Article

Geoenvironmental Characterisation of Heap Leach Materials at Abandoned Mines: Croydon Au-Mines, QLD, Australia

Anita Parbhakar-Fox

Transforming the Mining Value Chain (TMVC) ARC Industrial Transformation Research Hub,
School of Physical Sciences, University of Tasmania, Private Bag 79, Hobart, Tasmania 7001, Australia;
anitap1@utas.edu.au; Tel.: +61-400-850-831

Abstract: Heap leaching is a well-established metallurgical technology which allows metal recovery (e.g., Au, Cu, U) from low-grade ores. However, spent heap leach materials remaining at abandoned or historic mine sites may represent a potential source of contamination. At the Croydon Au-mines, heap leaching operations (1984–1985) were performed on mineralized rhyolites hosting sulphides including pyrite, galena, arsenopyrite and minor sphalerite. Characterization of spent heap leach materials (n = 14) was performed using established geochemical and mineralogical techniques, supplemented by automated mineralogical evaluations. Whilst these materials contained low sulphide-sulphur (0.08 to 0.41 wt %) and returned innocuous paste pH values (pH 5.1 to 8.6), they were classified uncertain by net acid producing potential/net acid generating criteria. This was likely due to the reaction of secondary mineral phases (*i.e.*, beudantite, hidalgoite, kintoreite and Fe-As-Pb oxides) during these tests. It is hypothesised that during heap leaching, gangue sulphides have differentially reacted with the cyanide lixiviant, pre-conditioning the formation of these complex secondary phases during surficial oxidation, after heap leaching termination. These materials are considered to represent a moderate geoenvironmental risk as dissolved Pb in basal leachates is in excess of the World Health Organization (WHO 2006) guideline values. Considering this, these materials should be included in ongoing rehabilitation works at the site.

Keywords: heap leach; AMD; automated microscopy; mineral-liberation-analyser; mineralogy

1. Introduction

Heap leaching is a hydrometallurgical processing technology used for metal recovery from crushed low-grade ores [1]. It was first used for Au recovery in the late 1960s and is now a well-established global mineral processing practice for other commodities [2]. For example, it accounts for 20% of the worldwide copper production [3], and has been considered for Ni, Zn and U recovery [4,5]. Fundamentally, the process involves passing an appropriate lixiviant (*i.e.*, chemical solution) through crushed ore placed on an impermeable pad to enhance dissolution of metals [6]. The pregnant liquor is collected by a drainage system at the base of the pile, and channeled to a designated pond [2]. From here it is pumped to a processing facility where the target metal is extracted using an appropriate solution recovery technology (e.g., solvent extraction or electrowinning; [1]). The barren leach solution is finally pumped back to a designated pond, modified and reapplied to the heap [2]. Commonly used lixiviants are either acidic or alkaline, with sulphuric acid used for copper oxides (leach period: 4 to 6 months), cyanide leaching for gold/silver bearing ores (leach period: 60 to 100 days) and oxidative sulphuric acid for secondary copper sulphides *i.e.*, supergene porphyry ores (leach period: 1 to 3 years; [1]). Heap leaching is an attractive processing technique because metal

recovery can be performed on-site at relatively low operating costs *i.e.*, need for energy intensive comminution is omitted [1]. However, due to the low-grade nature of ore nominated for heap leaching, the physical footprint of these operations is considerable to permit economic metal recovery, occupying hundreds of hectares of land [7]. Moreover, there can be issues regarding slow and inefficient recovery and poor heap permeability [1], indicating that a repository of potentially hazardous waste may remain on mine sites after closure. Characterisation of waste rock and tailings materials at historic, legacy or abandoned mine sites is commonly undertaken as these are recognised sources of acid and metalliferous drainage (AMD) or present hazardous dust risks [8,9]. However, spent heap leach piles also pose contamination risks to water, soil and air [10–12] and must also be assessed as part of an abandoned mine characterisation study. To demonstrate this, the geoenvironmental risk posed by heap leach materials at the abandoned Croydon Au-mines, Queensland were studied with the objectives of: (i) determining their geoenvironmental properties; and (ii) examining the detailed primary and secondary mineralogy of these hydrometallurgically processed and weathered materials. Based on these observations, rehabilitation options for these materials were recommended, and a framework for assessing such spent materials proposed.

2. Materials and Methods

2.1. Site Description and Sampling

The Croydon gold mining district is situated approximately 15 km northeast of the Croydon Township, and 520 km west of Cairns, north Queensland (Figure 1A). The geology of the district comprises of Mesoproterozoic rhyolites of the Croydon Volcanic Group (CVG) and the Esmeralda Supersuite (granite-monzogranites and lesser granodiorites; [13]). Mineralization is hosted by the Parrot Camp and Carron rhyolite units of the CVG, comprising rhyolitic tuffs and massive rhyolitic quartz-feldspar porphyries with pyroclastics respectively [14]. Mesothermal mineralization differs between the Federation and La Perouse pit (Figure 1B), at the prior it is present as 0.2 to 6 m wide vughy white quartz veins containing pyrite, galena and arsenopyrite within altered (quartz-sericite-kaolinite) and graphitic volcanics [14]. At La Perouse, Au is contained in a sheeted set of anastomosing, en echelon vughy quartz veins from 0.5 to 10 m thick with galena, pyrite, arsenopyrite and free gold [14].

Modern mining operations commenced in 1981 when small open cut mining operations targeted reef gold [13]. By 1984, large scale open cut operations had commenced at Federation and La Perouse, with a full-scale cyanide heap leach operation (dynamic on/off pad design) established (1984 to 1985) recovering 134 kg of Au, and 152 kg of Ag from 141,702 tonnes of ore [15]. By 1989 underground mining had started at La Perouse, targeting 2.84 Mt of ore at 3.4 g/t Au [13]. However ore reserves were close to exhaustion in 1990, with operations concluding a year later. The mine workings have remained undisturbed since this time. Currently, the Abandoned Mines Unit, Department of Natural Resources and Mines, Queensland are custodians of the site; with liabilities for the waste rock piles alone estimated as AUD $1.8 million [13].

