then filtered with filter paper No.40 and "NAG pH" was measured in 50 ml sample solution using a pH meter. Then, 50 ml of the sample solution was titrated with NaOH standard solution until reaching a pH of 4.5 or 7. Table 1 shows NaOH concentrations used for the titration.

Table 1 NaOH concentration used for titration

NAG pH	pH	Used NaOH concentration
NAG pH < 2	4.5	0.5 N
2 < NAG pH > 4.5	7	0.1 N
2 < NAG pH < 4.5	4.5	0.1 N

The "NAG" was calculated in term of kg H_2SO_4 t^{-1} [7, 8, 9] and the calculation of NAG followed equation (2) [10]. The cut-off NAG pH for prediction of acid forming potential was divided into 3 ranges [9] as shown in Table 2.

$$NAG = 49 \times V \times M/W \qquad (2)$$

Whereas; V = Volume of NaOH (ml)
M = Mole of NaOH (mole/l)
W = Weight of sample (g)

Table 2 Cut-off prediction of acid forming potentials by NAG Test

NAG pH	Calculated NAG	Predicted quality
≥ 5	0 - 2	Low or nonacid forming
2.5 < NAG pH < 5	2 - 50	Moderate acid forming
≤ 2.5	> 50	High acid forming

Results and Discussion

1) Tailings characterizations

1.1) pH

pH values of all tailing samples from sampling location A to E were neutral to slightly alkaline (pH 7.2-8.4) as shown in Figure 2. In CIP/CIL gold extraction process (Carbon In Pulp/Carbon In Leach), the pH is normally maintained at approximate 10.5 to prevent volatilization of $HCN_{(g)}$ and the discharged slurries to TSF are already more alkaline. Over time, pH of the tailings will gradually decrease during rain water infiltration and CO_2 uptake from atmosphere [11, 12, 1, 13]. The pH values measured at the shallower samples at 0.2 m depth (pH 7.56) were slightly lower than the values of the deeper samples at 2.5 m depth (pH 8.28). This is due to an influence of CO_2 dissolved in rain water to become H_2CO_3 affecting pH reduction [14]. Hence, the pH of tailings nearer to the surface would be lower than the deeper tailings.

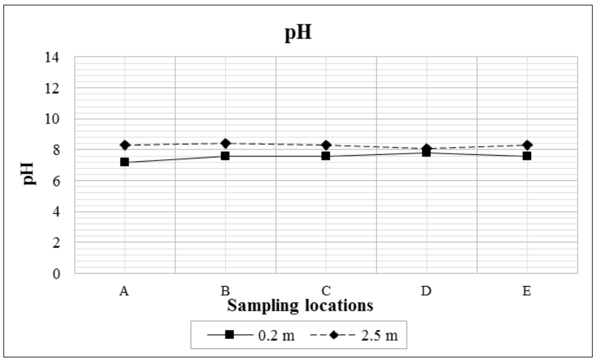

Figure 2 pH with the depth of tailings at sampling locations.

1.2) Metals

Heavy metal concentrations (Ni, Cu, Zn, Co and Fe) in tailings samples are presented in Table 3. Distribution of the metals found in tailings is highly variable in composition and rather labile depending on processing technique; its composition may also change over time [14]. Concentrations of most metals at 0.2 m sampling locations tend to be lower than the concentrations at 2.5 m sampling locations, except for Zn, because rainfall tends to dilute the concentration of metals on tailings close to the surface of TSF (0.2 m). When tailings are discharged from the spigot forming a deposition, the slurry flows towards the center of the TSF; fine particles flow into the central pond and precipitate to form sediments; metals are then adsorbed onto the sediments. Thus, concentration of metals at sampling location E was found to be the highest (Figure 3 shows only Fe concentration, but other metals show the same trend). This finding is in line with the results of E. B. Nsimba's study (2009) [15].

According to the results shown in Table 3, Fe concentration was highest both at 0.2 and 2.5 m (22,800 to 35,000 mg/kg) because it is a major composition of soil and present at high levels in the environment. The result suggested that high concentrations of Fe in tailings could react with CN^- to form iron cyanide complexes (strong acid dissociable cyanide, strong metal cyanide complexes). While Co was found in very low concentrations, it can also react with CN^- to form strong complexes. Others metals such as Ni, Cu, and Zn were found at very low concentrations which also produce relatively unstable forms of complex when react with CN^-.

