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Del. I1.2.2. Site specific report on traditional pre-sampling and post-sampling investigations

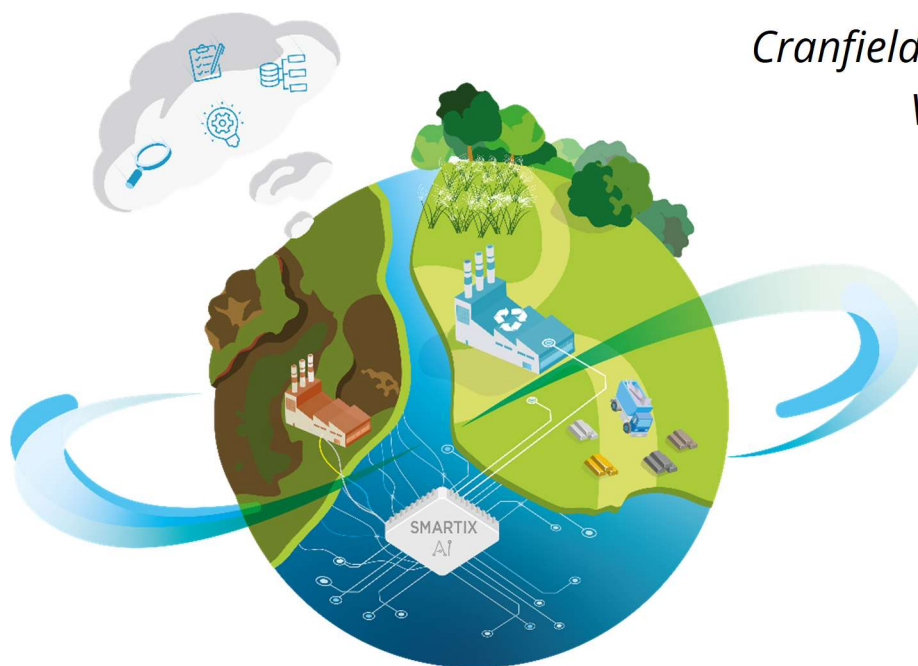
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Version 3.0



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The Materials Processing Institute together with its project partners has the objective of achieving a systematic, long-term beneficial outcome from recovery and regeneration of Past Metallurgical Sites and Deposits (PMSD) in the INTERREG region of Europe under an EU funded REGENERATIS project. Its aims are the innovative circularity to recover raw materials while regenerating the polluted sites.

This report is submitted in fulfilment of the requirements of work package I1.2.2

1 INTRODUCTION

The NWE-REGENERATIS project (Interreg North-West Europe) aims to recover (metals, minerals, and land) from PMSDs using urban mining methods and valorise the site. Three pilot sites were selected one of which was the former integrated steelworks at Teesside.

As an integrated steelworks which processed from raw materials to finished product there was a number of known areas used for the storage of waste products dating back as far as the 1900s.

The significant areas of previous industrial activity are those of the Redcar works complex (comprising the blast furnace, coke ovens, sinter plant and materials handling areas), the Lackenby steelmaking complex (comprising the basic oxygen steel and continuous casting plants), the Grangetown Prairie (site of the Cleveland Iron Works), the zone designated as Landfill and Waste Management Facilities (comprising the SLEMS waste management facility, the High Tip Landfill and a metals recovery area) and the South Bank zone (site of the Clay Lane furnaces and the South Bank Coke Ovens).

Samples were taken from site for chemical analysis, laboratory testing, material separation testing, pyrometallurgical testing and hydrometallurgy.

2 SELECTION OF AREA FOR GEOPHYSICAL INVESTIGATION

A number of areas were identified for consideration all of which have been used for waste management. These are shown in Figure 1.

