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A Geometallurgical Approach to Tailings Management: An Example from the Savage River Fe-Ore Mine, Western Tasmania

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Abstract: At the Old Tailings Dam (OTD), Savage River, Western Tasmania, 38 Mt of pyritic tailings were deposited (1967 to 1982) and have since been generating acid and metalliferous drainage (AMD). Mineral chemistry analysis confirmed high concentrations of refractory cobalt in pyrite (up to 3 wt %). This study sought to determine, through a series of bench scale tests, if Co could be liberated using biohydrometallurgical techniques. Four bulk tailings samples were collected across the OTD, from up to 1.5 m depth, targeting three sulphide-bearing facies. The study was conducted in four stages: (1) bacterial adaption using BIOX® bacteria; (2) biooxidation optimization with pH, temperature and Fe medium parameters tested; (3) flotation test work to produce a sulphide concentrate followed by biooxidation; and (4) Fe and Co precipitation tests. The BIOX® culture adapted to the bulk composite (containing 7 wt % pyrite) in ~10 days, with biooxidation occurring most efficiently at pH 1.5–1.6 and 40 °C whilst the Fe medium concentration was identified as a less-controlling parameter. Flotation produced a 71% pyrite concentrate with total oxidation occurring after 14 days of biooxidation with 99% of Co leached. At pH 3, Co was effectively separated from Fe, however Ni and Cu were also present in the pregnant liquor solution and therefore required refining before production of cobalt hydroxide, the intermediate saleable product. This study shows that adopting a geometallurgical approach to tailings characterisation can identify if mine waste has commodity potential and how best to extract it therefore unlocking the potential for unconventional rehabilitation of AMD affected sites.

Keywords: tailings; mine waste; reprocessing; biooxidation; acid and metalliferous drainage

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1. Introduction

The mining industry produces approximately 14 billion tonnes of mine tailings per annum [1]. These tailings are the remaining fine grained (1–600 µm) ground-up material left after the ore has been extracted from the mined material [2,3]. In addition, the associated process water, which includes dissolved metals and ore processing reagents, is also emitted [2,4]. Tailings are typically discharged to purpose-built storage facilities and commonly are covered with either an engineered, vegetation or water cover [1,5–7]. As implied by their designation as waste, they have low economic value and can pose significant geoenvironmental risks if, for example, they contain sulphide minerals, e.g., pyrite or pyrrhotite [8]. If left uncovered, under surficial conditions, these sulphides are susceptible to oxidation producing acid and metalliferous drainage (AMD) characterised by metal-laden acid-sulphate waters). AMD can occur throughout the life of the mine (LOM) with numerous case studies published or otherwise reported, e.g., [9–12] among others.

Current mining practice mandates the adoption of strategic waste planning and management practices in accordance to environmental legislative practices enforced in that particular jurisdiction (e.g., Solid Waste Disposal Act Amendment, 1980; Environmental Management and Pollution Control Act, 1994; Directive 2006/21/EC; Leading Practice Sustainable Development in Mining, 2011). However, historical mining operations adopted disposal and waste management practices, which would be considered inappropriate by today's environmental standards [13,14]. Attempting to retrospectively manage historical tailings proves challenging as widely documented in the scientific literature, e.g., [6,15–18]. Alternatively, if such tailings were regarded as potential resources and geometallurgically characterised (i.e., combined use of mineralogical and mineral chemistry tools to enable the selection of a metallurgical processing methodology), there could be economic and environmental opportunities arising from their reprocessing using modern techniques. Such an approach is becoming increasingly adopted for both historic and modern tailings as recently reported at the Henty gold mine, Tasmania, and the Century zinc mine, Queensland, among others, e.g., [19,20]. However, conventional mineral processing methods may be inappropriate for such secondary sulphide ores as relating to the deportment mode of the element of interest, thus despite the resource potential, tailings processing may yet prove uneconomic [21]. In such cases, biohydrometallurgical processing could be considered, e.g., [22–24] among others.

In Tasmania there are reportedly 215 sites where AMD occurrence has been documented and therefore require rehabilitation [25]. At such sites, performing geometallurgical test work could assist in the development of a long-term innovative management strategy. This would have the economic benefit of reducing on-going environmental management costs, production of a saleable commodity and the new inert tailings waste could be used as a dry cover material in other mine waste management strategies. This study focuses on the Old Tailings Dam (OTD), located at the Savage River mine, Western Tasmania, recognised as an AMD impacted site [25]. AMD management at the site by the Tasmanian State Government has been ongoing since 1997. The OTD contains 38 Mt of pyritic tailings, which are actively generating AMD as described in [26]. To manage this, the State Government has evaluated several options including establishing a water cover [26], introducing native vegetation and investing in a hard engineering solution. These options appear less plausible, due to geotechnical complications, pending further engineering studies. A laser ablation ICPMS (LA-ICPMS) study on pyrite contained in these tailings was performed to determine the tenor and deportment of several metals including Co, Cu, Ni, Ag and Au [27]. High concentrations (up to 3 wt %) of Co, a critical metal used in rechargeable batteries, electroplating and various metal alloys, with a current value of >US $ 50,000/t [28] reported. Cobalt in pyrite is refractory, therefore, its recovery via well-established extractive metallurgy techniques (pyrometallurgical and hydrometallurgical methods; [29]) is unsuitable as it would yield uneconomic recoveries. Instead, Co extraction via biohydrometallurgical leaching (defined as the conversion of an insoluble metal into a soluble form thereby extracting the target metal into an aqueous solution [23,30]) was considered more suitable. This works via indirect oxidation mechanisms whereby bacteria oxidise Fe^{2+} to Fe^{3+} (with a proton released which maintains low pH conditions as preferred by the bacteria and allows Fe to stay in solution). The Fe^{3+} oxidises pyrite at the surface enabling metal release, gets converted back to Fe^{2+}, and this cycle is repeated if the chemical conditions remain favourable for the bacteria. Examples of tailings bioleaching are given in [30–35] among others.

This study examines if biohydrometallurgical processing of the OTD materials could liberate economic concentrations of Co. The specific study objectives were to: (i) determine if bacteria used in the BIOX® process, as is common in Au recovery projects, could oxidise as-received OTD materials; (ii) optimize bioleaching test work by defining the optimal pH, temperature and Fe-medium operating concentrations to use; (iii) perform flotation experiments on the tailings and identify how to improve the test work in order to produce a high-pyrite concentrate; and (iv) collect the final pregnant liquor and perform metal precipitation tests to improve Co recovery and produce a saleable intermediate Co salt product. The results from this study were collected as a first step towards informing a full-scale study compliant with the Australasian Code for Reporting of Exploration Results, Mineral Resources and Ore Reserves (JORC Code) to help the Tasmanian Government decide if tailings reprocessing is a plausible option for the future management of this AMD-impacted site.

2. Site Description

2.1. Local Geology and Mineralisation

A description of the geology of Tasmania is given in [36]. The Savage River mine is located approximately 243 km from Launceston on the northwest coast of Tasmania as seen in Figure 1.

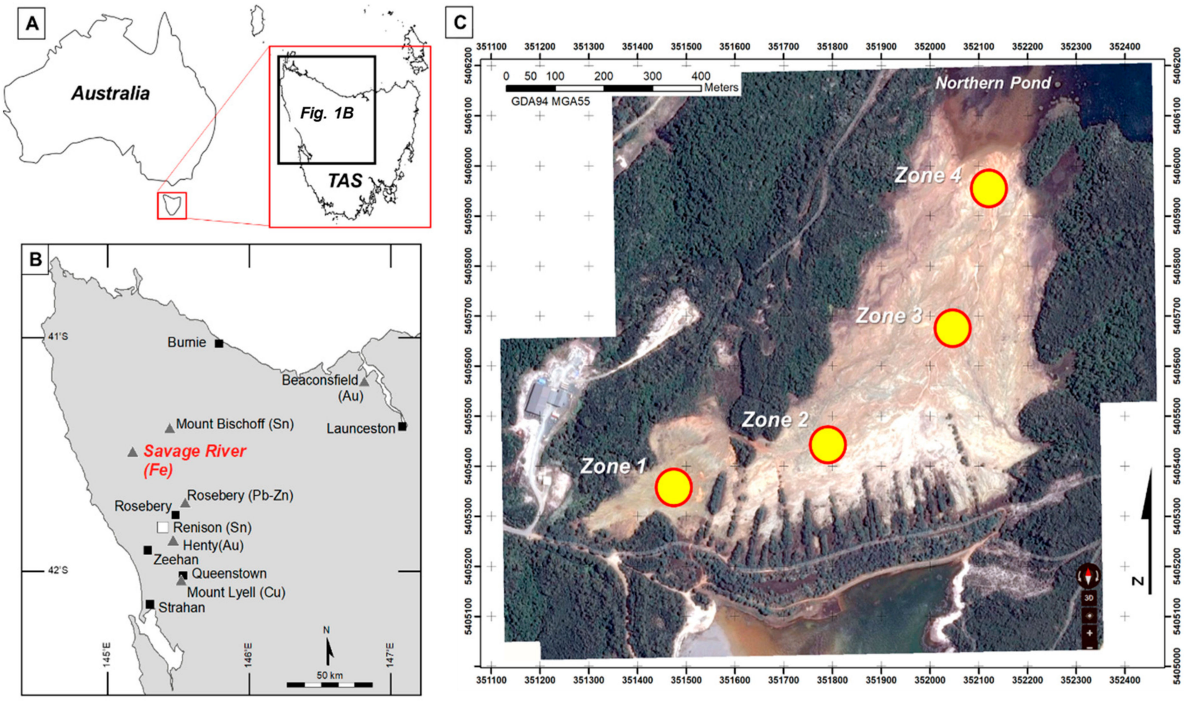

Figure 1. (**A**) Location of Tasmania in Australia; (**B**) Location of Savage River in Western Tasmania showing the location of other major mines and their commodities; (**C**) Image of the Old Tailings Dam (OTD) with the location of samples collected in this study marked with yellow circles.

