

# Effects of pH on arsenic mineralogy and stability in Poldice Valley, Cornwall, United Kingdom

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## Abstract

Many abandoned mine sites in Cornwall, UK, are characterised by elevated concentrations of arsenic (As), which can cause contamination of surrounding soil and water resources. These sites have important historical value that requires access to be maintained, despite exposure of humans to toxins that may lead to health issues including hyperpigmentation keratosis (including skin cancers) and liver fibrosis. The abandoned mine tailings at Wheal Maid has been assessed for As-bearing mineralogy and stability taking into account the public footpaths made by the local council to areas of potential contamination.

**Keywords:** Arsenic, Mining, Weathering, Scorodite, Thermodynamic, Mineralogy, Environmental Contamination, Oxygenated

## Introduction

Human exposure to high arsenic (As) levels can lead to numerous health issues. These include hyperpigmentation keratosis (including skin cancers) and liver fibrosis (ATSDR, 2013). Arsenic may form toxic dust that can rest on garden soils and footpaths that young children may ingest via hand to mouth (Bowell *et al.*, 2013). Arsenic is a known toxin (Pascoe *et al.*, 1994) and numerous studies have demonstrated higher As uptake in children (Eligali, 1994). However, a preliminary study of inorganic As and methylated metabolites in urine from adults and children in Cornish mining villages showed elevated urinary As contents (Farmer & Johnson, 1990). High As concentrations are commonly found associated with the desired ore products during the mining process and are typically discarded with the rest of the mine wastes (Craw & Bowell, 2014).

Mining for copper and tin in Cornwall began at least by the early eighteenth century (Hunt & Howard, 1994). Towards the end of the nineteenth century, Cornwall dominated copper, tin and arsenic production globally (Buckley, 2005). Prolonged periods of mining without environmental regulations have had

a significant impact to the surroundings (Bowell *et al.*, 2013). One such mine, the Wheal Maid is located in the Poldice Valley in central Cornwall (Figure 1). This site is of particular interest due to its popularity for outdoor recreation, the lack in reclamation of mine dumps, and its prominence in the production of As. Mine waste and derelict As kilns are still present at the site (Camm *et al.*, 2004). Runoff from the workings flow through tributaries approximately 2 km before entering the Carnon River to the southeast. The objective this study are to: (1) identify all potentially harmful contaminants and As-bearing minerals present at the site, (2) assess and evaluate the most common As-bearing minerals in an oxygenated mine tailings dam, (3) collect and analyse water, rock and soil samples from Wheal Maid and along the Carnon River, and (4) determine the minerals controlling As mobility and the effects of varying pH conditions. Thermodynamic and crystallographic data collected in (2), combined into an internally consistent thermodynamic database, can help to predict and explain the occurrence and assemblages of arsenates and associated minerals.

A conceptual model for the Wheal Maid mine tailings facility (Figure 2) was developed from observation of the general topography and the following assumptions are made through discussions during work onsite. These assumptions are made purely in a look-see basis so may not be representative for the study area. The assumptions are as follow:

1. Water falls onto the tailings facility from rainfall
2. Water from rainfall enters the Carnon River through surface runoff and infiltration of the tailings facility
3. Water flows downstream moving from tailings pond 1 to tailings pond 3 and enters the Carnon River through a controlled water barrier
4. Water in the tailings pond infiltrates only a minor amount of water into the deep “Great Adit” groundwater system and mixes with the tailings water leaving the facility at the controlled water barrier
5. Surface runoff is neglected in the model as it is not quantified, and the amount is deemed negligible compared to the flows from the tailings ponds and the “Great Adit” system.

## Methods

### *World Health Organisation Guideline*

Water samples representative of the mine tailings and the Carnon River were collected, and characterised following guidelines (Table 1) where available of the World Health Organization’s Guidelines for Drinking-water Quality (WHO, 2011).

## Field Methods

### *Water sampling*

Water samples were collected in June 2018 at each of the three tailings ponds and 400 m along the Carnon River (Figure 1). Sampling teflon vials were prepared in the lab using ultra-pure deionised and distilled water (to 18.2 MΩ cm resistivity at +25 °C) produced by the VWR Ultrapure water system, P series, to prevent contamination from bacterial growth. Each vial was filled with ultra-pure water that was removed before sampling. The VWR water system is built following Standard Operating Procedures, and a Certificate of Calibration for the temperature and resistivity

meters built into the system (VWR, 2019) At each sampling location, samples were taken using a Whatman syringe filter and two drops of 2% aqueous nitric acid (HNO<sup>3</sup>) were added (dwi, 2005). The location the pH was measured on site while collecting each sample using a Mettler Toledo 5-easy plus pH probe. The pH probe is calibrated on-site using three buffer solutions, pH 4.0, pH 7.0 and pH 9.21. Detection limit is not applicable. This process was replicated at least three times at each site.