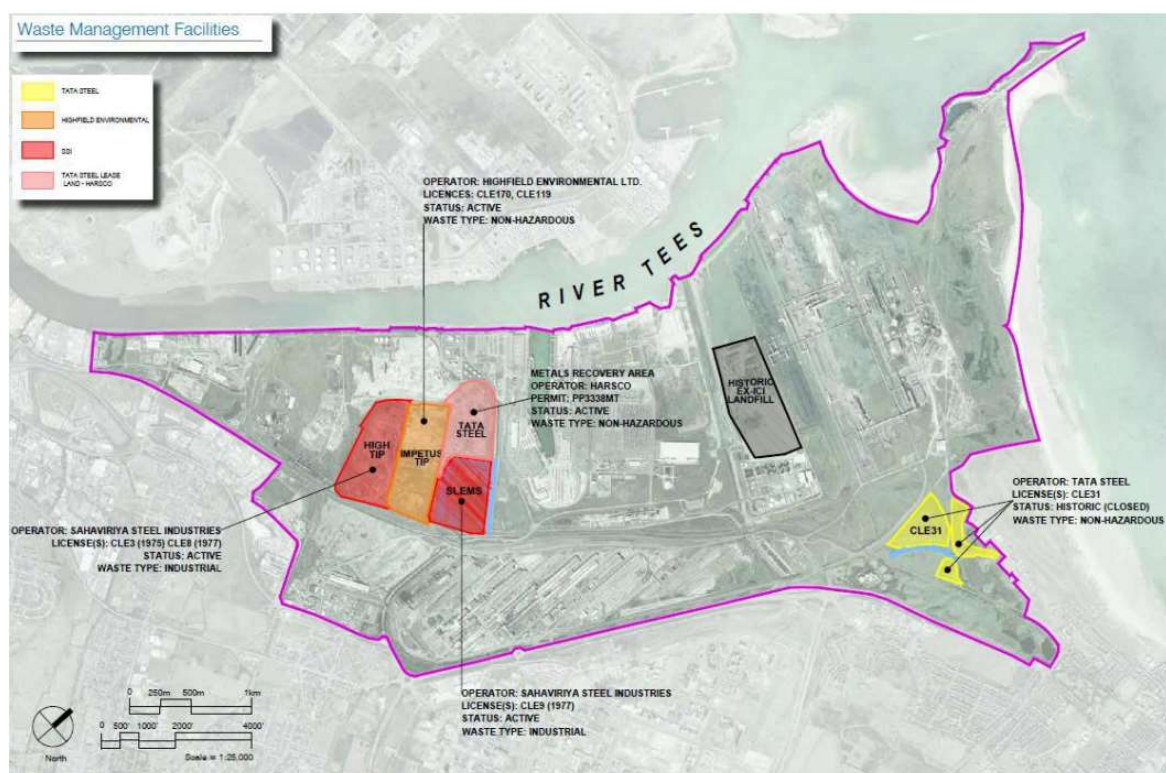


Figure 1. Waste management facilities within PMSD-I1 Teesworks.

The area initially selected was the South Lackenby Effluent Management System (SLEMS) landfill site, shown in Figure 2. An area of 22 hectares, this is a waste handling and treatment facility for Basic Oxygen Steelmaking (BOS) oxide waste. It comprises a series of settling ponds in the southern section of the site. An aqueous suspension of BOS oxide and blast-furnace waste (slurry) was pumped from the BOS plant into these ponds.

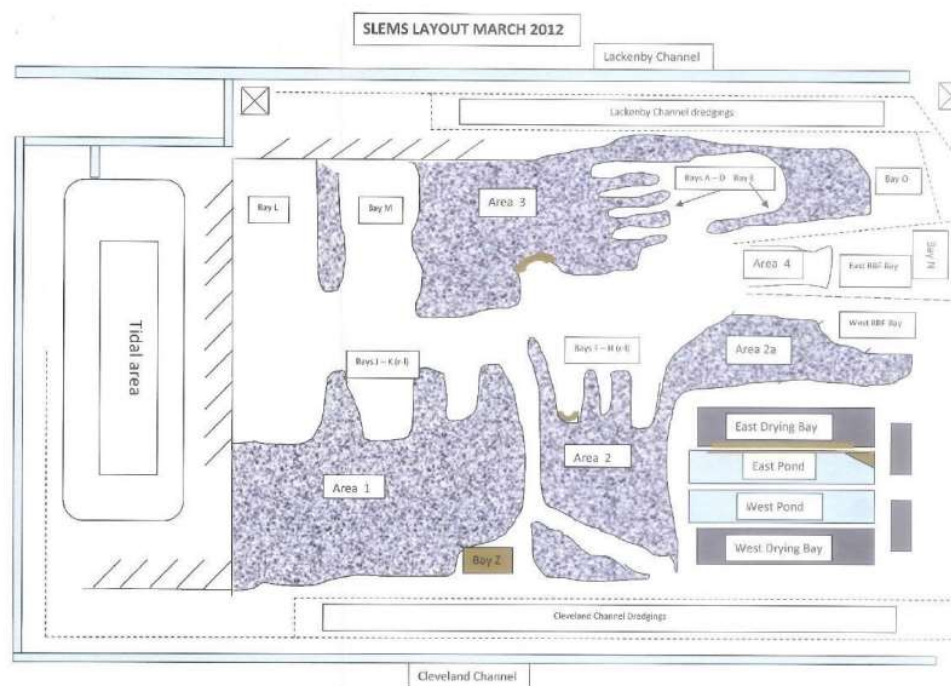


Figure 2. SLEMS site plan

Settled material was dredged from the ponds and deposited in adjacent drying bays before being placed at a final deposition point within the landfill.

