

Review

Evolution of Sulfidic Legacy Mine Tailings: A Review of the Wheal Maid Site, UK

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Abstract: Historic tailings dams and their associated mine waste can pose a significant risk to human and environmental health. The Wheal Maid mine site, Cornwall, UK, serves as an example of the temporal evolution of a tailings storage facility after mining has ceased and the acid-generating waste subjected to surficial processes. This paper discusses its designation as a contaminated land site and reviews our current understanding of the geochemistry, mineralogy, and microbiology of the Wheal Maid tailings, from both peer-reviewed journal articles and unpublished literature. We also present new data on waste characterisation and detailed mineral chemistry and data from laboratory oxidation experiments. Particularly of interest at Wheal Maid is the presence of pyrite-bearing “Grey Tailings”, which, under typical environmental conditions at the Earth’s surface, would be expected to have undergone oxidation and subsequently formed acidic and metalliferous mine drainage (AMD). The results identified a number of mechanisms that could explain the lack of pyrite oxidation in the Grey Tailings, including a lack of nutrients inhibiting microbial Fe(II) oxidation, passivation of pyrite mineral surfaces with tailings processing chemicals, and an abundance of euhedral pyrite grains. Such research areas need further scrutiny in order to inform the design of future tailings facilities and associated AMD management protocols.

Keywords: acid mine drainage; mine waste legacy; metal pollution; pyrite; mineral oxidation



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1. Introduction

The Wheal Maid tailings dam is a legacy valley infill tailings repository located in the Gwennap Mining District, Cornwall, UK (Figure 1A). During the 1970s and 1980s, it received fine-grained mineral processing wastes (predominantly tailings) from the mill facilities at two adjacent mines: Mount Wellington and Wheal Jane [1]). It is amongst the most highly contaminated sites in the United Kingdom, based on its formal designation as Contaminated Land under Part 2A of the Environmental Protection Act 1990. This designation was on the grounds that the exposed tailings cause a *significant possibility of significant harm* to human health and that the pollution of controlled waters is being caused (Table S1, [2]). Arsenic was designated as being amongst the most major contaminants present, and it was concluded that there is *significant possibility of significant harm* to site users (most commonly mountain bikers) due to the potential for the ingestion, dermal contact, and inhalation of arsenic-contaminated soils. As well as this, arsenic, cadmium, chromium, copper, iron, lead, nickel, and zinc were also designated as *currently resulting* in the pollution of controlled waters. This was concluded as *currently occurring* for the St Day Stream due to “leaching from contaminated soils through the lower dam” and *likely occurring* for the St Day Stream and groundwater adjacent to Wheal Maid due to “leaching from contaminated soils through culvert walls” and “leaching from contaminated soils”, respectively [2].

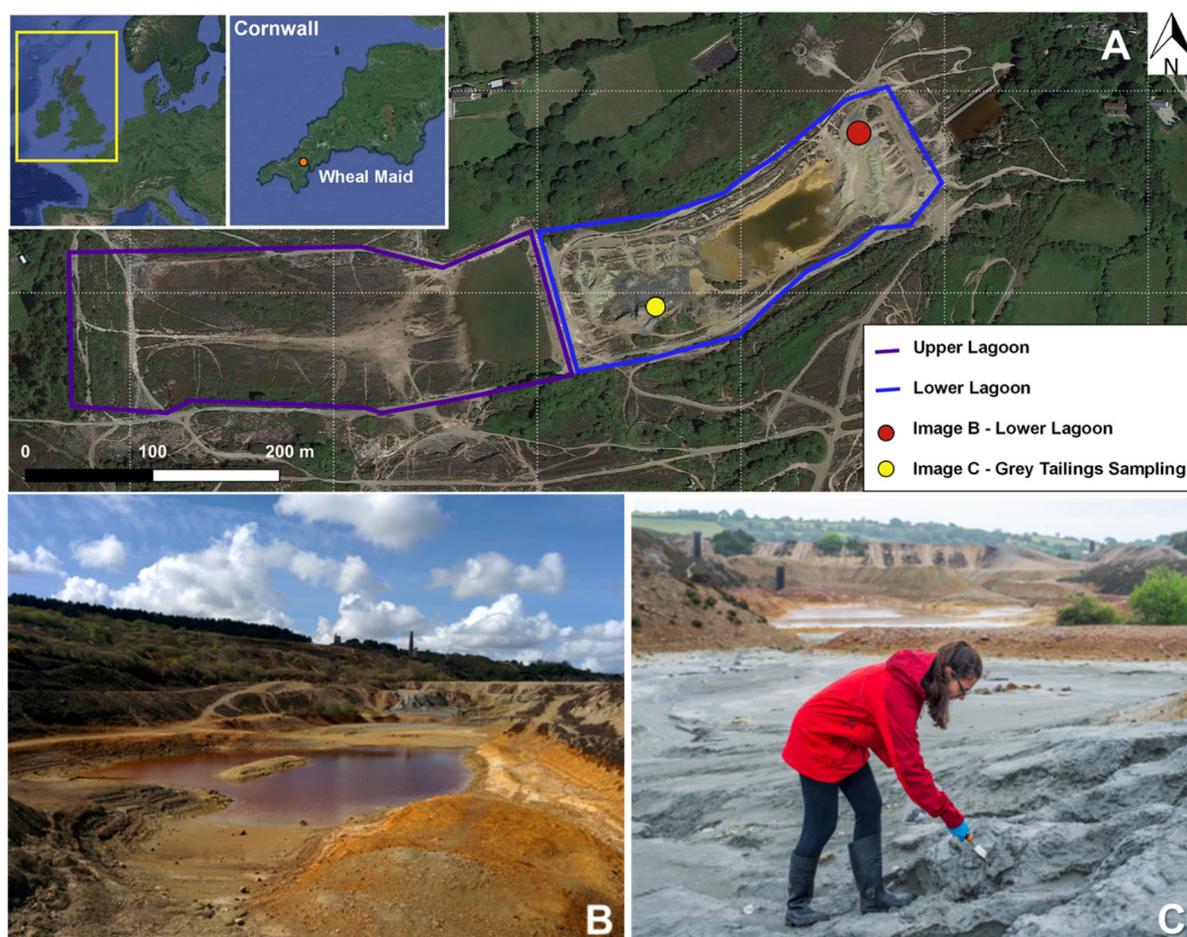


Figure 1. (A) Site location and layout. Grid Reference 50° 14' 15" N 05° 09' 34" W, showing the location of the site in Cornwall, UK and the tailings dam (upper lagoon shown in purple, lower lagoon in blue, location of 1B shown by red marker, location of 1C shown by yellow marker); images compiled in QGIS. (B) Photograph of the lower lagoon (R. Crane). (C) Photograph of sampling the Grey Tailings (C. Wilson, LLE Photography).

The mine waste at Wheal Maid comprises an acid producing system (Figure 1B). This is due to the abundance of sulfide-bearing minerals (particularly pyrite, FeS_2) that undergo oxidation upon exposure to air and moisture, producing sulfuric acid and leading to metal ion dissolution [3]. This is a relatively slow process when O_2 is the oxidant, but Fe^{3+} is much more effective; certain microorganisms gain energy from oxidising Fe^{2+} to Fe^{3+} , and some can also oxidise reduced forms of S to sulfate. As such, microbial iron and sulfur oxidation can increase the rate of pyrite oxidation by up to five orders of magnitude at a low pH [4]. These microorganisms are referred to as acidophiles, and they significantly contribute to the formation of acid mine drainage (AMD). Pyrite can exist with other chalcophile elements such as As, Cd, Cu, Pb, Sb, Sn, and Zn [5], which are mobilised by the acidity produced by microbial pyrite oxidation. Acidophilic microorganisms can increase sulfur oxidation during the dissolution of arsenopyrite [FeAsS], chalcopyrite [CuFeS_2], marcasite [FeS_2], and sphalerite [ZnS], as well as pyrite [6]. Thus, once oxidised, potentially toxic elements previously adsorbed onto the surface or associated with pyrite are released to the solution [7,8]. Although many acidophiles can obtain carbon autotrophically, their growth and metabolic activity in mine waste may be limited by the availability of other essential nutrients, such as nitrogen and phosphorus [9–11].

The site has been studied through various research and teaching activities at the Camborne School of Mines, University of Exeter, UK. The purpose of this article was to review the state-of-the-art knowledge on the mine waste mineralogy and geochemistry, using both

published and unpublished data, and interviews with local people with knowledge of the site (Table S2). New data characterising mineral chemistry and data from experiments conducted to stimulate mineral oxidation are presented, with the methodology given in the relevant sections. We highlight some unconventional aspects where the mine waste does not behave as expected and identify gaps in knowledge that limit our understanding of metal behaviour and environmental risks at the site.

