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Characterisation and hydrometallurgical processing of nickel from tropical agromined bio-ore

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ABSTRACT

Hyperaccumulator plants (“metal crops”) can be used for selective extraction of Ni from low-grade resources with high concentration factors, thereby producing a high-grade “bio-ore”. This so-called agromining (or phytomining) technology involves farming select metal crops on ultramafic soils, mineral wastes, or overburden that are sub-economic Ni resources for conventional extractive technology. Key to profiting from agromining is the efficient recovery of Ni and by-products from the bio-ore, either directly from freshly harvested biomass or from the ash after incineration. Bio-ore of wild grown specimens of the Ni hyperaccumulator plants *Rinorea bengalensis* and *Phyllanthus securinegoides* were collected in Malaysia. After incineration, the ash composites contained 5.5 and 12.7 wt.% Ni for *Rinorea* and *Phyllanthus* respectively, along with substantial amounts of Ca, K, C, Mg, P, Na, S and Cl. Other minor impurities included Si, Fe, Al, Mn and Zn. The solids were characterised in detail by SEM-EDS, XRD and XANES. The effect of solution chemistry on the leaching behaviour of the bio-ore (dried biomass and ash) was also assessed. A hydrometallurgical process for recovering Ni from the bio-ore was then demonstrated. The processes involves the bio-ore (ash) being water-washed, yielding >90% recovery of K to solution. After water washing, >95% Ni recovery was achieved by H₂SO₄ leaching at 60°C, although long residence times and high acid concentrations were required. Ni(OH)₂ was then precipitated from solution using the K₂CO₃ rich wash-water. The bio-ore generated precipitant was compared with NaOH and MgO used industrially.

Keywords: *bio-ore; phytomining; agromining; nickel; tropical hyperaccumulator*

1. INTRODUCTION

Hyperaccumulator plants, which are rare plants that accumulate metal in their living tissues to concentrations up to 6% (dry wt.), can be used for the extraction of Ni from ultramafic soils naturally enriched in Ni, or from mineral wastes polluted with Ni, in a process known as phytomining or agromining technology (Chaney et al., 1998; Reeves, 2003; Van der Ent et al., 2013a; Van der Ent et al., 2015a). In this process, hyperaccumulator plants (“metal crops”) are farmed and the biomass is harvested. This biomass, now considered a “bio-ore”, is significantly upgraded in terms of Ni content (up to 20% dry wt.) with the added benefit of being free of impurity elements that occur in traditional ore such as Fe and Al (Chaney et al., 1998; Zhang et al., 2014).

Using plants to recover metals from sub-economic resources (ultramafic soils) on a commercial scale has benefits as the costs of growing and harvesting metal crops are minimal compared to traditional mining operations (Chaney et al., 2007), particularly given the high costs involved in conventional recovery of Ni from low grade lateritic resources. Considering the high surface area of land required to achieve large tonnage Ni production by agromining, the technology will not likely compete with traditional methods of ore extraction and Ni processing, but rather be complementary to access Ni-resources in soil materials and overburden below conventional cut off grades (<0.8 % Ni). Nickel hyperaccumulator plants are effective at accumulating high levels of Ni in biomass from soils that contain less than 0.1% total Ni (Van der Ent et al. 2015a; Sumail 2015).

Globally, the largest ultramafic regoliths with Ni-enriched laterite soils are in tropical regions, mainly New Caledonia, Indonesia and the Philippines where Ni hyperaccumulator plants occur natively (Van der Ent et al., 2013). These regions such as in Central Sulawesi in Indonesia and Palawan in the Philippines are also important centres for lateritic Ni mining operations. Nickel agromining is envisaged to be part of a progressive rehabilitation strategy of strip-mined land in which local communities ‘farm’ selected “metal crops” and deliver harvested biomass to the local Ni industry for off-take and processing (Van der Ent et al., 2013b). The technology was recently proposed as a way to generate income to support metallurgical testing and feasibility studies during often-lengthy timeframes to site development (Willis, 2015). As such, processing of bio-ores should be low-tech, robust and simple to operate, scalable, and suitable for remote areas in the Asia-Pacific region.

In initial Ni agromining trials in Oregon (USA), the bio-ore (after ashing) produced was fed to an electric-arc furnace to smelt Ni metal (Chaney et al., 2007). While this is technically feasible, it was noted that the relatively high grade and unique bio-ore composition free of most impurities makes it well suited to be processed to Ni catalysts for the organic chemistry industry (Losfeld et al., 2012) or to be turned into higher value Ni chemicals, such as for the electroplating industry (Barbaroux et al., 2012). The use for electrochemical Ni products places higher demands on purity, but is a higher value product, and may increase the economic viability of agromining. Ashing the harvested biomass has benefits such as reducing the mass of the original material by 10–20-fold, potential to recover energy (heat) from incineration, and transforming organo-nickel compounds into nickel oxide (NiO). In

terms of product recovery, previous studies have used either sulphuric acid (H_2SO_4) to leach biomass to produce Ni micronutrient fertiliser, followed by solvent extraction (Barbaroux et al., 2011), or a combination of concentrated H_2SO_4 leaching of the ash followed by sodium hydroxide (NaOH), ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) and sodium fluoride (NaF) additions, fractionated crystallisation and evaporation to manufacture a purified ammonium nickel sulphate hexahydrate ($\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) product (Barbaroux et al., 2012). Earlier work has also shown that the high concomitant concentrations of Ca (20–40%), Mg (1–5%) and K (7–11%) are a major obstacle for deriving pure Ni-salts from the bio-ore in a streamlined process (Barbaroux et al., 2011).

In this study, bio-ore was produced from *Rinorea bengalensis* and *Phyllanthus securinegoides*, two of the most promising species for tropical Ni agromining. The bio-ore was chemically and mineralogically characterised, and the leaching behaviour of the dried and incinerated biomass was assessed. A process flowsheet producing nickel hydroxide ($\text{Ni}(\text{OH})_2$) and recycling alkaline reagents was evaluated (see Figure 1). The ash was water-washed to recover K, the washed ash was then leached with H_2SO_4 to extract Ni, and finally the Ni was recovered from solution by precipitation as $\text{Ni}(\text{OH})_2$ using potassium carbonate (K_2CO_3) solution. The energy released during incineration could be used for drying and to heat process solutions. Excess K-solution and the gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) residue could be recycled to the Ni farm as fertiliser to counter depletion of these elements in the soil over time.

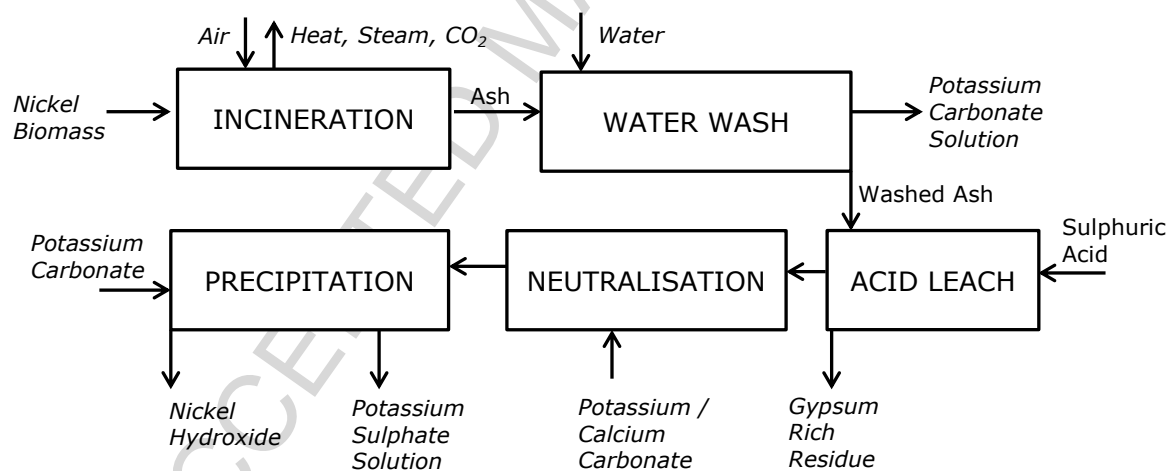


Figure 1. Process flow diagram for the hydrometallurgical processing of nickel biomass.

2. MATERIALS AND METHODS

2.1 Biomass collection and ash preparation

The biomass of *Rinorea bengalensis* and *Phyllanthus securinegoides* consisting of ligniferous parts (twigs, branches) and leaves was collected near Nalumad in Sabah (Malaysia) from plants growing in their natural habitat. These were wild, not cultured, plants growing on ultramafic soils not disturbed by mining activities. Information on the ecology and ecophysiological characteristics of *Rinorea bengalensis* and *Phyllanthus securinegoides* are provided in Van der Ent, Erskine *et al.* (2015) and Van der Ent and Mulligan (2015). Approximately 15 kg of biomass of each species was collected and subsequently dried at 65°C for four days in a dehydrating oven. Sub-samples of each of the fractions of the dried biomass were collected for elemental composition assays. For the *Rinorea* biomass, 2 kg of dried material was kept separate and finely ground with a ball mill (ligniferous and leaf fractions separately); the remainder of the biomass of both *Phyllanthus* and *Rinorea* was then burnt to produce ash in an open furnace. Although the combustion temperature can affect the mineralogical composition of the ash (Boominathan *et al.*, 2004; Zhang *et al.*, 2014), self-supported open air burning of the dried biomass, as opposed to a heated furnace, was preferred here because heat production may potentially be utilised in the full-scale process, and because of its simplicity. Samples were collected from each biomass fraction and analysed using ICP-AES (for major and trace elements) and ICP-MS (ultra-trace elements) after microwave-aided acid digestion unless indicated otherwise. Finally, a composite bio-ore from the ligniferous and leaf wood fractions, representing the approximate composition of harvested material from agromining operations, was prepared for each of the species and used in the following experiments.