At the largest Croydon mine operations site (Figure 1B) two pits lakes now remain (Federation: 320 m × 160 m × 35 m; and La Perouse: 270 m × 180 m × 40 m), two waste rock piles (Federation/La Perouse pile: 1.5 million and 35,000 m^3), one stockpile (25,000 m^3), three heap leach piles (55,000 m^3; Figure 1C), a catch dam (170 m × 65 m), a seepage collection pond (100 m × 30 m) and relict mining infrastructure including a crusher platform [13]. Federation pit captures runoff and seepage from the main Federation/La Perouse waste rock pile, which contains range of sulphidic waste materials [13]. The seepage pond constructed below this drains to the catch dam (average pH 2.9), however during the wet season, water overflows into Tabletop Creek. The water quality of Tabletop Creek is poor with elevated concentrations of Al, As, Cd, Cu, Ni, Pb, S and Zn relative to local background/upstream value measured [13]. However, the net contribution to the poor water quality from the heap leach piles has yet to be determined.
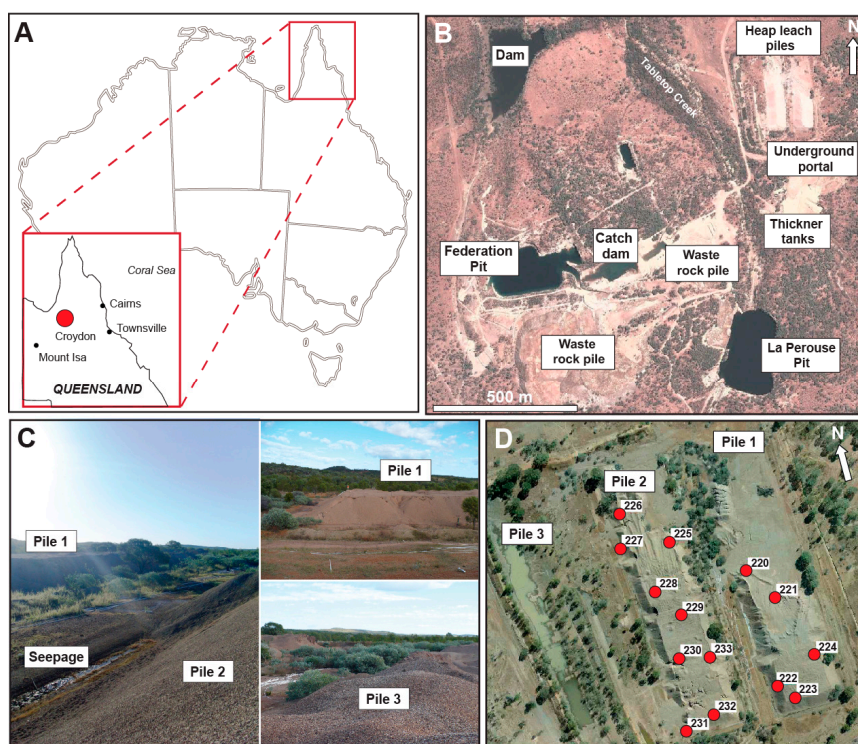
Figure 1. (**A**) Map of Australia with the location of the Croydon mining district shown in the inset; (**B**) Croydon mine workings, showing the abandoned Federation/La Perouse site (image from Google Earth); (**C**) Heap leach piles with seepage observed at the base; (**D**) Heap leach sample locations (220 to 233).

Motivated by this, fourteen heap leach grab samples (HL_220 to HL_233) were collected February 2010 from the surface of piles 1 and 2 only where safely permitted (Figure 1D). This provided an insight into the characteristics of the most weathered materials only (*i.e.*, no samples were collected from within the piles due to logistical constraints). These materials consisted of approximately 2 kg of gravel size (average diameter ~1 cm) angular-sub-angular weathered clasts. Approximately 500 g of this material was milled to <125 µm for geochemical and mineralogical analyses, with a split used to make polished grain mount samples (2.5 cm diameter).

2.2. Mineralogical Investigations

The bulk mineralogy of select samples (*n* = 5; samples: 222, 225, 227, 231 and 233) was measured by X-ray diffraction (XRD) at the University of Ballarat. Powdered samples were micronised (to ~10 µm) with 2 g splits of this material analysed using a D500 diffractometer (Siemens, Berlin, Germany; detection limit of 0.5 wt %). Mineral phases were identified by computer-aided (X'Pert and Eva, Woburn, MA, USA) searches of the 2009 ICDD PDF4/Minerals subfile. Quantitative XRD results were obtained using SiroQuant™ V.3.0 (Sietronics, Canberra, Australia). Polished grain mounts containing between 8 to 25 clasts were prepared for these same samples and analysed using an FEI Quanta 600 SEM equipped with 2 EDAX ultra-thin window Si(Li) energy dispersive X-ray (EDS) detectors (Central Science Laboratory, University of Tasmania). Each sample was first evaluated in a SEM-EDS study to closely examine the secondary mineralogy of these samples and obtain a first pass indication of the potential deleterious element deportment. Second, they were evaluated using a mineral liberation analyser (MLA), to classify and quantify the secondary mineralogical phases. Specifically, the sparse phase liberation technique was performed [16] with a nickel standard used. This permitted the microscale identification of sulphides and allowed for their evaluation using the acid rock drainage index (ARDI) [17].