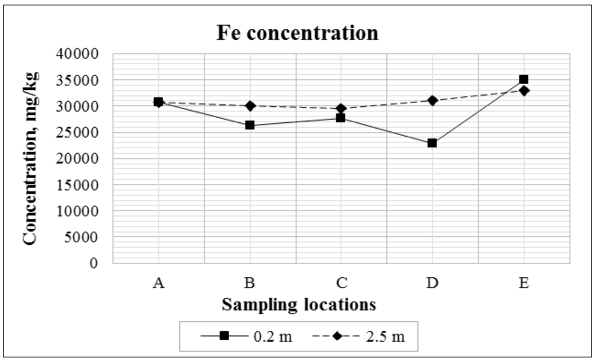

Figure 3 Iron concentration varies with sampling locations and depths.

1.3) Residual cyanides

From the experimental results, it was observed that cyanide concentrations increased in the centre of the TSF (sampling location E), as was found for concentration of metals. Cyanide can be adsorbed weakly on common soil and sediment components.[3] From Figure 4, CN_{Free} concentrations at depths of 0.2 and 2.5 m are very low at all locations, while CN_{SAD} tends to increase with proximity to the centre of the TSF, in line with the results from E. B. Nsimba (2009).[15] At sampling location D (at 0.2 m depth), concentrations were found to be 0.64, 1.06, 3.89, and 4.95 mg/kg, respecttively, where all cyanide concentrations reach the maximum. Average cyanide concentrations at 0.2 m depth (0.44, 0.76, 3.15 and 3.90 respectively) were found to be higher than the concen- trations at 2.5 m depth (0.35, 0.63, 2.83 and 3.46 res-pectively). This could be due to the fact that the tailings at 0.2 m depth were produced more recently than tailings at 2.5 m depth, which had undergone a natural cyanide attenuation pro-cess over a longer period.

All samples were found to have very low concentration of CN_{Free} (0.16-0.64 mg/kg). Over time, CN_{Free} gradually decreases because of natural cyanide attenuation by volatilization (major process) at pH<9.24, but pH in all samples were found in a range 7.2-8.4 indicating that CN_{Free} in TSF can volatile easily and undergo biodegradation from which CN_{Free} can be rapidly oxidized by aerobic microorganisms to NH_3 and CO_2. A study by K. Oudjehani (2002) [16] demonstrated high potential of indigenous microorganisms to both directly and indirectly mineralize CN_{Free} in fresh and aged tailings of gold mine, especially when cyanide presents in reactive forms (readily soluble compounds and weak metal cyanide complexes). CN_{WAD} concentration was found to be very low, ranging from 0.37–1.06 mg/kg, which may be a result of the natural cyanide attenuation process such as volatilization and formation of complexes in aged tailings deposited in TSF for a long time [17, 16]. There is also a possibility that CN_{WAD} in tailings could be decomposed through microbial action under aerobic and mildly acidic conditions, releasing free cyanide and reducing concentration in the tailings. Calculated CN_{SAD} from CN_T and CN_{WAD} concentration is in a range 1.96-3.89 mg/kg which is higher than the concentration of CN_{Free} and CN_{WAD}, indicating the predominance of strong complexes in the tailings. The results of S. Laha and R. G. Luthy's study (1991) [18] indicated that due to its resistance to biodegradation, CN_{SAD} is stable and pH of tailings is normally high, preventing dissociation to release free cyanide in this pH range. CN_T concentration observed is in the range of 2.33-4.95 mg/kg which is below the standard of residual cyanides concentration in term of CN_T specified in Thai Environmental Regulations of Soil Quality Standards, Notification of National Environmental Board No. 25, B.E. 2547 (2004) issued under the Enhancement and Conservation of National Environmental Quality Act B.E. 2535 (1992) [19] as shown in Table 4.