2.2 Elemental analysis

The different dried biomass-fraction samples were manually crushed and ground. Sub-samples (200 mg) were then digested in 4 mL concentrated nitric acid (HNO₃; 70 wt.%) and 1 mL hydrogen peroxide (H₂O₂; 30 wt.%) in a microwave oven, diluted to 45 mL with deionised water before ICP analysis. Similarly, samples of the ashed biomass were also digested and analysed. Quality controls included NIST references and internal standards. The elements tested were: Ni, Co, Cr, Cu, Zn, Mn, Fe, Mg, Ca, Na, K, S and P. In order to determine the total C content of the ash, approximately 150 mg of finely-ground (<100- μ m) ash was weighed into tin foil boats and analysed on a LECO (UK) TruSpec CHN combustion analyser at 1100°C; carbonate was removed using hydrochloric acid (HCl) to differentiate between the organic (C_{org}) and carbonate (C_{CO₃}) carbon. The data presented is based on select repeat experimentation and quality checks in the assaying process. Typically, the experimental error accounting for sampling, dilutions and variation in ICP is +/- 5% with a 95% confidence interval. However, there is additional error introduced by sample variability and in particular between different specimens of a given plant species.

2.3 XRD, Synchrotron XAS and SEM-EDS analysis

Dominant crystal phases were identified using X-ray diffraction (XRD) on finely ground powder samples (ball-milled and sieved to <100 μ m) using a Bruker D8 Advance X-Ray diffractometer with a Cu-target, diffracted-beam monochromator, and scintillation counter

detector. The settings in the instrument were: 40 kV, 30 mA, 3–80° 2 θ , 0.05° step size or increment, with 10 seconds per step. The XRD data were analysed using DIFFRAC plus XRD Evaluation Search/Match Version 8.0 software supported by the International Centre for Diffraction Data's PDF-4/Minerals database.

Ash samples of *Phyllanthus* and *Rinorea* were analysed at the Australian National Beamline Facility (ANBF) beamline (20B) at Tsukuba, Japan to obtain X-ray absorption near edge structure (XANES) spectral signatures at the Ni K-edge. The storage ring electron beam energy was 2.5 GeV with a maximum beam current of 300 mA. Monochromation was achieved using a water-cooled channel-cut Si(111) crystal monochromator with a 1 mm beam size in both the horizontal and vertical directions, and harmonic rejection was achieved by detuning to 50% intensity. Fluorescence data were recorded using a Canberra-Eurisys 36-element Ge-detector positioned at 90° to the incident beam, with the sample positioned at 45° to the incident beam. The X-ray beam energy was calibrated simultaneously with data collection using a Ni metal foil recorded in transmission downstream of the sample, where the first peak of the first derivative was assumed to 8331.6 eV. All samples and standards were diluted to ~1000 mg kg⁻¹ in boron nitride, contained in polycarbonate cuvettes covered with Kapton tape and then analysed at between 5 and 15 K using a closed-cycle He cryostat. Data reduction of the X-ray absorption spectroscopy data, including calibration, averaging and background subtraction of XANES spectra, were performed using the EXAFSPAK software package (G.N. George, Stanford Synchrotron Radiation Lightsource, Menlo Park, CA, USA).

Scanning Electron Microscopy (SEM; Phillips XL30 with Electron microprobe JEOL 8800L) was used for collecting high magnification electron images and energy dispersive spectra (EDS) of the ash samples with a particular focus on determining the Ni-bearing phases in the microstructures.

2.4 Leaching scoping tests

Batch leaching of dried biomass, ash and thermally reduced ash was undertaken to assess the effect of different solutions chemistry on a range of starting materials at ambient temperature, 20°C. Eight different leaching solutions were tested under identical conditions (2 g of ground *Rinorea* dried leaf biomass (2.2% Ni) with 20 mL of various acids and bases for 16 hours using and end-over-end shaker at 400 rpm) to determine leachability. These solutions were: H₂SO₄ (20%; 228 g L⁻¹), HNO₃ (35%; 529 g L⁻¹), HCl (16%; 238 g L⁻¹), citric acid (100 g L⁻¹), NH₄OH (30%; 264 g L⁻¹), (NH₄)₂CO₃ (100 g L⁻¹), acetic acid (20%; 210 g L⁻¹) and malic acid (100 g L⁻¹). Similarly, batch leaching was undertaken on the ash of *Rinorea* leaf (7.2% Ni) and leaf rich *Phyllanthus* (29% Ni) composites using the same set of leaching solutions (1 g sample of ash in 20 mL solution), also for 16 hours. The composites in the leaching scoping tests were not the same composites used in the washing and sulphuric acid leaching tests due to sample availability. The nickel content of different plant specimens of the same species can vary greatly. The leaf biomass and ash composite leachates were then filtered thru a 0.45 μ m syringe filter, and the clear supernatant was diluted by combining 1 mL of the extract with 9 mL of deionised water before analysis by ICP-AES. Samples of thermally reduced ash of the *Rinorea* composite were also leached in 1 M H₂SO₄ and 30% NH₄OH (0.5 g in 10 mL, stirred) and then diluted by putting 3 mL of sample to 7 mL of 4% HNO₃ before analysis by ICP-AES. Finally the biomass and ash composites were assayed by strong acid digestion: 1 gram of

Rinorea biomass and 0.5 gram of *Phyllanthus and Rinorea* ash composite were mixed with 6 mL HNO₃ (70%) and 3 mL HCl (32%) and digested for 2 hour at 125°C on a hot block. Then 0.5 mL digest solution was added to 9.5 mL of deionised water before analysis by ICP-AES. The leaching extractions were calculated by dividing the mass of the element leached by the mass of the element reported in the assay.

2.5 Thermal reduction

Samples of the *Rinorea* ash composite (5.5% Ni) were heat treated in a reducing gas environment at either 700°C or 950°C. This procedure was carried out in an electrically-heated tube furnace inside a quartz tube, using a top-blown fluidising particle technique. The CO/Ar gas mixture was introduced through a 5-mm-inner diameter (ID) alumina injection tube from the top, blowing and circulating the particles at the bottom of a 30-mm-diameter, closed-end quartz tube. Three grams (-/+ 0.01g) of sample were introduced into the quartz tube, which was then placed in the tube furnace that had been pre-heated to the desired temperature. After reduction, the quartz tube containing the sample was quickly removed from the furnace and quenched in a water bath held at room temperature.

2.6 Water-washing and sulphuric acid leaching of ash

Water washing and H₂SO₄ leaching trials were performed on the ash material to assess the kinetics and extent of these reactions. The pH measurements were carried out using a temperature compensated pH probe that was calibrated at room temperature in pH 4.00 and 7.00 buffers. Solution samples (1 mL) were isolated from solids by membrane (0.45 µm) filtration and stabilised in solution by 10X dilution in 2 wt.% nitric acid (HNO₃) solution (3.02 g L⁻¹). For mass balancing purposes and to isolate the solids for assaying and further experiments, final solution and solids were separated by vacuum filtration and the solids were dried to constant mass at 60°C. Samples of the solids were subject to microwave assisted digestion in concentrated acids 7 mL of HNO₃ 70 wt.% (1057 g L⁻¹) and 3 mL HCl 37 wt.% (551 g L⁻¹). Washing and leaching experiments were carried out in baffled glass reactors with agitation provided by Teflon coated magnetic stir bars for the water-washing and weak acid leaching and overhead agitation for the strong acid leaching (1 or 5 M H₂SO₄). The experiments were naturally aerated. For the leaching experiments, heating to 60°C was achieved using a hot plate with electronic temperature control. For the leaching extraction figures, recoveries were calculated based on the calculated head composition considering the final solids and solution assays. The solution phase metal content was adjusted to take into account evaporation effects and the slightly diminished volume due to sampling.

2.7 Precipitation of nickel hydroxide

Nickel was precipitated in two stages from the *Rinorea* final leachate that was prepared by sequentially water washing, leaching in 1 M H₂SO₄, adjusting to pH 4.5 by addition of fine and reactive lime (CaO) and then filtering off the solids formed, which were mainly CaSO₄.2H₂O. The reactions took place in a magnetically stirred 250-mL baffled glass reactor maintained at 50°C where the basic chemical was either magnesia (MgO (EMAG45)), NaOH (1 M) or the K₂CO₃-rich liquid from the previous water-washing of the *Rinorea* composite. After one hour, the slurry was transferred to a graduated cylinder where the solids settling rate

was recorded. The solution was then separated from the solids by vacuum filtration. The solution proceeded to a second ('scavenger') stage of precipitation where the pH was adjusted to ~8.5. All the Ni(OH)₂ solids were dried at 105°C for 18 hours prior to being assayed with acid digestion as described previously (see section 2.2).

