Effects of Capping and Uncapping of Closed Tailings Dam Site on Soil pH, Free Cyanide and Some Heavy Metals: Case Study of a Ghanaian Gold Mine

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Abstract

Large scale gold mining in Ghana has intensified during the beginning of the 20th century. However, the development of environmental legislation and effective monitoring of the process to address environmental impacts of gold mining activities in the country has been slow. The use of cyanide compounds during gold processing is extensive. Consequently, mining operations and their waste disposal methods constitute major source of pollution by cyanide and other heavy metals in mining communities in Ghana. Tailings samples were taken from capped tailings sites, uncapped (solidified tailings) sites and a non-mined soil at depths of 0–15 and 15–30 cm. The randomised complete block design with three replications was used. The pH (soil : water-1 : 2.5), free cyanide, water soluble and EDTA-extractable heavy metals were determined. The levels of Cu and Zn in capped and solidified tailings were within permissible levels, while the concentration of EDTA-extractable As was above internationally accepted maximum limit. The concentrations of EDTA-extractable As and also water soluble Pb and As, at the 0–15 cm depth, were in the following decreasing order: solidified tailings > capped tailings > non-mined soil ($P < 0.05$). The arsenate of the solidified tailings was possibly strongly adsorbed by Fe oxides of the laterite of the capped tailings. The capping of tailings led to significantly lower concentrations of free cyanide and EDTA-extractable As (0.4–0.43 mg kg^{-1}) compared to the solidified tailing (1.3 mg kg^{-1}) at the 0–15 cm depth ($P < 0.05$). The lower free cyanide levels could be attributed to the formation of strong complexes of ferricyanide [Fe (CN)$_{63}^{-}$] and ferrocyanide [Fe (CN)$_{64}^{-}$]. Capping of mining waste with laterite could not reduce cyanide to levels per Canadian standards for agricultural land.

Introduction

Prospecting for gold is a major activity in Ghana and modern gold mining has occurred on a large-scale since the beginning of the 20th century, and the mineral sector has been a major recipient of foreign direct investment (ICMM, 2007). However, developing desired environmental legislation and environmental monitoring to address the inevitable environmental impacts of mining have not been comparable with the zeal that supported policy reforms to attract foreign investments to the mining sector (Awudi, 2002). In Ghana, the extensive use of cyanide compounds in the extraction of gold by more than 13 large-scale gold mines that employ cyanide heap-leach processes is a major source of toxic contaminants to the environment (Khodadadi *et al.*, 2005; Awudi, 2002; Patil & Paknikar, 2000). Mining operations and waste disposal methods, therefore, constitute major causes of pollution by cyanide and heavy metals, and other environmental problems (Chakraborty & Choudhury, 2009).

Soil contamination has been identified as one of the main threats to soil quality (European Commission, 2006a). Governmental and regional institutions are increasingly giving attention to issues of soil pollution (European Commission, 2006b). Subsequently, initiatives have started to limit and prevent further soil degradation and to examine applicable remediation measures (Poggio *et al.*, 2008). The Ghana Environmental Protection Agency (EPA) has, unfortunately, concentrated on monitoring the levels of heavy metals and other pollutants in water (water quality) to the detriment of monitoring soil quality in mining environments.

Although there has been extensive reclamation of lands used for mining and the containment of heavy metals at tailings sites, documentation of these activities is inadequate. The scientific approach in assessing the effectiveness of the different soil/tailings decontamination methods is lacking. No definite scientific conclusions can be drawn based on records of the routine study without any control treatments and replications. The capping of contaminated tailings with lateritic soil does not remove the contaminants from the soil (Kertulis-Tartar *et al.*, 2006). This is, however, the main method of remediating heavy metals contained in tailings sites at AngloGold Ashanti, Obuasi mine. The objective of the study was, therefore, to determine the extent of decontamination of free cyanide and some heavy metals and also changes in the *p*H of capped tailings compared to uncapped tailings and non-mined site.

Materials and methods

Site description

The study was conducted at a closed tailings dam site, located 200 km north-west of Accra in Ghana, at latitude 6°12'0" N and longitude 1°40'0" W (Maplandia, 2005). The gold deposits occur along a zone of intensive shearing and faulting within the Precambrian greenstones. The mineral deposits are of two types, comprising of quartz veins containing high-grade free gold and the main sulphide ore in which narrow veins contain gold trapped within arseno-pyrite. The soils of the area are classified as Ferralsols (FAO and IUSS, 2006). The study area in the Ashanti Region lies within the forest zone of Ghana. It consists of vast areas of primary forest of *Triplochiton-Celtis* association and has a bimodal rainfall pattern. The average rainfall is 1250 mm per annum. The average maximum and minimum temperatures are 30 and 20 °C, respectively.

