

Research Article

Mineralogical and Geochemical Controls of Arsenic in an Active Tailings Dam

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Abstract: The aim of this study was to assess arsenic (As) mobilization in an active tailings dam through mineralogical and geochemical characterization study. Arsenite is the predominant As species in the dam with more than 50% of the arsenic bound to the organic fraction. Pyrite and arsenopyrite are the principal opaque minerals remaining in the tailings with relic grains showing rims of oxidation (hematite/goethite). Illite, kaolinite and carbonates act as pH buffers and consume the acid generated during pyrite oxidation and raise the pH to near neutral measured in the tailings dam. At near neutral conditions As is mobilized, which likely combines with the Fe and Ca oxides formed to form ferric-calcium arsenates and deposited in the tailings dam. Some As appear to equilibrate with atmospheric CO₂ and are converted into calcium carbonates with release of arsenic into solution.

Keywords: Arsenic, arsenopyrite, pyrite, tailings

INTRODUCTION

Arsenic-bearing minerals commonly occur in association with gold ores, with As constituting up to 1 wt.% of the ore. Hence, gold mining and mineral processing operations produce mill arsenic bearing tailings that are stored in impoundment dams (Blowes and Jambor, 1990; Yannopoulos, 1991). The gold tailings typically comprise sulphur bearing minerals, such as pyrite, arsenopyrite and iron oxides (hematite and goethite (Blowes and Jambor, 1990). Common gangue minerals found in the tailings include quartz, feldspars and micas. In these tailings As occurs in pore solutions and in arsenic-bearing minerals not destroyed during processing. Further breakdown of arsenic-bearing minerals and redistribution of arsenic occur in the tailings dam. Oxidation of residual sulfide minerals by atmospheric oxygen and bacteria releases As Blowes and Jambor (1990) and results in the formation of crystalline Fe(III) oxides/hydroxides (goethite and ferrihydrite) and sulfate minerals. As species and other metal elements are co-precipitated with or adsorbed onto weathering derived precipitates like iron oxides. Arsenic as a surface-bound inner or outer complex species is more mobile than those incorporated into solid phases (Jambor, 1994). Hence the amount of arsenic available for release into aqueous environment may show time dependent increase in behavior. Secondary mineral phases precipitation and dissolution reactions may be induced to maximize arsenic in solid and minimize the amount in pore waters (Bowell *et al.*, 1994; Brandberg *et al.*, 1993). However, these precipitation processes are not completely effective because pore water-tailings reaction tend to result in

near neutral pH solutions where As oxidation and solubilization in the presence of molecular oxygen occur (Blowes and Jambor, 1990).

Previous investigations of arsenic in mine tailings (Courtin-Nomade *et al.*, 2002b; McGregor and Blowes, 2002) focused on As distribution in inactive tailings storage facilities that are located in temperate regions. Furthermore, the ore beneficiation and processing employed did not involve the intentional use of bacteria. To date, there are limited studies that characterize As in an active tailings dam located in a tropical, humid environment. The mine under study is located in a tropical, humid environment. Bacteria oxidation pretreatment method is employed to digest the sulfide ores to liberate the encapsulated gold and release arsenic and other metals, which are stored in the Sansu tailings dam. Examining the chemistry of active tailings allows study of present conditions that can facilitate predictions of later chemical processes in the dam.

The present study therefore characterizes the distribution and speciation of As in the active tailings dam by mineralogical analyses and speciation assays via sequential chemical extractions of sediment samples from five drill holes. Detailed profiles of solid phase As provide a basis for interpreting its distributions in terms of processes responsible for As interactions and complexation in the dam. Partitioning of dissolved As between oxidized and reduced species is achieved and also explained by Eh and pH measurements.

Site description: The 6 km² tailings dam contained over 34 million tonnes of tailings material deposited

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over a 10 year period. The dam contains 30 m deep impounded tailings material at the north western portion and 6 m at the southern portion. The tailings depositional history affects pore water composition since it determines the hydrogeological environment and the pore water movement through the dam. The age determines the extent of mineral reactions that have taken place under a given set of conditions.

Mine records show tailings from 1993 when the impoundment opened to 1996 tailings were from oxide ores. During 1997 tailings were from oxide and sulfide ores, from 1998 to 2000 they were exclusively from sulfide ores and since 2000 tailings are from both types of ore. Since 2000 tailings are clearly traceable across the impoundment at depths of 2 to 3 m. From 1998 to 2000 sulfide ore tailings also are traceable across the impoundment. The early oxide tailings were found only in holes at the western and northern parts of the dam where the impoundment is deeper.

