Understanding the Mechanism of Arsenic Mobilisation and Behaviour in Tailings Dams*

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Abstract

This study was carried out on leaching of tailings at 30 °C and 40 °C. The mineralogical and chemical composition of the tailings material were determined by Quantitative X-Ray Diffractometry (QXRD) and Scanning Electron Microscopy combined with Energy Dispersive Spectroscopy (SEM-EDAX). The study revealed that the tailings contain sulphides (arsenopyrite and pyrite) which can leach to produce arsenic (As) and other ions in solution. The acid released during leaching depends on the temperature of leaching. More acid was produced at higher temperature (40 °C) than lower temperature (30 °C). It was established that arsenic precipitation from solution was higher at higher temperature (40 °C) than lower temperature (30 °C). Mimicking the study in a typical tailings environment, it could be proposed that As mobilisation will be enhanced at lower temperature (30 °C) than at higher temperature (40 °C).

Keywords: Tailings, Leaching, Arsenopyrite, Heavy metals and Temperature

1 Introduction

Alkaline cyanide leaching of gold from refractory ores usually requires finely ground ores (80 % passing 106 µm) for efficient metal recovery. This produces very fine tailings with a relatively high specific surface area whereby unstable compounds in the tailings material can undergo decomposition. Some of these unstable materials are pyrite, arsenopyrite and other sulphides which can be easily oxidized once exposed to air and water (Warhurst and Noronha, 2000; Fan et al., 2016). The oxidation of these sulphides will produce metal laden acid which can be mobilised into the geoenvironment (Wang and Mulligan. 2009: Heikkinen and Raisanen, 2009; Carvalho et al., 2014).

The release of As and other heavy metals from tailings into the geo-environment can adversely affect the biota (Bain et al., 2000; Armienta et al., 2001; Jung, 2001; Romero et al., 2010) which manifests in the following: keratosis, neuropathy, liver fibrosis, anemia, burning sensation of eyes, chronic lung disease, gangrene of toes/black foot disease, body weakness, skin cancer and solid swelling of legs, osteoporosis, decreased birth weight, kidney disease, cancer, and skeletal damage in humans, and in plants, stunted growth via inhibition of phosphate enzyme activities and protein synthesis (Ter Welle and Slater, 1967; Sckerl and Frans, 1969; Clijsters and Van Assche, 1985; Lu, 1990; Burlo et al., 1999; Guha, 2003; Stoeva et al., 2005; Choong et al., 2007).

Therefore, effluent from tailings is normally treated before it is discharged into the geo-environment using the following methods: chemical precipitation, ion-exchange, adsorption, membrane filtration and coagulation/flocculation (Dabrowski *et al.*, 2004; Fu and Wang, 2011; Hua *et al.*, 2012; Koomson and Asiam, 2013).

The efficiency of these methods will largely depend on the nature of the effluent. Therefore, it is necessary to understand the geo-chemical process occurring in the tailings mass. The present study seeks to understand the influence of temperature on the leaching of tailings material.

2 Resources and Methods Used

2.1 Tailings Characterisation

The tailings material used in this study was obtained from a gold mine in Ghana. The mineralogical composition of the tailings material was determined using: quantitative X-ray diffractometry (QXRD; Phillips PW 1050 X-ray generator equipped with Sietronic automated data collection). Scanning electron microscopy (SEM; FEI Quanta 450 FEG) combined with energy dispersive spectroscopy (EDAX; Apollo X SDD) was used to determine the morphology and spot composition of the sulphide minerals. Chemical composition was determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer 5300 DV) after acid digestion of sample. Particle size distribution was determined by laser diffraction using Mastersizer 2000 (Malvern Instruments Ltd., U.K.). Specific surface area of the tailings was determined by the Brunauer, Emmett and Teller (BET) method (Brunauer *et al.*, 1938) using Gemini VII 2390 (Micrometrics, USA).

2.2 Leaching

Various slurries (each containing 40 wt% solids) conditioned to pH 2 were isothermally leached on a rotating orbital mixer incubator rack (Ratek) at 260 rpm at 30 °C for 7 days. Samples were removed at 24 h interval and the pH was measured. The slurry was then centrifuged at 4500 rpm for 30 min using the Heraeus multifuge 3S-R centrifuge. The supernatant solutions were then carefully collected, and filtered through a 0.25 μ m Teflon membrane. The filtrate was then analysed for As and Fe using an ICP-OES. The experiment was repeated at 40 °C.

3 Results and Discussion

3.1 Mineralogical Analysis

The results of QXRD is presented in Table 1. It can be inferred that the tailings material consists mainly of quartz and muscovite. The minor materials are chlorite and siderite. The results of the chemical composition of the tailings is presented in Table 2. The major elements are Fe, S, Ca and As. Although no sulphide was identified in the QXRD analysis, SEM-EDAX analysis (Fig.1) indicated that arsenopyrite and pyrite were present in the tailings material. It can therefore be inferred that these sulphide materials can oxidise. Hence, the presence of trace amounts of hematite could be due to the weathering product of the sulphides.