Soil/tailing sampling

Samples of soils/tailings were taken from four sites. Three of the sites were within the operational areas of the mine under study. The non-mined (control) site, which constituted the fourth site within the mines concession, but not yet mined, was included for the comparison on the extent of contamination by free cyanide and some heavy metals. These sites were capped tailings dam, uncapped tailings dam and non-mined soil. Soils were sampled at depths of 0–15 and 0–30 cm from the uncapped solidified tailings and the control sites. At the capped tailings site, the refilled topsoil was predominantly made up of laterite.

The area sampled for each of the sites was 1 ha. The zig-zag pattern of sampling was adopted, and 30 soil core samples were taken from each site and bulked. The quartering technique was used to obtain a soil composite of approximately 500 g for subsequent preparation and the preliminary

analyses to establish the baseline properties of the soil. Three replications of samples were taken for each soil/tailing and at each of the 0–15 and 0–15 cm depths.

Soil preparation

The composite soil samples were air-dried. The soil clods were crushed with the hand and pebbles and other foreign materials removed. The soils were stirred daily to hasten the drying process. The samples were then passed through a 2-mm nylon mesh. A sub-sample from the < 2 mm fraction was ground with a pestle and mortar, and passed

through a 0.15-mm sieve for the determination of As, Pb, Cd, Fe, Zn and Cu. The values of the background soil properties of the study sites are presented in Table 1 and Table 2.

Determination of soil physical properties

Some composite soil samples (n = 3) were taken at the 0–15 and 15–30 cm depths to determine the baseline properties of the soil. The physical properties of the soil were determined using the procedures described by Anderson & Ingram (1993). The bulk density was measured as a ratio of the mass

TABLE 1
Some properties of soils (n = 3) at the 0 to 15-cm depth in the study area

| Soil property | Site | | | |
	Non- mined	Capped tailings I	Capped tailings II	Solidified tailings
Organic carbon (%)	2.13 (0.09)*	0.63 (0.03)	0.55 (0.02)	1.02 (0.04)
Total N (%)	0.19 (0.03)	0.06 (0.0)	0.06 (0.0)	0.10 (0.01)
C: N ratio	11.21 (1.03)	10.50 (0.98)	9.16 (0.7)	10.20 (0.03)
pH (1: 2.5 - soil: water)	5.10 (0.03)	6.79 (0.07)	6.70 (0.07)	7.22 (0.12)
Extractable P - Bray I (mg kg^{-1})	6.58 (0.08)	16.57 (0.14)	4.17 (0.07)	1.53 (0.02)
Exchangeable cations				
Ca^{2+} (cmol$_c$ kg^{-1})	3.47 (0.03)	11.75(1.24)	10.15 (0.0)	15.39 (3.05)
Mg^{2+} (cmol$_c$ kg^{-1})	1.60 (0.02)	8.54 (0.1)	3.47 (0.06)	9.61(0.38)
K^+ (cmol$_c$ kg^{-1})	0.21 (0.02)	0.42 (0.03)	0.41 (0.05)	1.40 (0.13)
Na^+ (cmol$_c$ kg^{-1})	0.13 (0)	0.42 (0.03)	0.38 (0.02)	1.67 (0.07)
Total exchangeable bases				
(cmol$_c$ kg^{-1})	5.41 (0.07)	21.13 (1.32)	14.41 (1.05)	28.07 (2.98)
Exchangeable acidity				
(cmol$_c$ kg^{-1})	0.35 (0.01)	0.10 (0)	0.10 (0.01)	0.05 (0)
Effective cation exchange				
capacity (cmol$_c$ kg^{-1})	5.76 (0.06)	21.23 (1.32)	14.51 (1)	28.12 (2.77)
Bulk density (g cm^{-3})	1.26 (0.05)	1.33 (0.12)	1.32 (0.08)	1.39 (0.12)
Total porosity (%)	52.45 (2.86)	49.81(1.71)	50.19 (3.03)	47.54 (2.48)
Soil texture				
Sand (%)	43.65 (3.19)	48.93 (2.71)	73.64 (3.03)	34.62 (1.88)
Silt (%)	46.34 (2.7)	41.06 (1.63)	24.35 (0.9)	61.37 (3)
Clay (%)	10.01 (0.78)	10.01 (0.82)	2.01 (0.01)	4.01(0.03)

*Values in parenthesis represent the standard error of means.