3. RESULTS

3.1 Bio-ore characterisation

Open air burning of the dried biomass yielded an ash with a mass factor reduction of about 16-fold (9–18 for wood and twigs, and 10–27 for woody green twigs and leaves) with minimal loss of the contained mineral elements. The elemental composition and level of Ni accumulation in different plant parts varies substantially as shown in Table 1. In the dried biomass, the Ni content was relatively high in the *Phyllanthus* leaves (1.1%) and the *Rinorea* twigs (0.8%) compared with the wood fractions of the respective species. The distribution of Ni in the biomass fractions is hence an important consideration in agronomic management. In order to achieve the highest Ni concentrations in the bio-ore, leaves and young green twigs can be preferentially harvested.

The major elements in the biomass are Ca, K, Ni, Mg (Table 1B), Na and C (not measured), and once ashed, some of the fractions contain over 10 wt.% Ni (Tables 1B and 2) which is a substantially higher grade than conventional ore. The ash, also contains minor amounts of P, S, Cl (not measured), Mn, Zn and Si, but only trace amounts of Al, Co, Fe, As, B, Ba, Bi, Cd (Table 1C), Cu, Cr (data not shown), Hg, Li, Mo, Pb, Sr, Ti and V (Tables 1B, 1C and 2). Note that Cl was not assayed but was apparent in both samples from EDS solid phase analysis with a more prominent Cl signal for the *Phyllanthus* ash.

Table 1 A. Element concentrations in the dried biomass.

Species	Al	Ca	Co	Fe	K	Mg	Mn	Ni	P	S	Zn
BIOMASS	µg g ⁻¹	%	µg g ⁻¹	µg g ⁻¹	%	%	µg g ⁻¹	%	µg g ⁻¹	µg g ⁻¹	µg g ⁻¹
<i>Phyllanthus</i> (woody twigs)	6	0.1	15	6	0.2	0.0	18	0.1	289	342	7
<i>Phyllanthus</i> (leaves)	16	1.2	23	18	0.6	0.4	182	1.1	765	1286	59
<i>Rinorea</i> (green twigs)	69	7.7	20	138	1.1	0.6	83	0.8	1011	2349	248
<i>Rinorea</i> (woody twigs)	15	4.4	12	10	0.5	0.1	22	0.2	420	1046	33
<i>Rinorea</i> (wood)	8	0.5	14	8	0.3	0.1	6	0.03	334	332	7
<i>Rinorea</i> (leaves)	36	2.0	21	13	0.6	0.2	101	0.4	557	1862	64

Table 1 B. Element concentrations in the ash.

Species	Al	Ca	Co	Fe	K	Mg	Mn	Ni	P	S	Zn
ASH	$\mu\text{g g}^{-1}$	%	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	%	%	$\mu\text{g g}^{-1}$	%	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$
<i>Phyllanthus</i> (woody twigs)	401	32.9	80	877	8.7	2.1	1481	10.3	8964	19871	1166
<i>Phyllanthus</i> (leaves)	334	9.4	138	961	3.8	2.1	1559	11.3	4741	8661	862
<i>Rinorea</i> (green twigs)	121	46.4	58	537	8.0	2.1	448	4.1	5865	9657	1101
<i>Rinorea</i> (woody twigs)	248	52.4	39	416	5.5	1.6	281	2.0	3367	6557	376
<i>Rinorea</i> (wood)	614	47.9	53	897	7.0	2.0	319	2.2	4463	6977	555
<i>Rinorea</i> (leaves)	309	35.0	143	563	10.2	2.0	1329	7.2	6099	10793	1014

Table 1 C. Trace element concentrations in the ash.

Species	As	B	Ba	Bi	Cd	Hg	Li	Mo	Pb	Sr	Ti	V	Si
ASH	$\mu\text{g g}^{-1}$												
<i>Phyllanthus</i> (woody twigs)	0.6	132	20	0.5	0.7	0.2	0.5	9	4	152	4.1	1.5	965
<i>Phyllanthus</i> (leaves)	0.6	140	4.2	0.5	2.1	0.1	0.8	9	4	26	3.0	2.7	717
<i>Rinorea</i> (green twigs)	0.3	86	21	0.5	1.0	0.2	0.1	9	2	259	1.8	0.3	389
<i>Rinorea</i> (woody twigs)	0.2	91	14	1.8	0.6	0.1	0.1	7	4	237	2.1	0.0	362
<i>Rinorea</i> (wood)	0.1	81	13	1.3	0.6	0.1	0.2	9	5	194	2.9	0.5	569
<i>Rinorea</i> (leaves)	0.6	310	23	0.6	0.3	0.2	0.5	8	2	225	5.3	0.9	2142

For the water washing and H₂SO₄ leaching trials, ash composites were prepared by mixing the ligneous and leaf fractions in the approximate ratio of 2:1 (by weight) for *Phyllanthus* and *Rinorea*, respectively. These composites provide an average feed material that reflect more closely the feed from a agromining operation. Note that the blend does not correspond

directly to the samples assayed for Table 1 which is why there is some variation in the composition, notably a higher Ni content. The composition of the ash blend is shown in Table 2.

Table 2 Elemental composition of the ash composites.

%	Ca	Ni	K	C _{org}	C _{CO₃}	Mg	S	P	Na	Si	Fe	Mn	Zn	Al
<i>Phyllanthus</i>	10.8	12.7	7.2	5.9	1.7	1.4	1.2	0.8	1.1	0.33	0.13	0.13	0.09	0.05
<i>Rinorea</i>	25.4	5.5	8.5	2.6	4.8	1.2	0.8	0.6	0.02	0.24	0.07	0.07	0.07	0.04

The morphology of the ash samples of *Phyllanthus* and *Rinorea* is shown in Figure 2. Fine ash material can be seen in the *Phyllanthus* image along with a larger particle. On the surface of the large Ca-rich wafer-structured *Rinorea* ash, very small particles (nm scale) can be seen which were found to be rich in Ni by EDS point analysis.

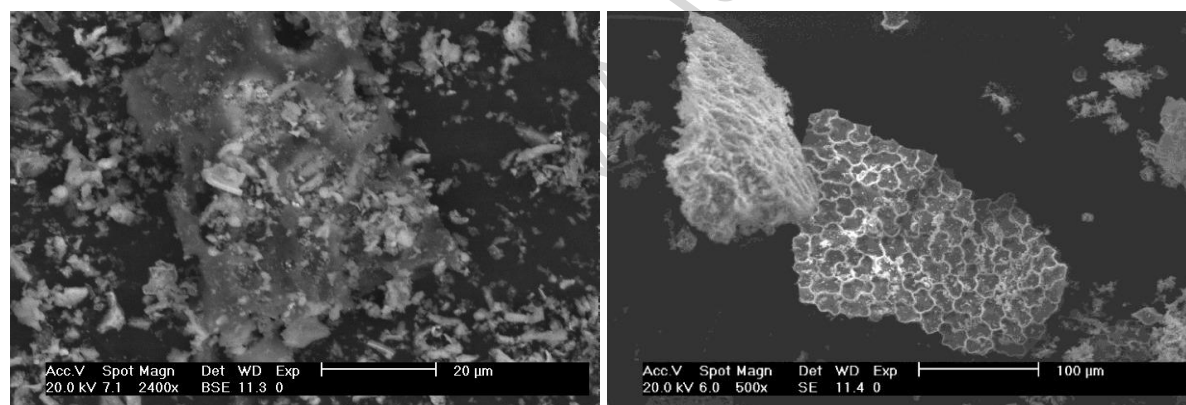


Figure 2 SEM micrographs of the ash composites: backscattered electron (BSE) image of *Phyllanthus* ash (left) and secondary electron (SE) image of *Rinorea* ash (right).

The ashes were characterised by XRD to obtain information on the contained mineral phases. Figures 3 A and B show the XRD-spectra of *Phyllanthus* and *Rinorea* ash. Nickel phases identified were NiO, oxygen deficient NiO_{0.97} and (Mg,Ni)O, which forms a solid solution series (e.g.: Mg_{0.4}Ni_{0.6}O). Substantial amounts of K₂CO₃, CaCO₃ and K₂Ca(CO₃)₂ were also identified. No CaO was detected, because CaCO₃ only readily converts to CaO at temperatures above about 900°C according to chemical thermodynamic data (HSC, 2009). The synchrotron XANES data, which reports on all Ni present in the sample, supports the XRD-analysis, and shows that NiO is the dominant phase, whereas Ni(OH)₂ is very minor, as expected given the high temperatures during incineration (Figure 4). As the ash is a complex material and the ashing environment was not controlled, Ni may also be distributed amongst other phases that are either amorphous or not present in the XRD mineral database (PDF).

Some Ni was also reduced to its metallic state. This depends on the local oxidation/reduction environment during incineration of the biomass. For example, in the presence of H₂, bulk NiO was nearly completely reduced to Ni in three hours at 205°C (Benton & Emmet, 1924). A small Ni [1,1,1] characteristic peak can be seen in both ash samples at 2θ of 44.5° (Richardson et al., 2003). Particles of light grey metallic Ni (<0.1 mm) can be seen distributed over the surfaces of the *Phyllanthus* ash sample in Figure 5; the metallic Ni-particles in the ash exhibited a response when exposed to a strong neodymium magnet.