Operations consist of five open cut workings exploiting a group of magnetite-rich lenses irregularly distributed within a series of highly metamorphosed rocks of marble, schist and metabasic rocks [37,38]. Urqhart [37] described magnetite as associated with amphibolite or disseminated in meta-sediment. Urquart [37] also stated that folded, steeply dipping Precambrian Whyte Schist underlies most of the area and is separated by an inferred major fault from less metamorphosed and deformed Precambrian Corinna Slate to the SW. Urqhart [37] and Coleman [38] identified pyrite as the dominant gangue sulphide often forming irregular grains up to 3 mm across. It can occur ophiolitically overgrown with small blades of actinolite or tremolite, and intergrown in coarser areas of magnetite as seen in Figure 2A. Urqhart [36] described chalcopyrite as restricted to pyrite where it occurs as 'bleb' like inclusions (Figure 2B) and as small interstitial patches or discontinuous seams in grain boundaries at the contacts of pyrite with either magnetite or other gangue phases [37,38]. Our investigations show that isolated chalcopyrite grains associated with silicate gangue, as shown in Figure 2C, and similar-sized pyrite-magnetite associated grains are also present, as seen in Figure 2D.

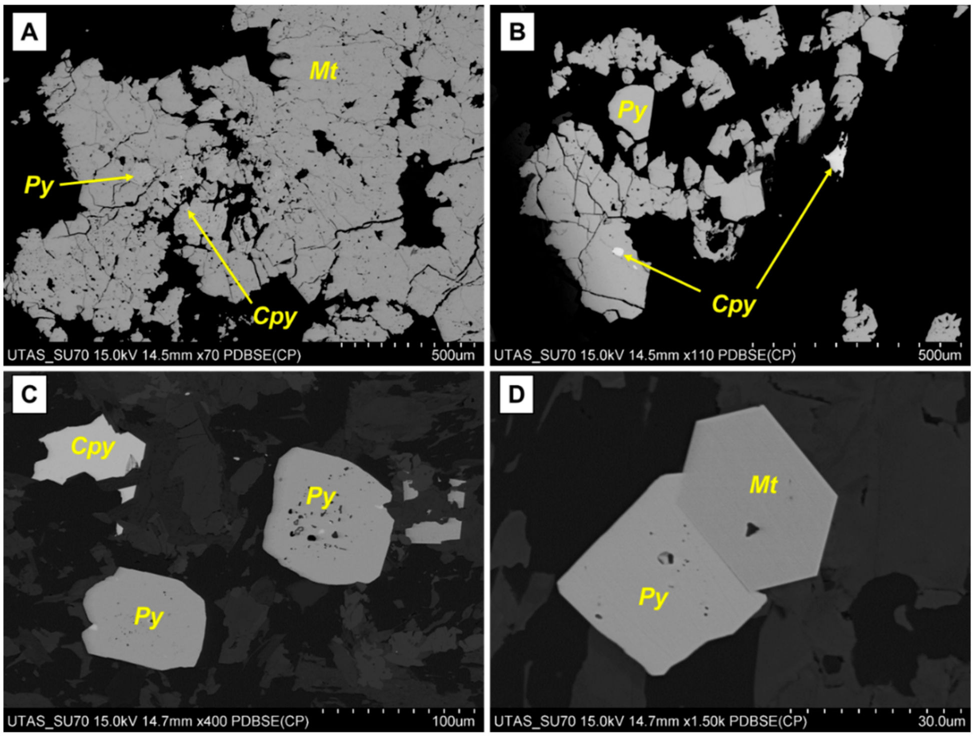

Figure 2. Back scattered electron images of Savage River ore and sulphide gangue; (**A**) Massive magnetite containing pyrite and chalcopyrite intergrowths; (**B**) Massive pyrite containing chalcopyrite blebs; (**C**) Pyrite and chalcopyrite in a silicate matrix; and (**D**) Pyrite-associated magnetite grains (abbreviations: Cpy, chalcopyrite; Mt, magnetite; Py, pyrite).

2.2. Mining and Mineral Processing

Production did not begin at Savage River until 1967 and in 2017 the resource was reported by Grange Resources at 377.5 Mt at 47.7% Davis Tube Recovery (DTR) and the ore reserves at 86.6 Mt at 52.5% DTR with a projected mine life until 2025. A description of ore extraction and mineral processing is given in [39]. In summary, drilling and blasting are undertaken to prepare the ground prior to mining with conventional off-highway rear-dump trucks and hydraulic excavators used to transport the excavated material [40]. Within the orebody all blast holes are sampled for grade control. Ore processing involves tipping of ore into two gyratory primary crushers, reducing it to 200 mm and transporting it to a 100,000 MT capacity ore stockpile via truck or overland conveyors. The ore is ground by two autogenous and two ball mills. The ore is magnetically separated to recover magnetite and the gangue is pumped to a tailing storage facility. The magnetite concentrate slurry is pumped from the concentrator to Port Latta via an 83 km pipeline where it is pelletised, transferred by conveyor onto a stockpile, and shipped nationally and internationally [40].

2.3. Geoenvironmental Risks

For the first three decades of operation, pyrite oxidation associated with the waste rock and tailings was not adequately restricted and legacy AMD now emanates from the site. Environmental degradation to within 30 km of the Savage River has been reported particularly downstream of its confluence with Main Creek where 90% of its invertebrate biodiversity and 99% of its invertebrate abundance have been lost [40]. Several of the active AMD sources have been progressively rehabilitated by the State Government [41]. However, the OTD, located 1.3 km from the processing plant, remains a significant challenge with known AMD seeps discharging into the Main Creek Tailings Dam where it is currently neutralised. Pyritic tailings were deposited from Centre Pit South and Centre Pit North by end of pipe spilling into the southwest corner of the dam [42]. Tailings were sprayed from a fixed spigot point and the dam wall was raised in lifts proximal to this point, resulting in the deposition of coarser, heavier and more permeable material against the southern dam wall [42]. This caused the water table in the tailings to decrease adjacent to the wall and resulted in extensive tailings oxidation and AMD generation. Jackson and Parbhakar-Fox [26] reported that a significant reservoir of reactive tailings remain on the site, although material present under the Northern Pond, as seen in Figure 1C, appears stable due to the overlying water cover (with those tailings covered by water at a depth >1.5 m particularly protected from oxidation). If these tailings continue to be passively managed they will pose a long-term geoenvironmental risk and instead require active rehabilitation.

3. Materials and Methods

3.1. Tailings Collection

In February 2016, four individual bulk tailings samples (between 16 and 21 kg) were collected from Zones 1 to 4 as defined in [26] with locations given in Figure 1. Materials were collected from 0.5 m to 1.5 m depth to enable the sampling of Facies C (fine interbedded medium-grained sulphide sand and clay), D (oxidised paleo-hardpan) and E (sulphide sand) as defined by [26] and had been recognized as Co endowed [27]. These materials were transported to ALS-Metallurgy Burnie laboratories where they were dried and weighed with the bulk chemistry, bulk mineralogy and acid forming characteristics for each individual sample measured. Samples were kept refrigerated until their use. The bulk chemistry of these materials was determined by several methods at ALS Global, Perth (Method Code: MEICP41; aqua regio digest and ICP analysis of solution, SIR07—leach of sulphates and Leco Furnace of residue, SIR08—total S by Leco Furnace, CIR06a—HCl leach of carbonates followed by Leco Furnace of residue, CIR07—total carbon by Leco Furnace) with concentrations of Fe (%), Cu (ppm), Co (ppm), As (ppm), Mo (ppm) Ag (ppm), Zn (ppm) Ni (ppm) and Pb (ppm), C (%), organic C (%) (or Corg), S (%), S^{2-} (%) primarily sought. The commonly used BIOX® process was selected for use in this study. Traditionally, this is used for the pre-cyanidation treatment of refractory Au-ores with demonstrated applications given in [43–46]. The BIOX® process uses a mixture of naturally occurring bacterial population comprising *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* (oxidises sulphur compounds only) and *Leptospirillum ferrooxidans* (oxidises iron substrates only). These chemolithotrophic bacteria can oxidise a range of sulphides (e.g., pyrite, arsenopyrite, pyrrhotite, chalcopyrite, chalcocite, covellite, stibnite, pentlandite and galena) under controlled conditions [23].

3.2. Bacterial Adaption

The first step in any bioleaching experiment is ensuring the bacteria are well adapted to the feed material as traditionally, lab-held stock inoculum is adapted to a 'clean' sulphide feed (i.e., pyrite with an absence of additional trace metals). Approximately 750 g of the composite tailings sample was weighed and added to 4000 mL of a 9 K nutrient medium as defined by Silverman and Lundgren (1959; comprising 150 mL of salt A ($(NH_4)_2SO_4$ + K_2HPO_4 + KCl), 30 mL of salt B ($MgSO_4·7H_2O$), 150 mL of salt C ($CaNO_3$) and 150 g $FeSO_4·7H_2O$). Following its stabilisation, 400 mL of the stock BIOX® was added. The conditions employed were those used typically in the BIOX® process as conducted at the ALS-Metallurgy Burnie laboratory, i.e., pH 1.4–1.8, 40 °C, 425 rpm stirrer speed and 0.2 L/min O_2 flow. The experiment was monitored at least once daily with measurements of pH, redox and dissolved oxygen collected. In addition, the free acid and ferrous iron concentration were measured by titration methods at least every second day. Approximately 60 mL of the slurry was collected manually via syringe from the experiment on days 1, 3, 5, 7 and 10 (as is commonly performed in this type of experiment to monitor the bacteria and liquor chemistry). This was pressure filtered with the liquor and solids weighed and assayed (ALS Global, Perth, Method Codes: MEICP41 and MEICP02 For Co and AA20a for Fe; ICP-MS and -AAS methods).