TABLE 2
Some properties of soils (n = 3) at the 15 to 30-cm depth in the study area

Soil property	Site			
	Non-mined	Capped tailings I	Capped tailings II	Solidified tailings
Organic carbon (%)	0.71 (0.03)*	0.61 (0.04)	0.51 (0.01)	0.94 (0.05)
Total N (%)	0.08 (0.01)	0.06 (0.0)	0.05 (0)	0.08 (0.01)
C: N ratio	8.88 (0.41)	10.17 (1.2)	10.20 (1)	11.75 (2.06)
pH (1: 2.5 - soil:water)	3.78 (0.52)	6.82 (0.85)	7.01(0.410	7.15 (0.09)
Extractable P - Bray I (mg kg^{-1})	1.70 (0.23)	3.06 (0.18)	0.83 (0.09)	1.70 (0.2)
Exchangeable cations				
Ca^{2+} (cmol$_c$ kg^{-1})	1.34 (0.02)	5.87 (0.21)	10.95 (0.36)	15.49 (0.55)
Mg^{2+}(cmol$_c$ kg^{-1})	0.80 (0.03)	2.67 (0.09)	3.47 (0.11)	3.74 (0.07)
K$^+$ (cmol$_c$ kg^{-1})	0.14 (0.01)	0.27 (0.01)	0.32 (0.04)	0.91(0.01)
Na$^+$ (cmol$_c$ kg^{-1})	0.07 (0)	0.10 (0.01)	0.17 (0)	0.96 (0.05)
Total exchangeable bases (cmol$_c$ kg^{-1})	2.35 (0.2)	8.91 (0.08)	14.91 (1.5)	21.10 (2)
Exchangeable acidity (cmol$_c$ kg^{-1})	1.10 (0.04)	0.10 (0)	0.05 (0)	0.05 (0)
Effective cation exchange capacity (cmolc kg^{-1})	3.45(0.31)	9.01 (0.29)	14.96 (1.1)	21.15 (2.77)
Bulk density (g cm^{-3})	1.44 (0.05)	1.37 (0.03)	1.35 (0.03)	1.43 (0.010
Total porosity (%)	45.66 (2.63)	48.30 (1.89)	49.06 (1.67)	46.04 (0.96)
Soil texture				
Sand (%)	37.86 (2.2)	39.69 (1.95)	71.42 (4.7)	32.83 (1.56)
Silt (%)	38.04 (3)	54.29 (2.7)	26.55 (1.06)	65.17 (3.11)
Clay (%)	24.10 (1.33)	6.02 (0.05)	2.03 (0.03)	2.00 (0.01)

*Values in parenthesis represent the standard error of means.

of oven-dry soil to the volume of oven-dried soil. The porosity was extrapolated from the bulk density of the soil samples and particle density of a mineral soil, assumed to be 2.65 × 10^3 kg m^{-3}. The texture of the soil, indicated by the percent sand, silt and clay, was determined by the Bouyoucos method. The soil water content for data correction, as described by Anderson & Ingram (1993), was followed.

Chemical properties

The *p*H of the soil was determined in a soil : water ratio of 1 : 2.5 (Anderson & Ingram, 1993). The exchangeable bases (Ca^{2+}, Mg^{2+}, K$^+$ and Na$^+$) were extracted using 1.0 *M* ammonium acetate (*p*H 7) (Rowell, 1994). The Ca^{2+} and Mg^{2+} in the extract were determined by atomic absoption spectrophotometer while the Na$^+$ and K$^+$ were measured by flamephotometer. The effective cation exchange capacity (ECEC) was calculated by summation of exchangeable bases and exchangeable acidity. Extractable P was determined by the Bray No.1 method described by Anderson & Ingram (1993). The wet oxidation method of Walkley and Black, as modified by Damian

& Damian (2007), was used to determine total organic carbon. Total N was measured using the Micro-Kjeldahl method (Anderson & Ingram, 1993).

Extraction of heavy metals

Two heavy metal extraction procedures were used. These were the methods using DIN 38414 S4 (DIN-NORMEN, 1984) and ammonium ethylene-diamine-tetra-acetic acid (EDTA) (ADAS, 1986). The DIN 38414 S4 (DIN-NORMEN, 1984) was used for determining the water soluble fraction of the heavy metals As, Pb, Cd, Cu, Zn and Fe. Deionised water, that allows the test material to establish the pH, was added to each sample at a liquid to solid (L/S) ratio of 10:1. The soil suspension was shaken for 24 h on a reciprocating shaker at 125 r.p.m. After the extraction, each resulting solution was filtered through a 0.45-µm filter paper and the leachate analyzed for soluble heavy metals.