2. The Wheal Maid Site and Its History

2.1. Site Overview

The Wheal Maid tailings facility comprises two tailings lagoons (an upper and lower lagoon) that are separated by three retaining dams constructed perpendicularly to the valley walls [1] (Figure 1C). The site is approximately 8 ha and holds approximately 220,000 m³ of tailings [2]. The St Day stream flows west to east through the site via a 1.2-m-wide culvert, which discharges into the Carnon River at the eastern edge of the site. Part of the Great County Adit runs north to south below the site. The site is underlain by a minor aquifer, but there are no licenced groundwater supplies near to the site [2]. The average annual temperature is approximately 11–12 °C, with an average annual rainfall of 900–1000 mm [12]. Wheal Maid and the areas surrounding the site have been designated as being either culturally or ecologically important. In July 2006, the Cornwall and West Devon Mining Landscape, which encompasses the Gwennap Mining District, was added to the UNESCO World Heritage List. These mining landscapes were added as they “reflect the substantial contribution the area made to the industrial revolution and formative changes in mining practices around the world”. Wheal Maid is also co-located or adjacent to priority habitats: lowland heathland and deciduous woodland [13]. The area to the north, where the previous Poldice mine is located, is a Site of Special Scientific Interest (SSSI).

2.2. Site History

Mining activity started at the site in the early 1700s. During 1780–1806 and 1819–1840, Wheal Maid worked as part of the Great Consolidated Mines, which was a collective of mines found within the Carnon Valley, primarily exploited for copper, but some tin was also recovered. At the time, the Great Consolidated Mines was the richest copper mine in the world. From 1852–1873, the mines then formed part of the St. Day United, which was later renamed Poldice Mines. During the late 1900s, the Mount Wellington Mine began to rework the mineral deposits at Wheal Maid.

By 1976, mining was no longer occurring at Wheal Maid; instead, Cornwall Tin and Mining Ltd. began construction on the downstream and intermediate embankments and on the concrete culvert. Cornwall Tin and Mining Ltd. still had active processing facilities at the nearby Mount Wellington Mine, and they disposed of their mill tailings by pumping the slurry along the valley and into the lower tailings lagoon (Figure 1B). The surface plant at Mount Wellington was then bought by Billiton Minerals UK. They constructed the upstream embankment and a further 395 m of culvert at Wheal Maid. In late 1979, they began to reprocess material in the downstream dam along with other material from the Carnon Valley. All these reworked deposits were then pumped into the upstream dam at Wheal Maid.

Mount Wellington Mine closed in 1981, with control of the tailings dams passing to Carnon Consolidated Tin Mines Ltd., who also owned the nearby Wheal Jane tin mine. Various studies were carried out, but no further deposits were pumped into the dams. The upper lagoon was partially restored by seeding in an attempt to prevent wind-blown dust. The results of that can be seen today, with a growth of a variety of vegetation across the dam surface. The site is now owned by the Gwennap Parish Council, who bought the site for GBP 1 in 2002 [2].

2.3. Historic Processing and Storage of Waste Materials

To understand the composition and behaviour of the tailings that are causing contaminated land issues, it is important to understand the processes by which they were produced. At the nearby mines Mount Wellington and Wheal Jane, mineralisation is predominately hosted within this series of metamorphosed Upper Devonian sedimentary rocks, locally termed “Killas” [14]. The main lodes worked in the area are parallel to sub-parallel, trending from EW through to ENE-WSW and contained As, Cu, Fe, Sn, Ti, and Zn. They also showed minor amounts of Ag, Au, Bi, Pb, and Sb and W [15]. Both Mount Wellington and Wheal Jane mined the same mineralised structure, “B” Lode. This was a flat, dipping (5–40°) quartz–tourmaline–chlorite–sulfide structure. Concentrates of Sn, Cu, and Zn were produced by these working mines [14].

There is limited information on how rock was processed at Mount Wellington. After discussions with previous workers at Wheal Jane (Table S2), the two mines carried out very similar processing techniques. Therefore, the processing technique at Wheal Jane is briefly discussed here. Firstly, ore was crushed and ground in three primary crushing stages. Stage one was underground using a jaw crusher to reduce the feed to around 150 mm [16]. The other two primary crushing stages were carried out at the surface, using cone crushers to reduce the size of the feed to 10 mm. Then, two secondary crushing stages were carried out, including wet screening and classification to remove slimes. This obtained a yield material at 10 mm. The next stage was primary grinding, which was achieved through open circuit rod milling, followed by closed circuit ball milling. This ground 90% of the material to >300 µm [16].

After this, the ore was passed through a bulk sulfide float with a regrind circuit attached to it. The tailings contained the tin bearing minerals and the floats contained sulfide minerals, including Cu, Zn, and associated Ag. Here, differences in the surface properties of minerals were exploited using the processing technique of froth flotation [17]. Reagents were added to attach to certain minerals to make them water repellent. Blowing air through the slurry caused the minerals to attach to the air bubbles and float for collection. The tailings from the bulk sulfide flotation circuit were then hydrolysed, with the coarser fractions being fed to shaking tables from which concentrates were classified. Tin minerals have a much higher specific gravity than the waste rock. Therefore, it was possible to separate the two using shaking tables [16].

A notable feature of Cornish mining is that centuries old mine waste can be reworked to obtain minerals that were at the time discarded on the waste pile [17]. This is true for the tailings at Wheal Maid, which have been reworked and deposited extensively through time. There is no real record of where the waste was derived from and when it was deposited into the lagoons. Both Mount Wellington and Wheal Jane were involved, at some time, in the reworking of the tailings. However, Wheal Jane had its own storage facility for tailings, so did not deposit tailings at the site.

It is common practice for tailings to be stored in isolated areas, laid down underneath pools of water, and retained behind dams. Being stored under water means the potential for the tailings to come into contact with the atmosphere is greatly reduced, thus limiting the amount of oxidation occurring [18]. Isolation and well-constructed dams are essential to prevent any contamination from entering groundwater, surface waters, or dust generation. Wheal Maid, with its two tailings ponds with three retaining dams, is classed as a cross-valley impoundment, as the dams are orientated perpendicular to the valley walls. Pools of water at the site change in volume with varying weather conditions. In areas, the embankment of the lagoons have undergone some collapse, and it is known that groundwater from the lower lagoon seeps into the St Day stream [2].

3. Characterisation of the Wheal Maid Waste

3.1. Waste Types and Mineralogy

3.1.1. Review of Previous Data

This section summarises available information on the different waste materials found at the site and their mineralogy. The four main waste types at Wheal Maid were identified based upon both physical properties of the materials and their occurrence at the site, categorised as Marbled Tailings, Grey Tailings (Figure 1C), Mine Waste, and Capping Material (Table 1) [1].

Previous research used X-ray diffraction (XRD) to identify the main minerals present at Wheal Maid as quartz [SiO₂], tourmaline [a borosilicate], pyrite, and muscovite [an aluminosilicate] (Table 1; van Veen et al., 2016). Similarly, [19] identified the major minerals as quartz, chlorite [(Mg,Fe,Li)₆AlSi₃O₁₀(OH)₈], and muscovite, with aluminosilicates [kaolinite, dickite], borosilicates [tourmaline, schorl], iron sulfates [pyrite jarosite, jarosite], goethite [FeO(OH)], and cassiterite [SnO₂] as accessory minerals. No specific As-bearing minerals were identified in either study, although arsenopyrite [FeAsS] and other As phases have been reported at nearby locations [15].

Table 1. The different mine waste types located at Wheal Maid.

Material Type	Physical Appearance	Photographs	Location at the Site	Minerals Identified by XRD [20]
Marbled Tailings	Visually distinctive red/brown/yellow mottled tailings. Predominantly made up of clay/silt, with sand and some gravel.		Located within the lower tailings lagoon.	Major: quartz, tourmaline, albite, and muscovite. Minor: nacrite, clinocllore, and pyrite.
Grey Tailings	Distinguishable due to the presence of pale, yellow pyrite minerals, with a grey fine to medium sand matrix.		Found in a distinct area within the central western part of the lower lagoon.	Major: quartz, muscovite, tourmaline, and pyrite. Minor: albite, nacrite, and secondary rozenite.
Mine Waste	Granular material with varied particle size, but it typically contains clay/silt, sand, and gravel fractions.		Found around the perimeter of the tailings depository and was used to construct the dams.	Major: quartz, muscovite, tourmaline, and nacrite. Minor: albite and clinocllore.
Capping Material	Found to be granular and contains roughly equal amounts of clay/silt, sand, and gravel material. Although, the gravel fraction visually appeared to be finer and more regularly sorted than the mine waste.		Caps underlying tailings across both of the lagoons.	Major: quartz, muscovite, tourmaline, and nacrite. Minor: albite and clinocllore.