After samples were taken for laboratory work, during the preparation for geophysical examination, the SLEMS landfill was repurposed for work involving land development at Teesworks. Although a temporary use the time scales were such that it was not feasible to perform any site work at this location during the project.

An alternative area for geophysical study was sought within Teesworks. Following site visits to identify potential sites it was agreed that the CLE31 landfill site would be a suitable location see Figure 3.

CLE31 (Fig.3) is a closed waste disposal site and was used primarily for the disposal of blast furnace and steelmaking slag with a small percentage of general site waste. The site was used from the 1930s until it was closed in 2002.



Figure 3. CLE31 landfill site

3 PRESAMPLING - SLEMS

Extensive historical data is available from previous onsite investigations. Arcadis have reported (2018) excavation data in the SLEMS area based on a limited number of boreholes and trial pits. The ground was reported as comprising BOS oxide in the form of a slightly gravelly silt underlain with slag, refractory bricks and other wastes. The average BOS oxide content found was 63% and 37% slag. The elemental analysis of the material is provided in Appendix A.

3.1 SAMPLING

As part of an ongoing piece of work on the SLEMS a significant quantity of material, approximately 8000 tonnes, had been removed from the landfill and placed in under cover storage. This is shown in Figure 4.



Figure 4. SLEMS material in undercover storage

Eighteen samples of approximately 30 Kg each were taken from 15 locations around the heap. 15 samples were sent to Cranfield University for laboratory work involving hydrometallurgy. The remaining 3 were duplicates of sample 1 which were distributed between the Materials Processing Institute for material separation and laboratory melting trials and CTP for mineralogical separation testing.

3.2 CHEMICAL ANALYSIS

In addition to the historical analysis listed in Appendix 1 the recovered samples were subjected to elemental analysis by the Institute, an external test house (AMG) and Cranfield University. The results can be seen in Table 1.

Table 1. Elemental Analysis of SLEMS Material

	Institute	AMG	Cranfield
Aluminium	0.53	0.58	0.00
Carbon		5.08	4
Calcium	4.72	4.42	2.59
Chromium	0.03	<0.05	0.01
Copper	0.02	0.6782	0.01
Iron	50.56	53.03	46.87
Potassium	0.14		0.04
Magnesium	0.68	0.95	
Manganese	1.05	0.99	0.86
Nickel	0.01	<0.05	0.01
Phosphorus	0.07	0.103	
Lead	0.26	0.09	0.24
Sulphur	0.17		
Silicon	1.35	1.84	0.30
Tin		<0.05	0.01
Titanium	0.06	0.06	0.01
Zinc	1.41	1.6	1.46

3.2.1. Rapid characterisation

Rapid determination of metal concentrations was determined using a portable X-Ray fluorescence spectrometer (pXRF) (Olympus Delta Premium USA). Three samples (~200 g) were collected in LDPE bags from each of the 15x bulk samples. These were measured in triplicate through the bags in the integrated test stand accessories using the Geochem mode for 30 seconds in real-time, on both beams 1 and 2. No pre-treatment was applied to the samples.

The results from XRF analysis are provided in Figure 5.