2.3. Geochemical Analyses

Static acid base accounting tests were performed on all heap leach samples (School of Physical Sciences, University of Tasmania) to determine if they had been efficiently leached. Tests included paste pH, Sobek testing and single addition net acid generation (NAG) tests following procedures given in [18] and [19]. During paste pH testing, solutions were measured in triplicate (per sample) using a Eutech Instruments 510 pH meter. To ensure accuracy, the pH meter was calibrated to pH 4 and 7 using standard buffer solutions (purchased from Merck Ltd., Frenchs Forest, Australia) after each sample measurement. Sample blanks (deionised water) were tested before and at the end of each sample batch. Electrical conductivity (EC) was measured using a TPS WP-81 meter, with the probe calibrated prior to use with a 0.01 M KCl solution. Static testing standards KZL-1 (sericitic schist), and NBM-1 (altered feldspar porphyry; both obtained from the Canada Centre for Mineral and Energy Technology, Ottawa, Canada) were also assessed. The relative standard deviation calculated between the standard measurements was <5%. Acid neutralising capacity and sulphate analyses were conducted at ALS Global (method codes: EA013 and ED040T respectively).

Total sulphur values (for calculation of maximum potential acidity) were measured using a Thermo Finnigan 1112 Series Flash Elemental Analyser (Central Science Laboratory; University of Tasmania). Methionine ($C_5H_{11}NO_2S$) and BBOT ($C_{26}H_{26}N_2O_2S$) standards were used, with blanks analysed at random to calculate instrument precision.

To measure chemical composition, all samples were analysed by X-ray fluorescence (XRF) using a Philips PW1480 X-Ray spectrometer (School of Physical Sciences, University of Tasmania) following the procedure outlined in [20]. Corrections for mass absorption were calculated using Philips X40 software with De Jongh's calibration model and Philips alpha coefficients [21]. Trace element analyses were performed using an Agilent 7700 ICPMS (School of Physical Sciences, University of Tasmania). Calibration standards were made up using both single and multi-element standard solutions. Trace element standards were made up to 10, 100, 200 and 1000 ppb and included the elements Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Ba, Pb and U. The resulting data was processed using MassHunter software (Agilent, Santa Clara, CA, USA).

3. Results

3.1. Mineralogical Characteristics

The bulk mineralogy of these materials (Figure 2) is consistent between, and within, the sampled piles with quartz (72 to 77 wt %), muscovite (13 to 17 wt %) and kaolinite (2 to 9 wt %) dominating. Minor pyrite was identified in sample 222 only (0.5 wt %) with jarosite identified in all samples (0.6 to 4 wt %) both of which are potentially acid forming [22].
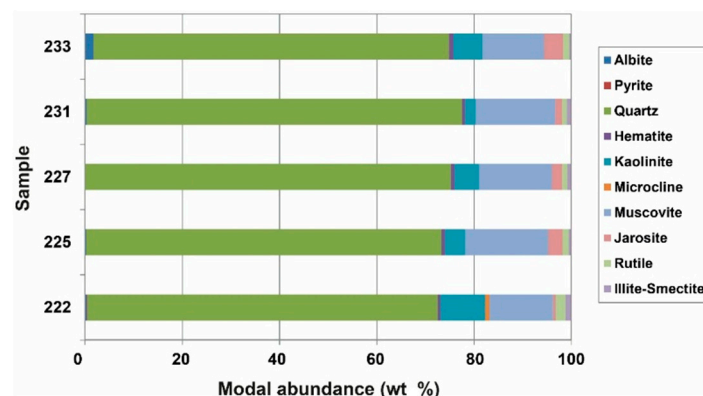
Figure 2. Bulk mineralogy (measured by XRD) results for samples selected from heap leach Piles 1 and 2 (*n* = 5; samples: 222, 225, 227, 231 and 233; detection limit: ~1 wt %).

Backscattered electron (BSE) and secondary electron (SE) images revealed that these heap leach materials are highly altered and weathered; with relict sulphides and several secondary phases identified and a range of textures displayed (Figure 3). In general, these materials are considered to be in the latest-stages of weathering as per the mine waste paragenesis proposed by [23].
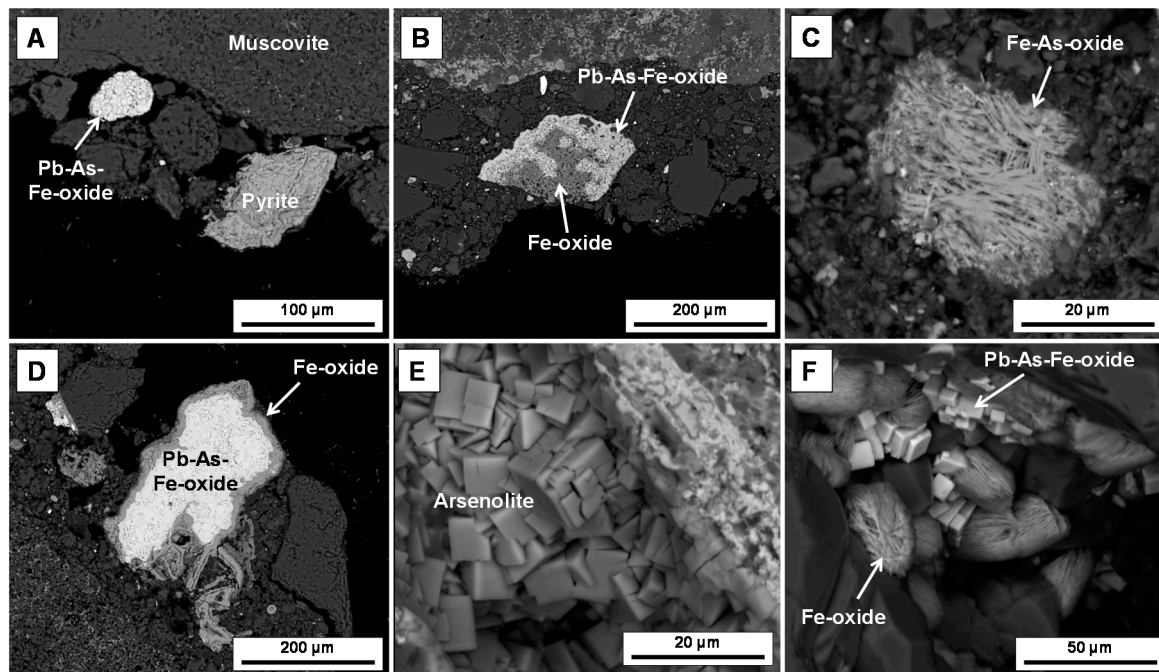
Figure 3. (**A**) Weathered pyrite grain associated with muscovite, with internal striations displayed but no visible reaction products, with a secondary Pb-As-Fe oxide phase also observed; (**B**) Pb-As-Fe oxide phase associated with Fe-oxide, both displaying porous texture; (**C**) Pb-As-Fe oxide phase rimmed by Fe-oxide; (**D**) Fibrous habit Fe-As oxide with diffuse grain boundary; (**E**) Cubic arsenolite; (**F**) Cubic Pb-Fe-As oxides intergrown with fibrous Fe-oxides.