Scanning Electron Microscopy Mineral Liberation Analysis (SEM-MLA) performed by [20] provided evidence that the Grey Tailings contain a much higher abundance of pyrite than the Marbled Tailings, with mean values of 18.4 and 0.1 wt.% recorded, respectively. Sphalerite (mean 0.2 wt.%) and chalcopyrite (mean 0.1 wt.%) were also identified within several of the Grey Tailings samples. Oxidised Fe minerals, including ferrosaponite (a smectite clay mineral) and Fe-OH-As, were higher in the Marbled Tailings than the Grey Tailings, with 22.6 and 1.6 wt.%, and 15.0 and 0.4 wt.% recorded, respectively. Other minerals of note in the Marbled and Grey Tailings included: quartz (mean values of 16.5 and 36.4 wt.%); montmorillonite (a phyllosilicate clay mineral) (mean values of 7.2 and 11.6 wt.%); and chamosite (an Fe(II)-bearing chlorite clay mineral) (mean values of 14.4 and 4.4 wt.%).

The particle size distribution (PSD) for the Grey Tailings was reported to be 75% sand and 25% clay/silt ($n = 1$), and the Marbled Tailings were 14%–15% gravel, 34%–35% sand, and 50%–52% clay/silt ($n = 2$), demonstrating that they were relatively fine grained (URS, 2007). The range of measurements for the Capping Material included 13%–77% gravel, 15%–55% sand, and 8%–41% clay/silt ($n = 9$), and for Mine Waste, it included 9%–57% gravel, 26%–54% sand, and 16%–36% clay/silt ($n = 5$), indicating their more coarse nature (URS, 2007). These are similar to the range reported by Crane et al. (2017), who found that the PSD for a composite sample for the entire site comprised 18.2 wt.% gravel (particle size range 2–64 mm), 70.3 wt.% sand (particle size range 0.063–2 mm), and 11.5 wt.% silt/clay (particle size range < 0.063 mm).

SEM was used to observe the texture of each waste material before and after it was subjected to hydrogen peroxide (oxidative) leaching [20]. Images of the Grey Tailings showed that both serrated and non-serrated pyrite grains were initially present; the serrated pyrite grains indicated that some degree of oxidation had already occurred. After leaching, the previously serrated grains were generally more corroded. However, euhedral pyrite grains remained present in the residue; therefore, even in very strong oxidising conditions, some pyrite grains are resistant to oxidation. SEM images of the Marbled Tailings showed that they contained sulfide minerals before being subjected to the oxidation test. The residue displayed minimal amounts of sulfides; instead, sulfates were present and therefore oxidation of sulfide minerals had occurred.

3.1.2. Methodology

Additional samples of the Grey Tailings and Marbled Tailings (Figure S1) were dried, powdered, and analysed by XRD (Siemens D5000 Powder Diffractometer, 40 kV, Cu $K\alpha 1/2$).

3.1.3. Results of Additional XRD Analysis

The results of the additional XRD mineralogical characterisation were similar to those previously reported, with the Grey Tailings containing pyrite, quartz, and uvite (a borosilicate). Sulfide minerals were absent from the Marbled Tailings, and instead, oxidised phases such as jarosite [$KFe_3(SO_4)_2(OH)_6$] were observed, along with quartz, muscovite, clinocllore (an aluminosilicate), and dravite (a borosilicate).

3.1.4. Mine Waste Mineralogy Summary and Discussion

Both the fine-grained Grey and Marbled Tailings contained sulfide minerals, with considerably more pyrite present in the Grey Tailings, which reflects the grey colouring. Minerals containing oxidised Fe and S were present in the Marbled Tailings, and, together with the presence of fewer sulfide minerals, we could assume that the Marbled Tailings represent a more oxidised form of the Grey Tailings. While experiments showed that the sulfides in the Marbled Tailings were oxidised by hydrogen peroxide, some pyrite remained present post-oxidation in the Grey Tailings. The resistance of fine-grained pyrite in the Grey Tailings to oxidation in the environment and to hydrogen peroxide is unexpected, as pyrite is typically readily oxidised under such experimental and environmental conditions. Further investigations into the limited oxidation of pyrite in the Grey Tailings are required.

3.2. Geochemical Analysis of Bulk Waste Samples from Wheal Maid

3.2.1. Review of Previous Data

Materials collected from Wheal Maid have been characterised for their metal content and associated risks to human health. Solid waste, groundwater, and surface water samples were analysed for their metal content [1]. Waste samples were collected based on a square grid pattern and taken at or near the surface (up to 30 cm deep). Samples were digested in aqua regia digest then analysed by ICP-MS. The results were compared to UK Soil Guideline Values or Generic Assessment Criteria, based on residential land use without plant uptake. Concentrations of As in all waste samples (Figure 2) considerably exceeded the screening value of 20 mg kg^{-1} (site mean 1182 mg kg^{-1}), while concentrations of Pb exceeded the screening value of 450 mg kg^{-1} in 9 samples (geometric mean 143 mg kg^{-1}) [1]. Other metals did not generally exceed their screening values. Values for soil pH varied across the site from 2.41 to 6.13 (Figure 2), and the lowest readings were reported from samples of the finer grained Grey and Marbled Tailings [1]. The tailings exhibited an average paste pH of 2.39, which confirmed their acid producing properties [13]. The presence of pyrite was suggested to be the main source of low pH at the site.

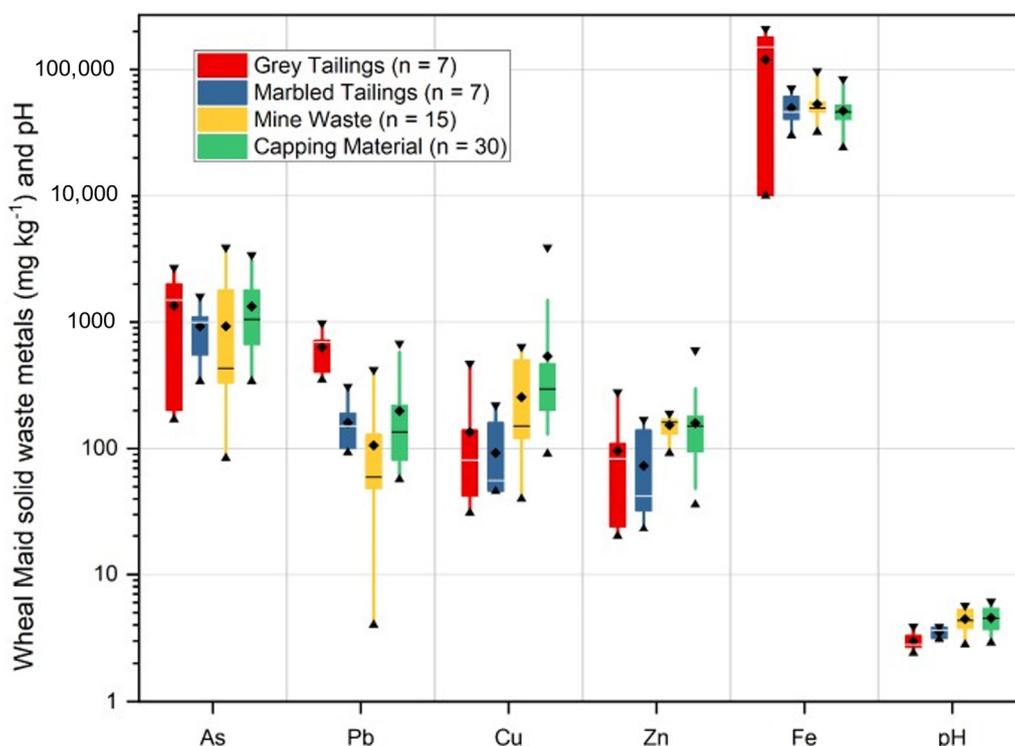


Figure 2. Concentrations of metals and pH in Wheal Maid waste samples (figure drawn from data collected by [1]). The box covers the interquartile range, the line is the median, and the diamond is the mean. The whiskers are drawn at the 5th and 95th percentile, and the maximum and minimum values are shown with triangles.