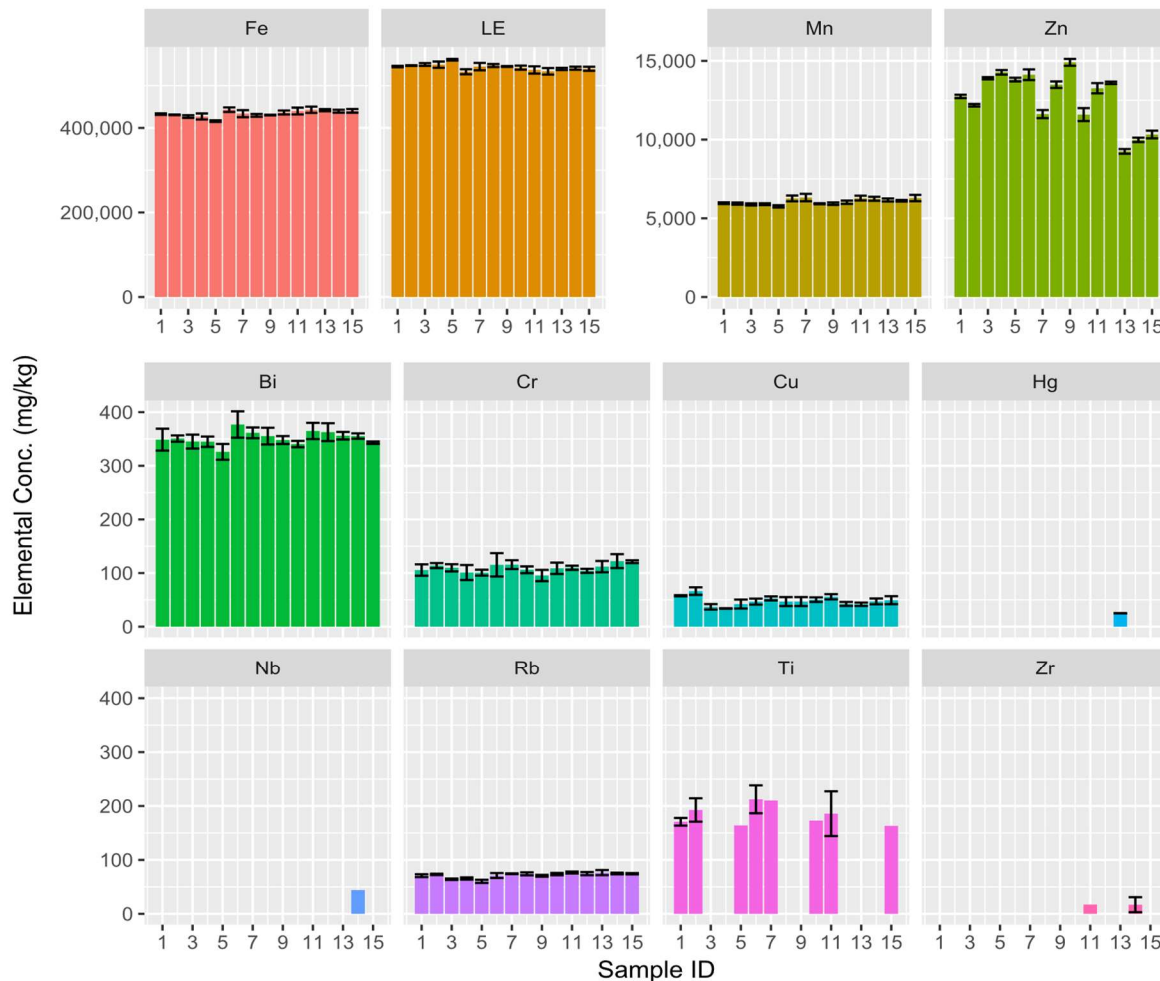


Figure 5. Elemental concentration from SLEMS samples determined by portable XRF.

3.3 MINERAL SEPARATION

Mineral separation work was carried out at CTP in Belgium and at Buntings Magnetics in the UK.

As mentioned previously one of the 30Kg samples of the recovered material was supplied to CTP in to carry out separation tests using mineral processing techniques on a lab scale. The proposed treatment line included screening and magnetic separation equipment. Wet screening with different mesh sizes allowed tightening of the particle size range to improve the efficiency of the magnetic separation processes. Magnetic separation allowed the recovery of valuable ferrous metal fractions separately from non-ferrous fraction.

Separation tests using mineral processing techniques including wet screening and magnetic separation equipment were carried out on a lab scale. The chemical analysis of the material showed that the screening did not allow the separation of a richer ferrous fraction as each granulometric range had a very similar chemical composition (55-57% Fe). In addition, the material was found to be predominantly magnetic. The performance of magnetic separation tests using various equipment operating in dry and wet conditions led to the removal of most of the material at very low magnetic susceptibilities. Magnetic separation techniques did not

seem efficient for SLEMS BOS oxide material. The full results were reported in Del. T2.1.1 Preliminary report on Mineral Processing lab scale tests on samples from Teesside site [1]

A similar exercise was initiated by The Materials Processing Institute with Buntings Magnetics as an external tester. A sample of the SLEMS material was sent to Buntings Magnetics for electrostatic and magnetic separation testing at the laboratory scale. The results are included as Appendix B.