3.3. Optimization Experiments

Following adaption, investigations into defining the optimal conditions for bioleaching (to maximize Co in the pregnant liquor) were explored in stirred batch reactor tests, with three parameters tested. Experiments focused on varying: (i) pH- with four conditions tested (1.3 to 1.4, 1.5 to 1.6, 1.7 to 1.8, and 2.0 to 2.1); (ii) temperature (35 °C, 40 °C, and 45 °C); and (iii) iron concentration in the nutrient medium (4 K, 12 K, and 16 K). These experiments were monitored at least once daily with measurements of pH, redox and dissolved oxygen made. In addition, the free acid and ferrous iron concentration were measured by titration methods at least every second day. Approximately 60 mL of the slurry was collected from each experiment at least every other day (starting at 0) for up to 19 days. These slurries were pressure filtered with the liquors and solids assayed (ALS Global, Perth, Method Codes: MEICP41, MEICP-02 For Co and Fe).

3.4. Flotation Testwork

To determine if creating and bioleaching a concentrate is feasible for efficient Co liberation, an experiment was initiated in January 2018. Approximately 10 kg of each sample was used to make a bulk tailings composite sample and ground to 84 µm. This was subjected to a rougher/cleaner flotation test (using a 30 L flotation cell set with the agitator speed set at 800 rpm) to produce a sulphide concentrate [47]. The frother, methyl isobutyl carbinol (MIBC) was added manually at 100% purity though a syringe with a natural pH (i.e., no modifications; ~pH 5.3). The collector, potassium amyl xanthate (PAX) is widely used in pyrite flotation and therefore was selected for use in this test work. Air was fed through a plastic break tube (metric airbrake type A) to the top of the agitator shaft. The air travels down the hollow shaft and dispersed from the bottom of the impellor. A stator at the bottom of the float cell was used to assist with air bubble dispersion, slurry agitation and turbulence. All solutions used in the experiment were prepared with concentrated analytical grade reagents. An airflow rate of 40–60 L/min was applied during flotation. The float was a three-stage rougher at 5 min, 3 min, and 3 min with the floated and unfloated particles collected. Both were assayed for elements including Co, Cu, Fe, Ni, S, Au, As, C, Pb, and Zn (ALS Global, Perth, Method Code: MEICP-02 using ICP-MS). The flotation recovery was calculated based on solid weight distributions between the two products with the final rougher concentrate used in the bacterial oxidation experiments described in this study. These were batch ground using a stirred milled (vertical shaft) to a *p80* of 40 µm.

To determine the Co concentration in the rougher concentrate, one grain mount sample was prepared and analysed using a Resonetics RESOlution system equipped with a 193 nm wavelength Coherent COMPex Pro ArF excimer laser (Australian Scientific Instruments, Fyshwick, ACT, Australia), coupled with the Agilent 7700 quadrupole ICP-MS (Ar plasma) at the CODES analytical laboratories (University of Tasmania). Spot analyses (29 µm) were performed with a laser energy of 85 mJ used. Ablation data was processed offline using new in-house software with appropriate consideration for detection limits and QA/QC protocols followed. Calibration standards used in this analysis included Peru Pyrite, STDGL3 and GSD-1G.

The BIOX® bacteria (Outotec, Espoo, Finland) were once again adapted, but this time to the rougher concentrate (i.e., higher sulphide content) for 8 days (pH:1.1 to 1.6; 40 °C; 9 K nutrient medium; stirrer speed: 350 rpm; dissolved oxygen: 2.1–4.4 ppm) prior to the continuous stirred tank experiments.

Three 5 L tanks (B1, B2, and B3) were arranged in a cascade with the pulp passed from one taken to the next by manual periodic transfer. The reactor tank feed in each was made up of 240 g of high density pulp of pyritic concentrate (9.74 wt % solids) suspended in 3000 mL and inoculated with 300 mL of the adapted BIOX® bacteria. The tanks were left to run for 7 days with the pH, redox and dissolved oxygen measured at least every three days. The pH was maintained around pH 1.5 by adding limestone (up to 25 g) or sulphuric acid (up to 12.5 mL). On day 7, approximately 1/3 of the pulp was manually transferred from each and passed to the next tank, with fresh concentrate material introduced into B3, passed to B2 and B1 where material was finally removed. This transferal process occurred every 3 days (i.e., allowing enough time for bacterial equilibrium to be reached in each tank), with the quantity of added solids increased over time (i.e., 90 g for the first two transfers, 120 g for the third, and 150 g for the final three). Approximately 60 mL of the bioleached slurries were collected at transferal times and at the end of the experiment on day 27. These were pressure filtered with the liquor and solids analysed (ALS Global, Perth, Method Codes: MEICP41, MEICP-02). Final leached cobalt and pyrite oxidation rates were calculated using: (i) data obtained from sampling solids; (ii) measuring concentrations directly and comparing to the head grade; and (iii) results obtained periodically during the experiment (e.g., cobalt concentration in solution).

3.5. Iron and Cobalt Precipitation Tests

To recover Co, experimental Fe precipitation test work (sighter tests) was first performed with 125 mg of the combined BIOX® liquor (i.e., composite of all transfer liquors plus end liquors) used. This experiment was to determine the pH at which Fe and Co are effectively separated (with Fe precipitated out) to enable the recovery of a purer Co product. The pH targets were 2.2, 2.8, 3.5, and 4.0. Once a suitable end-point was determined, the bulk BIOX® liquor was subjected to limestone dosing to precipitate out Fe, with Co precipitation the last remaining step. First, Co required oxidising therefore both H_2O_2 (40% strength) and NaOCl (15%) were tested. Finally, NaOH (5%) was added to reach pH 4.5 to precipitate out the desired product, cobalt hydroxide.

3.6. Mineralogical Characterisation

Measurements of bulk mineralogy were performed throughout the experiments with X-ray diffractometry (XRD) performed using a Bruker D2 Phaser XRD instrument with a Co X-ray tube. Approximately 2 g of each sample was micronized in ethanol using a Retsch miconising mill with zirconium oxide grinding elements for 10 min. The ground residue was oven-dried at 40 °C overnight and lightly disaggregated in an agate pestle and mortar prior to analysis. Each sample was loaded into XRD sample holders and analysed between 5° and 90° 2θ using a 0.02° step size and a counting time of 0.5 s per step. The D2 phaser operated at 30 kV and 10 mA using a 1 mm fixed divergence slit, a 2.5° soller slit and a Fe-filter. Mineral phases were identified using the Bruker DIFFRAC.EVA software package with the PDF-2 (2012 release) database. Mineral abundances were estimated by Rietveld refinement using TOPAS (Version 4) pattern analysis software. As an internal standard was not added to the sample (as is conventional in XRD studies) results were considered semi-quantitative at best and those minerals identified < 5% have been assigned but not semi-quantified.

Scanning electron microscopy (SEM) studies of the ore, tailings bulk composite, rougher concentrate, rougher tailings and bioleaching residues were performed, to compliment XRD results, at the Central Science Laboratory, University of Tasmania. Each dried powdered sample was mounted on double sided carbon tape placed on a 10 mm diameter steel puck, and carbon coated prior to analysis. A Hitachi SU-70 field-emission scanning electron microscope (FE-SEM) fitted with a 5-segment solid state BSE detector and an Oxford Instruments Aztec EDS system equipped with an X-max 80 SDD EDS detector was used with the operating volume set at 1.5 kV for imaging. Both back scattered electron (BSE) and scanning electron images (SEI) were collected to allow the examination of reaction products. Oxford Aztec software was used to acquire and process the data.

4. Results

Results from the initial batch tank reactor experiments (with results from optimization test work also given) and the continuous stirred tank reactor experiments are, for clarity, given in separate sub-sections.

4.1. Batch Stirred Tank Reactor Experiments

4.1.1. Tailings Feed Characteristics

The tailings mineralogy is dominated by hornblende and chlorite, with 7 wt % pyrite measured in the bulk composite indicating that, as a bacterial feed, this material is relatively lean as typically, sulphide concentrate materials used in bacterial oxidation experiments contain higher quantities, e.g., 70 wt % pyrite [32]. Additionally, no other obvious mineralogical sources of cobalt (e.g., skutterudite, gersdorffite) were identified. Material collected from all zones were Co bearing, as seen in Table 1, with a maximum measured in Zone 2 (580 ppm) However, the bulk Co is notably lower (by two orders of magnitude) in the head grade than for individual pyrite grains as reported in [27]. Nickel was also noted as high (up to 3 wt %) in individual pyrite grains [27], with concentrations similar to Co in the bulk samples as seen in Table 1.

Based on the sample mineralogy, the composite sample is considered acid forming as carbonate minerals are absent, with a measured net acid producing potential of 214 kg H_2SO_4/t (calculated following the AMIRA P387A Handbook methodology whereby acid neutralising capacity is subtracted from the maximum potential acidity). Tailings from Zone 1 report the lowest maximum potential acidity (17 kg H_2SO_4/t) as these are more oxidised tailings (i.e., coarser grain size due to proximity to the fixed spigot point; [26]). Despite this, results confirm the net geoenvironmental risk if passively managed, i.e., the OTD will continue to generate AMD.

Table 1. Chemical composition of Zones 1 to 4 bulk samples and the composite. Please note that As, Au, Mo, and Ag were below instrument detection limits of 10, 2, 5, and 2 ppm respectively.