Since the URS report was published, Soil Guideline Values have been replaced by Category 4 Screening Levels (C4SL); these include screening criteria for public open spaces (e.g., parks) which may be more appropriate for an open access site such as Wheal Maid [21]. In this scenario, the provisional C4SL for arsenic is 170 mg kg^{-1} and for lead is between 580 and 1400 mg kg^{-1} depending on the exposure pathway. Almost all measured concentrations of As at Wheal Maid (56 out of 59) and some Pb concentrations (6 out of 59) exceeded these screening values and therefore may pose a risk to human health. Of the Pb exceedances, five were from Grey Tailings, which represent a significant proportion of

those samples. The highest concentrations of As were encountered in the coarser grained Mine Waste and Capping Material.

The metal content of waste samples was also investigated by [13]. Samples were collected at a depth of 0.2 m at equal distances around the base of the lower lagoon and analysed for metal concentrations following the methodology of ASTM D6009-12. In brief, samples were homogenised, subjected to total acid digestion, and then analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES). Results were largely in agreement with [1], again showing reasonable variability in metal and metalloid concentrations across the site. For example, Fe concentrations varied from 32.7–241 g kg⁻¹, As from 186–5360 mg kg⁻¹, Pb from 41–973 mg kg⁻¹, Cu from 33–1910 mg kg⁻¹, Zn from 95–6360 mg kg⁻¹, and Cd 3–40 mg kg⁻¹ [13].

Correlation plots (Figure S2) showed that concentrations of metals were generally positively correlated (e.g., concentrations of lead, copper, zinc, and iron were generally higher when concentrations of arsenic were higher), although few significant trends were observed when the samples were divided into the different types. One exception was the Grey Tailings, which showed significant positive correlations between arsenic and iron ($R^2 = 0.97$), arsenic and zinc ($R^2 = 0.75$), and significant negative correlations between pH and iron ($R^2 = 0.85$) and pH and arsenic ($R^2 = 0.83$). This suggests that arsenic and iron are closely associated in these samples, with the highest concentrations occurring in the samples with lower pH.

3.2.2. Methodology

Additional analyses were performed to characterise the bulk geochemistry of the mine wastes. Two samples of Grey Tailings and Marbled Tailings (Figure S1) were oven dried overnight and analysed by X-ray fluorescence (XRF, Wheal Jane Laboratories Ltd., Cornwall, UK). An additional sample each of Grey Tailings and of Marbled Tailings were split into two, digested in aqua regia, and metal concentration analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

3.2.3. Mine Waste Geochemistry Results

The results of the XRF analysis showed that the samples mostly comprised Si, Fe, Al, and S, reflecting typical rock forming minerals and the abundance of S minerals in the waste (Figure 3A,B). There was considerable variability in the proportion of elements between the samples. Significantly higher concentrations of S and Na were present in one of the Grey Tailings samples. Concentrations of As were much higher in the Marbled Tailings (14–55 g kg⁻¹) compared to the Grey Tailings (1.7–2.5 g kg⁻¹), and Pb was only detected in the Grey Tailings (1.3–1.4 g kg⁻¹), while concentrations of Cu (0.2–0.5 g kg⁻¹) and Zn were broadly similar (0.1–0.4 g kg⁻¹) in both sample types.

The ICP-MS results (Figure 3C) were broadly in the same range as the XRF results, but there were some differences: As was higher in the Grey Tailings (25 g kg⁻¹) compared to the Marbled Tailings (3.7 g kg⁻¹), and Pb was higher in the Marbled Tailings (4.3 g kg⁻¹) compared to the Grey Tailings (0.9 g kg⁻¹).

3.2.4. Mine Waste Geochemistry Summary and Discussion

Regarding the risk to human health, the concentrations of As and Pb are of the highest concern. Concentrations of As were very high across the site and exceeded the screening values for public open space in most cases. The Grey Tailings contained the highest Pb concentrations, with most exceeding the screening value for public open space. Few correlations were observed between the different metal concentrations, and the pH suggests they are likely to be controlled by separate geochemical or mineralogical variables. However, As and Fe concentrations were significantly correlated in the Grey Tailings, which may suggest that As is linked to the presence of iron minerals (e.g., pyrite) in these samples.

Interestingly, data reported here and by [1] where the wastes were subjected to acid digest and analysed for metals with ICP-MS showed that concentrations of As were some-

what lower in the Marbled Tailings compared to the Grey Tailings. This contrasts with the XRF data, which showed that the Marbled Tailings contained higher As concentrations. This effect could be explained by heterogeneities in the waste composition. As XRF analysis is performed on bulk materials and therefore not limited by elemental or mineralogical solubility in acid, it potentially is a more representative analytical technique. However, further investigations would be necessary to confirm the suitability of acid digestion for quantifying As concentrations in these materials.

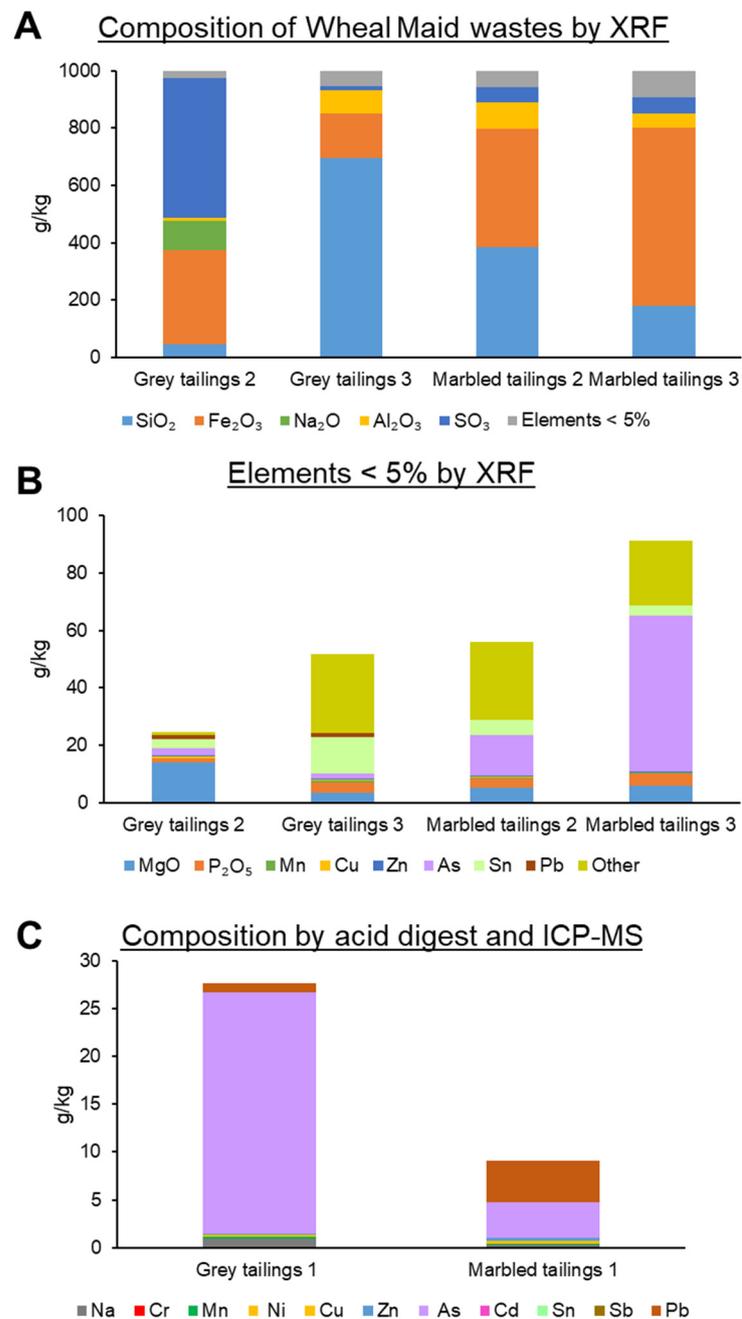


Figure 3. Bulk geochemistry of Grey and Marbled Tailings. (A) XRF results. (B) Elements < 5% by XRF. (C) Composition by acid digest and analysis by ICP-MS, values are the average of two replicates; results for Fe (323 g kg^{-1} in Grey Tailings and 324 g kg^{-1} in Marbled Tailings) are not shown for scale.

3.3. Mine Waste Mineral Chemistry

Given the importance of acid-forming sulphides (pyrite), further investigations were undertaken to characterise their mineral chemistry. Here, we report new data comparing pyrite present in the Grey Tailings with pyrite in the Marbled Tailings.