This test work clearly indicated that the magnetic fraction (iron oxide) was fully distributed through the material and in every size fraction. There was little or no enrichment of the materials by either electrostatic or magnetic separation.

3.4 BIOLOGICAL AND CHEMICAL HYDROMETALLURGY

Fifteen samples taken from Teesworks were sent to Cranfield University and these were subjected to hydrometallurgical testing. Hydrometallurgy is a process by which desirable elements are extracted by leaching them from a material using a solvent or biological agents.

3.4.1 Batch testing

3.4.1.1 Bioleaching

To assess the impact of various parameters on the dissolution of metals from BOS dust the Taguchi orthogonal array design L9 (3^4) was chosen. This design involved optimising four parameters, including solid concentration (1, 5 and 10% w/v), energy source concentration (1%, 2% and 3% w/v), inoculum concentration (1, 5 and 10% v/v) and pH (1.5, 1.75, and 2), in three different levels under 9 different conditions (Table 2). The inoculum aids in the growth of the microbes. Actively growing culture of *Acidithiobacillus ferrooxidans* (DSM 583) was sourced from the Leibniz Institute (DSMZ), Braunschweig (Germany). The culture was adapted to 5% (w/v) of BOS dust as detailed in [2]. As a growth medium, modified basal salt medium (MBSM) consists of 2 g of $(\text{NH}_4)_2\text{SO}_4$, 0.25 g of K_2HPO_4 , 0.25 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.10 g of KCl and 0.01 g of $\text{Ca}(\text{NO}_3)_2$ in 700 mL of deionised water and a ferrous iron ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) solution with different concentration according to Table 2 in 300 mL deionised water was used [3]. Experiments were performed under 100 ml working volume. A two-step bioleaching approach was employed for this study [4]. In the first step, the growth media were placed into 250 mL flasks, and the pH was adjusted to the different levels (Table 2, parameter D). Before inoculation, an equal amount of growth medium volume was discarded from the flask to create volume for inoculum. The flasks were inoculated with different concentrations (Table 2, parameter C) and incubated at 30°C on an orbital shaker at 150 rpm (Figure 6). Throughout the experiment, the oxidation-reduction potential (ORP) and pH of the culture were monitored on a daily basis, with pH being adjusted as necessary, except for the goethite material where pH and ORP were only monitored and adjusted on the designated sampling days (days 0, 1, 3, 5, 8, 11, 16). In the second step, after 2 days of incubation, different amounts of materials were added into the flasks (Table 2, parameter A).

Table 2: Taguchi L9 (3⁴) experimental design for both BOS-D. Conc. stands for concentration.

Conditions	Factors and their variation levels			
	BOS-D			
	Solid conc. (A)	Energy source conc. (B)	Inoculum conc. (C)	pH (D)
C1	1	1.11	1	1.5
C2	1	2.22	5	1.75
C3	1	3.33	10	2
C4	5	1.11	5	2
C5	5	2.22	10	1.5
C6	5	3.33	1	1.75
C7	10	1.11	10	1.75
C8	10	2.22	1	2
C9	10	3.33	5	1.5

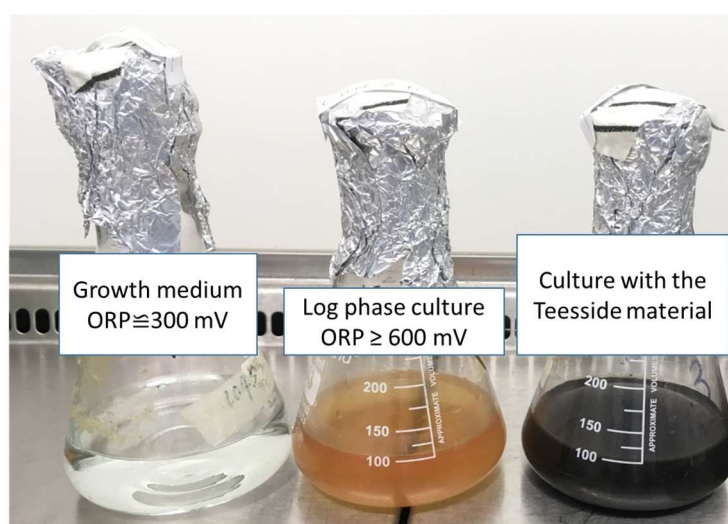


Figure 6. Flasks showing growth medium phase and with Teesworks sample.