	C	**Corg**	**S**	**S^{2-}**	**Fe**	**Cu**	**Co**	**Zn**	**Ni**	**Pb**
	%	**%**	**%**	**%**	**%**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**
Zone 1 Head	<0.03	<0.03	0.7	0.6	9.4	98	60	32	75	15
Zone 2 Head	0.06	<0.03	15.9	14.2	18.1	2120	580	88	595	25
Zone 3 Head	0.03	<0.03	10.6	9.54	14.1	1480	440	102	375	30
Zone 4 Head	<0.03	<0.03	9.5	8.6	13.6	1640	380	76	305	35
Composite Head	0.06	<0.03	9.16	8.2	14	1400	360	74	325	30

Corg: Organic carbon.

4.1.2. Bacterial Adaption

The solid concentration of the bacterial adaption composite feed was 12%, with the pH maintained between 1.4 and 1.6. During the experiment, a steady redox increase was observed for the first three days (420 to 496 mV) suggesting successful adaption with the rate increasing sharply (net increase of 90 mV) between days 2 and 3 in particular. At day 10, a final redox potential of 685 mV was measured, and as it had only risen by 5 mV since day 9, it was considered a suitable end-point to confirm bacterial adaption to the composite feed. Measurements of free acid and ferrous ion concentrations decreased steadily over the 10 days, suggesting progressive pyrite oxidation. This was confirmed by analyzing solid and liquor materials periodically collected from the tank. Sulphide content decreased from 8.22% to 0.18%. Because Co is lattice bound in pyrite, its content also decreased in the remnant solids with 89% liberated by day 10 and 63 mg/L Co measured in the corresponding liquor, with a calculated Co liberation of 93%. Cobalt content in the liquor gradually increased to 80 mg/L on day 24 (i.e., after the termination of the adaption experiment the tank was maintained to host the OTD adapted specific inoculum). Bulk mineralogical analyses of the post-reaction material revealed that trace pyrite was present (i.e., below reporting confidence level), with gypsum (25 wt %) and jarosite (7 wt %) the dominant oxidation products.

4.1.3. pH Modification

Following the successful adaption of these bacteria to the lean feed, the pH experiments were conducted. The temperature was maintained at 40 °C with a 9 K nutrient medium used. Direct calculations of sulphide oxidation were performed (determined by performing a mass balance using sulphur and sulphate-sulphur assay values) and showed that the feed material contained partially oxidised sulphide material at the start (likely originating from Zone A as suggested by the low sulphide-sulphur content measured; Table 1). Bacterial assisted oxidation appeared most effective at lower pH conditions as near total oxidation was calculated, whilst only 88% and 76% was calculated for pH 1.7 to 1.8 and pH 2.0 to 2.1 experiments, respectively, at day 19, as seen in Figure 3A.

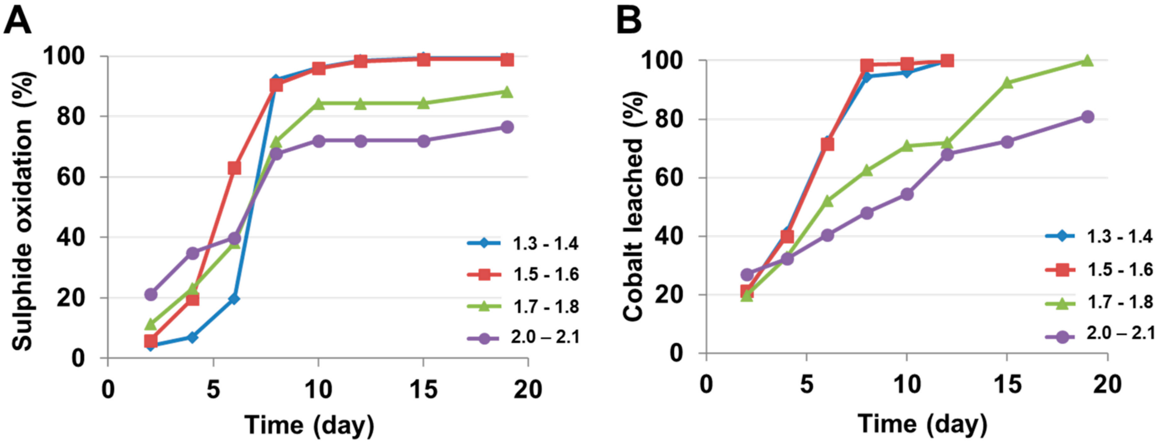

Figure 3. Calculated percentage of (**A**) sulphide oxidation and (**B**) cobalt in leachate for pH-modified experiments.

Measurements of Co in the resulting liquor showed that maintaining the experiment at pH 1.5 to 1.6 is the most efficient pH condition. However, by day 10, a similar quantity of Co was measured from the pH 1.3 to 1.4 experiment. These results show the BIOX® consortia do not behave efficiently under higher pH conditions with the percentage of leached Co decreasing with increasing pH, as seen in Figure 3B, which agrees with the documented behavior of these bacteria [23]. Maintaining the pH conditions at 1.3–1.4 was, at times, difficult as the generation of protons as part of the reaction caused the pH to drop below pH 1, therefore, high quantities of limestone had to be added (>25 g) although this is a noteworthy CO_2 source which these bacteria do indeed require [23].

4.1.4. Temperature

The BIOX® consortia behave most efficiently at 40 °C, but to test if catalysis could be accelerated at a higher temperature, or alternatively a cooler temperature could be used to save on energy costs (associated with heating) two variation experiments were established at 35 °C and 45 °C. The pH was maintained at 1.5 to 1.6 and a 9 K nutrient medium was used. Up until day 7, sulphide oxidation was broadly similar in the three experiments with approximately 58% having occurred, as seen in Figure 4A. After this time, a slight acceleration in oxidation rate occurred at 45 °C up to day 8 after which the rate decreased until day 15 when it plateaued having achieved 98% oxidation. As BIOX® uses three bacteria, their individual activities fluctuate, in response to temperature, during the experiment. The observed results may be explained by the diminished activity of *Acidithiobacillus thiooxidans* which thrives at 28–30 °C and at temperatures above 37 °C sulphur oxidation progresses at a significantly slower rate. Further, as pyrite oxidation is exothermic the internal tank temperature may indeed have exceeded the set temperature further impacting its activity [23].

In contrast, oxidation progress dropped from day 8 onwards at 35 °C with a near-cessation of activity from day 10 onwards with only 86% oxidation achieved by day 19, as seen in Figure 4A. It is likely that the other mesophilic bacteria present are better adapted to warmer conditions, as prior to adaption the bacteria had been kept in a stock tank where the temperature was held at 40 °C. Indeed, as seen in Figure 4A, at 40 °C, the oxidation rate remained reasonably consistent for the duration of the experiment with 100% oxidation achieved by day 12. Co leaching shows greater efficiency at higher temperatures with $>95\%$ by day 10 but can be seen to have evolved generally over three stages (best shown at 35 °C). Initially, the mesophilic bacteria are active, next, oxidation rate begins to diminish and finally, bacterial growth rate declines, as seen in Figure 4B [23].

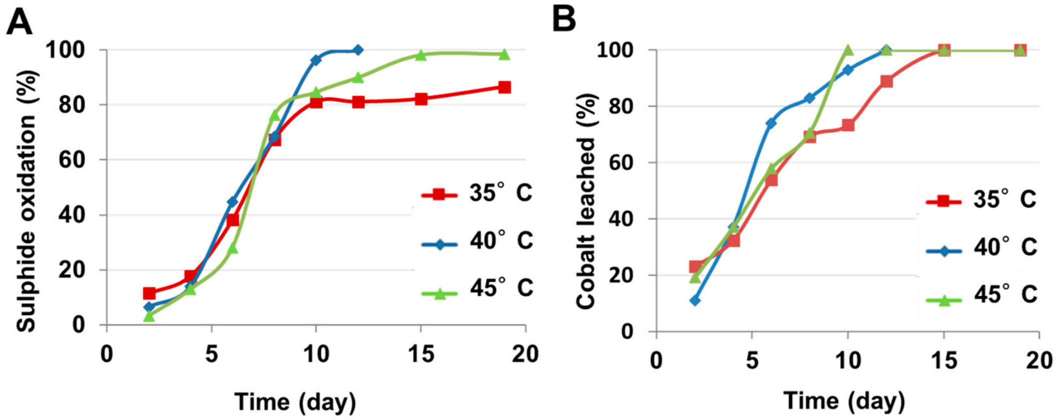

Figure 4. Calculated percentage of (**A**) sulphide oxidation and (**B**) cobalt in leachate for temperature-modified experiments.

4.1.5. Nutrient Medium Amendment

The BIOX® consortia require sustenance to maintain activity, with the provision of Fe in the nutrient medium vital to generate ferric irons in solution by which pyrite is oxidised and Co leached. To test the sensitivity of these bacteria to changing Fe conditions, three experiments were established using 4 K, 12 K, and 16 K mediums (containing 66.6 g, 200 g, and 266.6 g $FeSO_4 \cdot 7H_2O$ respectively). In these tests the pH was maintained at 1.5 to 1.6 and at 40 °C. Results from the earlier 9 K experiment are not shown as they were performed as part of the earlier adaption test work and are therefore not comparative. Both 4 K and 16 K medium reported similar sulphide oxidation and cobalt leach rates with >97% in solution by day 8 as seen in Figure 5A,B. This demonstrates that in this experiment, this is not a key-control on bacterial activity, and a 4 K medium could be easily used in place of 9 K to reduce operational costs associated with this type of test work.