Relict subhedral-anhedral pyrite grains show an altered internal texture with fractures observed though no immediately obvious reaction products have formed (Figure 3A). In addition, porous Pb-As-Fe oxides are observed, and as Pb dominates (approximately 40% to 45%), these are most likely galena oxidation reaction products (Figure 3A). However, similar phases are shown in Figure 3B, where instead these Pb-As-Fe oxides are associated with Fe-oxides (likely bernalite; Table 1), both of which demonstrate a porous, boxwork texture. A similar relationship is observed in Figure 3C, however, the Fe-oxide phase (likely ferrihydrite) forms a distinct rim around the Pb-As-Fe oxide phase (likely carminite, Table 1). In the absence of Pb, some Fe-As oxide phases (*i.e.*, products of arsenopyrite oxidation) appear fibrous (Figure 3D) with a poorly defined grain boundary. Cubic arsenolite, a common reaction product of arsenopyrite oxidation is observed (Figure 3E), and appears relatively fresh (*i.e.*, no pits or fractures) in these materials. A similar cubic morphology was exhibited by a Pb-Fe-As oxide phase intimately associated with Fe-As oxide also demonstrating fibrous habit (Figure 3F), therefore indicating availability of a large surface area for exchange reactions to take place. Measurement of surface waters taken immediately downstream of the heap leach pad [13] show elevated Pb (~60 μg/L) relative to the baseline concentration (<7 μg/L) and the WHO (2006) drinking water guideline value (10 μg/L). In contrast, arsenic was below the WHO (2006) drinking water guideline value of <10 μg/L [13].

MLA results allowed for the identification of these complex secondary phases (present in minor-trace quantities). First, a range of primary sulphides were identified (in abundance order): pyrite, arsenopyrite, galena and sphalerite, in addition to anglesite, beudantite and kintoreite (Table 1) which

were not reported by XRD. Larger sulphide grains (>20 μm diameter) displayed anhedral morphology and associated with the mineral phases listed in Table 1. For example, Figure 4A shows a pyrite grain which is associated with four phases, with the unknown phase likely to be a secondary Fe-oxide (as indicated by EDS). In contrast <20 μm diameter sulphide grains were typically encapsulated in quartz and appear unweathered (Figure 4B–D. In relative terms secondary minerals dominate over primary sulphides indicating the efficiency of heap leaching at this site. ARDI evaluations performed on pyrite indicated these are non-acid forming, with the majority of individual grains scoring <20/50.

Table 1. Secondary mineral phases identified by mineral liberation analysis (●—present; A—absent).

| Mineral Phase	Formula	222	225	227	231	233
Alunite	$KAl_3(SO_4)_2(OH)_6$	A	●	●	●	●
Anglesite	$PbSO_4$	●	●	●	●	●
Arsenolite	As_4O_6	●	●	●	●	●
Bernalite	$Fe(OH)_3$	●	●	●	●	●
Beudantite	$PbFe_3(OH)_6SO_4AsO_4$	●	●	●	●	●
Carminite	$PbFe_2(AsO_4)_2(OH)_2$	A	●	●	●	●
Fe-oxide	$FeOOH$	●	A	●	●	A
Ferrihydrite	$Fe_2O_3 \cdot 0.5(H_2O)$	●	●	●	●	●
Finnemanite	$Pb_5Cl(AsO_3)_3$	A	●	A	A	A
Hematite	Fe_2O_3	●	●	●	●	A
Hidalgoite	$PbAl_3(AsO_4)(SO_4)(OH)_4$	●	●	●	●	●
Kintoreite	$Pb(Fe)_3(PO_4)_2(OH,H_2O)_6$	A	A	●	●	●
Pitticite	$Fe_2(AsO_4)(SO_4) \cdot (H_2O)$	●	●	●	●	●
Schultenite	$PbHAsO_4$	A	●	●	A	●
Segnitite	$PbFe_3H(AsO_4)_2(OH)_6$	●	●	●	●	●
Surite	$(Pb,Ca)_3(Al,Fe,Mg)_2((Si,Al)_4O_{10})(CO_3)_2(OH)_2$	●	●	●	●	●
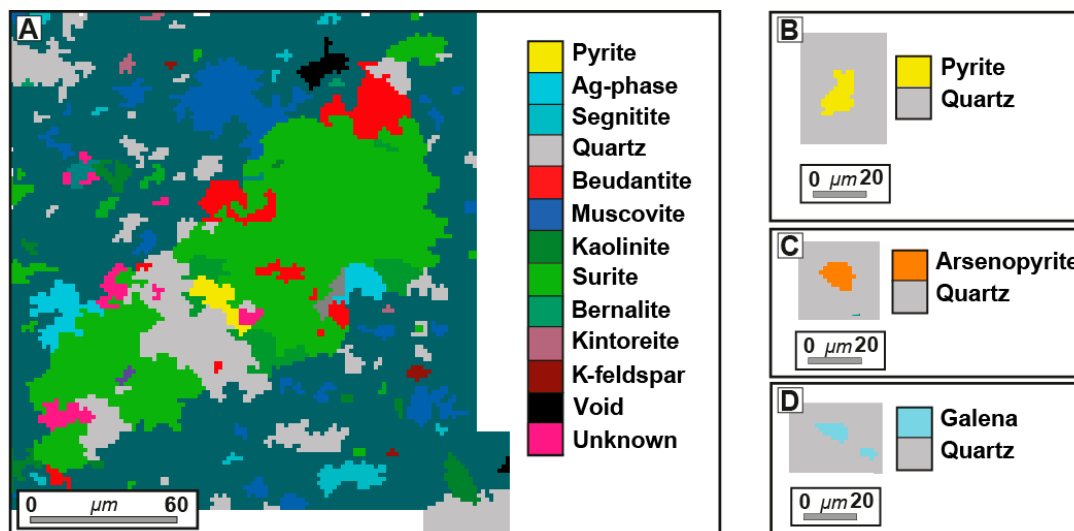
Figure 4. Classified mineralogy images showing: (**A**) anhedral pyrite with complex mineral associations (including surite, kaolinite, quartz and an unknown phase, likely iron oxide); (**B**) fine grained pyrite encapsulated in quartz; (**C**) fine grained arsenopyrite encapsulated in quartz and (**D**) fine grained galena encapsulated in quartz.