MATERIALS AND METHODS

Sampling: To understand the nature of arsenic source, 65 sediment samples from 5 drill holes were taken from the beach material by means of a PILCON Wayfarer 1500 portable site investigation percussive rig and an AMS stainless steel core sampling auger. The samples were split for mineral identification and photographed.

Hundred 100 water samples from the tailings pond, seepage sump and holding ponds, monitoring wells and downstream water were taken biweekly by means of Watermark Dome-End 36 inch disposable polyethylene bailers and discharged into acid washed Nalgene bottles for analyses at the Chemistry laboratory of New Mexico Bureau of Geology and Mineral Resources (NMBGMR), Socorro.

Physico-chemical analysis: Main physico-chemical parameters (pH, Eh and temperature) were measured on site with a Mettler Toledo MP 125 pH/Eh/T meter. Dissolved Oxygen (DO) was measured using Oakton DO 100 meter. Alkalinity was determined by means of a LaMotte alkalinity test kit. Total water chemistry and arsenic in water samples were analyzed by a graphite furnace atomic absorption spectrophotometer (GFAA Spectra 600) at the NMBGMR.

Mineralogical investigations: Sediment analyses included chemical, mineralogical and physical characterization. Chemical analyses were performed on the sediment samples for Ca, Mg, As, Al, Fe, K, Na, SiO₂, Cu, Zn and Pb by microwave digestion followed by ICP-MS determination (USEPA method 3051) at the NMBGMR, Socorro. Materials selected for mineralogical studies were air-dried at 25°C in order to preserve trace elements speciation.

Bulk elemental composition was determined by X-Ray Fluorescent Spectroscopy (XRF) at the New

Mexico State University, Las Cruces. The mineralogical composition was determined on a RIGAKU DMAX/2 X-ray Diffractometer. Powder XRD analysis of the samples was performed using CuK α radiation (40 kV/25 mA and scan speed of 2°/min). Minerals were identified using the Jade mineral identification software. Micro-morphology and elemental composition were determined by examining polished one-inch cylinder samples by an electron microprobe analysis (EMPA) on a COMICA SX-100 equipped with an EDS system and 4 wavelength dispersive spectrometers. An accelerating voltage of 15 KV and a probe current of 20 nA were used at 10 s counting time, using a beam diameter up to 5 μ m. Standard reference materials used to calibrate the instrument include natural and synthetic silicates, oxides and sulfide minerals (pyrite). Heavy mineral fraction from the sediments was separated using sodium metatungstate and examined in a petrographic microscope. Petrographic analyses were done on selected samples from two cores. Twenty four mineral grains were analyzed in detail. Grain sizes were measured using the filar scale on the microscope eyepiece.

Organic matter content was determined according to the combustion method. Sediment paste pH was measured in water (2:5 solid/water ratio) using the Mettler Toledo MP 125 m.

Carbonates were determined using the calcium and magnesium carbonate method developed by Dreimanis (1962). Sequential chemical extraction was performed on composite samples to examine the chemical forms of arsenic solid phases in the tailings, using the partial extraction techniques developed by Tessier *et al.* (1979) and Chao and Zhou (1983). The sequential steps of the procedure are described in Table 1. All extractions were conducted in plastic centrifuge tubes to avoid loss of sample and cross contamination. Between each successive extraction samples were centrifuged at 20,000 rpm.

RESULTS

Field observations: Figure 1 shows a split tailings core. Visual examination of the Sansu core indicates ponding-induced stratification of the Tailings Sediments (TS). There are three prominent types of layers; these are gray sulfide-bearing Sediments (S), dark-gray to black carbon-rich sediments layers types (CM) and red-brown-gray oxide layers (Ox). These layers vary from cm scale to tens of cm. Some layers appear to be varying mixtures of the two types of sediment (Fig. 1).

Tailings sediments are characterized by high SiO₂ (64.12-68.63%) and Al₂O₃ (10.52-13.69%). The result of extensive hydrothermal alteration and metasomatism of the ore are evidenced by high normative amounts of corundum, orthoclase, pyrite and calcite.



Fig. 1: Split tailings from a 15 cm core taken at 2 m from that shows stratification: S-sulfide and Ox- oxide and CM-carbonaceous material

Table 1: Clay analyses of sediments and tailings dam material. H-high, L-low and bd- below detection

Sample ID	Illite	Kaolinite	Smectite
NST	H	L	bd
WST	H	L	bd
SAD 3			bd
2 nd Raise material	H	L	bd
3 rd Raise material	H	H	L
4 th Raise material	H	H	L

X-Ray Diffraction (XRD) analyses show the presence of quartz, muscovite (sericite) and clay minerals as the dominant crystalline phases, which is

consistent with the mineralogy of the Obuasi gold ores. Gypsum was identified as the major sulfate mineral in the sediments. Illite, smectite and kaolinite were identified as the predominant clay minerals in all the samples. XRD analyses suggest that quartz comprise more than 50% volume of the samples, which agrees with CIPW norm calculation. No crystalline As-rich secondary phase such as scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). Tailings embankment material consists of mainly quartz, feldspar, muscovite and clay minerals. Typical XRD patterns are shown in Fig. 2.