Ammonium EDTA forms strong complexes with many heavy metals, which are released from the exchange complex (Kabata-Pendias, 2001), organically complexed pools (Podlesakova *et al.*, 2001) and from carbonates and hydroxides of iron (Beckett, 1989). The EDTA extractable fraction of heavy metals was, therefore, determined instead of the total amounts because it represents the plant available form. The procedure used is briefly described below. Ten grams of pulverised air-dried soil was weighed and then placed into a 100 ml plastic container with an air-tight lid. Fifty millilitres of 0.05 *M* ammonium-ethylene-diamine-tetraacetic acid (NH$_4$-EDTA) (pH 7) was then added. The container with the screwed lid containing the soil: NH$_4$-EDTA mixture was shaken at room temperature on a mechanical shaker at 125 r.p.m. for 2 h.

The soil slurry was then passed through a Whatman 45 filter paper into a sterile 100 ml conical flask. The filtrate was brought to exactly 100 ml with the extraction solution, and the filtrate was analyzed using the atomic absorption spectrophotometer (AAS, Spectra AA 220).

Determination of free cyanide

Field moist soil samples were used for the determination of free cyanide concentration. The moisture content of the soil was noted for data correction of dry mass determination. Although the same procedure of the DIN 38414 S4 (DIN-NORMEN, 1984) extraction for the determination of heavy metals was followed in the determination of the free cyanide content of soils, the samples were shaken for only 30 min in air-tight black plastic bottles due to the high volatilization of the hydrocyanic acid component of free cyanide. The soil suspension was allowed to settle and immediately decanted for CN$^-$ determination. The procedure described by De (2000) was used for cyanide determination. Concentrations of cyanide >1 mg l^{-1} was determined by the titrimetric method using silver nitrate solution and 4-dimethylamino-benzylidinerhodanine indicator. The colorimetric method was used for determining cyanide concentrations <1 mg l^{-1}. The HCN collected in NaOH in a gas washer was reacted with chloramine T. The resultant CNCl was then mixed with pyridine-barbituric acid reagent and the resulting red-blue dye measured using a spectrophoto-meter at 578 nm.

Statistical analysis

The Genstat statistical package (Genstat, 2008) was used for the analysis of the data. The effects of the capping on pH and the levels of free cyanide and heavy metals (As,

Pb, Zn, Fe, Cd and Cu) were determined using the analysis of variance (ANOVA). The data on free cyanide was log-transformed, in the form $\log_{10}(\times + 1)$, for the analysis of variance and back transformed before the separation of means. The least significant difference (LSD) was used for the separation of means at the 95% confidence level.

Results

Data on the effects of reclamation measures on the levels of water soluble heavy metals (As, Pb, Cu, Zn, Fe and Cd), *p*H, free cyanide and EDTA extractable metals (As, Pb, Cu and Zn) of soils, respectively, in the study area are presented in this section. The effect of reclamation measures on the concentrations of EDTA extractable heavy metals (As, Pb, Cu, Zn) of the non-mined soil, capped and solidified tailings are presented in Table 3. The mean EDTA extractable As levels of the non-mined soil at the 0-15 and 15-30 cm depths were 20.27 ($\pm$0.5) and 9.1 ($\pm$0.06) mg kg^{-1}, respectively. The levels of EDTA extractable As in the

capped tailings ranged from 28.5 to 198.1 mg kg^{-1}, while that of the solidified tailings was 725.6 mg kg$^{?1}$ at the 0–15 cm depth (Table 3).

The results of the effects of the capping of tailings with laterite on the levels of water soluble heavy metals (As, P, Cd, Cu, Zn and Fe) are in Table 4. The results of the influences of capping on *p*H and free cyanide are also presented in Table 4. The concentrations of free cyanide in the capped and solidified tailings were 0.2–0.47 mg kg^{-1} and 0.73–1.3 mg kg^{-1}, respectively, compared to that of the non-mined soil (control) 0.01 mg kg^{-1} (Table 4). The levels of free cyanide in the capped soil at the 0–15 cm depth varied from 0.4–0.43 mg kg^{-1} and that of the solidified tailings was1.3 mg kg^{-1} (Table 4). The mean *p*H of the non-mined soil at the 0–15 and 15–30 cm depths were 5.53 and 5.43, respectively (Table 4). The *p*H of solidified tailings at the 0–15 and 15–30 cm depths was, however, 7.27 while the *p*H values recorded for capped tailings varied from 6.37 to 6.79 (Table 4).