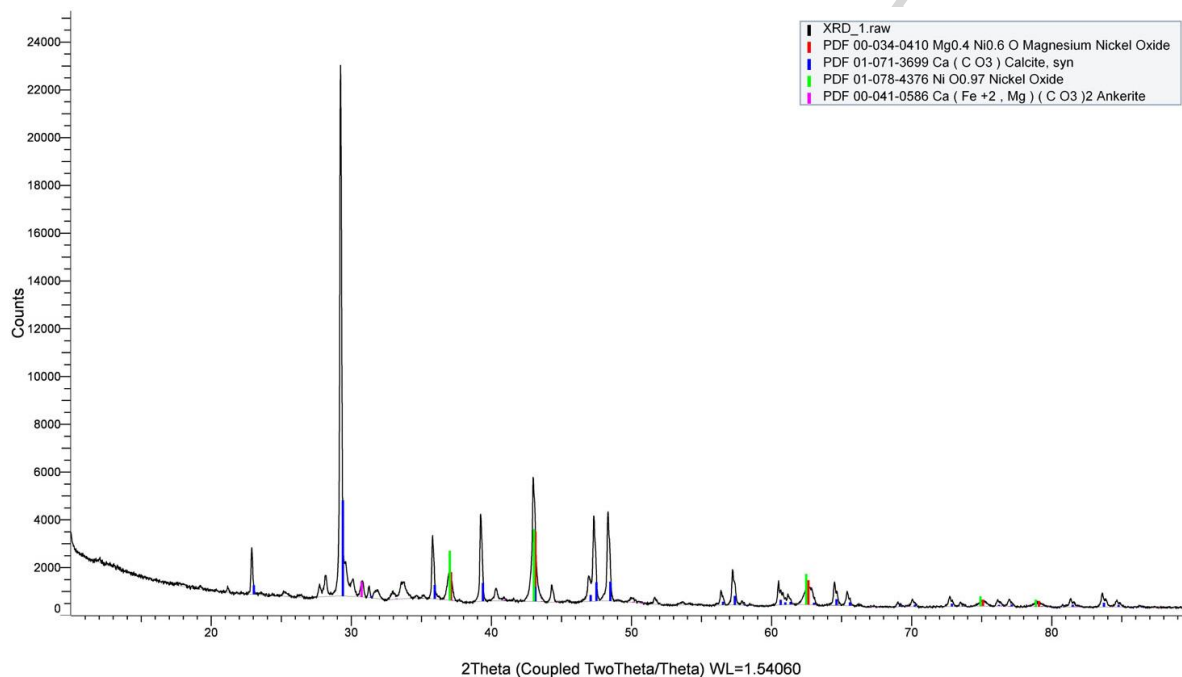


Figure 3A. XRD-spectra of *Phyllanthus* ash.

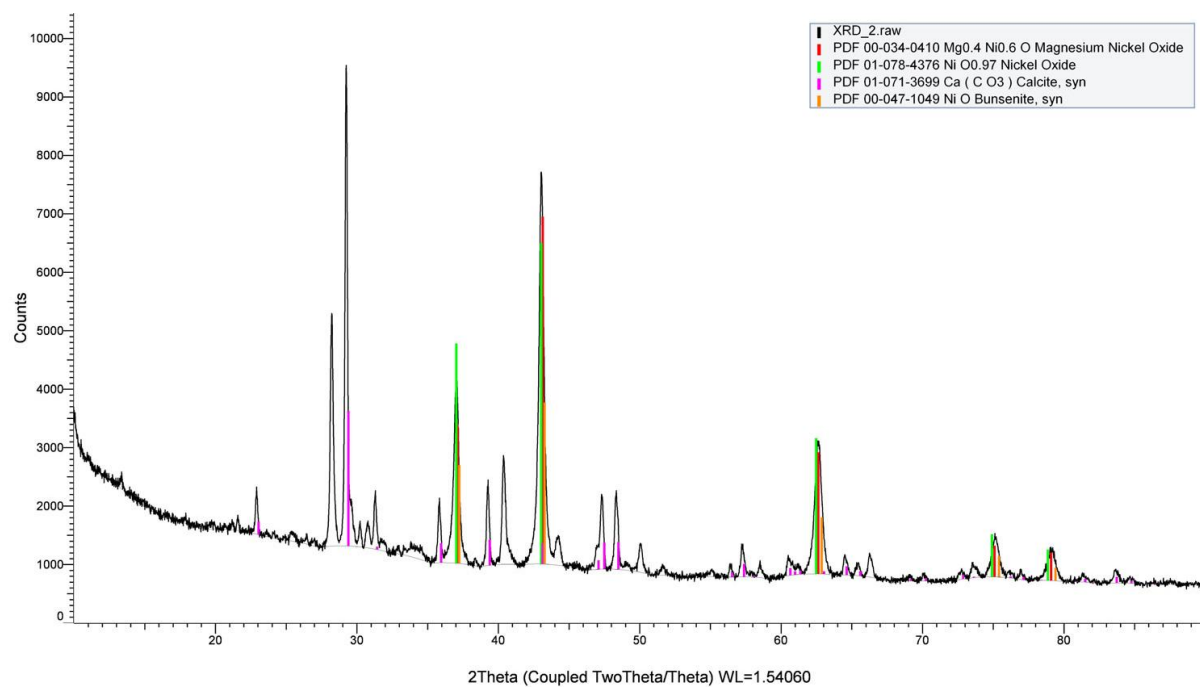


Figure 3B. XRD-spectra of *Rinorea* ash.

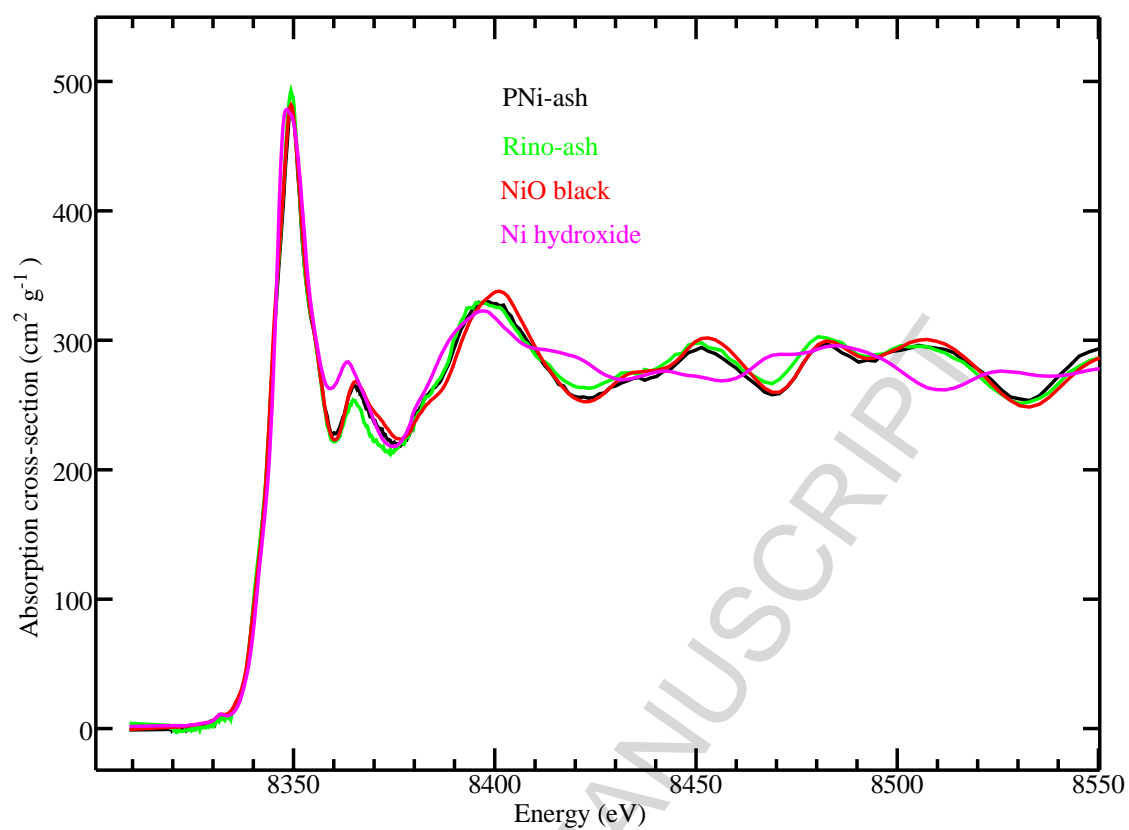


Figure 4. Ni XANES spectra of *Phyllanthus* (PNi) and *Rinorea* (Rino) ash and NiO and Ni(OH)₂ standards. PNi-ash denotes *Phyllanthus* bio-ore (black), Rino-ash denotes *Rinorea* bio-ore (green), NiO is black nickel (II) oxide (red) and Ni (II) hydroxide (pink).