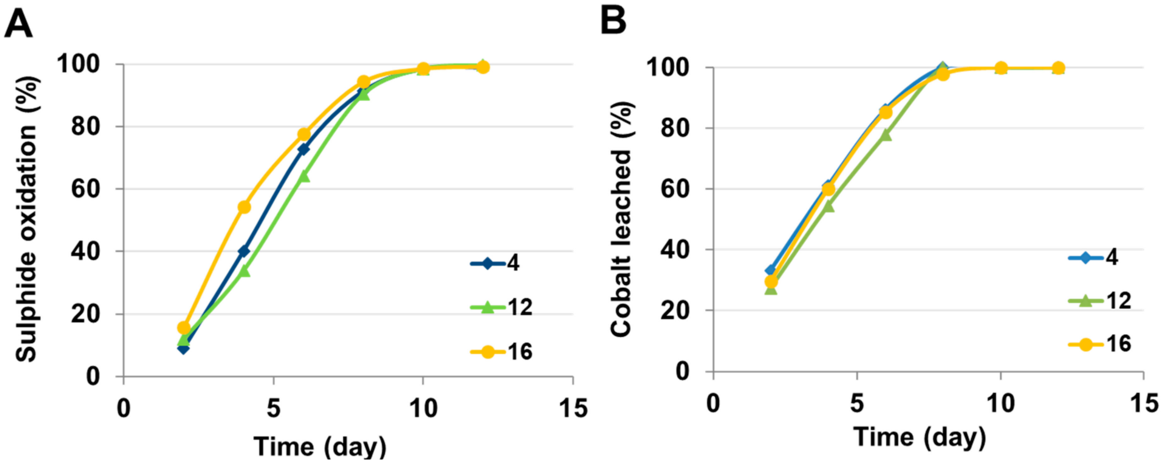

Figure 5. Calculated percentage of (**A**) sulphide oxidation and (**B**) cobalt in leachate for iron amendment in nutrient medium (4 K, 12 K, and 16 K) experiments.

4.2. Continuous Stirred Tank Experiments

4.2.1. Sulphide Concentrate Production

After flotation, approximately 70.5% pyrite was measured in the rougher concentrate, however talc was also concentrated by this process, increasing from 1 wt % in the tailings composite to 17 wt %. Antigorite (8 wt %), actinolite (3 wt %) and trace chlorite were also identified as shown in Figure 6. Magnesium silicates are common gangue components in sulphide ores with their presence inhibiting metallurgical recovery [48]. The mineralogy of the rougher tailings was like that of the composite feed with chlorite (32 wt %), antigorite (27 wt %) and actinolite (23 wt %). Pyrite was still present as a minor component (2 wt %; Figure 6) and remains classified as potentially acid forming (PAF) although the relative neutralising potential had increased by 8 kg H_2SO_4/t compared to the tailings feed as seen in Table 2. These results highlight that the efficiency of the initial float must be improved to generate an inert 'new' tailings product.

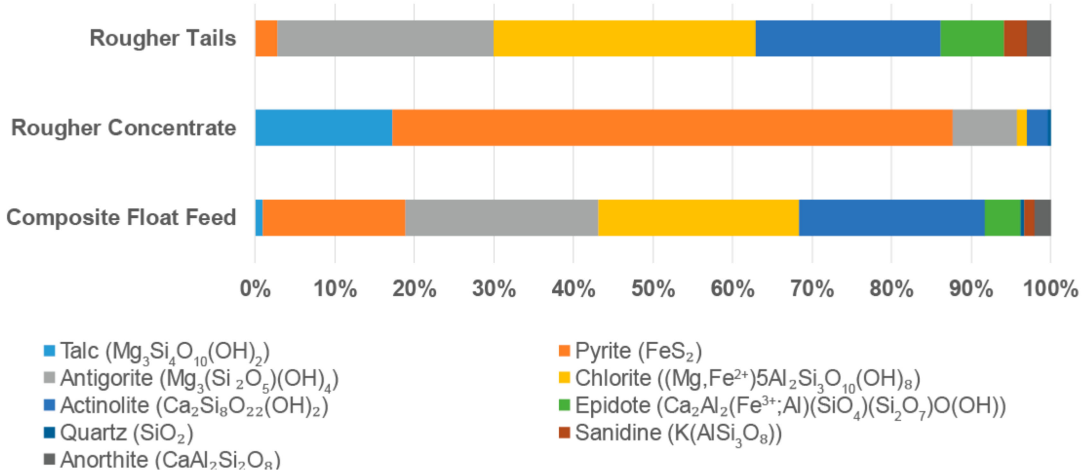

Figure 6. Bulk mineralogy (measured by X-ray diffractometry (XRD)) of the composite float feed, rougher concentrate (used in biooxidation experiments) and rougher tailings.

Table 2. Chemical composition and geoenvironmental properties of composite head, rougher concentrate and rougher tailings (ANC: acid neutralizing capacity; MPA: maximum potential acidity; NAPP: net acid producing potential calculated by MPA-ANC; NAG: net acid generation; PAF: potentially acid forming).

Parameter	Unit	Tailings Feed	Rougher Concentrate	Rougher Tailings
Fe	%	14	37	9.5
Cu	ppm	1100	5910	452
Co	ppm	350	1840	70
Ni	ppm	350	1385	170
Pb	ppm	30	80	5
Zn	ppm	114	166	80
S	%	7.53	44.9	1.09
Neutralising characteristics				
Fizz Rating	-	1	0	1
ANC (Sobek)	Kg H_2SO_4/t	14	0	22
Acid generating characteristics				
MPA	Kg H_2SO_4/t	230	1374	33
NAPP	Kg H_2SO_4/t	216	1374	11
NAG	Kg H_2SO_4/t	45	115	15
NAGpH	-	2.3	2.1	2.6
ARD Classification		PAF	PAF	PAF

Concentrating Co during flotation successfully occurred when compared to the head sample, as seen in Table 2, with an increase in 350 ppm to 1840 ppm. Similarly, Ni and Cu were also high in the rougher concentrate, as shown in Table 2, with an average concentration of 1935 ppm and 462 ppm respectively. Measurements of Co in pyrite reported a range of 2 to 27,800 ppm with an average value of 2460 ppm suggesting the rougher concentrate has a head grade of 0.2% Co as seen in Figure 7. This would be considered a potentially economic grade when compared to other Co-bearing deposits, for example, laterites containing 0.05% Co have been considered mineable [45].

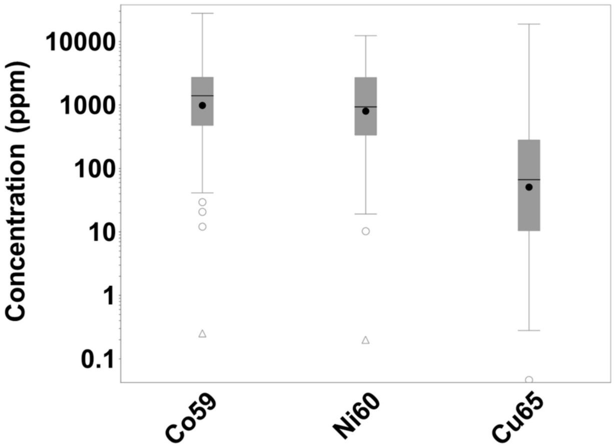

Figure 7. Box and whisker plot (*n* = 143) showing cobalt, nickel and copper concentration in pyrite from the rougher concentrate (NB. the box covers the interquartile range, the line is the median and the circle the mean. The whiskers are drawn at the threshold to identify near and far outliers based on the Tukey statistic).

Similarly, high Ni (range: 4.5 to 12,360 ppm; average: 1960 ppm) and Cu (0.28 to 18,830 ppm; average: 460 ppm) were measured. An investigation of the deportment mode of these three elements confirmed that both Co and Ni are likely refractory, as seen in Figure 8A. Copper in pyrite is observed as chalcopyrite inclusions with their size estimated as < 10 μm as shown in Figure 8B. Overall, the net-content of Co was considered high enough to be a good feed to use in the continuous tank experiments.

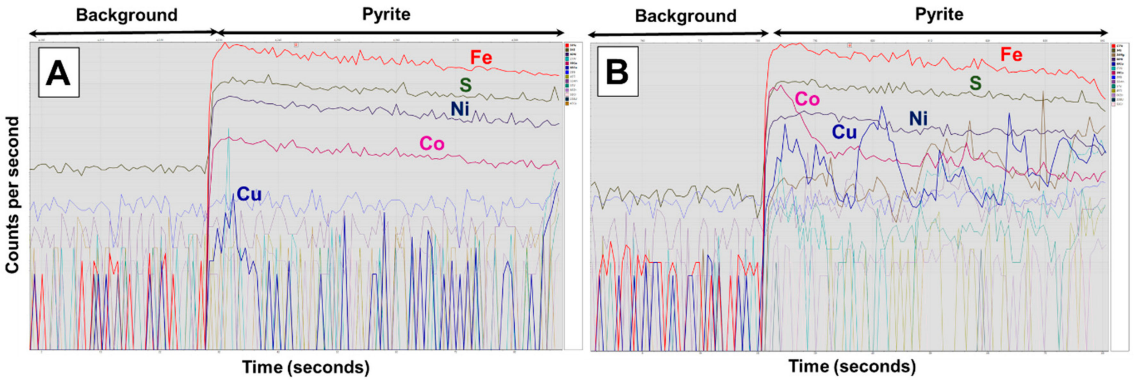

Figure 8. Examples of laser ablation ICPMS (LA-ICPMS) traces for pyrite contained in the rougher concentrate. (**A**) Co and Ni appear as refractory within pyrite as their trace is roughly similar to that for Fe and S; (**B**) Cu inclusions are seen within pyrite (i.e., appearance of large spikes) with Co showing zoning in the pyrite grain.

4.2.2. Cobalt Liberation

Bioleaching in each tank proceeded using the optimal conditions determined in Section 4.1 and following a standard BIOX® experiment. The sulphide concentrate material was placed in each tank and allowed to react for seven days and after this, material was manually transferred every three days from one tank to the next until the end of the experiment at day 28, as seen in Figure 9. As fresh material was placed into tank B3, sulphide content in the assayed solid was highest, with tank B2 intermediate and tank B1 containing the least. For the first 5 days (pre-transfer), sulphide oxidation progressed efficiently in tank B3, with a drop from 40% to 0.5% with 94% Co liberated, as seen in Figure 9A. On addition of new feed, an average of 13.75% sulphide-sulphur was present in the column suggesting that some oxidation of material occurred (i.e., 66%) with, on average 620 ppm Co remaining in the solid. This is greater than the measured bulk Co that went into the tanks (head assay: 350 ppm) implying that whilst sulphide oxidation is ongoing, Co may be precipitating in salts or even adsorbing to solid reaction products such as jarosite.