TABLE 3
EDTA extractable heavy metal content of soils in the study area

Soil	EDTA extractable metals (mg kg^{-1})			
	As	*Pb*	*Cu*	*Zn*
Non-mined (0-15 cm)	20.3 g	1.63 e	2.71 f	5.71 g
Non-mined (15-30 cm)	9.1 h	1.06 f	2.53 e	6.44 f
Capped tailings (site 1) (0-15 cm)	28.5 f	2.90 g	4.42 d	12.67 de
Capped tailings (site 1) (15-30 cm)	107.1 e	4.63 b	2.77 g	14.40 b
Capped tailings (site 2) (0-15 cm)	198.1 d	4.23 c	6.54 a	11.87 e
Capped tailings (site 2) (15-30 cm)	515.5 b	4.93 a	4.87 d	13.10 c
Solidified tailings (0-15 cm)	725.6 a	4.01 d	6.01 b	12.77 d
Solidified tailings (15-30 cm)	371.9 c	4.04 d	5.43 c	21.33 a
Canadian limits for contaminated industrial	50	1000	500	1500
(agricultural) sites	(20)	(375)	(150)	(600)

.Note: Means with the same letters are not significantly different from one another at the 95 % level of significance.

TABLE 4
Levels of water soluble heavy metals, free cyanide and pH of soils in the study area

| Soil | Water soluble metals (mg l⁻¹) | | | | | | pH | Free cyanide (mg kg⁻¹) |
	As	Pb	Cu	Zn	Fe	Cd		
Non-mined (0-15 cm)	0.177e	0.023f	0.002c	0.007d	1.043a	0.002b	5.53e	0.01f
Non-mined (15-30 cm)	0.047e	0.019f	0.008b	0.009d	0.540b	0.001b	5.43f	0.01f
Capped tailings (site 1) (0-15 cm)	0.322d	0.054c	0.004c	0.020cd	0.124c	0.013b	6.53b	0.40d
Capped tailings (site 1) (15-30 cm)	0.641 c	0.045d	0.008b	0.037bc	0.084cd	0.015ab	6.37d	0.47c
Capped tailings (site 2) (0-15 cm)	0.444d	0.048d	0.002c	0.043ab	0.094c	0.008b	6.50c	0.43cd
Capped tailings (site 2) (15-30 cm)	0.932b	0.035e	0.010b	0.047ab	0.021d	0.037a	6.37d	0.20e
Solidified tailings (0-15 cm)	2.672 a	0.135a	0.008b	0.037bc	0.136c	0.029a	7.27a	1.30a
Solidified tailings (15-30 cm)	0.817bc	0.092b	0.023a	0.056a	0.117c	0.021a	7.27a	0.73b
lSD (0.05)	0.192	0.008	0.005	0.018	0.082	0.028	0.097	0.06

Discussion

Effect of capping with lateritic soil on the concentrations of EDTA extractable heavy metals of soils and tailings in the study area

The mean EDTA extractable As levels of the non-mined soil at the 0–15 and 15–30 cm depths were within the Canadian limits for agricultural sites (CCME, 1991). Only the Canadian international standard was referred to due to the lack of standards set for soils by the Ghana Environmental Protection Agency. The capping of tailings with lateritic soil is the main method of remediating heavy metals contained in tailings sites at the closed tailings dam site. The levels of As in non-mined soil were generally lower than those of the capped tailings and solidified tailings at the 0–15 and 15–30 cm depths ($P < 0.05$) (Table 3). At the 0–15 cm depth, the concentration of As in the capped tailings was significantly less than that of the solidified tailings ($P < 0.05$). There might have been the leaching of AsO_4^{3-} from the solidified tailings at the 15–30 cm depth to the previously unpolluted lateritic soil. Laterite consists of Fe oxides that strongly adsorb arsenate (AsO_4^{3-}) (Chakravarty *et al.*, 2002). This could also have contributed to the significantly lower ($P < 0.05$) levels of EDTA extractable As in the capped tailings compared to the solidified tailings.

Although the levels of EDTA extractable As in the capped tailings were significantly reduced ($P < 0.05$) compared to the solidified tailings at the 0–15 cm depth (Table 3), they were above the Canadian maximum permissible limit of 20 mg kg⁻¹ for agricultural sites. These recapped soils would, therefore, not be suitable for agricultural purposes unless further remediation measures are adopted to reduce As to an acceptable level.