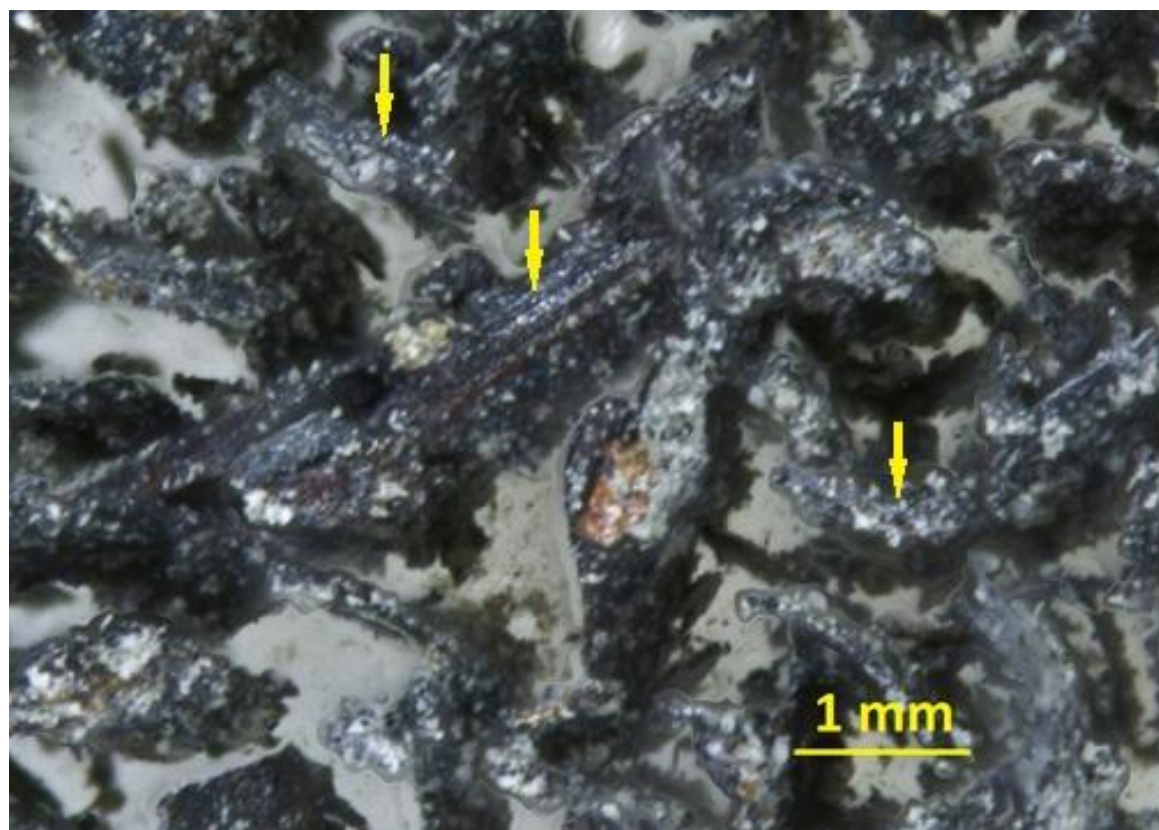


Figure 5. Optical microscope image of *Phyllanthus* ash. Yellow arrows highlight areas more concentrated in reduced nickel on the surface of the ash that appear as fine light grey particles which are relatively evenly distributed.

3.2 Leaching and Water Washing

3.2.1 Leaching scoping studies

Scoping leaching tests were undertaken to evaluate the effectiveness of various solutions in extracting the main components of dried *Rinorea* biomass as a function of solution chemistry. The results presented in Table 3. Approximately half of the Ni can be readily leached directly from the biomass along with significant K and Mg. Ca extraction was notably higher with the stronger acids HCl and HNO₃.

Table 3. Leaching extraction (%) of *Rinorea* biomass, 10% solids, 16 hours, 20°C.

Solution	Ca	K	Ni	Mg
H ₂ SO ₄ 20%	3	21	51	28
Citric acid 100 g/L	10	31	59	34
HCl 16%	26	33	56	32
NH ₄ OH 30%	5	35	47	31
HNO ₃ 35%	26	33	54	30
(NH ₄) ₂ CO ₃ 100 g/L	1	23	43	21
Acetic acid 20%	8	47	55	34
Malic acid 100 g/L	12	30	52	30

For the ashed *Rinorea* and *Phyllanthus* samples (Tables 4A and 4B, respectively) the strong acids exhibited the highest Ni extraction with the order being HCl>HNO₃>H₂SO₄>Acetic, Citric, Malic>(NH₄)₂CO₃>NH₄OH. The extent of Ni leached was higher for *Rinorea*. Dissolution of Ca, Mg is suppressed in NH₄OH, however, Ni also does not readily dissolve in ammonia from these ashes.

Table 4A. Leaching extraction (%) of *Rinorea* ash, 5% solids, 16 hours, 20°C.

Solution	Ca	K	Ni	Mg
H ₂ SO ₄ 20%	<1	40	18	36
Citric acid 100 g/L	16	49	12	34
HCl 16%	49	52	41	48
NH ₄ OH 30%	<1	69	2	<1
HNO ₃ 35%	48	48	26	43
(NH ₄) ₂ CO ₃ 100 g/L	<1	47	10	16
Acetic acid 20%	61	74	16	41
Malic acid 100 g/L	5	48	11	33

Table 4B. Leaching extraction (%) of *Phyllanthus* ash, 5% solids, 16 hours, 20°C.

Solution	Ca	K	Ni	Mg
H ₂ SO ₄ 20%	1	38	8	29
Citric acid 100 g/L	51	48	4	23
HCl 16%	50	48	31	46
NH ₄ OH 30%	<1	53	1	<1
HNO ₃ 35%	49	47	20	40
(NH ₄) ₂ CO ₃ 100 g/L	<1	39	3	6
Acetic acid 20%	57	76	5	29
Malic acid 100 g/L	33	46	5	25

The effect of a reducing heat treatment on the ashes on leaching was tested for both H₂SO₄ and NH₄OH solutions. From Table 5 it is evident that the heat treatment at 700°C resulted in significant improvements in Ni extraction for both systems while the 950°C heat treatment was detrimental to the acid leach and only slightly improved the NH₄OH leach. Ni extractions were calculated assuming 5.5% Ni in the *Rinorea* ash composite as determined by the initial characterisation.

Table 5. Leaching extraction of 0.5 g of *Rinorea* ash and reduced *Rinorea* ash in 10 mL solution.

Elements Extracted (g-kg solids)	Ash (Full Digest)	1M H ₂ SO ₄	30% NH ₄ OH	Ash reduced (700°C) 1M H ₂ SO ₄	Ash reduced (700°C) 30% NH ₄ OH	Ash reduced (950°C) 1M H ₂ SO ₄	Ash reduced (950°C) 30% NH ₄ OH
Al	0.3	0.2	0.001	0.3	0.001	0.4	0.001
Ca	282	13	0.01	11	0.02	12	0.1
K	90	18.1	4.4	16	4.7	22	2.4
Mg	13	7.8	0.004	5.5	0.01	0.9	0.002
S	8.4	419	0.6	386	0.8	350	0.6
Ni	55	14	0.5	27	13	4.4	0.8
Ni (%)	100	25	0.9	49	23	8.1	1.4

3.2.2 Water washing of the ash

In order to partially mitigate the high cost of acid for the process, the ash was first subjected to a water wash to remove the soluble acid-consuming fraction, mainly consisting of K₂CO₃. The recovered K₂CO₃ could be recycled to the agromining farm and used as a fertiliser, or it could be used as a neutralising agent in a later stage of the process by precipitating Ni(OH)₂.

The ash washing experiments were conducted in two stages. The first stage wash produced a concentrated K-salt solution as 25 g ash was mixed with 50 mL deionised H₂O until the pH stabilised after a minimum contact time of 1 hour. In the second washing stage the solid residue from the first wash was mixed at a lower solids density with 200 mL of deionized H₂O for 1 hour.

Table 6 shows the composition of the wash solutions of both stages. The first washing stage recovered a concentrated and reasonably pure solution of K with some Na, S as well as Cl (not assayed) for both the *Rinorea* and *Phyllanthus* ash. The K-salts are highly soluble, for example, the solubility of K₂CO₃, K₂SO₄ and KCl is 52.30, 9.95, 25.39 mass percent (100*(g-solute / (g-solute + g-water))) at 20°C, respectively (CRC Handbook 2006). Samples of the first wash solutions were evaporated and the crystals analysed by XRD where it was found that the *Rinorea* wash water-derived crystals were predominantly K₂CO₃·1.5H₂O along with KCl and K₂SO₄, while the *Phyllanthus* wash-water derived crystals were mainly KCl and K₂SO₄ with little K₂CO₃·1.5H₂O. In the second washing stage, some Fe, Al and P were dissolved into solution with a small amount of additional K and Na. Dissolution of Ni, Mg and Ca in either of the washing stages was low being less than 0.5%.

The final solution pH for wash stages 1 and 2 (respectively) are 10.9 and 10.0 for *Rinorea* and 13.9 and 10.9 for *Phyllanthus* suggesting that the *Phyllanthus* ash contained some (Na/K)OH. Prior to the solid-liquid separation at the end of the second wash, the pH was adjusted to 8.8 by addition of dilute H₂SO₄ to remove additional water-soluble components while leaving the majority of the Ni in the solid phase.