Table 1 Mineralogical	Composition	of Tailings
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Mineralogical composition of major minerals in tailings		
Mineral	wt %	
Quartz	48	
Muscovite	41	
Chlorite	5	
Siderite	4	
Hematite	<1	
Amorphous Content	<1	
Total	~ 100	

Element	Concentration (mg kg ⁻¹)	
As	490	
Cu	64	
Fe	60000	
S	2650	
Ca	2300	

3.2 Leaching

The results of particle size analysis of the tailings material is presented in Fig 2. It can be inferred that the d_{50} is 29.10 µm. The tailings' specific surface area was found to be 3.58 m²/g indicating a relatively high surface area. Hence, these parameters can enhance the leachability of tailings.









Fig. 2 Tailings Particle Size Distribution Curve

results of leaching at temperatures 30 and 40 °C are presented in Fig. 3 and Fig. 4 respectively. It can be seen that at 40 °C the As dissolution is found to increase to 3.36 mg/l within 24 h and thereafter, it decreased rapidly to 0.06mg/l after 168 h. The pH trend at 40 °C increased from 2 to 5.2 within 168 h (Fig. 5). The Fe dissolution at 40 °C is found to increase to 382.70 mg/l after 24 h and shows a sinusoidal trend decreasing gradually to 15.76 mg/l after 168 h. At 30 °C, on the other hand, As dissolution was observed to increase gradually from 0.03 mg/l at 24 h to 0.2 mg/l at 168 h. Fe dissolution increased rapidly to 55. 30 mg/l after 24 h and decreased gradually to 0.31 mg/l after 168 h showing a similar trend to that at 40 °C.



Fig. 3 Fe and As Release Concentrations measured as a Function of Time at 30 °C

The experimental observation revealed that a brownish precipitate was seen in the case of leaching at 40 °C while a greenish-yellow colouration was found at 30 °C. Furthermore, the change in pH trend at 30 °C is higher than 40 °C indicating the leaching at 40 °C produces more acidic solution. This can be explained as follows: the Fe species at 40 °C shows the presence of Fe ³⁺ as inferred by a brownish precipitate during experimental investigations. However, at 30 °C, the

precipitate formed showed a greenish-yellow colouration. From this, the mechanism of hydration of Fe species may be described as follows:

At 30 °C;
$$Fe^{2+} + 2H_2O$$

 $\rightarrow Fe(OH)_2$
 $+ 2H^+$ (1)
At 40 °C $Fe^{3+} + H_2O$
 $\rightarrow Fe(OH)_3$
 $+ 3H^+$ (2)

From Equation 1, it is observed that the overall/net acid produced by Fe^{2+} hydration is lower than that of Fe^{3+} (equation 2) and this explained the observed trend in Fig. 5.

The dissolution of Fe is higher at 40 °C than 30 °C. For example at 30 °C, Fe dissolves rapidly and reaches a peak (55 mg/l) at 24 h and thereafter decreased rapidly to about 9 mg/l at 48 h. In contrast, at 40 °C, Fe increased rapidly in solution to 383 mg/l and was sustained until 100 h and thereafter it decreased gradually to about 15 mg/l at 168 h. The mechanism of Fe precipitation in solution can be given as follows:

$$Fe^{2+} + \frac{1}{4}O_2 + \frac{5}{2}H_2O \rightarrow Fe(OH)_3 + 2H^+$$
(3)

Thus, the presence of oxygen will enhance the precipitation reaction since the solubility of gases decreases with increasing temperature (Gerrard, 1976). The amount of oxygen in solution at 30 °C will be more than 40 °C. Consequently, the precipitation of Fe at 30 °C will be higher than 40 °C resulting in a delayed precipitation of Fe as observed at 40 °C.

Furthermore, the behaviour of As can be explained as follows: at 40 °C, there is more Fe^{3+} in solution. As a result, As is removed rapidly from solution as ferric arsenate whereas at 30 °C most of the Fe had precipitated after 50 h during which period As had not sufficiently dissolved. Hence there were insufficient Fe^{3+} in solution to precipitate the dissolving As, therefore, its concentration was high.

This study has shown that leaching temperature has marked influence on Fe and As species in solution. Mimicking the leaching reactions in a typical tailings environment, it could be proposed that As mobilization will be enhanced at lower temperature than at higher temperature.



Fig. 4 Fe and As Release Concentrations measured as a Function of Time at 40 °C



Fig. 5 Leaching of Fe and As pH Trends as Function of Time at 30 and 40 °C

4 Conclusions

This study revealed that sulphide bearing tailings can leach and produce As and Fe in solution. The acid released during leaching depends on the temperature of leaching. More acid is released at a higher temperature than at lower temperature. It was found that As precipitation will be higher at higher temperature than lower temperature.

Mimicking reactions in a typical tailings environment, it could be proposed that As mobilization will be enhanced at lower temperature $(30 \text{ }^{\circ}\text{C})$ than a higher temperature $(40 \text{ }^{\circ}\text{C})$.

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