The levels of EDTA extractable Pb, Cu and Zn in the non-mined soil, capped tailings and solidified tailings were significantly different from one another ($P < 0.05$). However, they were generally lower than the Canadian standards for both agricultural and contaminated (Table 3). The levels of these three metals in the soils capped tailings and solidified tailings of the AngloGold mining could, therefore, be considered safe to humans and other organisms.

Effects of capping on the levels of water soluble heavy metals in the study area

The separation of means indicated that the levels of free cyanide, water soluble As, Pb and Zn in the 0–15 and 15–30 cm depths of non-mined soil was significantly less at the 5% probability level than those of recapped tailings and solidified tailings (Table 4). These higher levels of As and Pb, that are hazardous heavy metals, are of concern since the levels of water soluble As and Pb in the treated effluent discharged after bacterial degradation into the environment (Table 4) was higher than the GEPA (2006) standards for effluent discharge and the WHO (2004) guidelines for drinking water quality. The leaching of As and Pb from the capped and solidified tailings could further increase their concentrations in water bodies.

The water soluble Pb contents of the capped tailings were also significantly less than that of the solidified tailings at the 0–15 and 15–30 cm depths ($P < 0.05$) (Table 4). The concentrations of dissolved Fe in non-mined soil, at the 0–15 and 15–30 cm depths, were significantly greater than that of the capped and solidified tailings ($P < 0.05$) (Table 4). Except at the 0–15 cm depth of capped tailings (Site 1), the levels of Zn in

soil solution were significantly less in non-mined soil compared to the other treatments. These results are contrary to the finding of Salt *et al.* (1995), who reported that at lower soil pH, the adsorption of metal decreases and, thus, increases their concentration in soil solution.

Calcium ions (Ca^{2+}) compete effectively with cationic metals for adsorption sites (Kiekens, 1983; Pierangeli *et al.*, 2003). The Ca^{2+}, derived from the $Ca(OH)_2$ added to tailings slurry to increase its pH when discharged at the tailings dam, could have led to the displacement of Zn^{2+} from and, or a preferential adsorption of Ca^{2+} onto the exchange complex. The solubilization of zinc minerals of the sulphidic minerals (ZnS) contained in the processed tailings might have increased the concentration of mobile Zn^{2+} in solution (Kabata-Pendias, 2001). These, coupled with the leaching of Zn^{2+} from the 0–15 cm depth of the non-mined soil, could explain the increased concentration of Zn in soil solution at higher soil pH in the tailings.

The concentration of cadmium in non-mined soil was similar to that of the capped soil at the 0–15 cm depth ($P > 0.05$). The difference between the levels of Cd in the 0–15 cm depth of the capped and solidified tailings was significant ($P < 0.05$). This indicates that the capping of tailings could be used to contain and reduce the level of exposure of Cd in tailings. The trend of the results for Cu in solution indicated that there were significantly lower levels at 0–15 than at 15–30 cm in the capped, solidified and non-mined soil. The reverse of this pattern was observed for water soluble Pb (Table 4). The higher levels of Cu in the lower soil horizons might be due to its attraction to

soluble organic ligands that form complexes which increases the mobility of Cu in soils (United States Environmental Protection Agency, 1992). On the other hand, Pb compounds of low solubility are formed in the presence of organic and inorganic ligands (Evanko & Dzombak, 1997). This, coupled with the reaction of soluble Pb in soil with carbonates, clays, sulphates and hydroxides that lead to its retention of Pb (United States Environmental Protection Agency, 1992), could be the reason of the significantly lower Pb in the 0–15 cm depth compared to the 15–30 cm depth.

Effects of capping on the levels of free cyanide in the study area

The concentrations of free cyanide in the capped and solidified tailings were significantly greater than that of the non-mined soil (control) ($P < 0.05$) (Table 4). The levels of free cyanide in the capped soil at the 0–15 cm depth was significantly lower than that of the solidified tailings ($P < 0.05$). This might be explained by the formation of strong complexes of ferricyanide [Fe $(CN)_6{}^{3-}$] and ferrocyanide [Fe $(CN)_6{}^{4-}$] (Ebbs, 2004). The capping of tailings with lateritic soil could, therefore, be an effective method of reducing the levels of free cyanide in contaminated soil. However, there is still the need for the adoption of other remediation measures that would lead to a further precipitation and immobilization of free cyanide in the capped and solidified tailings to levels that are not significantly different from that of the control (non-mined soil). Nonetheless, the levels of free cyanide in capped tailings (sites 1 and 2) at the 0–15 cm depth (Table 4) were less than the Canadian maximum permissible limit of 0.5 mg kg^{-1} for agricultural land and, therefore, could be used for arable crop

production. This is in contrast with the free cyanide level of solidified tailings that is above the Canadian maximum permissible limit for agricultural land and obviously makes it unsuitable for agriculture.