3.3.1. Methodology

Nine samples comprising seven Grey Tailings and two Marbled Tailings were analysed at the CODES Analytical Facility (June 2015), University of Tasmania. A Resonetics Resolution 193 nm excimer laser ablation system, coupled with an Agilent 7700s ICP-MS was used. Only spot analyses were performed, with beam diameters of 20 and 30 μm used, with a dwell time of 10 ms on all masses. Spots were ablated with a repetition rate of 5 Hz, with a laser energy of 50 mJ, and a fluence of 3.0 J cm^{-2} . Ablation was performed in an ultra-high purity He atmosphere, and the resulting aerosol was mixed with an Ar carrier gas before introduction to the ICP-MS. Data were collected over 80–90-s intervals with a 30-s pre-ablation acquisition (background) interval and 50–60-s sample ablation, during which time the ICP-MS collects data for each element. Pyrite was analysed while the Fe signal remained constant.

The calibration standards GSD-1G, STDGL2b-2, and Peru pyrite were used [22]. GSD-1G is a synthetic basaltic glass with nominal trace element contents of approximately 30 mg/kg, and it is available for purchase from the USGS. STDGL2b-2 is a lithium-borate fused disc of ore concentrate powder doped with certified element solutions. Peru pyrite is an in-house standard used for sulfur quantification. These standards were used to calculate element contents and correct for instrument drift. Analyses were corrected for linear drift, and data reduction was undertaken following the methodology developed by [23]. Between 15 and 30 spots were analysed per sample mount with a range of elements analysed: Al, Si, S, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Zr, Nb, Mo, Ag, Cd, Sn, Db, Te, Gd, Hf, Ta, W, Au, Hg, Tl, Pb, Bi, Th, and U. For quantification, Fe was used as the internal standard element.

3.3.2. Mineral Chemistry Results

Results for selected metals are reported in a box and whisker plot (Figure 4). Pyrite was considered to be enriched in As with a range of 16 to 54,800 mg/kg measured (mean: 8210 mg/kg, $n = 212$). This was notably higher in the Marbled Tailings (mean: 35,300 mg/kg; $n = 20$) than the Grey Tailings (5390 mg/kg; $n = 192$), though it is noted that fewer analyses were performed in the prior, thus potentially skewing the results. Lead was also high in both tailing types, ranging from 0.2 to 9920 mg/kg in the Grey Tailings (mean: 873 mg/kg; $n = 192$) and 56 to 1590 mg/kg in the Marbled Tailings (mean: 371 mg/kg; $n = 20$). Zinc also showed a similar trend, ranging from 0.3 to 22,300 mg/kg in the Grey Tailings (mean: 247 mg/kg; $n = 190$) and 7 to 3530 mg/kg in the Marbled Tailings (mean: 276 mg/kg; $n = 20$). Copper was, on average, more endowed in the Grey Tailings (247 mg/kg, $n = 191$ compared to 145 mg/kg, $n = 20$) as was Co (58 mg/kg, $n = 187$ compared to 4 mg/kg, $n = 20$). Both tailing types contained cassiterite inclusions in pyrite with mean value of 85 mg/kg and 675 mg/kg reported for the Grey and Marbled types respectively. Finally, Cd concentration was, on average, low, with 4 mg/kg and 3 mg/kg, respectively, measured for the Grey and Marbled Tailings.

3.3.3. Mine Waste Mineral Chemistry Summary and Discussion

Assuming that the Marbled Tailings represent a more oxidised form of the Grey Tailings (Section 3.1), it would appear that As and Sn are enriched post-oxidation, Co and Ni are lost (perhaps to the aqueous phase), while the other metals are neither enriched nor depleted. Enrichment of As could be due to the sorption to Fe(III) phases, but Sn is typically recalcitrant, so it is unclear why this would occur. Although the concentrations of metals appear more varied in the Grey Tailings compared to the Marbled Tailings, this may be due to fewer samples being analysed. Interestingly, the data correlated with the results from the XRF analysis (Section 3.2), which showed higher concentrations of As in

the Marbled Tailings compared to the Grey Tailings. This could lend support to the theory that aqua regia digests potentially underestimate the concentration of As in some of the Wheal Maid materials, and again further investigations are warranted.

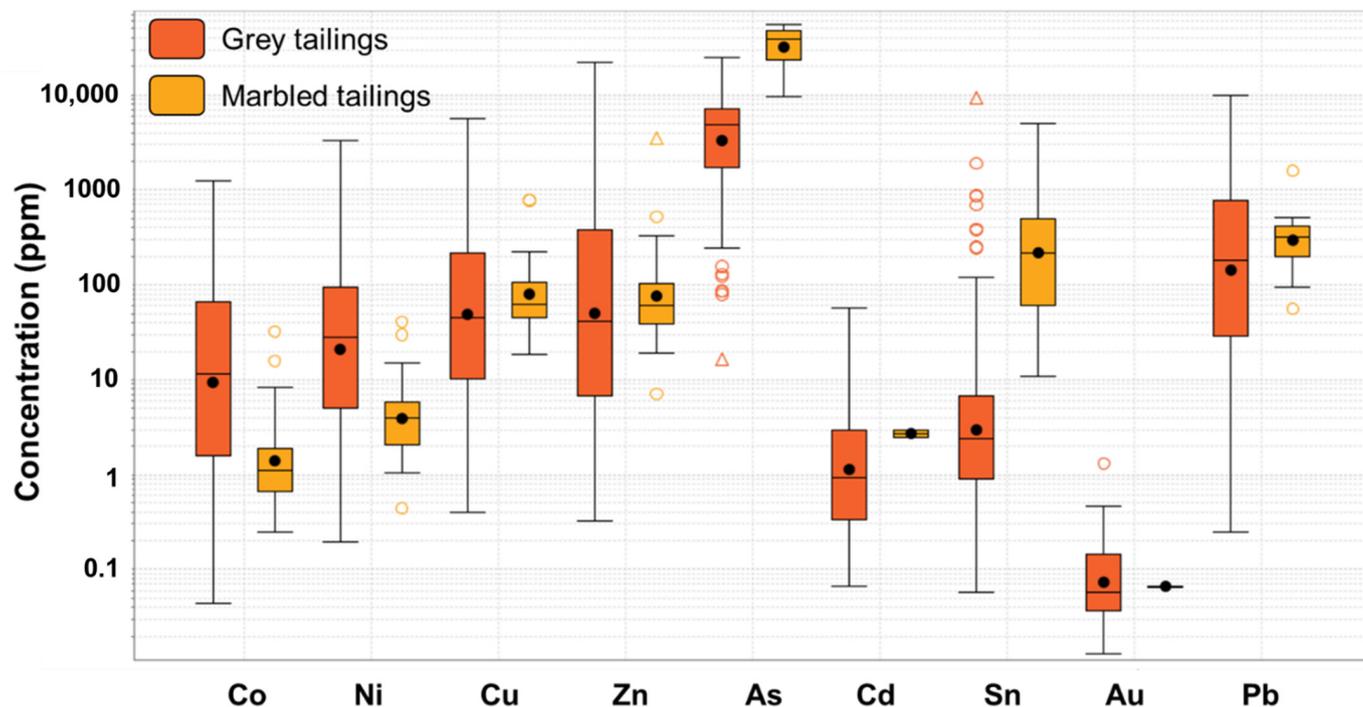


Figure 4. Box and whisker plot summarizing the concentrations (ppm (mg/kg), *y*-axis) of select elements in pyrite contained in Grey Tailings (dark orange) and Marbled Tailings (orange) sampled in 2015 (NB. Log-scale; data is shown on a Tukey box and whisker plot: the box covers the interquartile range, the line is the median, and the circle the mean. The whiskers are drawn at the threshold to identify near and far outliers based on the Tukey statistic).

3.4. Mine Waste Bioaccessibility and Leachability

3.4.1. Review of Previous Data

Total metal concentrations do not necessarily relate to the number of metals that are available for biological uptake, and as such, they may lead to the environmental risks being overestimated. To better assess the risk to human health, the bioaccessibility of As in relation to oral uptake was determined in nine solid waste samples by a four hour physiologically-based extraction test (PBET) [1]. Relatively little of the arsenic in the Grey Tailings ($n = 1$, total As 1510 mg kg^{-1}) and Marbled Tailings ($n = 2$, total As $1010\text{--}1140 \text{ mg kg}^{-1}$) was bioaccessible (1.5%–2.6%); however, it was higher in the Mine Waste ($n = 2$, total As $536\text{--}1977 \text{ mg kg}^{-1}$, <1–10%) and the Capping Material ($n = 4$, total As $976\text{--}3440 \text{ mg kg}^{-1}$, 5.8%–12.0%) [1].