Clay analyses on thirty samples show that illite is present in all the samples. Kaolinite/smectite is present in tailings embankment material. The results of the analyses are summarized in Table 1.

Petrography: Eighteen mineral grains identified were sulfides, mainly arsenopyrite, pyrite, marcasite and pyrrhotite. Six arsenopyrite grains identified showed oxidation rims of iron oxides (goethite), which indicates incipient oxidation of the arsenopyrite, suggesting local reduction of Fe sulfide mineral. Goethite identified on some grains may be part of the original ore. Banded goethite and leucoxene (pseudorutile) were observed in a sample also suggesting oxidation. An arsenopyrite grain was observed overgrown by marcasite (Fig. 3a). Pyrite grains were between 200-300 μm . Pyrrhotite grains were between 20-30 μm and often encapsulated

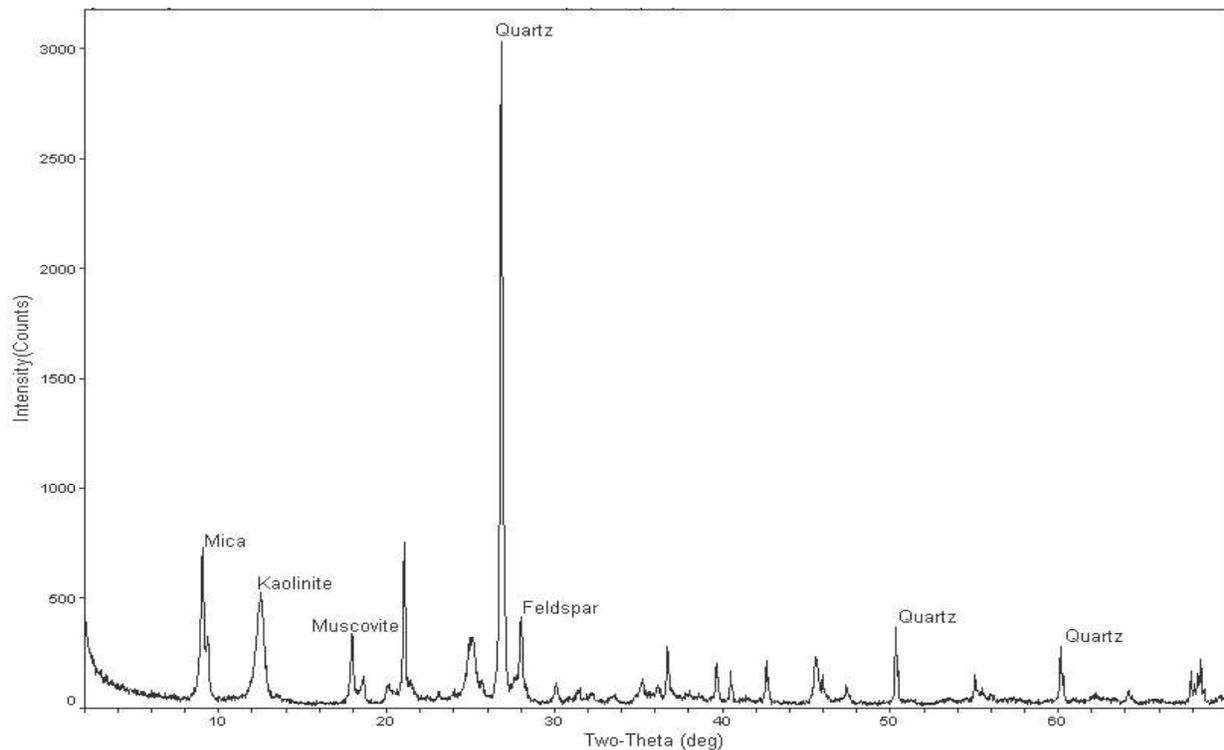


Fig. 2: X-ray pattern of tailings embankment material showing results of phase identification. Minerals identified are quartz, mica, kaolinite, feldspar and muscovite