### *Rock/Soil sampling*

Rocks and soils were samples June 2018 at five sites from high to low topography to determine the leachability of material from these solids. The top 10 to 20 cm of the surface material was removed prior to collecting these samples. This method was adopted to avoid solids may have been affected by surface chemical weathering. Samples were then retrieved and stored in separate labelled transparent sample bags (dimensions: 76 × 83 mm). Sampled sediments greater than 6 cm is size were considered as rocks, and those less than 0.5 cm as soil.

## Sample Analysis

### *Water sample analysis*

The collected water samples were stored in a refrigerator prior to analysis. Each was analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and the inductively coupled plasma mass spectroscopy (ICP-MS) for the major and minor elements respectively. The analysis was completed on a Varian 720 ICP-AES (axial configuration) equipped with autosampler and a Bruker M90 ICP-MS equipped with autosampler. In each analysis, 5 known and 5 blank samples were analysed simultaneously. The detection limits of all elements are all below 0.0001 mg/L which have been removed from the later calculations. ICP-analyses were run together with certified reference material TMDA-70 (fortified lake water) during each analysis session. The known and blank samples with the TMDA-70 were used to calculate the uncertainties of each analysis and check accuracy and reproducibility. The uncertainty of all elemental analyses were found to be less than +/- 10% when evaluated with TMDA-70.

### *X-ray diffraction*

Samples for diffraction analysis were prepared by side-filling the powder, against a ground-glass surface, into a 1.5 mm wide sample holder and consolidating it by gentle tapping. X-ray powder diffraction data were then collected with Cobalt (Co) Potassium (K) alpha ( $\alpha$ ) radiation, using a PANalytical X'Pert Pro diffractometer, with Bragg-Brentano para-focusing reflection geometry. The X-ray peaks produced are evaluated using the database provided by the PANalytical HighScore Plus software with the ICDD (International Centre for Diffraction Data) database. The minimum tip width for the searched peaks is 0.01, which corresponded to a relative error of 1%, the counting statistical error.

### *Geochemical Calculations*

Thermodynamic calculations in this study were computed with PHREEQC (version 3.5.0.14000) together with a modified version of the WATEQ4F.v4 database (Parkhurst & Appelo, 2013). This database was selected for this study because it includes the all of elements considered for this study of water quality in a mine tailings environment. The solubility constant of scorodite in the database was changed from  $10^{-20.25}$  to  $10^{-24.5}$ . This scorodite solubility constant value is different from that published in literature (Zhu *et al.*, 2019), as pure scorodite does not occur in the natural environment. Thus, the modified value for the scorodite + goethite system is more fitting for an acid mine drainage environment.

### *Additions to PHREEQC database*

Nordstrom *et al.*, 2014 described the PHREEQC thermodynamic database as an over-determined network in a theoretical sense, but also contains large uncertainties. This inconsistency led to the idea of evaluating previous literature on how solubility measurements were made, in return to limit the use of solubility products measured where large impurities were present. Wagman *et al.*, 1982 pointed out that typically two methods have been used to evaluate thermodynamic data, the sequential method, and the simultaneous fit method. In

this study, a mixture of both techniques have been used and the solubility products added to the PHREEQC input is shown in Table 2.

## **Results**

### *Mineralogy of the Mine Site*

Mineralogical samples collected from the Wheal Maid were found to be similar in composition confirming a similar style of mineralisation. Whole-sample XRD demonstrated that the predominant mineralogy for sand, silt and clay fractions are quartz, muscovite and chlorite. Cassiterite, dickite, lizardite ( $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$ ), and tourmaline are also present. These occurrences depend on local geology and weathering of nearby outcrops. Of the samples taken, the products identified by XRD include jarosite, goethite and pyrite ( $\text{FeS}_2$ ). Minor rutile ( $\text{TiO}_2$ ), arsenopyrite ( $\text{FeAsS}$ ), arsenian pyrite ( $\text{Fe}(\text{As,S})\text{S}$ ), löllingite ( $\text{FeAs}_2$ ), tennantite-tetrahedrite ( $\text{Cu}_{10}(\text{Zn,Ag,Fe})_2(\text{As,Sb})_4\text{S}_{13}$ ) have previously been reported at these sites, but were not observed in this study (Bowell, *et al.*, 2013).