Tests designed to assess plant bioaccessibility were undertaken on the four different waste materials, with 10 or 11 samples of each type analysed [20]. Testing comprised firstly using 30% hydrogen peroxide to oxidise the substrate, then 1 M ammonium acetate to mobilise and extract the released metals. In general, the highest concentrations of bioaccessible metals were found in the Grey Tailings, followed by Capping Material, then Marbled Tailings, and then Mine Waste. Interestingly, although the Marbled Tailings contained the highest concentrations of total arsenic, they were not particularly bioaccessible (mean 195 mg/kg , maximum 281 mg/kg); this reflects the mineralogy results showing that the Marbled Tailings contained Fe oxides, which would not be susceptible to oxidation [20]. Instead, the highest concentrations of bioaccessible As were found in the Grey Tailings (mean 1420 mg/kg , maximum 3720 mg/kg). Concentrations of bioaccessible Cu and Zn

were also high in many samples, with the maximum values reported in the thousands of mg/kg. Concentrations of bioaccessible Cd, Sb, and Pb were low, with the exception of Pb in the Grey Tailings. The authors stated that their test did not predict actual plant uptake—to realistically predict the uptake of elements by plants, a wide range of parameters including biological, geochemical, and environmental factors need to be considered.

Leach testing was undertaken on different types of waste to assess the amount of water soluble metals [1]; testing followed the National Rivers Authority methodology whereby wastes were mixed with deionised water and analysed after 24 h. Results for As, Cd, Cr, Cu, Pb, Ni, and Zn were compared to Environmental Quality Standards (EQS) to assess the risk to controlled waters from metals leaching from contaminated wastes [1]. Leached metal concentrations exceeded the EQS in at least two of the 29 samples tested. The most significant were leachable Cu, which exceeded the EQS of $1 \mu\text{g L}^{-1}$ in 28 samples, and leachable Zn, which exceeded the EQS of $8 \mu\text{g L}^{-1}$ in 23 samples. The highest concentrations of leachable Cu, Pb, and Zn were reported in the Grey Tailings (4700, 9300 and $20,000 \mu\text{g L}^{-1}$ respectively), exceeding their EQS by more than three orders of magnitude, while the highest As concentrations were in the Capping Material ($3300 \mu\text{g L}^{-1}$).

The monitoring of groundwater in bedrock and perched groundwater in the wastes demonstrated that the concentrations of Cu ($1200\text{--}4400 \mu\text{g L}^{-1}$) and Zn ($1300\text{--}17,000 \mu\text{g L}^{-1}$) exceeded their EQS by two to three orders of magnitude and confirmed that the leaching of these metals is already occurring and is significant [1]. Concentrations of other metals of interest in groundwater were relatively low: As was below detection to $18 \mu\text{g L}^{-1}$, Pb was below detection to $70 \mu\text{g L}^{-1}$, and Fe was below detection. Soluble sulfate concentrations were high ($140\text{--}340 \text{mg L}^{-1}$), and the pH was acidic (4.05–5.24).

In surface waters, concentrations of Cu and Zn in the lagoon waters and in the St Day Stream also exceeded the EQS, again by orders of magnitude. Concentrations of Fe, As and soluble sulfate were also elevated. The St Day Stream flows into the Carnon River, a watercourse that is already severely impacted by metal pollution from mine waters and almost devoid of aquatic macrophytes and benthic macroinvertebrates [24]. PHREEQC modelling of the lagoon and mine runoff waters showed that, in places, it was supersaturated with respect to scorodite [$\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$], particularly when the pH was slightly acidic, e.g., pH 5–6 (Tang et al., 2021). The authors suggest that scorodite precipitation could be controlling the mobility of As in these locations, but increasing pH would lead to scorodite becoming undersaturated and to enhanced As mobility.

3.4.2. Mine Waste Bioaccessibility and Leachability Summary and Discussion

All bioaccessibility and leachability tests are operationally defined, but they do offer nuance beyond total metal concentrations. Finer grained materials would typically be considered to contain more bioaccessible metals due to their larger surface area; however, the results for oral bioaccessibility of As showed the opposite, with more bioavailable As in the granular materials. The Grey Tailings appear to pose the biggest threat to the environment in terms of metals mobilised by solubilisation in water [1] or oxidation [20].

The metals present in the wastes pose a risk to watercourses and aquatic ecosystems, with significant concentrations leachable and therefore likely to be transported to surface waters. High concentrations of leachable Cu and Zn in particular were prevalent in most samples tested, with As and Pb less common but also highly elevated compared to Environmental Quality Standards. However, the surface water quality in the area is already poor from the impacts of hundreds of years of historic mining and uncontrolled waste disposal in the region. Moreover, there are also a number of legacy mine sites, and their associated drainage adits, which also discharge into the Carnon River, including the Great County Adit, which is a much more significant contributor of pollutant metals than Wheal Maid [19,25,26]. Although it is unlikely that Wheal Maid makes a significant impact to surface water quality, this is often not the case in other areas where similar abandoned mine wastes are present. Moreover, such legacy wastes are also susceptible to future geomorphological change, such as a tailings dam failure, resulting in their discharge

into the environment. Their study is therefore of the upmost importance in order to predict the likely environmental impact, should such an event occur.

3.5. Mine Waste Microbiology

3.5.1. Review of Previous Data

The oxidation of pyrite is catalysed by a diverse group of bacteria that oxidise reduced sulfur and iron(II) compounds to gain energy for growth. Common mesophilic acidophiles (optimum temperature for growth 20–40 °C) that can oxidise both iron and sulfur include: *Acidithiobacillus* spp., *Acidiphilium* spp., *Acidiferrobacter thiooxydans*, and *Sulfobacillus* spp., while *Leptospirillum ferrooxidans* can oxidise iron but not sulfur [27]. To investigate what types of iron(II) and sulfur oxidising bacteria were present at Wheal Maid, DNA was extracted from samples of the wastes and the microbial communities analysed via 16S rRNA amplicon and metagenomic sequencing [28]. Two sampling locations were chosen on the western margin of the lower lagoon. Sampling location 1 was Marbled Tailings (oxidised sediment below the water level) and location 2 was Grey Tailings (unoxidised, rarely below the water level). Samples were taken at three depths at each sampling location (surface, 30 cm and 50 cm).

Microorganisms that facilitate the oxidation of Fe(II) and thus contribute to the formation of AMD were identified and include the *Leptospirillum*, *Acidiphilium*, and *Acidithiobacillus* genera [28]. The complexity of the microbial community varied depending on the location and depth of the sediment sampled. A more complex community was found at the three depths of Marbled Tailings compared with the Grey Tailings. Within the Marbled Tailings at both the surface and at depth, the most abundant sequences were assigned to the genus *Leptospirillum*, a known Fe(II) oxidiser and in the family *Xanthomonadaceae* (sequences said to be closely related to acid-tolerant *Metallibacterium* spp.). Other sequences that formed > 5% of the microbial community included those assigned to the *Acidiphilium* and *Acidithiobacillus* genera, the *Acidobacteriaceae*, *Sulfobacillaceae* and *Sinobacteraceae* families, the Acidimicrobiales order, and the Gammaproteobacteria and JG37-AG-4 classes. Some of these groups include metal-resistant acidophiles capable of metabolising via autotrophy or heterotrophy and oxidising S and Fe minerals. Some members of the *Acidiphilium* genus can also reduce Fe(III) to Fe(II) [29]. The Grey Tailings were dominated by relatively few sequences, and the surface sample contained the acidophilic *Stygiolobus* (~10%), *Sulfobacillus* (~32%), and *Acidithiobacillus* (~42%) genera, all which either oxidise or reduce S compounds. The 30-cm sample contained the genus *Leptospirillum* (~50%) and others at <10%, while the 50-cm sample was dominated by the acidophilic *Ferroplasma* genus (~25%) and the Bacteriovoraceae family (~50%, said to be a misclassification of novel acidophiles).

Samples were also subjected to shotgun metagenomic sequencing, with sufficient DNA obtained from three of the four samples tested [28]. Genes involved in metal resistance were identified in many of the genomes present, as were complete pathways for sulfate reduction and sulfur oxidation. Genes for carbon fixation via the Calvin cycle and nitrogen fixation were only found in 1 or 2 of the genomes, suggesting these functions can only be undertaken by a limited number of organisms in the Wheal Maid wastes, although various other pathways for carbon fixation were also present.