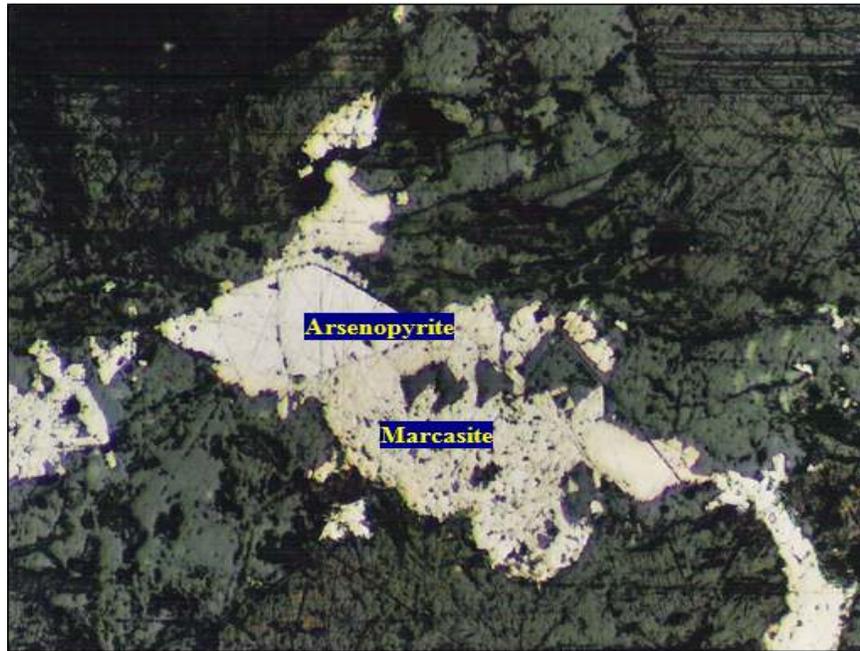


Fig. 3a: An arsenopyrite grain overgrown by marcasite. Field of view 40 mm

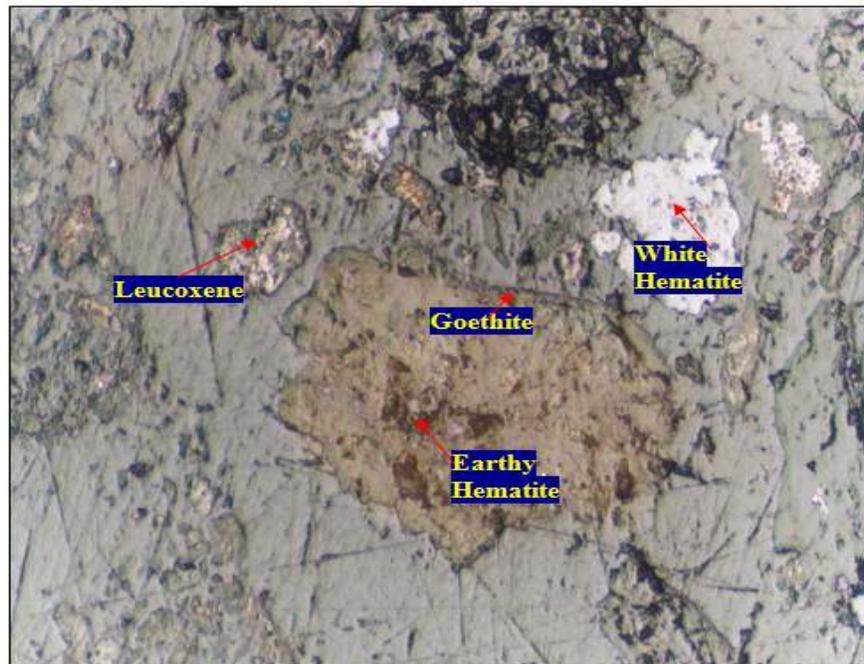


Fig. 3b: Biotite crystal oxidizing to goethite. Minerals identified are hematite, goethite and leucoxene. Field of view 40 mm

in pyrite. Locally, biotite phenocrysts may be oxidized to goethite (Fig. 3b). Total sulfide minerals were estimated at 0.7%. Arsenopyrite concentration was estimated at 0.4%.

Electron Microprobe Analysis (EPMA) and Scanning Electron Microprobe (SEM): Backscattered electron images of mineral grains from tailings material

indicate that sulfide grains are euhedral. Approximately 80% of sulfide grains identified have oxidation rims. Electron microprobe chemical mapping and image analyses were done to determine the sulfide mineral distribution and composition of oxide rims on pyrite and arsenopyrite grains. Scans on the oxide coating indicate high Fe with low but significant arsenic concentrations with minor calcium inclusions (Fig. 4).