3.2. Major and Trace Element Chemistry

Whole rock analyses (Table 2) confirm these as CVG rhyolites with SiO_2 (75.5 to 82 wt %) dominating followed by Al_2O_3 (8.2 to 10.6 wt %), Fe_2O_3 (3.1 to 5 wt %) and K_2O (2.2 to 3.1 wt %). A Tukey plot of the concentration range for select trace elements (Ag, As, Cu, Sb, Pb and Zn; given

in ppm) is shown in Figure 5. Precious metal contents in these leached materials are only trace with Au below the instrument detection limit (1 ppm) and Ag ranging from 3 to 9 ppm (median: 6 ppm). Lead dominates in these materials (3260 to 9730 ppm) followed by As (1090 to 3720 ppm), both of which are sourced in relict primary sulphides (e.g., Figure 4C,D) and the alteration phases listed in Table 1. Minor concentrations of Cu (70 to 204 ppm), Sb (15 to 35 ppm) and Zn (94 to 163 ppm) were measured. For comparison, these values were screened against Australian and New Zealand Interim Sediment Quality Guideline (ISQGs) values. The guidelines set both low and high trigger concentrations. The ISQG-Low (or trigger value) is a threshold concentration, below which biological effects are expected to be very low [24]. The ISQG-High is that above which adverse biological effects are expected to occur frequently [24]. Exceedances for As ($n = 14$; ISQG-High: 70 ppm), Pb ($n = 14$; ISQG-High: 220 ppm) and Sb ($n = 3$; ISQG-High: 25 ppm) were measured in these materials, indicating they present a potential geoenvironmental risk.
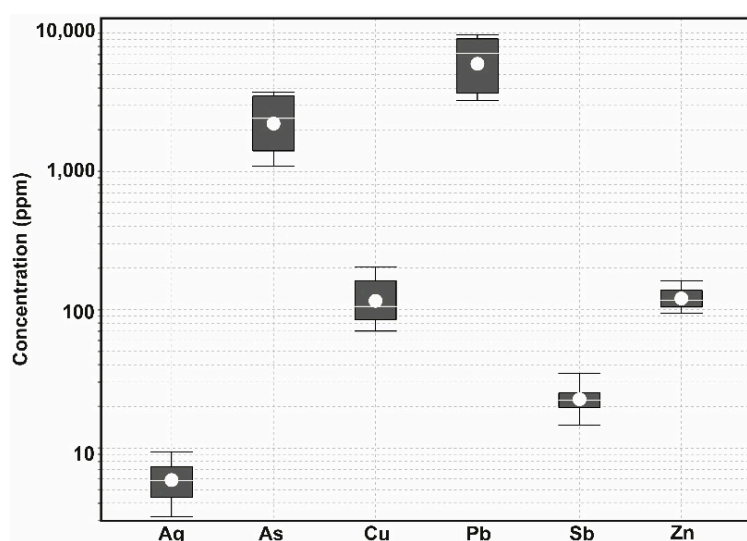

Figure 5. Box and whisker plot showing heap leach trace element chemistry ($n = 14$) with select environmentally significant elements shown. (NB. The box covers the interquartile range, the line is the median and the circle the mean. The whiskers are drawn at the threshold to identify near and far outliers based on the Tukey statistic).

Table 2. Whole-rock chemical analyses (wt %; LOI values not shown).

Sample	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	P$_2$O$_5$	PbO	As$_2$O$_3$
220	82.0	0.2	8.4	3.1	0.2	0.0	0.0	2.7	0.1	0.4	0.2
221	80.3	0.2	8.4	4.5	0.2	0.0	<0.03	2.4	0.1	0.4	0.2
222	77.8	0.3	10.1	4.0	0.2	0.1	0.0	2.8	0.1	0.4	0.2
223	77.1	0.3	10.6	4.0	0.2	0.1	0.1	3.2	0.1	0.4	0.2
224	78.1	0.3	10.4	3.5	0.2	0.0	0.1	3.1	0.1	0.4	0.2
225	78.3	0.2	9.7	3.3	0.3	0.1	<0.03	2.8	0.1	1.1	0.6
226	81.7	0.2	8.3	3.2	0.2	0.0	<0.03	2.7	0.1	0.5	0.3
227	78.3	0.2	9.4	3.6	0.2	0.1	0.1	2.9	0.1	0.9	0.5
228	79.1	0.2	8.2	4.5	0.3	0.1	<0.03	2.2	0.1	1.0	0.6
229	79.6	0.2	8.5	4.6	0.2	0.2	0.0	2.2	0.1	0.7	0.3
230	81.3	0.2	7.5	3.9	0.3	0.1	<0.03	2.2	0.1	1.0	0.6
231	78.3	0.2	9.7	4.0	0.2	0.1	<0.03	2.5	0.1	0.9	0.5
232	75.5	0.2	10.3	5.0	0.3	0.4	<0.03	2.4	0.1	1.0	0.5
233	77.6	0.2	9.0	4.5	0.2	0.1	<0.03	2.4	0.1	0.9	0.5