3.5.2. Mine Waste Microbiology Summary and Discussion

Fe(II) and S oxidising microorganisms were identified in both the Grey and the Marbled Tailings, which are capable of oxidising pyrite to form acid mine drainage. These include autotrophs that are able to metabolise using inorganic carbon sources, e.g., fixing it from atmospheric CO₂, so that they are not limited by the lack of organic carbon compounds that is typical of mine tailings. Genes for C and N fixation were present but only associated with a small number of organisms; this may limit the activity of microorganisms that rely on others to supply these essential nutrients. The microbial community was more diverse in the Marbled Tailings, which might reflect their lower metal content; having fewer

metals causes less toxicity and means that organisms can metabolise more efficiently with less energy needed for efflux or cell repair mechanisms.

3.6. Investigating the Lack of Oxidation in the Pyritic Grey Tailings

Given the continued presence of pyrite minerals in an oxidising surface environment (Figure 1C), further investigations were undertaken to identify the limiting factor in pyrite oxidation at Wheal Maid. Here, we report new data from laboratory experiments designed to stimulate physical, chemical, and biological mineral oxidation.

3.6.1. Methodology

A series of physical, chemical, and biological oxidation tests (Figure S1) were designed to investigate the conditions under which the wastes could be oxidised in a laboratory setting. In total, 26 flasks were prepared, with 50 mL of synthetic rainwater at pH 4.2 (2694-I, [30]) added to 5 g of Grey or Marbled Tailings in 300-mL conical flasks (Table S3).

- To assess if limited physical contact with atmospheric O₂ was contributing to the lack of oxidation, flasks were placed on an orbital shaker (50 rpm), while controls were held under static conditions.
- Nitric acid (0.1 M) was added to investigate whether the pyrite could be oxidised chemically by a relatively weak acid and oxidising agent (in contrast to the strong oxidation reaction of hydrogen peroxide and ammonium acetate used by van Veen et al. 2016). The physical tests above were used as controls.
- To investigate whether a lack of microbial activity was contributing to limited oxidation, flasks were inoculated with a model Fe(II) and S oxidiser, *Acidithiobacillus ferrooxidans* (grown on pyrite, 10% inoculum added), together with a nutrient solution of 0.5 g L⁻¹ Mg, 0.4 g L⁻¹ NH₄⁺, and 0.2 g L⁻¹ PO₄²⁻. The nutrient solution would also stimulate indigenous bacteria in the wastes. Controls for biological oxidation included adding nutrients but no cells and adding cells but no nutrients.

All experiments were conducted in triplicate, with single control flasks. All flasks were stored at room temperature on an orbital shaker (50 rpm), with the exception of the two no shaking controls. Experiments were performed for 25 days and changes in geochemistry were periodically monitored, including pH, using a calibrated electrode. To analyse Fe speciation in sediment slurry, 0.5 N extractable Fe(II) and 0.5 N hydroxylamine hydrochloride extractable 'total' Fe were measured using the Ferrozine assay, and Fe(III) was calculated by difference [31,32].

3.6.2. Oxidation Experiment Results

The oxidation of pyrite generates protons and lowers the pH, causing the release of Fe(III) to the solution at a low pH, while concentrations of Fe(II) in the solution may decrease due to oxidation to Fe(III), although this will also depend on the rate at which Fe(II) is solubilised. The monitoring data were analysed for these indicator parameters to identify if any experimental conditions had stimulated the oxidation of pyrite/sulfide minerals in the Grey or Marbled Tailings (Figure 5).

In the Grey Tailings (Figure 5A,C,E), concentrations of Fe(III) increased over time in the biological oxidation experiments but not in the physical or chemical experiments. The amount of Fe(III) produced was equivalent in the flasks where *A. ferrooxidans* and nutrients were added (pink line) and where just nutrients were added (yellow line), while slightly less Fe(III) was produced in the flasks where *A. ferrooxidans* and no nutrients (green line) were added (Figure 5C). This suggests that (a) biological factors may be limiting pyrite oxidation in the Grey Tailings and (b) that the Grey Tailings contain indigenous Fe(II) oxidising microorganisms that were stimulated when nutrients were added. In most flasks, it appears that Fe(II) concentrations initially increased but then decreased during the course of the experiment, with the exception of the nitric acid flasks, in which concentrations of Fe(II) remained high (Figure 5A). This could be due to minerals present in the Grey Tailings being more soluble at pH 1.0 generated by a nitric acid addition with chemical oxidation

being limited at such a low pH. In the other flasks, the pH remained around 2.0 for the duration of the experiment.

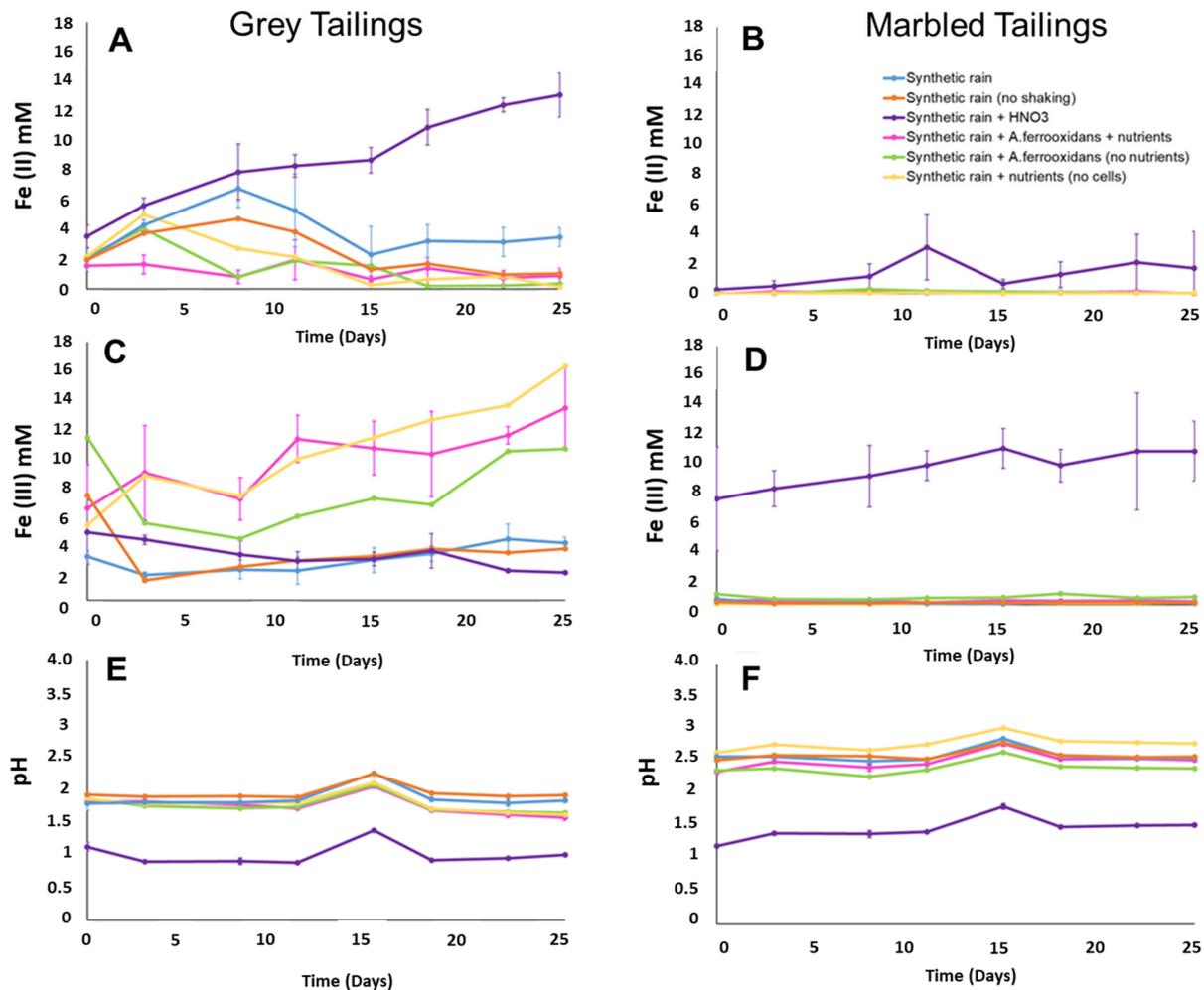


Figure 5. Monitoring data from the oxidation experiments. Physical oxidation compares shaken (blue) with no shaking control (orange). Chemical oxidation compares nitric acid addition (purple) with no acid addition (blue). Biological oxidation compares inoculating with cells and nutrients (pink) against controls with cells and no nutrients (green) and nutrients with no cells (yellow). Experimental data are the average of three replicates, error bars ± 1 standard deviation. Controls are single measurements. (A) Fe(II) in Grey Tailings. (B) Fe(II) in Marbled Tailings. (C) Fe(III) in Grey Tailings. (D) Fe(III) in Marbled Tailings. (E) pH in Grey Tailings. (F) pH in Marbled Tailings.