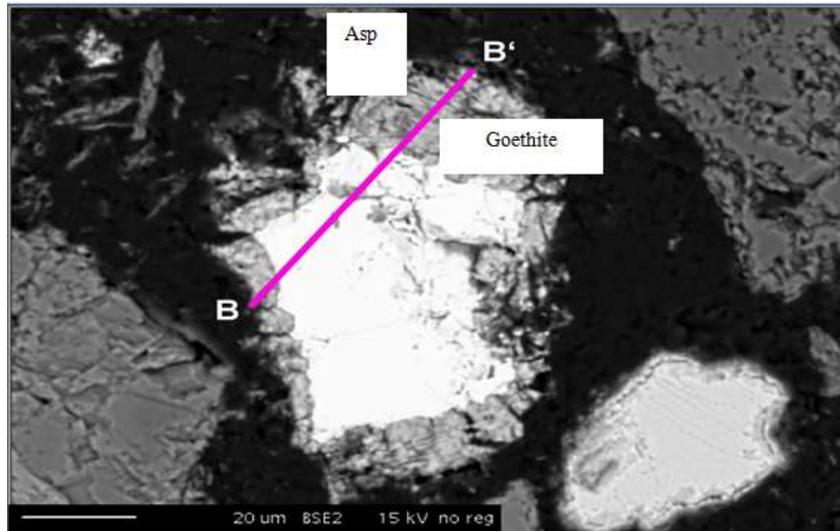
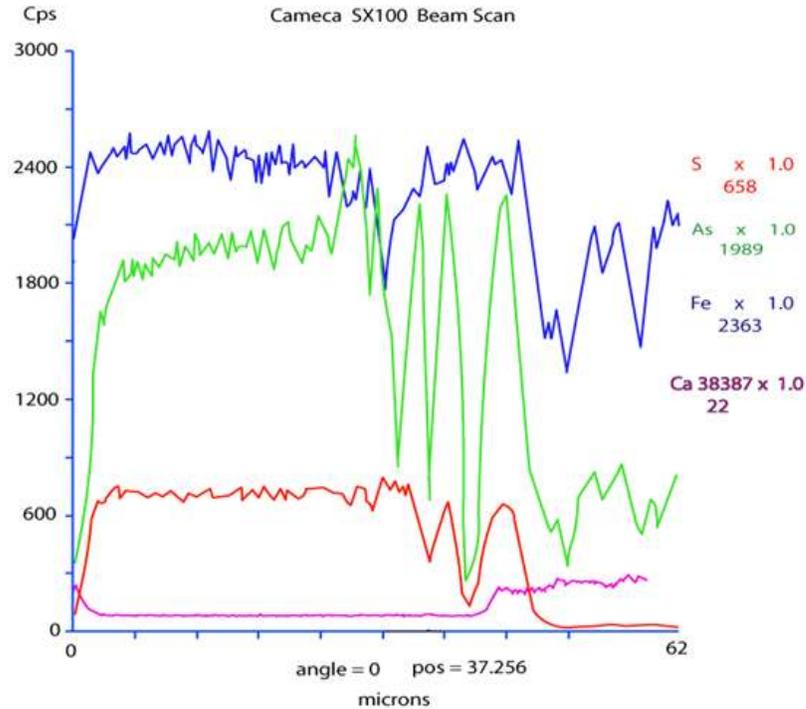


Fig. 4: Backscattered electron image and corresponding qualitative X-ray scans (for S, As, Fe & Ca) of arsenopyrite grain in a polished section and its alteration rim

It is not clear if the coating is an amorphous mixture of oxides or one of several minerals. Low analytical totals on the grains could probably be due to O₂ and C, which were not measured in the present study. However, appropriate amounts of O₂ were added to measured elements to convert them to oxides. A plot of molar Fe/As ratios versus totals of oxides (As₂O₅+FeO₄+CaO+ZnO+SO₃+CuO) is shown in Fig. 5. Three populated areas are located in Fig. 5. Region A represents areas with high analytical totals (~100) and low Fe/As ratios ≤1; this represent fresh material, B

represents areas with analytical totals between 30-60% and low Fe/As ≤1 representing areas that are oxidized but with no As loss. Region C represents areas with low analytical totals (30-60%) and Fe/As ranging between 1.5 and 2.7, this represents the oxidized zone with variable arsenic loss. High Fe/As ratios in grains indicate the removal of arsenic or addition of Fe, the former being more probable. The sum of Ca, As and S (as oxides) ranges from 0.20 to 2.69 wt% and averages 0.66%. The CaO content ranges from 0.01 to 0.13% and averages 0.3, while As₂O₅ concentrations range