3.3. Acid-Base Accounting

Weakly acid to alkaline paste pH values were measured, ranging from pH 5.1 (HL_220) to 8.6 (HL-229). Total sulphur contents (S_{total}; measured by EA) were between 0.08 to 0.41 wt %. Only three samples (225, 230 and 231) measured above the commonly used potentially acid forming (PAF) cut-off criterion of 0.3 wt % [17]. Maximum potential acidity (MPA) values calculated using $S_{sulphide}$ values ($S_{total} - S_{sulphate} \times 30.6$) gave a range of 2.4 to 11.8 kg H_2SO_4/t. Similarly, the acid neutralising capacity (ANC) of these materials is low ranging from 0 to 6.2 kg H_2SO_4/t. These materials were plotted on a NAPP *vs.* NAG pH classification (Figure 6; [19]) and all classified as uncertain with the exception of sample HL-220. This sample does not contain more $S_{sulphide}$ than several others in this suite, indicating that the lower NAG pH value (pH 4.4) is most likely due to the reaction of secondary phases as listed in Table 1. Indeed, for this suite NAG pH values (pH 4.4 to 8.9; median pH 5.4) are lower than anticipated based on the modal mineralogy, and indicates the potentially reactive nature of secondary phases formed since the end of heap leaching. Similar observations have been made for tailings materials dominated by secondary iron-oxides phases at historic sites e.g., [9].
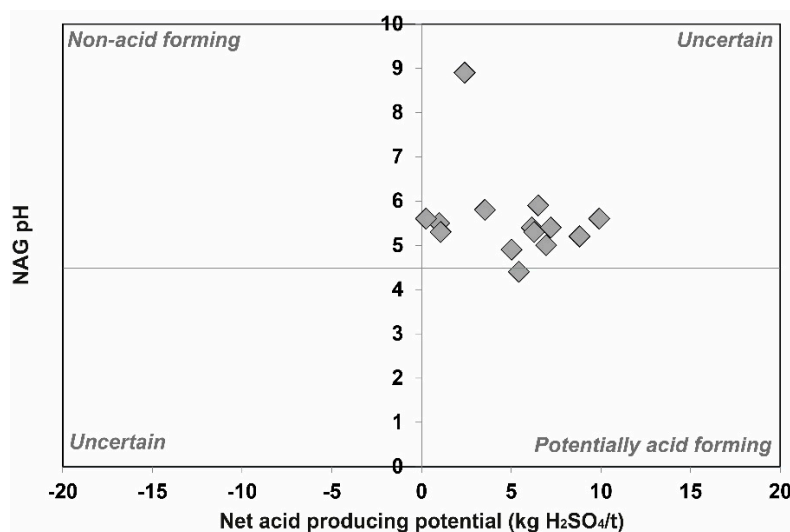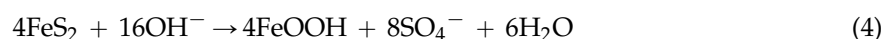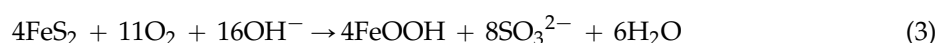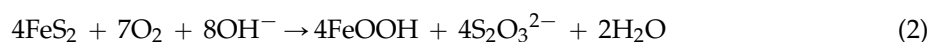

Figure 6. Net acid producing potential *vs.* net acid generation (NAG) pH plot showing the acid forming characteristics of the heap leach materials (*n* = 14).
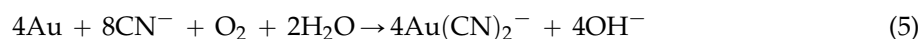
4. Discussion

4.1. Heap Leach Pile Evolution

At the Federation/La Perouse site, ore materials contained within the CVG include pyrite, arsenopyrite, galena, minor sphalerite and trace chalcopyrite [13]. Each react to varying degrees with the alkaline cyanide lixiviant [25]. In contrast, silicate minerals contained in these heap leach materials do not react [26]. The presence of gangue sulphides consumed reagents [27], likely resulted in high operational expenditure costs, potentially explaining the short-lived nature of hydrometallurgical operations at this site. Pyrite reactions with the lixiviant are shown in Equations (1) to (4); with reaction products included thiocyanate and several oxy-sulphur species [25]:

$$4FeS_2 + 8CN^- + 3O_2 + 2H_2O \rightarrow 4FeOOH + 8SCN^- \tag{1}$$

$$4FeS_2 + 7O_2 + 8OH^- \rightarrow 4FeOOH + 4S_2O_3{}^{2-} + 2H_2O \tag{2}$$

$$4FeS_2 + 11O_2 + 16OH^- \rightarrow 4FeOOH + 8SO_3{}^{2-} + 6H_2O \tag{3}$$

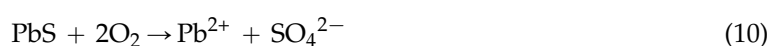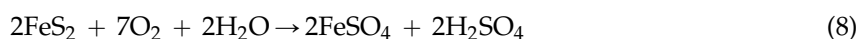$$4FeS_2 + 16OH^- \rightarrow 4FeOOH + 8SO_4{}^- + 6H_2O \tag{4}$$

Thiocyanate (as free or metal-complex cyanides) in industrial waste waters represents a significant geoenvironmental risk due to the acute toxicity for living organisms [28]. However, as Au complexes with CN^- (Equation (5); [27]) potential risks are negligible. If thiocyanate species had complexed and persisted in these materials, exposure to atmospheric conditions for three decades would likely result in their breakdown [28] as per Equation (6) [29], with ammonia (NH_3) eventually converted to nitrate (NO_3).