Table 6. Composition of filtrate after water washing the bio-ore ash composites.

Elements	Filtrate after Wash #1 (33% solids) (mg L ⁻¹)		Filtrate after Wash #2 (~9% solids) (mg L ⁻¹)	
	<i>Rinorea</i>	<i>Phyllanthus</i>	<i>Rinorea</i>	<i>Phyllanthus</i>
Al	<1	127	384	293
Ca	<1	112	<1	<1
Fe	<1	12	542	1240
K	27500	21000	83	33
Mg	<1	20	<1	2
Mn	<1	13	3	448
Na	55	1700	46	172
Ni	<1	15	5	13
P	5	9	374	658
S	2570	3980	<1	1
Zn	<1	7	<1	1

3.2.3 Acid leaching of water-washed ash

To establish the leaching behaviour as a function of solution acidity, the water-washed ash (16.8 g and 16.3 g for *Rinorea* and *Phyllanthus*, respectively) proceeded through two stages of acid leaching with increasing acid-strength as shown in Figure 6 A and B.

In the first stage, the washed ash was mixed with 150 mL of deionised water at 60°C then a solution of 1 M H₂SO₄ was dosed into the reactor every 20 minutes and the pH was lowered from an initial pH of 9.2 to a final pH below 1.5 after about 3–4 hours; the pH was buffered in the range of 7.5–5 as alkaline components of the ash reacted, consuming acid. During this first stage, the majority of the remaining K dissolved. For both experiments, the K in solution peaked and then recrystallised to some extent. It is likely that a K-Mg or K-Ni hydroxyl-sulphate double salt formed. The Ni did not readily dissolve during leaching, even when the pH was near 1.5, and this was unexpected considering Ni was present as NiO. The Ni-leaching kinetics were probably hindered due to the complex morphological and mineralogical nature of the ash. It is also possible that there was a passivation effect due to the presence of insoluble organic components.

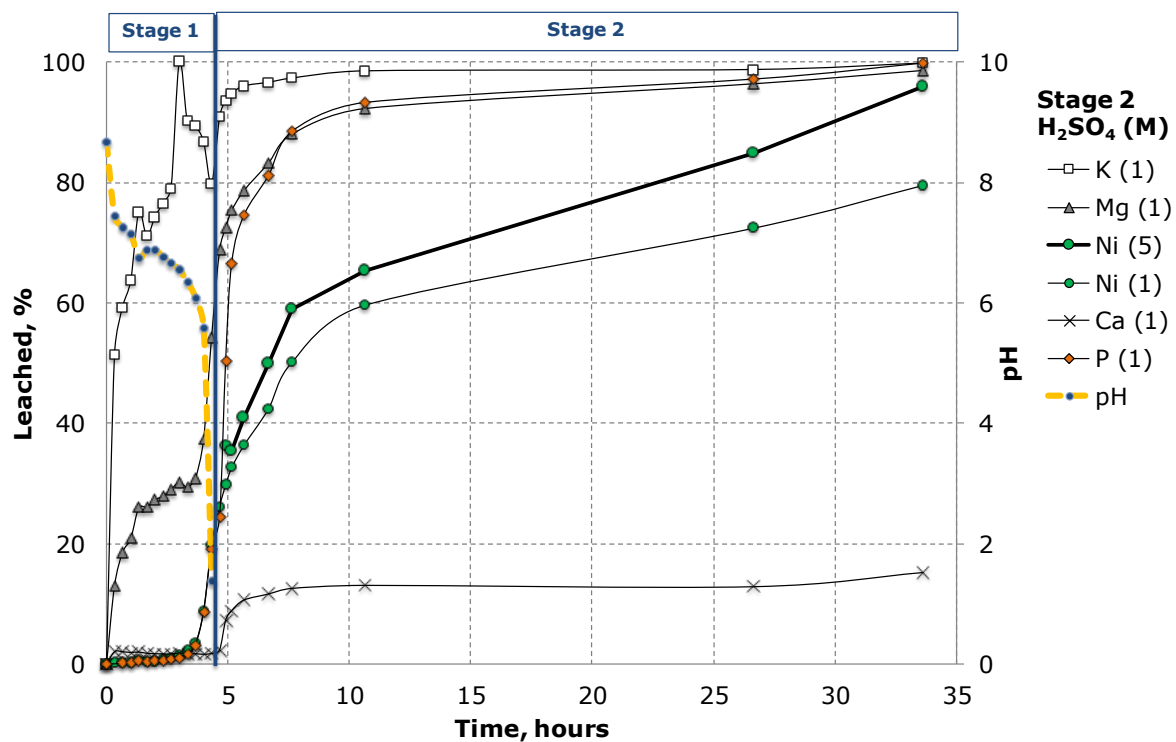


Figure 6A. Leaching behaviour of washed *Rinorea* ash. Two stages: (1) pH decreased from 8.7 to 1.5 over 4.7 hours by sequential addition of H_2SO_4 ; (2) residue from stage 1 is contacted with either 1 M or 5 M H_2SO_4 for 29 hours, only Ni shown for 5 M. All tests at 60°C .

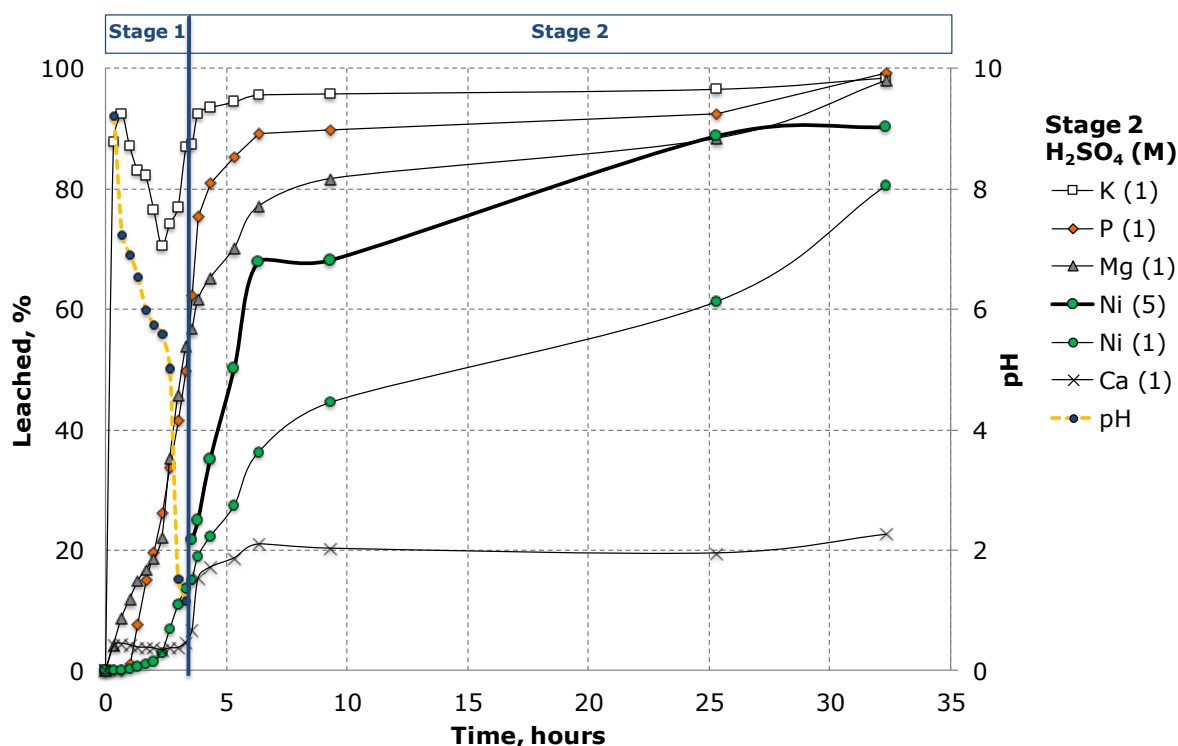


Figure 6B. Leaching behaviour of washed *Phyllanthus* ash. Two stages: (1) pH decreased from 9.2 to 1.3 over 3.3 hours by sequential addition of H₂SO₄; (2) residue from stage 1 is contacted with either 1 or 5 M H₂SO₄ for 29 hours, only Ni shown for 5 M. All tests at 60°C.

The residue from the first leaching stage was recovered and subsequently, in a stronger acid leaching stage, the solids were exposed to either 1 or 5 M H₂SO₄. For the second stage leach, 5 g of the residue was mixed with 50 mL of the acid at 60°C for 29 hours with samples collected periodically. Both acid strength and longer time favoured Ni extraction with 96% and 90% Ni recovered at 5 M and 80% and 81% at 1 M for *Rinorea* and *Phyllanthus*, respectively.

The major solution components at the end of the second stage leaching for the 1 M H₂SO₄ solution are shown in Figure 7. While the extent of Ni leached from the *Rinorea* was slightly higher than for the *Phyllanthus*, the higher Ni content of the *Phyllanthus* yielded a more concentrated leach solution.