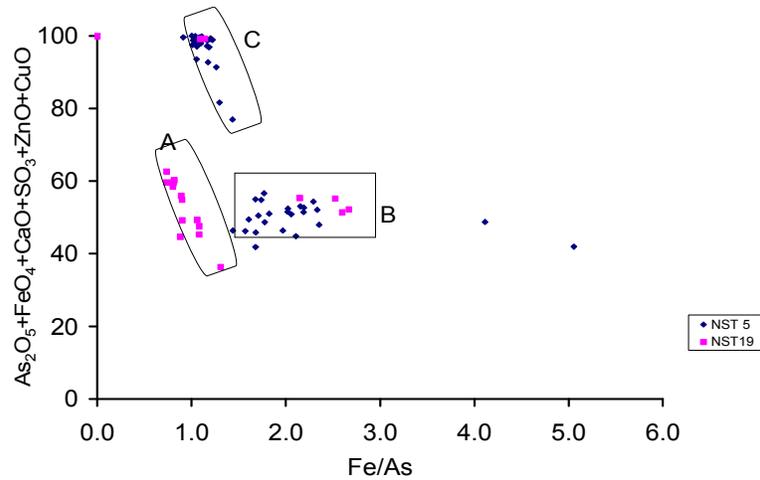


Fig. 5: A plot of Fe/As of an arsenopyrite grains versus $\sum (Fe_2O_3, As_2O_5, SO_3, CaO, ZnO, CuO)$. Oxides were calculated by adding appropriate amounts of O_2 since it was not measured during the analyses. Fe/As molar ratios range between 1.2-2.7

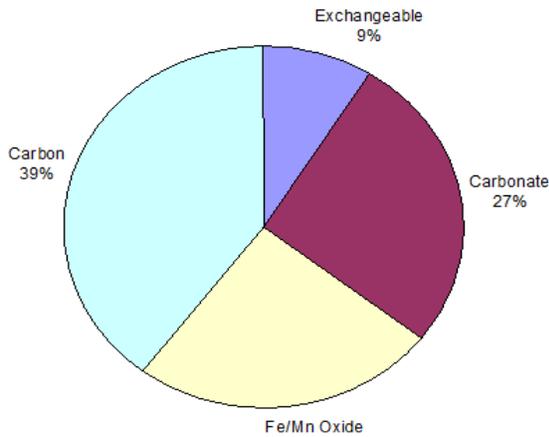


Fig. 6: Relative proportions of As associated with the exchangeable, carbonate, Fe/Mn-oxide and organic phases in sediment. Arsenic occurs mostly in organic fraction

between 0.26-0.97% and average 0.63%. These compounds can be accommodated in the goethite structure.

Sequential extraction: Sequential extraction of composite surface sediments shows As to be dominantly associated with organic matter (39%). The carbonate fraction contains 27% As whilst the Fe/Mn-oxides contain 25%. The exchangeable (ionically bound) fractions contained the smallest amounts: 9% As. This fraction represents the soluble arsenic minerals. The small amount of arsenic in this fraction indicates that soluble arsenic minerals may be weathered to more stable forms. Samples from different depths gave similar results. Figure 6 shows the proportions of As associated with the exchangeable, carbonate, Fe/Mn-oxide and organic phases in sediment. Arsenic occurs mostly in organic fraction.

DISCUSSION

Chemical conditions and controls: In the tailings dam near neutral pH values were measured in the pore waters, tailings pond waters, seepage pond waters and downstream waters. Mine discharge waters have a pH of 10 hence pH of mine tailings about 7.5 has to be the result of interaction of pore waters and tailings in the impoundment. These reactions must also generate the variations of pH seen down hole and from location to location in the impoundment. It is assumed that the tailings dam is in stage one of oxidation and equilibration recorded in abandoned tailings (Blowes *et al.*, 2005; 2003a) where carbonate minerals control pH generated by oxidizing sulfide minerals.

There are a number of significant differences between geochemical conditions in the Sansu tailings and abandoned tailings. There are no highly visible layers of secondary minerals like gypsum and iron sulfate minerals, such as jarosite and melanterite described by Sidenko *et al.* (2005), Patinha *et al.* (2004), Casiot *et al.* (2004), Courtin-Nomade *et al.* (2002b) and Paktunc *et al.* (1999) from tailings dams studies in Portugal, Russia and France. No visible layers exist within the Sansu tailings dam.

Ahn *et al.* (2005) identified secondary minerals like hematite, magnetite and calcium aluminum silicates (zoisite, $[Ca_2Al_3(SiO_4)_3OH]$) in the Nakdon tailings dam in South Korea. These minerals were identified in XRD patterns of the tailings sediments. The X-ray diffraction patterns of tailings sediments did not show the presence of iron minerals such as hematite even though hematite was identified in the petrographic studies. The tailings studied in temperate regions were generated mainly from the roasting of sulfide ores whereas the tailings under study were generated from bacteria leaching of sulfide ores.