In the Marbled Tailings, the geochemical indicators for pyrite oxidation generally did not change over time (Figure 5B,D,F). Concentrations of Fe(III) were much higher in the nitric acid flask and increased slightly over time (Figure 5D); this indicates that Fe minerals in the Marbled Tailings were susceptible to dissolution via nitric acid. Concentrations of Fe(II) and Fe(III) were very low in the rest of the flasks, suggesting that (in the absence of nitric acid) the Fe minerals in the Marbled Tailings were not extractable by 0.5 N HCl or hydroxylamine HCl. The pH remained around 2.5 (or 1.5 in the nitric acid flasks) for the duration of the experiment.

Both wastes were acid generating, with significant drops from the pH 4.2 synthetic rainwater. The pH was slightly more acidic in the Grey Tailings compared the Marbled Tailings. The pH equilibration occurred within hours of the experimental set up and then remained constant over time; none of the experimental oxidation conditions caused the pH to change.

3.6.3. Mine Waste Oxidation Experiment Summary and Discussion

The oxidation of the Grey Tailings and the production of Fe(III) were stimulated by biological factors, particularly the addition of nutrients (Mg, P, N) that likely stimulated indigenous Fe(II) oxidising microorganisms, but also to a lesser extent by inoculation with a model Fe(II) and S oxidising bacterium. Given that the Grey Tailings have been shown to contain Fe(II) and S microorganisms [28], the results of the oxidation experiments suggest that the tailings may be lacking in the nutrients required to stimulate microbial growth and pyrite oxidation. However, XRF data showed that the Grey Tailings do contain some Mg and P in the solid phase (Figure 3), and site monitoring data showed the presence in groundwater of Mg (5.7–13 mg L⁻¹), Ca (12–37 mg L⁻¹), K (1.5–8.1 mg L⁻¹), nitrate as N (3.7–11 mg L⁻¹), and ammoniacal nitrogen (below detection–0.2 mg L⁻¹); phosphate was not analysed [1].

Another explanation for the limited oxidation of the Grey Tailings could be the presence of residual mineral processing reagents. Bulk characterisation showed that the Grey Tailings had a high concentration of Na (10% by XRF, Figure 3). As well as this, the S concentrations were much higher than would be expected based on the Fe to S ratio of pyrite. Site monitoring data showed that groundwater contained 10–23 mg L⁻¹ Na (URS, 2007). It is possible that the higher concentrations of Na and S were remnants of the reagents used in processing during sulfide floatation. Further work would be required to elucidate the mechanism behind how these reagents might protect the pyrite from oxidation. Indeed, this phenomena has been noted by previous authors that compared the oxidation rates of sulphide-bearing minerals when exposed to floatation chemicals (e.g., [33]).

Limited oxidation occurred in the Marbled Tailings experiments. This is likely due to these materials already being oxidised in the environment; evidence for this was observed in the XRD patterns showing the presence of jarosite and absence of pyrite in these materials, and also their red brown colour observed in the field indicated the presence of oxidised iron minerals.

4. Key Data Gaps and Recommendations for Future Research

Whilst the depth of investigation is notably shallow (<1 m) in these surficial studies, clear questions remain regarding the lack of pyrite oxidation in the Grey Tailings at Wheal Maid given their exposure to the surface environment (deposited from 1979–1981). This is significant because this oxidation reaction is an acid-generating process and would therefore likely result in the significant mobilisation of (currently solid phase) ecotoxic metals present within the Grey Tailings. On one hand, this represents an environmental liability, with significant amounts of minerals yet to be oxidised and likely to form acid mine drainage. Alternatively, if lessons could be learned regarding why these materials remain unoxidised, the findings could be applied to better manage sulfidic tailings at other mine waste disposal sites. We have identified three areas that warrant further investigation to understand the limited oxidation of pyrite in the Grey Tailings:

1. **Role of microorganisms:** Although Fe(II) and sulfur oxidisers have been identified to be present, are they not of sufficient abundance to contribute significantly to pyrite oxidation, particularly Fe(II) and sulfur oxidisers? Or is a lack of nutrients limiting their ability to oxidise pyrite at significant rates?
2. **Role of processing chemicals:** Do the high Na and S concentrations in the Grey Tailings represent the remnants of processing chemicals? Have processing chemicals affected the surface properties of the pyrite (i.e., causing passivation; [34] and so are responsible for limiting its oxidation in the environment?
3. **Role of pyrite mineralogy:** Previous research suggested that the morphology of the pyrite crystals in this particular waste may be inhibiting oxidation. Do the Grey Tailings contain a particularly high proportion of euhedral crystals?

Other areas for future research include: (i) increasing the depth of investigation; (ii) sequential extraction tests to see how metals are preferentially leached, which may help understand the key factors that affect metal mobility and the stability of the minerals

(e.g., [35]); and (iii) additional detailed mineralogical and bulk metal concentration characterisation of the solid mineral phases (e.g., [36]). In addition, there has not yet been a study into the nature of the arsenic present. XRD analysis did not identify any arsenic bearing minerals [20]. It is evident that there is an association of arsenic within pyrite, but there is no understanding of the crystal chemistry of the arsenic.

There has been some attempt to remediate the site with the seeding of heather (*Calluna vulgaris*) and gorse (*Ulex europaeus*) [37]. These plants are metallophytes, which have the ability to exclude metals and As from their above-ground biomass, and they were planted in an effort to reduce the amount of dust formation. Further investigations could cover the strategies used by these plants to exclude metals, as well as studying the native flora that have colonised the wastes.

Wheal Maid is designated as an Open Mosaic Habitat and is within the Cornwall and Devon Mining Landscape, which is a World Heritage Site [13]. Such designations are a reflection of the unique environmental and cultural significance of the site; a common occurrence for legacy waste. As such, in order for a remediation activity to be successful, any impact on these designations must be considered. One particular technology that is currently being researched for analogous mine waste is the application of in-situ leaching [13,38], which could, if successful, enable pollutant metal recovery but with a lower geomorphological impact than physical excavation of the tailings material (i.e., physical excavation followed by disposal), whilst also enabling recovery of any economically valuable metals, the value of which could be used to offset the costs of such intervention [39,40]. It is vitally important that such activities are also complemented with educational material (such as photos of the site and historic descriptions) in order to enable maintenance of the mining heritage, which is an important backdrop (i.e., sense of history) for local members of the general public, whilst also significant for economic activities in the region (i.e., mining heritage tourism).

Although there are no known direct analogues to Wheal Maid in Cornwall (most legacy sites in Cornwall contain coarser grain waste rock), anecdotally there have been some similarities presented by former academics at the University of Tasmania (Table S2). Research into tailings repositories in western Tasmania is underway, from the Hercules mine and deposited in Zeehan. Tailings here were observed to be “fresh”, and it is thought they too have undergone little oxidation. Unfortunately, there is very little publication on this site (currently being characterised), and only observations on the lack of oxidation occurring have been noted. Clearly, this subject warrants further attention, as Wheal Maid is most likely not a unique site. Understanding the reasons why the Grey Tailings are not oxidising could inform strategies to better design processing wastes to minimise the formation of acid mine drainage and the associated environmental impacts.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min12070848/s1>, Figure S1. Sample location map for 2019 experiments, modified from: Crown copyright and database rights 2019 Ordnance Survey (Digimap licence); sample photographs; and descriptions of waste samples collected and the analyses performed. Figure S2. Correlation plots for concentrations of metals and pH in Wheal Maid waste samples (figure drawn from data collected by [1]). Table S1. A list of the 26 significant pollutant linkages (SPLs), modified from [2]. Table S2. Interviews conducted with organisations and individuals with links to Wheal Maid. Interviewees were asked about their involvement with the site and to supply any documents to help develop a better understanding of the site. Table S3. A list of the different simulated environments to test oxidation. GT refers to Grey Tailings, MT refers to Marbled Tailings.

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