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^- \tag{5}$$

$$SCN^- + 2/5O_2 + 2H_2O \rightarrow SO_4^- + HCO_3^- + NH_3 \tag{6}$$

The common reaction products (*i.e.*, sulphate and FeOOH species) have since reacted under surficial conditions [23], forming the complex secondary weathering phases observed in these investigations (Table 1). On reaction with an aerated cyanide solution, galena and sphalerite may react as shown by the general reaction for divalent metal cations (*i.e.*, MS^-; Equation (7) [27]):

$$2MS^- + 2(x + 1)CN^- + O_2 + 2H_2O \rightarrow 2M(NC)_x^{(x-2)-} + 2SCN^- + 4OH^- \tag{7}$$
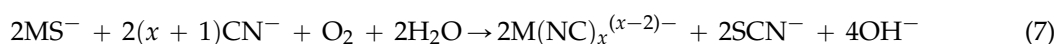
However, at alkaline pH (~9) the rate of galena dissolution rapidly decreases [30] therefore extensive reaction with the cyanide lixiviant (pH > 10) is unlikely. Therefore, phenomena such as preferential complexing of CN^- with Pb would not have been experienced as indicated by the absence of Au in the spent materials (*i.e.*, efficient leaching occurred; [31]). Instead, the addition of the cyanide lixiviant appears to have preconditioned galena to subsequent oxidation reactions occurring after heap leaching operations, particularly for larger, liberated particles (Figure 4A). Whilst some arsenic bearing minerals (e.g., realgar, As_4S_4; orpiment, As_2S_3) react with a cyanide lixiviant, arsenopyrite oxidises very slowly and therefore has very little adverse effect on Au leaching [32]. Instead, arsenopyrite and remnant pyrite have also undergone surficial oxidation after heap leaching operations (Equations (8) and (9); [8,33]) resulting in localised low pH conditions. In turn, this has permitted galena oxidation (Equations (10) [8,34]).

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \tag{8}$$

$$FeAsS + 7/2O_2 + 6H_2O \rightarrow Fe(OH)_3 + SO_4^{2-} + H_2AsO_4^- + 3H^+ \tag{9}$$

$$PbS + 2O_2 \rightarrow Pb^{2+} + SO_4^{2-} \tag{10}$$

The secondary phases listed in Table 1 appear exclusive to the spent heap leach materials, as with the exception of anglesite, jarosite and goethite; none were identified in waste rock materials at this site [13]. Whilst identification of these phases is relatively uncommon, they are reported as oxidation products forming in such environments, the majority of which are from the alunite supergroup [35,36]. For example, carminite is an alteration product of arsenopyrite forms in the oxidized zone of lead-bearing deposits, and is commonly associated with beudantite and anglesite [37]. In addition, arsenolite, pitticite, schultenite and segnitite are reported as secondary products forming under oxidised conditions experienced in mine waste piles [38]. These mineral phases are not readily soluble in water, instead favouring strong alkaline or acid solutions [38]. Therefore, during rainfall events, dissolved As in leachate is not significantly high at the base of the piles. In contrast, Pb was elevated in basal leachate, however the majority of Pb-bearing secondary phases (e.g., anglesite, kintoreite) are also insoluble under the pH range measured during paste pH experiments [39]. Instead, Pb is likely liberated from these secondary phases as a consequence of pyrite (and jarosite) oxidation, with an additional contribution from the Pb-bearing pyrite itself [13]. Based on these investigations, the spent heap leach materials should be considered to represent a moderate geoenvironmental risk. Lead is likely to continue leaching under these geochemical conditions, potentially impacting surface watercourses (*i.e.*, Tabletop Creek; Figure 1B), and will persist for the longevity of localised AMD.

4.2. Rehabilitation Options

Whilst there are several mine waste landforms remaining at the abandoned Croydon site, the heap leach piles represent a contaminant source. Therefore, they should not be overlooked when developing a future rehabilitation strategy. The assumption these materials are inert and permitting them to oxidize is no longer acceptable under current best practice guidelines for operational sites. For example, the US Bureau of Land Management has a robust cyanide heap leach management policy to protect the public and wildlife whereby all heaps are neutralised and detoxified, followed by regular site inspections e.g., [40]. A similar policy also exists in Australia [41]. In current practices, spent heap leach materials may be re-leached *i.e.*, dump leaching as part of a "scavanger circuit" [42]. However, at Croydon, *in-situ* re-leaching of these materials is not recommended as there are no valuable metals left to profitably recover, and the pad liner since degraded. Besides, the ore material was unlikely to have been mineralogically characterised and physically optimised for heap leaching (e.g., particle size, sulphide liberation; [27]). Therefore re-leaching for optimal recovery would require additional comminution before further lixiviant addition. Instead, such materials could be used in construction (*i.e.*, capping of other waste landforms; Mt Leyshon; [43], or aggregate/reclamation fill materials [44]). However, it is necessary for the material to be deemed non-hazardous using an established standard method such as the toxicity characteristic leaching procedure (TCLP; SW-846 Test Method 1311). Alternatively, rinse/leach experiments as performed at the Round Mountain mine, Nevada, US could be used [44]. At Croydon, these heap leach materials are dominated by non-reactive silicates, with acid-forming sulphides and their secondary products representing only a minor constituent. Therefore, to ensure no further sulphide oxidation and metal leaching, whilst costly these materials could be pre-treated to remove remnant sulphides by flushing with an oxidant such as H_2O_2 (commonly performed heap leaching termination; [27]). Following this, as many of the identified Fe-As-Pb bearing secondary phases are insoluble under surficial conditions, these materials may be sufficiently inert for reuse as aggregate/construction material. However, TCLP assessments would need to be undertaken to confirm this before rehandling.