### *Bulk Geochemistry*

#### **Hydrogeochemistry in the vicinity of the mine site**

To assess background levels of As in surface water, three tailings ponds and five river water samples were collected. The concentrations are compared with the WHO drinking water guideline values. Figure 3 delineates the As chemistry in each of the monitoring points. Other metal concentrations are presented in the appendix. The accumulation of metals in the tailings ponds results in highly acidic waters (pH 2-3) with As concentrations 2 orders of magnitude above the WHO drinking water guideline value (0.01 mg/L). Other elements with concentrations exceeding the WHO drinking water guideline values are Cd, Cr, Cu, Ni and Pb.

In the Carnon River, arsenic concentrations were 1 – 2 orders of magnitude above the 0.01 mg/L WHO water quality limits despite the pH being circum-neutral (pH 6-7). The pH of the waters was made near to neutral pH by the dilution of tailings pond waters with groundwater. Several elements including Cr, Cu and Ni had concentrations below the WHO limits in the river water, but Cd and

Pb concentrations remained to be above the drinking water guidelines.

## Discussion

### *Mass balance calculation*

Taking account of the conceptual model, water flows downstream from the tailings pond and enters the Carnon River through a controlled water barrier. The flow rate of the waters from the tailings pond and the underground source were not measure, hence, the mixing ratio of these waters was estimated through onsite observation of the quantity of water flowing from each source entering the river. The estimated mixing ratio of water entering the Carnon River comprises of 15% tailings pond water and 85% subsurface underground adit-water. This mixing ratio is understood to be representative as the majority of water entering the main river was observed to be from the underground source.

### *Geochemical Calculations*

The water chemistry at the monitoring points delineated in the previous section was used as inputs to the PHREEQC geochemical model and the saturation index (SI) of minerals was calculated. The SI of a mineral indicates the “tendency” of the water to want to precipitate the mineral, if the SI is at or above 0 (the solubility equilibrium, it indicates that the water wants to precipitate the mineral. The SI of the mine runoff waters before and after dilution with respect to scorodite is shown in Figure 4A which indicates that the SI ranges from -2.75 to +2.5. Scorodite is supersaturated in the second tailings pond water and in the marshland of the river which suggests that precipitation of the mineral is likely and can be a factor controlling As mobility in the waters.

Using the provided mixing ratios described, the water chemistry at the monitoring points were mass balanced and used as inputs to the PHREEQC geochemical model to produce the SI of scorodite downstream of the mixing zone (Figure 4B). The four orange bars represent the four monitoring points where predictions are made. Three out of four predictions are noticeably similar to the site measurement (blue bars). The constrains placed on the water calculations involved changing pH

(+/- 2 from pH 7) shown in Figure 4C. The bar charts suggest that changing pH alters the saturation index of scorodite significantly in the waters. With an increase of pH units (more alkaline), the water becomes heavily under-saturated in terms of the As-bearing mineral. However, in a more acidic environment (lower pH) the solubility of As is little affected.

The result of the mass balance indicate that an increase of pH leads to the waters becoming increasingly undersaturated with respect to scorodite. The SI of other As minerals have been studied but all minerals are shown to be heavily undersaturated in the waters, hence, scorodite is the most likely mineral to be controlling As concentration in the water. Thus, it may be expected that increasing the pH could lead to the enhanced concentration and mobility of As in the water. Due to the decades of infiltration of mine tailing water into the groundwater system, the dilution mechanism used previously does not prove to be effective as the water chemistry from the groundwater outlet is very similar to those found in pond C of the mine tailings.

## Conclusion

Wheal Maid mine tailings is integrated along a wider mining network known as ‘the Great County Adit’ that contains elevated concentrations of numerous potentially toxic metal(loid)s. The source of these metal(loid)s is related to past mine waste and disturbance of clay-rich country rocks leading to faster weathering rates from placing waste products in mine tailings sites. Arsenic concentrations in waters along the tailings dam and Carnon River range up to 3.6 mg/L which is more than 2 orders of magnitude above the WHO guideline value of 0.01 mg/L for drinking water.