Effects of capping on soil/tailings pH in the study area

The results show that the general pH of the non-mined soil of the study area was moderately acidic (Table 4). This is partly a reflection of the acidic nature of the parent material which predominantly consisted of asernopyrites (FeAsS). The leaching of basic cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) and replacement by H^+ ions could have also led to higher H^+ ion activity. Tailings generally exhibit acidic characteristics due to the oxidation of asernopyritic (FeAsS) gold bearing rock to produce H_2S (Alloway & Ayres, 1997). The pH of solidified tailings was, however, neutral at the 0–15 and 15–30 cm depths ($P < 0.05$) (Table 4). This could be attributed to the addition of liming material, [Ca $(OH)_2$], to reduce the pH of the tailings slurry discharged into the tailings dam as observed by Gonzalez & Gonzalez-Chavez (2006). An elevated amount of Ca^{2+} ions, therefore, occured in the resulting solidified tailings (Tables 1 and 2) that increased its pH and lowered its acidity. Gonzalez & Gonzalez-Chavez (2006) similarly recorded neutral to slightly alkaline pH values of 7.06–8.39 for mine tailings, and attributed it to the reaction of mine tailings with carbonates.

The capping of tailing led to significantly less alkaline conditions than that of the solidified tailings ($P < 0.05$) (Table 4) possibly due to inherently acidic pH (5.4 ± 0.04) of the laterite layer of soil. The pH values recorded for capped tailings would be more

suitable for arable crop production compared to solidified tailings at the 0–15 cm depth (Tables 1, 2 and 4), since most arable crops do well at *p*H values between 5.5 and 6.5.

Conclusion

The levels of Zn, Cu and free cyanide in capped and solidified tailings were within international standards for soils. The capping of tailing led to significantly less alkaline conditions than that of the solidified tailings. The slightly acidic *p*H of capped tailings would be more suitable for arable crop production compared with solidified tailings whose *p*H varied from neutral to slightly alkaline. The concentrations of As (EDTA-extractable and water soluble) were significantly higher in capped and solidified tailings compared to non-mined soil. The concentrations of EDTA-extractable As and also water soluble Pb and As, at the 0–15 cm depth, were in decreasing order, solidified tailings > capped tailings > non-mined soil ($P < 0.05$). The concentrations of EDTA-extractable As of the capped and solidified tailings were above the Canadian maximum permissible limit for agricultural land. There is, therefore, the need for the adoption of other As remediation measures if the land is to be used for agricultural purposes.

References

ADAS (1986), *The analysis of agricultural materials.* Manual of Methods. Agricultural Development and Advisory Service, London.

Alloway B. J. and **Ayres D. C.** (1997), *Chemical principles of environmental pollution.* Blackie Academic and Professional, London.

Anderson J. M. and **Ingram J. S. I,** (1993). *Tropical soil fertility and biology: A handbook of methods.* CAB International, Wallingford.

Awudi G. B. (2002). Role of Foreign Direct Investment (FDI) in the mining sector of Ghana and the economy. *Proceeding of the Foreign Direct Investment (FDI) and the Environment Conference. OECD.* Paris.

Beckett P. H. T. (1989). The use of soil extractants in studies on trace metals in soils, sewage sledges and sludge-treated soils. *Adv. Soil Sci.* **8**: 143–176.

CCME (1991). *Interim Environmental Quality Criteria for Contaminated Sites.* Report CCME EPC-CS34. Canadian Council of Ministers of the Environment, Winnipeg, Manitoba.

Chakraborty D. and **Choudhury D.** (2009). Investigation of the Behavior of Tailings Earthen Dam Under Seismic Conditions. *Am. J. Engng Appl. Sci.* **2**: 559–564.

Chakravarty S., Dureja V., Bhattacharyya G., Maity S. and **Bhattacharjee S.** (2002). Removal of arsenic from groundwater using low-cost ferruginous manganese ore. *Wat. Res.* **36**: 625–632.

Damian F. and **Damian G.** (2007). Detoxification of heavy metal contaminated soils. *Am. J. envir. Sci.* **3**: 193-198.

De A. K. (2000). *Environmental Chemistry,* 4th edn. New Age International Publishers Ltd, New Delhi.

DIN-NORMEN (1984). *Determination of Leachability by Water (S4).* German Standard Methods for the Examination of Water, Wastewater and Sludge. DIN 38414 S4. Sludge and Sediments (Group S).