4.3. Risk Assessment Framework

In general, a formal risk assessment framework for characterising spent heap leach materials must be adopted as global industry standard, as currently there is no clear, unified prescriptive framework or protocol. Certainly, such a characterisation approach is relevant to abandoned and historic sites, particularly if materials are inert and can be repurposed. The importance of introducing such a framework is ever increasing when considering the global uptake of hydrometallurgical processing with over 300 reported projects, particularly in South America [45]. Through undertaking predictive characterisation, opportunities to re-use materials based on robust scientific data can be identified at early life-of-mine stages and the materials used efficiently during the life-of-mine, or appropriate rehabilitation treatments (*i.e.*, for materials containing gangue sulphides) determined. One potential framework is presented in Figure 7 with automated mineralogy a critical component for resolving the secondary mineralogy which ultimately dictates the leachate chemistry, vital to understand to determine geoenvironmental risk. In contrast to this study, a vigorous sampling campaign which assesses materials from within the pile must be designed and followed. Through adopting such a characterisation approach, the true value of these materials in a circular economy [46,47] context can be ascertained, and a more sustainable approach to mine waste management realised.
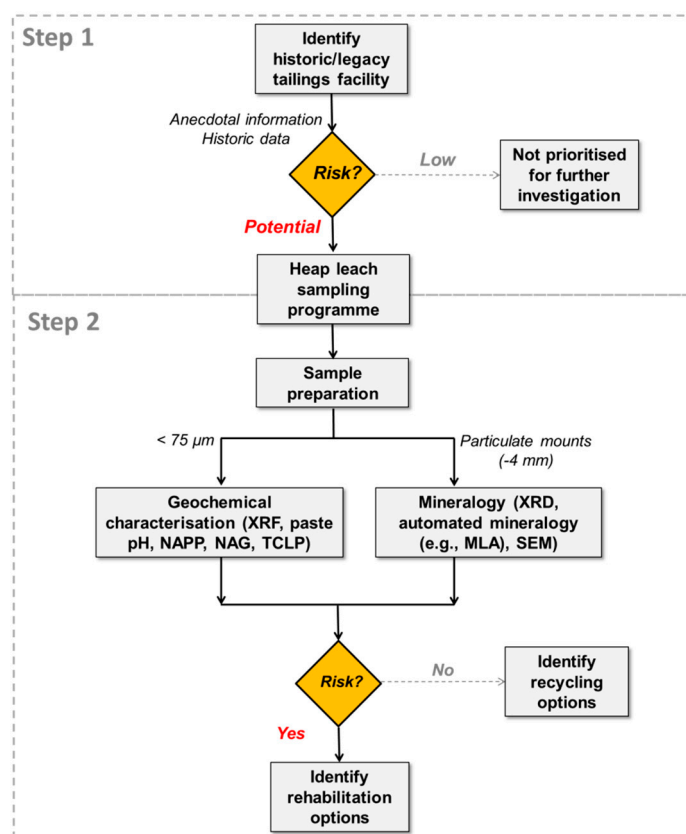
Figure 7. Proposed risk assessment framework for geoenvironmental characterisation of spent heap leach materials. If dealing with an abandoned site, Step 1 is mandatory, however, if characterising materials and an operational site, then it can be omitted. NB. This framework does not include an evaluation of the spent material's physical properties.

5. Conclusions

Hydrometallurgical processing of low-grade ore materials by heap leaching to recover metals including Au, Cu and U is a well-established global practice, which is increasingly being uptaken. However, the geoenvironmental consequences of passively managing spent heap leach piles at historic or abandoned site is poorly documented. At the Croydon Au-mines, Queensland, Australia, mining was intermittent since the late 1800s until 1991. In 1984, heap leaching of low-grade ore material was performed onsite using a cyanide lixiviant. These materials comprised of mineralized rhyolite-tuffs and massive rhyolitic quartz-feldspar porphyries, both of which hosted several sulphides including pyrite, galena, arsenopyrite and minor sphalerite. Whilst pyrite was the target mineral, it is likely that gangue sulphides also reacted to a degree, resulting in high OPEX costs to achieve optimal recovery. Therefore, hydrometallurgical operations were short-lived, concluding in 1985. Subsequently, three heap leach piles remained onsite containing partially reactive sulphides susceptible to surficial oxidation processes. Based on these geoenvironmental investigations, the following points are made:

- Fine-grained (*i.e.*, >20 μm diameter) sulphides were encapsulated in quartz and have remained fresh. In contrast, larger primary sulphides (e.g., pyrite, arsenopyrite and galena) particles experienced extensive oxidation. Consequently a diverse range of secondary mineral phases from the alunite supergroup, as well as other Pb-As-Fe oxide phases can are now observed.
- Minerals of the alunite supergroup are not observed in adjacent waste rock piles at this site, suggesting that the lixiviant has chemically preconditioned the gangue sulphides to oxidize via different reaction pathways, a hypothesis which requires further experimental clarification.

- Far from being inert waste landforms these heap leach piles are sources of Pb, with concentrations in their basal leachates exceeding WHO (2006) values by 6 times. Considering this, they represent a moderate geoenvironmental risk and should be included in future rehabilitation strategies developed for this site.
- Whilst costly, these materials could be rehandled and chemically pre-treated (*i.e.*, oxidized) to remove sulphides and then recycled (*i.e.*, for use as aggregate/construction fill), if TCLP assessments classify them as non-hazardous.
- Development of a global spent heap leach characterisation framework is required, and will be beneficial for rehabilitating such abandoned sites, and determining if indeed these materials have a place in the circular economy model.

Conflicts of Interest: The author declares no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AMD	acid mine drainage
BSE	backscattered electron
CVG	Croydon Volcanic Group
ISQG	interim sediment quality guideline
MLA	mineral liberation analyser
NAG	net acid generation
NAPP	net acid producing potential
SEM	scanning electron microscopy
TCLP	toxicity characteristic leaching procedure
WHO	World Health Organisation

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