At the dam there is no major stratification in Eh and pH as described by Blowes *et al.* (2003a, 2005), Savage *et al.* (2000, 2005) and Romero *et al.* (2006), in

tailings dams in Canada and Mexico. The tailings studied by these authors show pH stratification at values of 6.5, 5.5, 4.0 and 2.8 depending on whether acid generated by sulfide oxidation is neutralized by calcite, siderite, aluminum hydroxide or ferrihydrite. Rather there are fairly uniform Eh and pH conditions except from top to bottom. The pH in the tailings dam is near neutral and above neutral below 12 m depth. Equilibrium reactions between oxygen, sulfide minerals, carbonate minerals and sulfate appear to control chemical conditions from bottom to top of the impoundment.

Secondary mineral formation: The presence of secondary minerals elements by pH-controlled sorption processes and/or precipitation onto secondary minerals (e.g., Fe oxides) is a common phenomenon in tailings dam. This process is probably taking place in the active tailings dam since secondary minerals like goethite and hematite are present throughout the dam. Both goethite and hematite are known to sorb elements like As in their structure. In carbonate-rich tailings, where the acidity produced by sulfide oxidation is neutralized and pH values are near neutral (Blowes *et al.*, 2005). Sorption processes limit strongly the mobility of the bivalent metal cations. The concentrations of Fe (II/III), Al (III), SO_4^{2-} and other dissolved species are controlled by the formation of secondary solid phases such as gypsum and goethite, in response to changing pH and redox conditions.

Oxidation rims on sulfide grains (Fig. 4) suggest sulfide oxidation reactions are occurring in the sediments. However, there is no way to determine if the oxide rims were there in part or wholly the product of the BIOX process. Six arsenopyrite grains were identified and all showed oxidation rims of iron oxides (goethite), which indicates incipient oxidation of the arsenopyrite, suggesting local reduction of Fe sulfide mineral. Goethite identified on some grains may also be part of the original ore (Fig. 3b). There is abundant sulfate in pore water solutions but it is not clear if this sulfate is from oxidation of sulfide grains in the tailings or generated wholly during ore processing. Present discharge solution contained 1384 mg/L sulfate whilst pore waters contained up to 7000 mg/L SO_4^{2-} . The tailings pond also has SO_4^{2-} concentrations of 4228 mg/L. This suggests addition of SO_4^{2-} by sulfide oxidation assuming discharge sulfate has remained constant with time and evaporation and water additions by recharge rainfall are less than additions of discharge water. Pyrite is marginally unstable at the pH and Eh indicated by pore water analyses (Fig. 6). The oxidation of sulfide minerals requires oxygen, hence the low pore water Eh and high dissolved oxygen supports this mechanism.

Oxidation can occur by a series of inorganic reactions and action of bacteria.

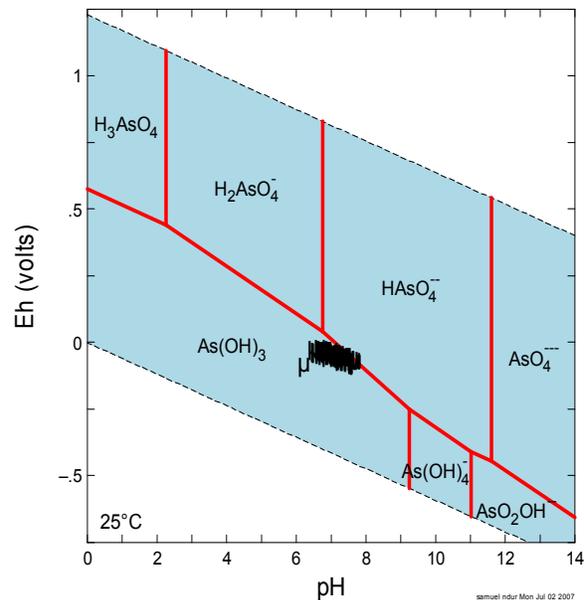


Fig. 7: Eh-pH diagram for S-As-H₂O showing 65 measurements of pore waters in 5 bore holes and 8 water locations. It is assumed that $[\text{S}] = 10^{-2}[\text{As}] = 10^{-4}$

Arsenic distribution in the tailings dam: Pore waters have concentrations of As up to 25 mg/L and the concentrations vary considerably with depth in the tailings. Other elements in pore water show considerable variation with depth with highs and lows at approximately the same depths in the locations sampled. It is not clear if these are entirely the consequence of chemical process or relict variations in tailings chemistry.