Table 3 Metal concentrations at various sampling points

Sampling locations with depth (m)	Metals concentration (mg/kg)				
	Ni	Cu	Zn	Co	Fe
$A_{(0.2)}$	10	51	69	8	30700
$A_{(2.5)}$	9	49	56	7	30700
$B_{(0.2)}$	8	44	78	5	26200
$B_{(2.5)}$	9	49	57	6	30100
$C_{(0.2)}$	8	46	74	6	27700
$C_{(2.5)}$	8	49	66	6	29600
$D_{(0.2)}$	8	36	53	4	22800
$D_{(2.5)}$	11	53	52	6	31100
$E_{(0.2)}$	9	54	69	7	35000
$E_{(2.5)}$	11	56	65	8	33000
Average 0.2 m	8.6	46.2	68.6	6.0	28480
Average 2.5 m	9.6	51.2	59.2	6.6	30900

Table 4 Soil quality standards

Soil quality standards	Cyanide and cyanide compounds (mg/kg)
1. Soil Quality Standards for Habitat and Agriculture	< 11
2. Soil Quality Standard for Other Purposes	< 35

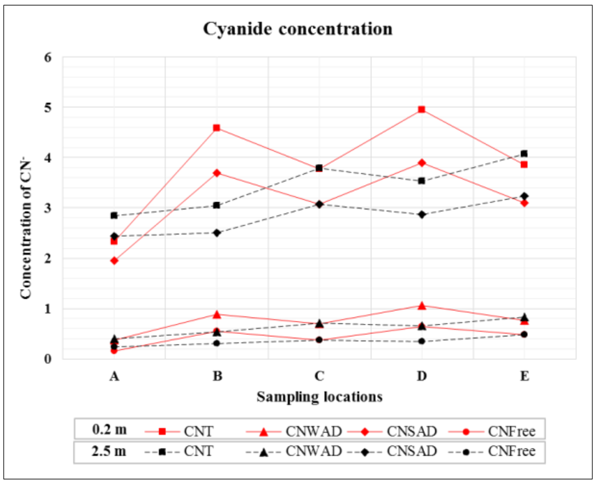

Figure 4 Cyanide concentrations at various sampling locations and depths

2) Net Acid Generation (NAG) Test

NAG pH values in the range of 5.02–6.10 and NAG in the range of 0.08–0.31 kg H_2SO_4 t^{-1} were observed in all samples. The NAG pH was less than the pH value because of the sulphur content from pyrite or sulphide ores in the tailings. After adding H_2O_2 to oxidize organic matter and sulphur in the sample, the pH decreases (NAG pH). From the experimental results, this NAG pH can represent a cut-off according to Table 2 and a graph between NAG pH and calculated NAG is shown in Figure 5. The graph indicates that all samples have low to non-acid forming potentials which suggests that strong metal cyanide complexes presented in the tailings and these strong metal cyanide complexes cannot dissociate to a significant extent because there is potential to generate H_2SO_4 from sulphide ores to reduce pH to a level favorable to dissociation of strong complexes.

Conclusions

The results demonstrate the stability of residual cyanides and low potential of cyanide to be released into the environment, especially tailings deposited in TSF for a period of time. Strong metal cyanide complexes especially iron cyanide complexes are predominantly presented in the tailings although there are lesser proportion of CN_{Free} and CN_{WAD} which are unstable forms because they can volatilize and undergo biodegradation through natural cyanide attenuation processes. The pH of the tailings is neutral to slightly alkaline which is unfavourable to strong cyanide complexes dissociation. From the results of NAG test, tailings have a low to non-acid forming potential to generate high acidity to dissociate strong metal cyanide complexes and release free cyanide, which is its most toxic form. CN_T concentrations in tailings are very low compared to Thai Environmental Regulations of Soil Quality Standards, indicating that it is not environmentally significant.

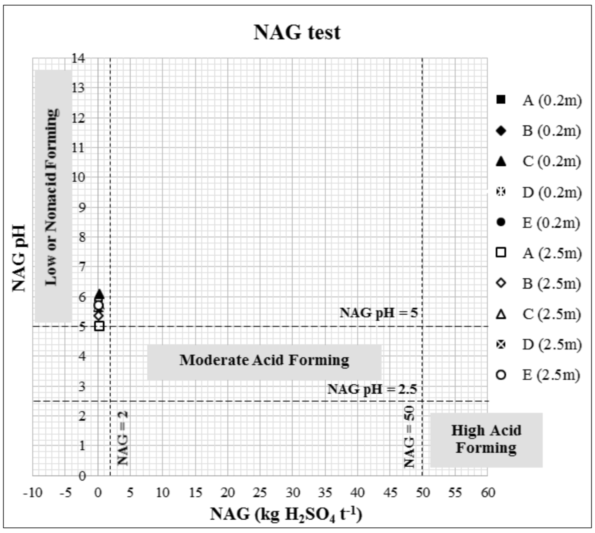

Figure 5 Results of NAG test.

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