Ebbs S. (2004). Biological degradation of cyanide compounds. *Curr. Opin. Biotechnol.* **15**: 231–236.

European Commission (2006a). *Thematic Strategy for Soil Protection, Communication from the Commission to the Council, the European Parliament, the Economic and Social Committee and the Committee of the Regions.* European Commission, Brussels.

European Commission (2006b). *Impact Assessment of the Thematic Strategy on Soil Protection. Communication from the Commission to the Council, the European Parliament, the Economic and Social Committee and the Committee of the Regions.* European Commission, Brussels.

Evanko C. R. and **Dzombak D. A,** (1997). *Remediation of Heavy-Metals-Contaminated Soil and Groundwater.* http://www.gwrtac.org

Food and Agricultural Organization and International Union of Soil Sciences (2006). *World Reference Base for Soil Resources. A Framework for International Classification,*

Correration and Communication. World Soil Resources Reports, 103. FAO, Rome. 128 pp.

Genstat (2008), *Genstat Discovery*, 3rd edu., Genstat Procedure Library Release PL15.2. VSN International Ltd, Hertfordshire, United Kingdom.

GEPA (2006). *Guidelines for Effluent Discharges into Natural Water Bodies. Maximum Permissible Levels.* Ghana Environmental Protection Agency, Accra.

Gonzalez R. C. and **M. C. Gonzalez-Chavez** (2006). Metal accumulation in wild plants surrounding mine wastes. *Envir. Pollut.* **144**: 84-92.

ICMM (2007). *Ghana. Country Case Study. The Challenge of Mineral Wealth: Using Resource Endownments to Foster Sustainable Development.* DC: ICMM, Washington.

Kabata-Pendias A. (2001). *Trace Elements in Soils and Plants.* 3rd edn. CRC Press, Boca Raton Fl.

Kertulis-Tartar G. M., Tu Q. M. L. and **Chirenje T.** (2006). Phytoreediation of an arsenic-contaminated site using pteris vittata L.: A two-year study. *Int. J. Phytoremediation* **8**: 311–322.

Khodadadi A., Abdolahi M. and **Teimoury P,** (2005), Detoxification of cyanide in gold processing wastewater by hydrogen peroxide. *Iran. J. envir. Health Sci. Eng*ng **2** (3): 177–182.

Kiekens L. (1983). Behavior of Heavy Metals in Soils. In *Utilization of Sewage Sludge on Land: Rates of Application and Long-term Effects of Metals,* (S. Berglund, R. D. Davis and P. L'hermite, eds). Reidel Publishing, Dordrecht.

Maplandia (2005), *Obuasi Municipal-Coordinates.* Google Maps World Gazetter: http://www.maplandia.com/ ghana/ashanti/ashanti/obuasi/obuasi

Patil, Y. B. and **Paknikar P. K.** (2000), Removal of Metal Cyanides from Waste Waters. *Process Biochem.* **35**: 1139–1151.

Pierangeli M. A., Guilherme L. R, Oliveira L. R, Curi N. and **Silvia M. L.** (2003). Efeito da força iônica da solução de equilíbrio na adsorção de cádmio em Latossolos brasileiros. *Pesquisa Agropecuária Brasileira* **38**: 737–745.

Podlesakova E., Nemecek J. and **Vacha R.** (2001). Trace Elements in Soil, Bioavailability, Flux and Transfer. In *Mobility and Bioavailability of Trace Elements in Soils.* (I. K. Iskandar and M. B. Kirkham, eds). USA.

Poggio L., Vrscaj B., Schulin R., Hepperle E. and **Marsan F. A.** (2008). *Metal pollution and human bioaccessibility of topsoils in Grugliasco (Italy).* Environmental Pollution. DOI: 10.1016/j.envpol.2008. 080009.

Rowell D. L. (1994). *Soil Science: Methods and applications.* Longman Scientific and Technical. Harlow.

Salt D. E., Blaylock M., Kumar P. B., Dushenkov V., Ensley B. D. and **Chet L.** (1995). Phytoremediation: A novel strategy for the removal of toxic metals from the environment using plants. *Biotechnol.* **13**: 468-474.

United States Environmental Protection Agency (1992). *Behavior of metals in soils.* (J. E. McLean and B. E. Bledsoe, eds) EPA Ground Water Issue, EPA/540/S-92/018,1-25.

World Health Organization (2004).*Guidelines for Drinking-water Quality,* vol 1. Recommen-dations, http://www.who.int/water_sanitation_ health/dwq/GDWQ2004web.pdf