This study indicated that the soil and water of mine tailings at Wheal Maid has the potential of releasing As and precipitating As-bearing minerals. The sampling programme captures information for the site during a relatively the summer period but could be improved by monthly sampling to monitor seasonal fluctuations in one year. The SI of scorodite was near to equilibrium indicating precipitation of the mineral is

likely, however, it doesn't conclude that it is the sole mineral controlling As concentrations. This study highlights the need to better understand As-bearing minerals and slight

environmental changes such as increase alkalinity in waters may cause serious consequences in an industrial setting.

**Figures**



Figure 1 Map of St Day, Cornwall, South-west England and the location of Wheal Maid.

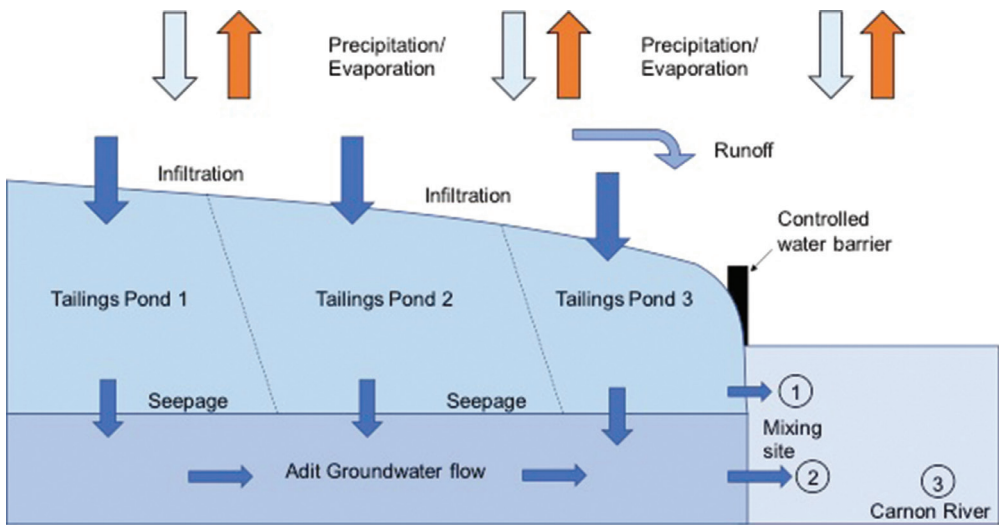
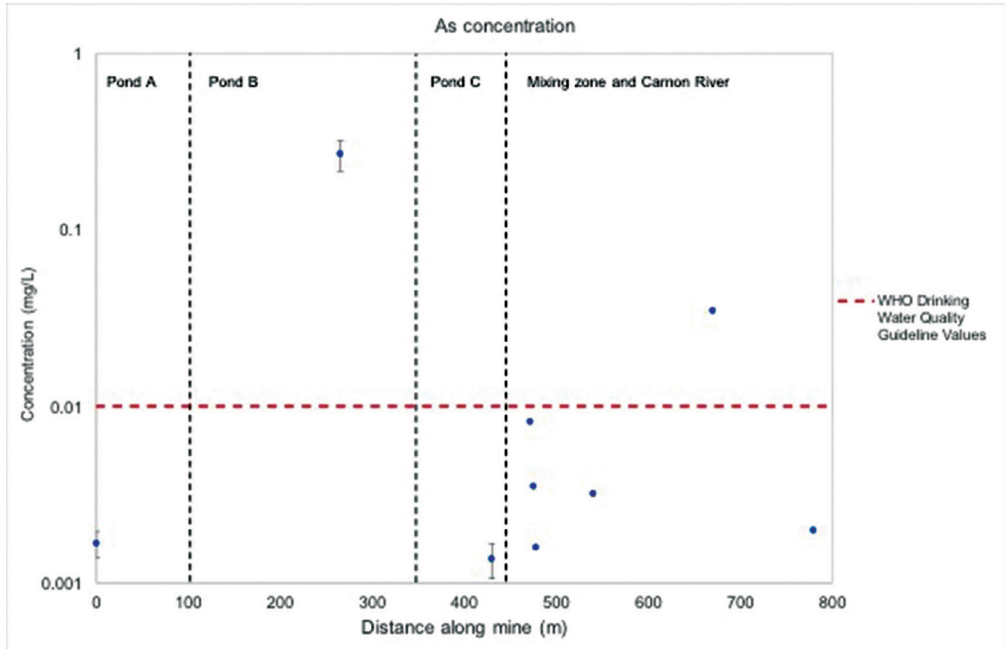


Figure 2 Conceptual model for the flow of water through the tailings to the Carnon River.