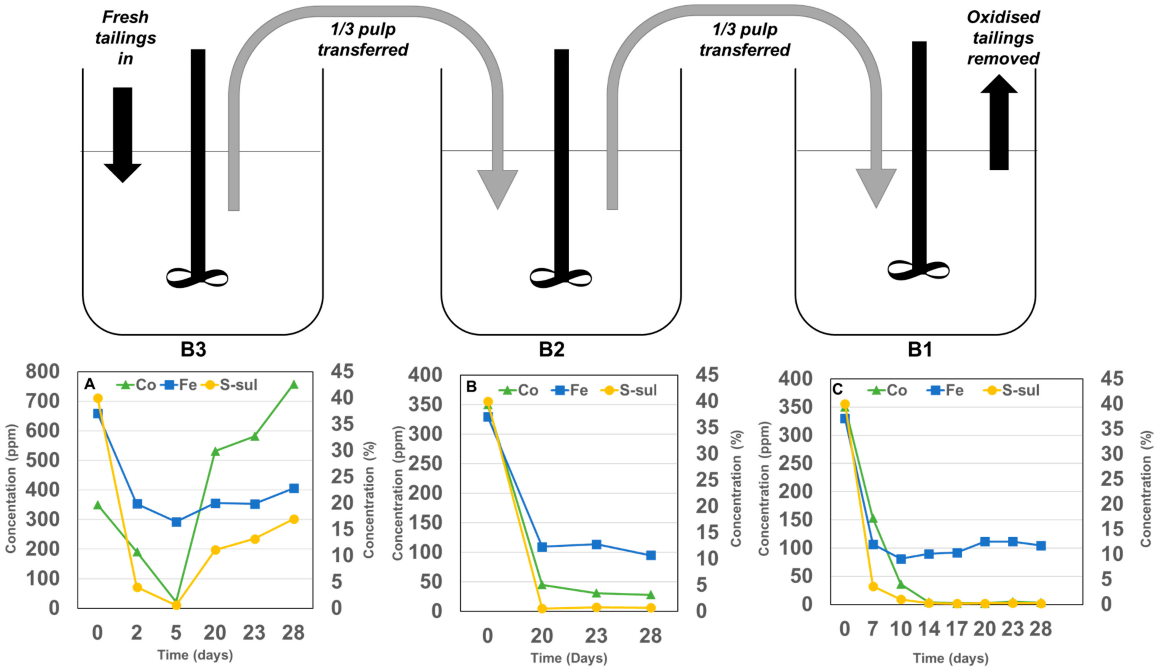

Figure 9. Schematic diagram of continuous tank experiments with transfer pathways, inputs and outputs shown and the concentrations of Fe (%), calculated sulphide-sulphur (%) and cobalt (ppm) in the solids periodically collected from tanks: (**A**) B3; (**B**) B2, and (**C**) B1.

In tank B2, fewer solid analyses were performed with solids from two transfers and only the end material analysed. The content of Co is an order of magnitude lower in tank B2 than B3 with 28 ppm remaining in the final material (i.e., 92% liberated when compared to the head grade) with a decrease observed over time (Figure 9B). The relative proportion of gypsum increased to approximately 50% (up from 23%; as seen in Figure 10 and Figure S1) providing further evidence (in addition to the low content of pyrite) of efficient oxidation. Therefore, the material transferred into tank B1 is considered to be well oxidised.

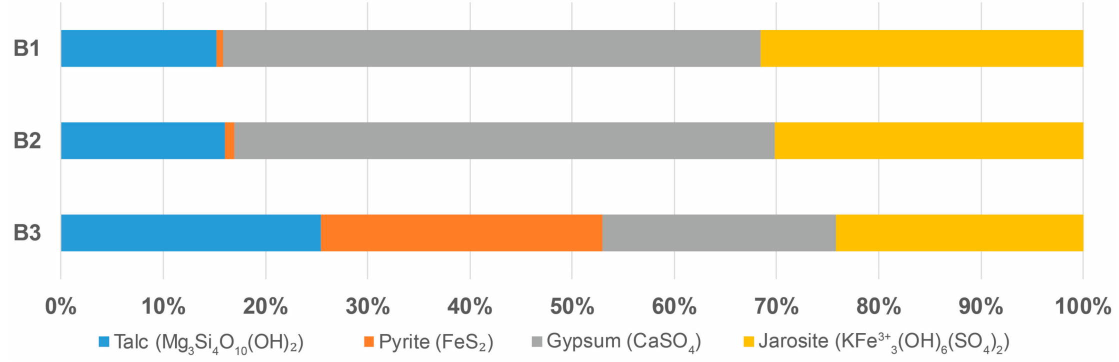

Figure 10. Bulk mineralogy (measured by XRD) of the residues collected at the end of the experiment from tanks B1, B2 and B3.

In tank B1, only chemical analyses were performed on solids from each transfer (i.e., here mass was removed, so each represent end-points of the experiment) and were compared against the chemistry of the rougher concentrate (i.e., day 0). By the 3rd transfer, 99% of Co was released from pyrite to the liquor solution and remained at around this level for the duration of the experiment as shown in Figure 9C. Bulk mineralogical measurements reported trace pyrite only (0.2%), with the dominant reaction products including gypsum (53 wt %), jarosite (32 wt %) and talc (15 wt %, shown in Figure 10 and Figure S1).

Final calculations were performed by dividing the residue assay by the feed assay to get the recovery (i.e., cobalt loss from solids). The three sets of samples indicate >99%, 96% and 53% recovery for B1, B2 and B3, which is considered a positive biooxidation response. Indeed, the final exit solid contained 2 to 5 ppm Co, suggesting that very little optimization is required for the actual biooxidation part of this experiment.

SEM investigations were undertaken to examine reaction products and showed that pyrite is present notably present in the original tailings composite, as seen in Figure S2, and concentrated significantly post-flotation (i.e., many bright phases are observable, as seen in Figure S2. This confirms bulk mineralogical observations, which suggest that the flotation reagents used are suitable. Much less pyrite is seen in the new rougher tails, but, it is still visible providing further evidence that flotation test work needs to be optimised (i.e., talc suppressed) in any further test work as Co is being lost and these new tails will still present an AMD risk (Figure S2). Residues collected from B3 show well-developed, large (up to 300 µm) tabular gypsum crystals are abundant, as seen in Figure S2, with minor cubic pyrite visible (approx. 10 µm, shown in Figure S2. In B2 residues larger gypsum crystals are observed and no pyrite. In the B1 final residue, the reaction products gypsum and jarosite are abundant.

4.2.3. Iron and Cobalt Precipitation Experiments

Controlling pH during sighter tests (to determine the pH at which Fe and Co separate) was difficult to set above a pH range of 2.4–2.6 where it would continue to increase (to an unpredictable end-point). Test E was overdosed so it was left to agitate for 2 h and it was noted that pH was still slowly rising at the time of termination. A visible reaction (fizzing, foam, and some fumes) occurred when adding the aglime to the BIOX® liquor. Assay results showed that Fe had dropped out considerably at pH 6.3, however, so had Co, as shown in Table 3. Instead, at pH 4.86, seen in Test D, Fe had decreased significantly from 19,950 mg/L in the feed liquor to 20.6 mg/L with similarly low Cu (0.90 mg/L) however again Co had also precipitated out (dropping from 127 mg/L to 64.9 mg/L). Whilst increasing the pH to 3.8 resulted in Fe dropping to 93.6 mg/L and Cu also to 38.2 mg/L, Co also decreased slightly. Instead, if the pH is 3, Co is not lost, but less Fe is precipitated out (with 124 mg/L remaining in the liquor). In reality, a pH between 3 and 3.8 would likely cause sufficient Fe removal with enough Co remaining in solution. However, setting at a pH in this range will cause difficulty in producing a pure Co product as Ni remained in this liquor, along with 82% of Cu. Thus, without additional refining steps, a Co-Ni-Cu concentrate will be produced.

Table 3. Chemical assay and end pH values measured in sighter test final liquors.

	pH	**Fe**	**Co**	**Cu**	**Ni**	**As**
Experiment		*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*
Test A	2.18	9730	135.5	275	96.7	3.6
Test B	3	124	135.5	218	96.3	1.7
Test C	3.8	93.6	126	38.2	86.2	1.8
Test D	4.86	20.6	64.9	0.9	30	0.7
Test E	6.3	0.80	1	<0.2	0.6	3.5
Feed Liquor	-	*19,950*	*127*	*267*	*90.8*	*6.8*

-: Not measured.

Whilst it may be attractive to manufacture the purest product, production of refined Co is highly complex, with the risk of variable purity. Considering this, precipitating out crude cobalt hydroxide ($Co(OH)_2$) was the target. First, Co was oxidized using H_2O_2 (40% strength), however, redox measurements did not increase suggesting this was not successful. Instead, NaOCl (15%; 5 mL) was added to 1 L of liquor with redox measurements ~921 Mv. When plotted on a Pourbaix diagram (against pH) Co oxidation was confirmed. Next, NaOH (5%; 8 mL) was added to pH 4.5 in order to precipitate out $Co(OH)_2$. A fine brown precipitate (several grams) developed following NaOH addition and the liquor changed from pink to clear over the experiment both of which indicate a successful experiment. However, assaying of the liquors reported that the start liquor contained 117 mg/L Co and 21.5 mg/L Fe, whilst the final liquor contained 111 mg/L Co and < 0.1 mg/L Fe implying the experiment should be refined. Further bench testing is needed to optimise Co precipitation, which could be achieved by increasing the pH (i.e., to > pH 6.3; as in Table 3 ~99% of Co had dropped out at this pH). This will ensure precipitation of the brown $Co(OH)_2$ product. However, it is necessary to remember that this is still not a pure product as Table 3 showed that Ni and Cu are likely present too (these were not assayed in the final Co precipitation tests). Thus, an extra refining step will be needed to remove Ni and Cu because at the measured concentrations, they are akin to penalty elements rather than additional streams of potential revenue.