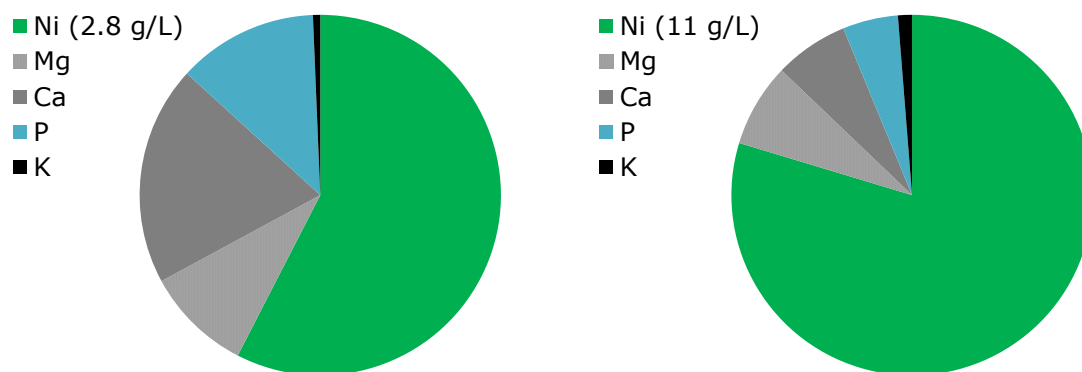


Figure 7. Major components (except S) of the final leach solution Stage 2 leach (1 M H₂SO₄). *Rinorea* left, *Phyllanthus* right.

The major components of the ash as well as the water wash and acid leach residues (dried at 105°C for 18 hours prior to assaying) are shown in Figure 8 A and B. For both the ash of *Phyllanthus* and *Rinorea*, K dissolved firstly followed by Mg and P and then Ni. The Ca content remained roughly consistent throughout, with S content increased as CaCO₃ was converted to CaSO₄·2H₂O. From the XRD-analysis, Ni in the first leach residue (pH 1.5) was shown to be present as NiO_{0.97}, NiMgO₂ and Mg_{0.4}Ni_{0.6}O.

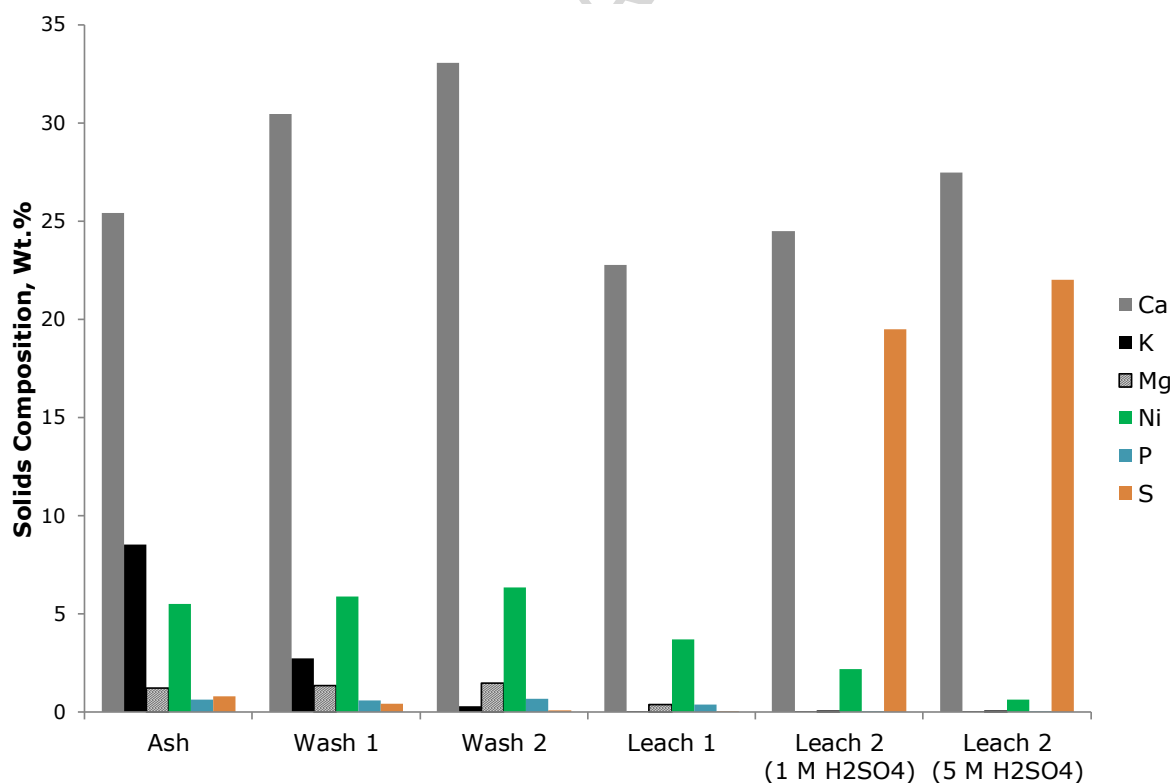


Figure 8A. *Rinorea* ash and residue composition after water washing and leaching.

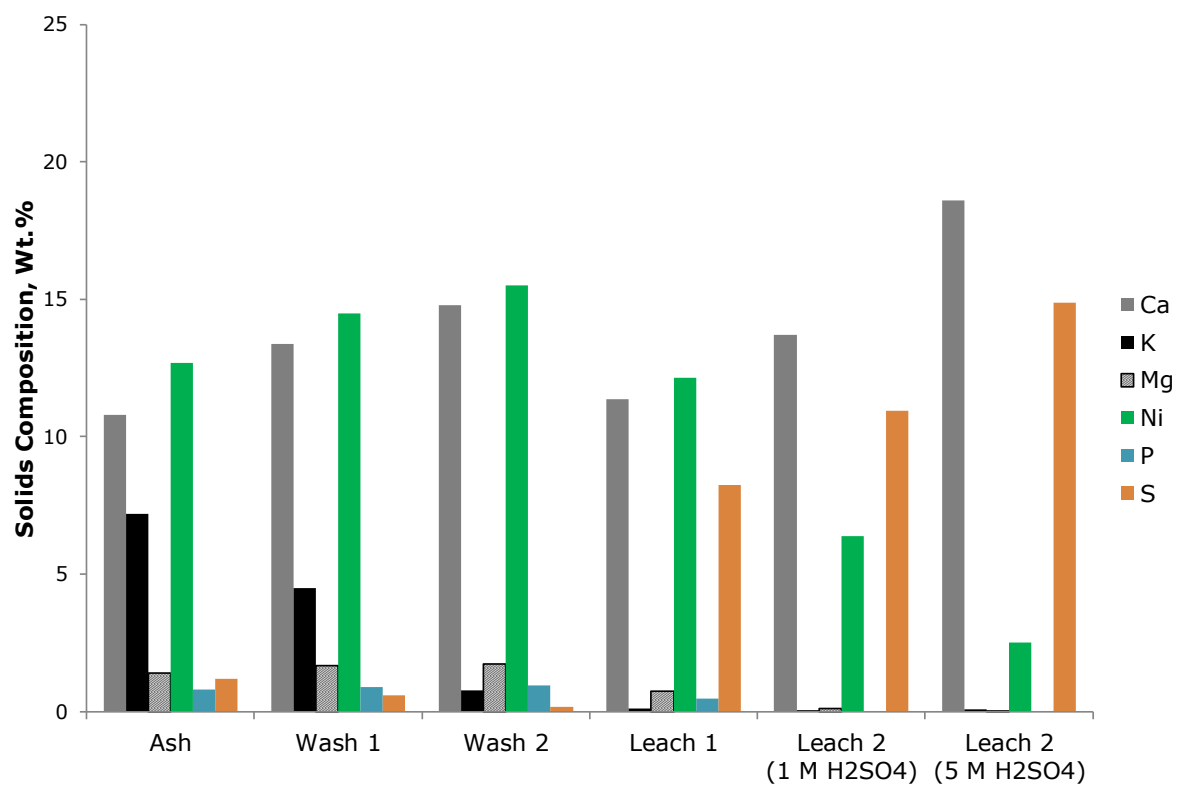


Figure 8B. *Phyllanthus* ash and residue composition after water washing and leaching.

3.3 Precipitation of Ni products from the leachate

The simplest route to obtain a Ni product from the leachate is to precipitate it from the solution as Ni(OH)₂. To assess the effect of the precipitating agent, Ni(OH)₂ was precipitated from *Rinorea* leachate solution using either 1 M NaOH, MgO (EMAG45), or the K₂CO₃-rich liquid (*Rinorea* ash wash 1 solution). The results are summarised in Table 7, where after two stages all three reagents precipitated >98% of the Ni in solution. From the Ni precipitated in Stage 1, the *Rinorea* wash 1 solution had a neutralisation potential approximately equivalent to a 0.92 M NaOH solution. More K₂CO₃-rich solution was added in stage 2 as the pH was buffered and took longer to reach the target pH >8.4; significant Ca was co-precipitated. Phosphorus also readily precipitated together with Ni(OH)₂ for all three systems.

Table 7. Composition of *Rinorea* leachate, precipitation filtrates (F) and solids (S, dried at 105°C for 18 hours), 200 mL of feed solution (leachate or filtrate 1).