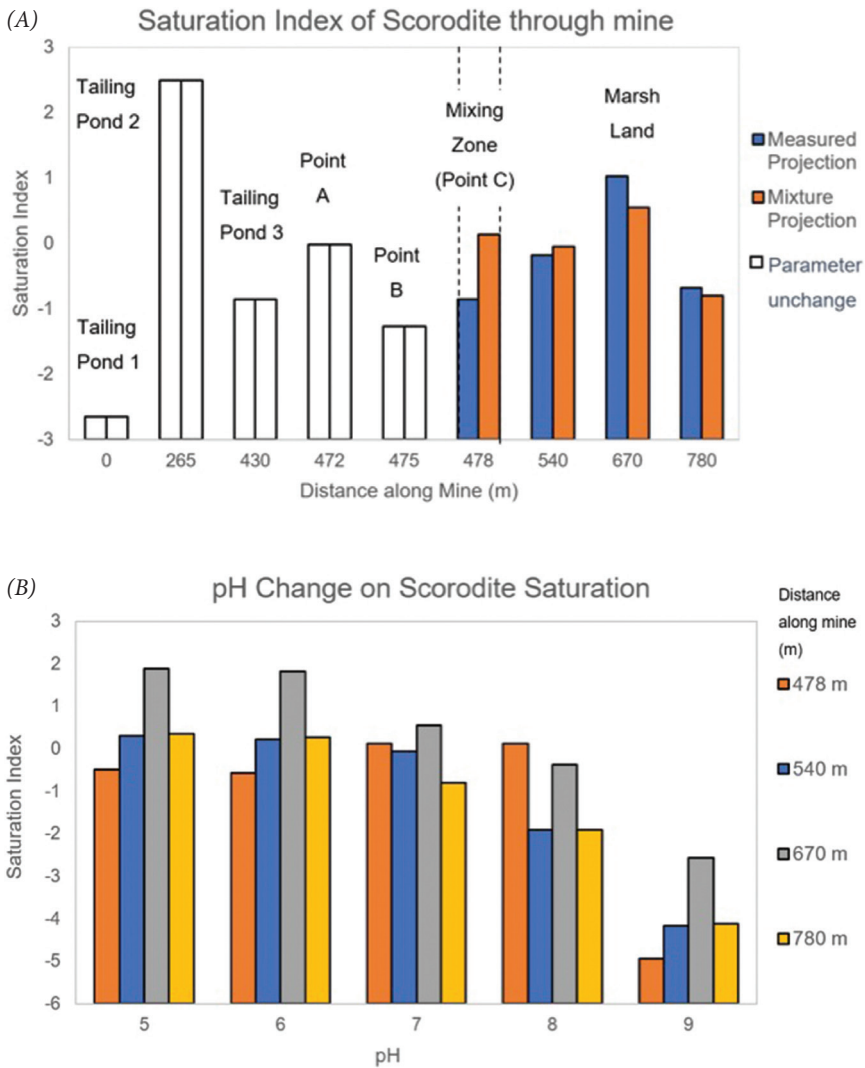
**Figure 3** Arsenic concentration in the water compared to WHO guidelines (WHO, 2011). The location names are as follow: (A) Tailings Pond A; (B) Tailings Pond B; (C) Tailings Pond C; (D) Carnon River.

**Table 1** WHO Drinking Water Quality Guideline Values (WHO, 2011).

Element	WHO Drinking Water Quality Guideline Values (mg/L)
As	0.01
B	2.4
Ba	0.7
Cd	0.003
Cr	0.05
Cu	2
Ni	0.07
Pb	0.01

**Table 2** Solubility data updates made to PHREEQC database.

Additional Phases	Log K	Delta h (kJ/mol)	Reference papers
Arsenosiderite	-21.6	-51.5	Paktunc et al., 2015
Pushcharovskite	-17.2	0	Plumhoff et al., 2020
Geminite	-15.9	0	Plumhoff et al., 2020
Liroconite	-4.92	0	Plumhoff et al., 2020
Zýkaite	-77	0	Majzlan et al., 2015
Haidingerite	-4.79	0	Bothe and Brown (1999b)
Scorodite	-24.5	0	Zhu, et al., 2019



**Figure 4** Saturation index of Scorodite along mine.  
 (A) Comparison of measured (blue) and mass balanced (orange).  
 (B) SI change varying pH +/- 2 from natural conditions of mass balanced values.

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