Profiles of As (III) and As (V) provide information on redox conditions prevailing in the tailings dam. Porewater speciation studies indicate As (III) concentrations are greater (up to 60%) than As (V) below 2 meters depth in the tailings dam reflecting the low Eh of this reducing environment. The relative high proportions of As (III) from mine effluent sources are also reported by Ficklin and Callender (1988). The concentrations of the two species plot on an Eh-pH diagram on the equilibrium line for As (III) and As (V) (Fig. 7).

This relatively high concentration of arsenopyrite with respect to pyrite in the Sansu tailings dam could also account for this observation. Nyashanu *et al.* (1999) report that bacterial leaching of concentrates with high ratios of arsenopyrite to pyrite produces more As (III) relative to As (V) in the initial stages of oxidation. They report relatively high concentrations of As (III) inhibit the activity of bacteria, resulting in the slowing down of the oxidation process. A similar process is probably occurring in the tailings dam since the amount of arsenopyrite in the tailings dam is approximately 50-65%.

Table 2: Sequential extraction procedure adopted for as in mine tailings samples

Fraction	Extractant	Target phase	Reference
Mg	1 M MgCl ₂ , pH 8.2, 1h, room temperature	Exchangeable (water soluble)	(Keon <i>et al.</i> , 2001)
NaOAc	1 M NaOAc, pH 5, 5 h, room temperature	Bound to carbonates	(Daus <i>et al.</i> , 1998)
NH ₂ OH.HCl	0.04 M NH ₂ OH.HCl, 6 h, 96°C±3°C	Bound to Fe-Mn oxides	(Keon <i>et al.</i> , 2001)
H ₂ O ₂	0.02 M HNO ₃ +30% H ₂ O ₂ , 2 h, 85°C±5°C	Bound to organic matter	(Loeppert and Inskeep, 1996)

Sequential extraction: Sequential extraction procedure was employed to determine the operationally defined arsenic binding. Processed ores average 1% arsenopyrite, but there is only 0.4% on average in the tailings. Therefore much of the arsenopyrite is destroyed during weathering and/or the BIOX process. Only a small fraction of the liberated arsenic is in pore waters, hence the arsenic must be in other minerals. As discussed above, no scorodite or other arsenic secondary minerals were found. Sequential extractions were used to identify the locations of the liberated arsenic (Table 2).

The fraction associated with the Fe/Mn fraction indicates that desorption from or dissolution of the Fe bearing solid phases would instigate the increase in arsenic extraction into the solution. The scavenging capacity of amorphous phases of Fe-oxides/hydroxides is well known and is often used to control trace element mobility (Welch, 1999). They are reactive in water-logged environments and retain an amorphous or weakly-crystalline structure due to alternate dissolution and re-precipitation. The scavenging capacity is attributed to their ability for non-stoichiometric co-precipitation with metals and large surface area that provides an abundance of sorption sites.

In the tailings sediments hematite and goethite were identified as original primary or secondary minerals formed by petrographic and X-ray spectral techniques. However, these methods do not necessarily confirm the presence of amorphous phases of Fe and Mn-oxides. Instead, they are inferred through partial extractions that are specifically designed for the selective dissolution of amorphous phases. The distribution of freed As in the tailings was not as expected. About 27% of the As extracted was removed with a reagent designed for selective dissolution of amorphous Fe-oxides (Fig. 5). Arsenic concentration in the carbonate fraction was (25%), which is slightly lower than the As in Fe/Mn fraction. It was unexpected to learn that about 39% of arsenic is contained in the organic fraction. Less As (9%) is associated with the exchangeable phase. It is not obvious why a significant portion of arsenic is associated with organic matter. It is here suggested that the organic material could originate from the ore that is mainly extracted from graphitic shear zones. In addition some of the bacteria employed in the BIOX Plant could end up in the tailings and thereby increase the organic content. The importance of organic materials or carbon in sequestering arsenic is reported by others. Welch (1999) shows that the carbonate fraction accounts for most of the arsenic in the Rio Grande, New Mexico.

CONCLUSION

- High ratios of arsenopyrite to pyrite produces more As (III) relative to As (V) in the initial stages of oxidation in the tailings dam.
- Much of the arsenopyrite is destroyed during weathering and/or the BIOX process.
- Illite, kaolinite and carbonates act as pH buffers and consume the acid generated during pyrite oxidation and raise the pH to near neutral measured in the tailings dam.
- No arsenic secondary minerals were found in the tailings dam.
- About 39% of the arsenic in the tailings dam is contained in the organic fraction of tailings sediments.

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