5. Discussion

5.1. Optimal Conditions for Biooxidation

Many factors can affect bacterial assisted leaching of metal sulphides as listed in Mahmoud et al. [23] including temperature, pH, redox potential, O_2 content and availability, CO_2 content, gas mass transfer, nutrients, Fe^{3+} and Fe^{2+} concentration, heavy metal content, aeration, and stirring rate. In this section we focus on only those which we consider having had the most control. The optimization testwork shows that the dissolution rate of Co is proportional to the decomposition of pyrite, thus using BIOX® under these varied experimental conditions will enable Co recovery even when using a lean tailings feed material such as the OTD composite. Geochemical measurements of ferrous ion content and free acid confirm that mineral dissolution is proceeding via the thiosulphate mechanism [49]. Essentially, solubilisation is through ferric iron attack on pyrite with thiosulphate produced as an intermediate, and sulphate the main end-product, as seen in Equations (1) and (2). The ferrous iron produced is oxidised to ferric iron by the bacteria, as seen in Equation (3), which efficiently oxidises pyrite, as shown in Equation (4).

$$FeS_2 + 6Fe^{3+} + 3H_2O \rightarrow S_2O_3{}^{2-} + 7Fe^{2+} + 6H^+ \tag{1}$$

$$S_2O_3{}^{2-} + 8Fe^{3+} + 5H_2O \rightarrow 2SO_4{}^{2-} + 8Fe^{2+} + 10H^+ \tag{2}$$

$$2Fe^{2+} + 0.5O_2 + 2H^+ - \mathit{bacteria} \rightarrow 2Fe^{3+} + H_2O \tag{3}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4 + 16H^+ \tag{4}$$

The results suggest that the optimal conditions for sulphide oxidation and release of refractory Co to the liquor are low pH (1.3–1.6) and higher temperature (40 °C) with the Fe-contents in the medium being of lesser importance if the bacteria are well adapted to the feed material (providing these other chemical conditions are maintained; Table 4).

Table 4. Percentage of Co leached per experiment after 4 days and at the batch experiment end.

Variable	Experiment	Co (%) Leached at 4 Days	Final Co (%) Leached
pH (40 °C, 9 K fixed)	1.3–1.4	39	100 (Day 12)
	1.5–1.6	39	100 (Day 12)
	1.7–1.8	32	100 (Day 19)
	2.0–2.1	32	81 (Day 19)
Temperature (pH 1.5–1.6, 9 K fixed)	35 °C	32	100 (Day 15)
	40 °C	36	100 (Day 10)
	45 °C	36	100 (Day 12)

Table 4. *Cont.*

Variable	Experiment	Co (%) Leached at 4 Days	Final Co (%) Leached
Nutrient medium (pH 1.5–1.6; 40 °C fixed)	4 K	60	100 (Day 9)
	9 K	37	100 (Day 12)
	12 K	54	100 (Day 9)
	16 K	60	100 (Day 10)

Several of these findings compliment those reported by [31] who examined an ore containing 40.3% Fe and 1.4% Co using bacteria obtained by the Bureau de Recherches Géologiques et Minières (BRGM) comprising *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, with *Leptospirillium*-like bacteria. Specifically, they evaluated the effect of Co concentration, pH, temperature, solid content, particle size, and dissolved iron contents. Cobalt concentration (range tested: 3–15 gL^{-1}) had no reported effect, with pH conditions between pH 1.1 and 2 most suitable for biooxidation. Below this pH, bacterial growth is inhibited, however, as pyrite biooxidation progresses, pH conditions below 1 may be occasionally experienced, which have repercussions on Co release. This highlights that regular monitoring (e.g., at least once every 24 h) of the geochemical conditions is critical, however, our experiments demonstrated that addition of limestone to bring up the pH can adversely affect sulphide oxidation rate. Morin and d'Hugues [33] reported temperature to have no significant effect upon cobalt solubilisation between 30 and 37 °C, with biooxidation inhibited at 40 °C. Our findings show this is not the case for the BIOX® consortia, who initially were ambient at 45 °C up to day 10 but showed diminished activity up to day 19. The rate of oxidation increased with solid contents until 10%, with the kinetics of biooxidation decreasing above this, regardless of the particle size (with <20 μm preferred). In our experiments, 12–17% solid content were used, therefore, to increase Co-leaching efficiency; an even lower quantity could be used in future experiments. Finally, Morin and d'Hugues [33] reported that ferric iron concentrations between 9 to 35 gL^{-1} slow Co release, and can reduce the final recovery by 10%, with lower concentrations yielding better results. Our results seem to contradict this as the measured dissolved iron concentrations were within this range for all except for the high pH experiment (2.0 to 2.1), which yielded less Co. This is likely due to *Leptospirillium*, which has the ability to tolerate ferric iron, being a formal part of the BIOX®consortia whereas in the BRGM consortia used, it was only later identified as present in the bacterial community.

D'Hugues et al. [32] examined, using the BRGM inoculum, how additional variables, including agitation rate and nutrient medium, affect Co release. Stirred tank reactors were constructed with the tested material containing 70% pyrite (with a head grade of 1.25% Co). They established that excessive turbulence and high agitation rates (i.e., tip speed: 2.6 $m \cdot s^{-1}$ radial flow turbine; 3.8 $m \cdot s^{-1}$ axial flow impeller) affect bacterial productivity by reducing bacterial contact with the solid substrate. Mahmoud et al. [23] made similar observations regarding the impact of agitation rates. In our experiments an agitation speed of 800 to 900 rpm was used, and therefore in the next stage of testing, it could be reduced to accelerate sulphide oxidation. Consideration should also be given to increasing the quantity of O_2 gas purged through the tanks as explored in [50,51]. Gwénaëlle Guezennec et al. [51] reported that when dissolved oxygen (DO) ranged from 4 to 13 ppm in bioleaching experiments (51% pyrite; 20% *w/w* solids) healthy bacterial oxidizing activity was observed, with sulphide dissolution efficiency increasing with DO concentration. However, when DO concentrations reached 17 ppm, a significant decrease of microbial activity (and O_2 consumption) was noted, showing there is a critical DO threshold. In our test work DO varied between tanks ranging from 1.43 ppm to 10.76 ppm. Whilst in the original adaption experiments average DO was 4.3 ppm the DO demand was lower as it is proportional to sulphide concentration. Thus, for our 70% concentrate, it is probable that greater quantities of DO should have been input into the tanks to increase the rate of biooxidation, as only after 14 days is 98% of sulphide oxidised.

Calculation of sulphide oxidation rate showed that bacterial adaption when using the rougher concentrate was not as efficient as when using the bulk (as-received) tailings composite, which was unexpected. One such reason might be toxicity effects to one of the bacterial strains in the BIOX® culture caused by the metals present at this concentration, as the typical tailings feed materials used in the laboratories do not have a similar chemistry to the OTD rougher concentrate. Tuovinen et al. [52] reported that *Acidithiobacillus ferroxidans* has inhibitory concentrations of Zn, Ni and Co: >10,000 mg/L; Cu: >1000 mg/L; and As: <200 mg/L. Trevors et al. [53] stated that similarly, *Thiobaccillus ferrooxidans* can tolerate concentrations of Zn, Ni, Cu, Co, Mn and Al at around 10 g/L. Thus, metals contained in the rougher concentrate are unlikely to be affecting the sulphur oxidisers. The iron oxidiser, *Leptospirillum ferrooxidans* is able to tolerate lower pH conditions and higher concentrations of U, Mo and Ag than *Thiobaccillus ferrooxidans* can, but it is more sensitive to Cu [54,55] therefore removal of coarse chalcopyrite during beneficiation may serve to improve results. Other factors also need to be considered including the buildup of toxic components in such stirred tank reactor tests as described by Mahmoud et al. [23].

In our test work, running continuous stirred tank reactors allowed for 98% Co liberation (in tank B1) in 14 days whilst for a batch stirred tank experiment (pH 1.5–1.6, 40 °C, 9 K medium) 93% was achieved in 10 days. Whilst these results are not directly comparable given that experiments were run at different times, they contradict findings presented in Mahmoud et al. [23] from [56] where using a continuous tank setup was much more efficient for Cu dissolution. Whilst our lab-scale testing implies batch testing is more efficient, on a commercial scale it is well established that running continuous stirred tank reactors is more beneficial because achieving good global mixing under low shear conditions is difficult [23,49,50]. Further, using continuous stirred tank reactors can reduce waste and cost as compared to batch tanks, for example, removing down-time inherent in batch processing [23,57]. Once conditions are at steady state, a continuous process will output a near-homogenous product (assuming all variable factors such as temperature, pH and feed constituent are constant; [57]). Considering this, any further test work performed using these materials should use a continuous tank set-up, which has been employed in many commercial scale projects including Co recovery at Kasese, Uganda [23]. The next target would be to optimize further to allow for at least 80% Co dissolution in 6 days, as was the case at Kasese [23] with parameters such as agitation speed, dissolved oxygen and% solids the next variables to examine.