			Ni	Ca	K	Mg	Na	S	P	Units	pH
<i>Rinorea</i> Ash Leachate			2.88	0.47	0.30	0.80	0.01	3.09	0.082	g L ⁻¹	4.0
Base	Add	Stream									
NaOH 1 M	21.8 mL	F-1	0.21	0.46	0.29	0.74	1.70	2.70	0.002	g L ⁻¹	7.4
		S-1	42	0.35	0.11	0.9	0.6	4.5	1.42	%	
	1.7 mL	F-2	0.005	0.46	0.29	0.75	1.89	2.81	0.001	g L ⁻¹	8.4
		S-2	44	0.45	0.14	2.3	0.9	4.5	0.08	%	
K ₂ CO ₃ <i>Rinorea</i> W-1	15.5 mL	F-1	1.13	0.48	2.88	0.78	0.03	3.07	0.001	g L ⁻¹	7.1
		S-1	39	0.34	1.05	0.5	0.01	3.8	2.17	%	
	15.3 mL	F-2	0.01	0.15	5.30	0.71	0.03	3.20	0.001	g L ⁻¹	8.4
		S-2	21	5.48	2.78	1.2	0.02	2.4	0.03	%	
MgO <i>EMAG45</i>	0.45 g	F-1	0.73	0.54	0.34	1.52	0.01	2.97	0.0001	g L ⁻¹	7.1
		S-1	35	0.45	0.05	5.4	0.01	4.1	1.55	%	
	0.40 g	F-2	0.002	0.59	0.36	2.05	0.01	3.55	0.001	g L ⁻¹	8.6
		S-2	24	0.53	0.04	12.1	0.01	3.4	0.01	%	

The solids settling rates were recorded after the first stage. The precipitate settling rate was highest for the MgO where the solids were 90% settled within 5 minutes. After 30 minutes, the K₂CO₃ and NaOH generated Ni(OH)₂ precipitates which had settled to 50 and 40%, respectively. The solution phase was noticeably clearer for the K₂CO₃ precipitated Ni(OH)₂ system. In practice, a flocculating agent would be used to enhance solids settling and solution clarity. The XRD patterns of all three precipitates were partially amorphous alpha phase Ni(OH)₂, comparable to the materials presented in Harvey et al. (2011). When precipitated from SO₄²⁻ solution, a portion of the SO₄²⁻ is integrated into the Ni(OH)₂ structure, for example, the stoichiometry of an industrial mixed hydroxide precipitate is approximately Ni₇(OH)₁₂SO₄ (Williams et al., 2013).

4. DISCUSSION

Effective recovery of a commercially attractive Ni product from bio-ore is important to make Ni agromining technology a viable proposition. As such, a Ni product may be obtained from the harvested bio-ore by either: (i) feeding the ashed bio-ore into an existing Ni processing facility; (ii) high temperature reduction to produce Ni metal in an electric-arc smelter; (iii) incineration of bio-ore under reducing conditions, followed by Ni-specific NH_4OH -leaching and reduction to produce Ni metal or; (iv) incineration followed by strong acid leaching and product recovery via precipitation.

When considering the strong acid leaching route, a range of products could be produced, for example: (i) Precipitation of $\text{Ni}(\text{OH})_2$ using a suitable base such as MgO , NaOH or K_2CO_3 . This is an intermediate product of a reasonably high grade, but it still contains impurity elements. The value of this product will be roughly 70–80% of the base Ni metal price. The $\text{Ni}(\text{OH})_2$ could also be calcinated to NiO to increase its grade; (ii) Purification of the solution using some combination of ion exchange, solvent extraction and precipitation, and then crystallisation of a high purity $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ product. This requires additional purification stages, thereby increasing the cost and complexity of such an operation. Heat energy will be required for the crystalliser, but this may be largely provided from a boiler associated with the biomass burning process. High purity $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ crystals will be more valuable than the $\text{Ni}(\text{OH})_2$, however, the market for such high-purity Ni salts is substantially smaller; (iii) Electrowinning of Ni metal from the purified NiSO_4 -solution. The latter also requires additional purification stages as well as the electrowinning plant. Such an electrowinning plant will require a stable source of electrical power, but the product, provided sufficiently pure, can be sold for the full Ni metal price.

The process described in this paper is operationally simple, highly scalable, and has low energy consumption, especially if the heat from the ashing of the biomass can be utilised. The thermodynamics of the incineration are such that losses of nickel due to volatilisation are negligible. However, the very fine Ni-rich ash particles are an environmental and health hazard, and burning of the biomass should therefore take place in a closed furnace with appropriate off-gas treatment. Furthermore, deportment of Ni to the gas phase should be carefully considered as different thermal processing conditions could potentially cause Ni to be volatilised. The high acid requirement and long residence times of the leaching to achieve high Ni recovery means that the equipment will be relatively large and that there will be a considerable neutralisation requirement. A counter-current process configuration would minimise reagent costs. The benefits of the proposed hydrometallurgical processing option are that the ash wash solution can be used as a neutralisation and precipitating agent and K-effluent solutions and gypsum rich residues may be recycled to offset the cost of fertilisation in the agromining farm.

5. CONCLUSIONS

Agromining enables access to large low-grade Ni resources located globally that cannot be economically extracted with conventional technology as they are well below the cut off grades for mining and processing. These laterite Ni resources are widely distributed,

especially in the Asia-Pacific Region; for example, Sulawesi has 15 400 km² ultramafic soils (Van der Ent et al., 2013). As such agromining provides a complimentary source of low-cost Ni in parallel to low-grade and high-cost conventional Ni producers. Agromining Ni is a low capital cost approach to extracting Ni, from resources as low as 0.1%, and has a relatively short lead-time to production. Bio-ore produced from metal crops in agromining is an attractive feedstock because of the intrinsically high Ni grade and the lack of many impurities when compared with conventional laterite ores. The *Phyllanthus* ash composite was especially high-grade containing 12.7% Ni.

Using a self-sustaining incineration process, the Ni was present mainly as the oxide distributed amongst phases such as NiO, NiO_{0.97}, MgNiO₂ and Mg_{0.4}Ni_{0.6}O. Elemental Ni was also present in the ash and it was demonstrated how controlled thermal treatment under reducing conditions may enhance the leaching behaviour of the ash. Controlling the combustion stage will be a key to develop the most efficient integrated pyro-hydrometallurgical process for this nickel biomass.

The ash was found to be highly amenable to water washing to recover an alkaline solution rich in K₂CO₃. The stage 1 water wash of the *Rinorea* ash at 33 wt.% solids had a neutralisation potential equivalent to 0.92 M NaOH in terms of precipitating Ni(OH)₂.

Leaching studies showed that strong acid treatment with long residence times were required to fully extract the Ni at 60°C. It is expected that the leaching performance could be improved by fine grinding, increased temperature and/or agitation. Sparging air might also result in a minor improvement in the leaching performance by promoting the oxidation of elemental Ni.

Recovering a Ni(OH)₂ product from the *Rinorea* ash leachate by precipitation was demonstrated using the K₂CO₃-rich solution from the *Rinorea* water-wash. The performance of the alternative precipitating agent was comparable to NaOH and MgO which are used in industry to precipitate Ni(OH)₂ products. A unique impurity in the bio-ore derived Ni(OH)₂ is P which has metallurgical implications if the ultimate use is to make stainless steel.

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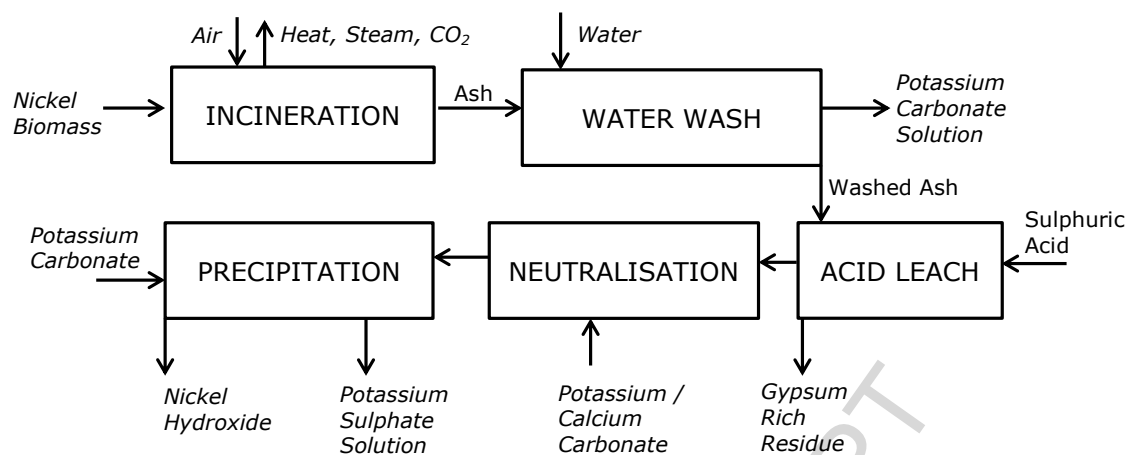
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Graphical abstract

Highlights

The biomass of the tropical nickel hyperaccumulators, *Phyllanthus* and *Rinorea*, was characterised

The leaching behaviour of the dried biomass and bio-ore ash was assessed

A hydrometallurgical process for treating the bio-ore ash was demonstrated

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