5.2. Flotation Testwork Evaluation

The largest source of Co loss in these experiments was during flotation where 70.5% pyrite was recovered in the rougher concentrate (with the new tailings stream still PAF). The presence of talc, a common gangue mineral in sulphide ores, has affected the flotation test work. It is naturally hydrophobic so reports to the concentrate thus reducing recovery [58]. Polymers are commonly used to depress talc, through their adsorption to its surface rending the mineral hydrophilic thus preventing bubble-particle capture. Typically, polysaccharides have been used as they are non-toxic and have selective inhibition properties with guar gum used [59]. However, guar gum is costly and its supply limited, so the efficiency of other polysaccharides (e.g., konjac gum) are being tested [59]. If flotation of OTD sediments is to be considered as part of an integrated tailings management scheme, then experimentation to find a locally derived plant-based polysaccharide, which effectively depresses talc could be a future opportunity aligning with sustainable mining practices. Routine examination of the degree of pyrite liberation using automated mineralogy [2] should be considered in future optimization to liberate more pyrite as whilst a *p80* of <38 µm was desired, SEM investigations showed some pyrite grains were up to 50 µm in diameter.

5.3. Metal Seperation

The Co refining stages of this study indicated that successful separation from Ni and Cu had yet to be achieved which is necessary to produce a saleable intermediate product. As an immediate first step, further bench-scale testing with pH adjustments (i.e., pH 5, 6, and 7) are necessary and, if possible, addition of NaOH before H_2O_2 should be tested [60]. Advantageously, Co exploration and its recovery is topical with many Australian companies targeting this commodity, thus new methods for its metallurgical recovery are being tested. For example, Co can be selectively extracted from Ni into an immiscible liquid organic phase using solvent extraction (SX; e.g., Kasese Cobalt, Uganda) [60,61]. There are advantages (e.g., fast exchange reaction kinetics) and disadvantages (aqueous-organic phase separation stage of SX is relatively slow requiring large settling ponds at high capital cost) of using SX and on a plant-scale, can cause ongoing challenges [60,61]. Newer technologies to enhance recovery include ion- and solvent-resin exchange (e.g., solvent impregnated resin, Lewatit® TP272; [61]). Application of this type of technology should be considered if pH alterations during the Co precipitation test work do not yield an acceptable recovery (i.e., > 60%).

5.4. Future Tailings Management

Extraction of the mine tailings for reprocessing is a significant undertaking which would require considerable funding (CAPEX and OPEX). Despite this, a diagrammatic flow sheet of what this could involve is shown in Figure 11. Consideration must be given to the rate at which tailings extraction will progress, as exposure of fresh tailings could induce AMD formation, therefore, kinetic testing of tailings to determine the lag-time to AMD is essential. Whilst these mine tailings likely originated from the Centre Pit, production of tailings has been ongoing to the present day, with these placed into the Main Creek Tailings Dam. Therefore, to further enhance a potential business case for remining, a geometallurgical study of these tailings should also be conducted, and if similar or higher Co contents are revealed, it is immediately strengthened. With a current price of >US $50,000/t [28]), and with a global thirst for this critical metal, the value of Co recovery could outweigh the ongoing costs of managing AMD at this site. However, this can only be determined once a Mineral Resource has been estimated that can be reported in accordance with The JORC Code 2012 (or other internationally accepted reporting code). This study focused on testing bulk samples collected from the upper 2 m, whilst in reality, against the northern dam wall the depth of tailings is 70 m, and the geometallurgical characteristics of these materials at depth is unknown. The next phase of investigation should seek to determine the geometallurgical properties of tailings at depth.

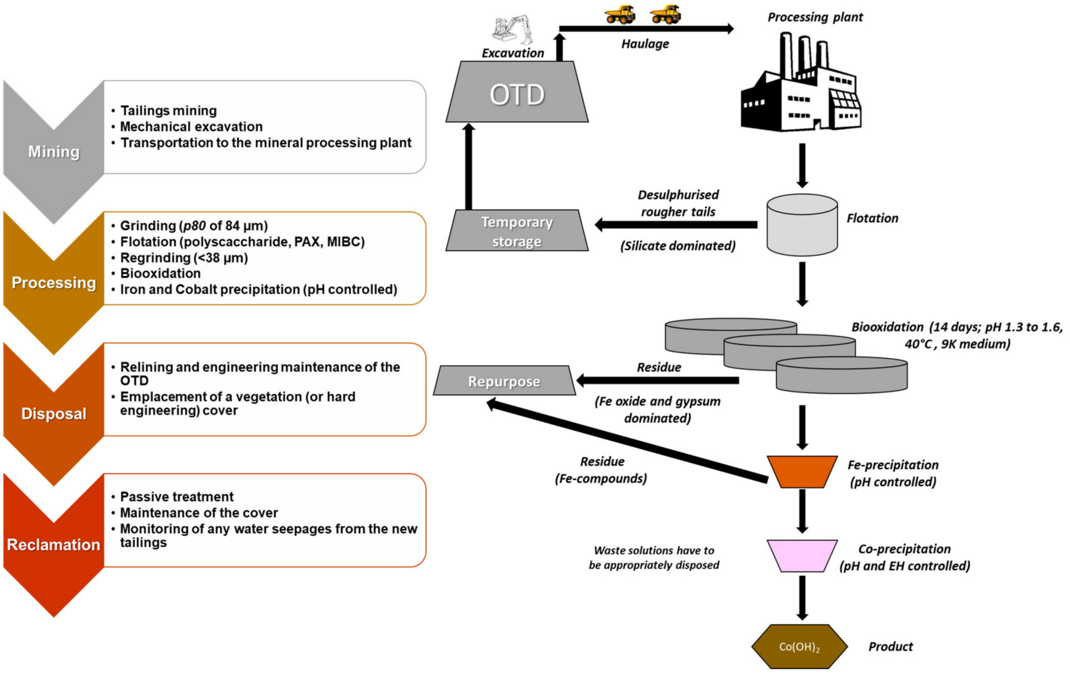

Figure 11. Diagram of potential tailings remining workflow. Here, new tailings are held in a temporary storage area before being returned to the OTD site following upgrade of the dam walls and lining. Residues from BIOX® and Fe-precipitation should be considered for further valorization; e.g., use of Fe-oxides and/or gypsum as part of a tailings cover design or pigment recovery (see [62]); all waste waters from mineral processing will need to be appropriately disposed).

Identifying new sources of metals can require new physical extraction methods. At this site, CAPEX and OPEX costs associated with remining could be minimized by considering in-situ biooxidation (similar to in-situ leaching; [63,64]). Such an approach is considered high-risk with difficulty obtaining environmental protection agency approval anticipated as it could inadvertently cause waste pollution if the operation is not well managed. Due to these considerable risks, as yet this is not a commonly used approach. In this proposed extraction process, a concrete curtain should first be sunk around the OTD to minimize contact between OTD pore waters and other surface and ground water courses. Next, a series of boreholes would be sunk across the OTD and bacteria pumped in (i.e., 4 K medium solutions). As sulphide oxidation is exothermic, it is anticipated that this heat would sustain the mesophilic consortia used (alternatively, utilising bacteria present at mine-impacted sites in Tasmania could be considered as they would be better adapted to local conditions). Water would also have to be pumped through the OTD (through an engineered fracture network) to then capture the pregnant liquor solution that would be delivered to the mineral processing plant where the process would begin at the iron precipitation step, as seen in Figure 11. This approach reduces handling costs, but it, as stated, high risk (potentially to ground and surface waters) which can be mitigated only if the concrete curtain is properly sunk and its integrity constantly monitoring with site-wide management strategies put in place. To determine if this is a feasible option, pilot-scale testing is required, whereby tailings would be placed in a large barrel (under ambient and modified conditions) with bacteria and water introduced and the resulting solids and liquor characterised (chemically and mineralogically).

6. Conclusions

At the Savage River mine, Western Tasmania, the historic OTD contains 38 Mt of reactive pyritic tailings that are actively generating AMD. Due to the geotechnical construction of the OTD, extending the natural water cover across the repository to prevent the ingress of oxygen (i.e., retard sulphide oxidation rate) is not economically feasible, nor indeed is establishing other types of covers. A geometallurgical study of the tailings, sampled from the upper 2 m, revealed that a potential Co resource may be present, with up to 3 wt % contained in pyrite. This study has shown that recovery of Co is possible from this material following flotation, biooxidation and precipitation tests to produce a $Co(OH)_2$ intermediate salable product. At the OTD, a rigorous sampling programme backed up by QAQC, is required that can form a base on which to estimate a Mineral Resource that can be reported in accordance with The JORC Code 2012 or other internationally accepted reporting code. However, our findings will assist with the undertaking of larger-scale bioleaching test work. This will in turn inform the business case for reprocessing tailings at this site. If a prefeasibility study is positive, then Co extraction from the tailings either traditionally via mining or in situ, may well be the most effective rehabilitation option to reduce AMD from this site, as the sulphide source will be sterilized and the new benign tailings can then be managed by today's environmental practices. Undertaking similar exploratory geometallurgical studies at other historical or legacy mine waste sites should be encouraged to inform whether reprocessing is a management option, as ultimately many positive impacts (environmental, economic, social) can be gained from deriving wealth from waste.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/8/10/454/s1, Figure S1: X-ray diffractometry patterns for the concentrate and solids taken from B1, B2 and B3 tanks at the end of the experiment; Figure S2: Back scattered electron (BSE) images of solid residues from the tailings composite, rougher concentrate and each tank. (A) Tailings composite material comprising bulk materials collected from Zones 1–4; (B) Pyrite contained in the tailings composite; (C) Rougher concentrate produced after tailings flotation; (D) New tailings stream produced after flotation; (E) Final bioleached residue from tank B3 (i.e., least oxidised); (F) Gypsum contained in the tank B3 residue; (G) Final residue from tank B2; H) Gypsum contained in tank B2; (I) Final bioleached materials from the most oxidized bioleached tank confirming the majority of pyrite had been oxidized (abbreviations: Gyp, gypsum; Jst, jarosite, Py, pyrite).

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