Results

To compare bioleaching efficiency on shake flask Mn, Zn, Pb, Al, Li, Co, Y, Ce were selected due to some of them being the most abundant metals, critical and rare earth elements. After 14 days of bioleaching, both materials, highest metal dissolution was achieved using 1% (w/v) solid concentration. From BOS dust, highest metal recovery from majority of selected elements, Zn, Pb, Al, Li and Y, was achieved under the condition of 1% solid concentration, 1% energy source concentration, 1% inoculum concentration, and pH 1.5 among nine conditions (**Error! Reference source not found.**). Under this condition, 54% Mn, 61% Zn, 13% Pb, 59% Al, 92% Li, 40% Co, 99% Y and 67% Ce were dissolved from BOS-D. These percentages correspond to 3.2 mg Mn, 11.2 mg Zn, 0.2 mg Pb, 1.6 mg Al, 0.004 mg Li, 0.004 mg Co, 0.001 mg Y and 0.0026 mg Ce extraction. Overall, 0.012 mg of REE, 0.09 mg of critical metals, 11.5 mg of heavy metals and 4.8 mg other metals were extracted from 1 g of BOS dust (Table 1).

Table 1. Bioleaching yield (%) and amounts of recovered elements from BOS-D

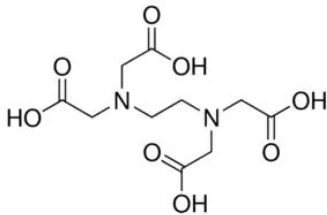
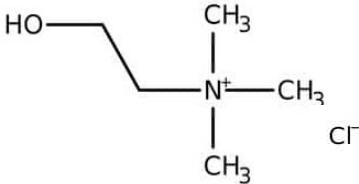
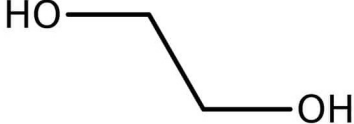
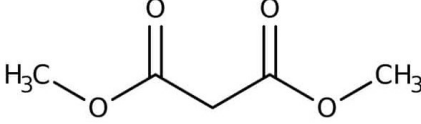
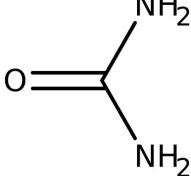
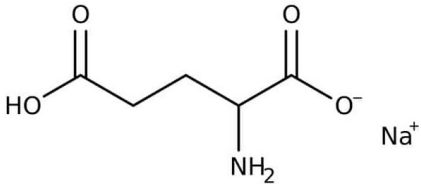
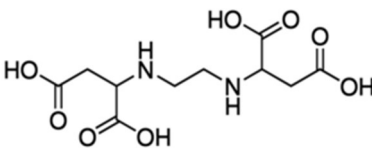
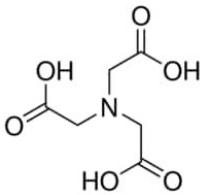
Element	BOS-D	
	Bioleaching yield (%)	Amounts of recovered element (mg)
Rare Earth Elements		
Yttrium	99	0.0013
Lanthanum	-	-
Cerium	67	0.0026
Praseodymium	163	0.0007
Neodymium	80	0.0014
Samarium	184	0.0006
Europium	833	0.0005
Gadolinium	259	0.0007
Terbium	1041	0.0006
Dysprosium	186	0.0005
Holmium	971	0.0005
Erbium	573	0.0007
Thulium	1475	0.0005
Ytterbium	420	0.0005
Lutetium	1488	0.0005
Total REE		0.012
Critical metals		
Lithium	92	0.00
Cobalt	40	0.00
Antimony	7	0.00
Copper	61	0.08
Total critical metals		0.09
Heavy metals		
Chromium	15	0.0
Nickel	23	0.0
Zinc	61	11.2
Cadmium	117	0.1
Mercury	253	0.0
Lead	13	0.2
Total heavy metals		11.5
Others		
Beryllium	1069	0.0
Boron	231	0.1
Aluminium	59	1.6
Vanadium	21	0.0
Manganese	54	3.2
Gallium	6	0.0
Barium	26	0.0
Rhenium	1391	0.0
Total other metals		4.8
Total elements		16.4

3.4.1.2 Chemical leaching

The solvometallurgy study investigated the efficiency of solvents to extract metals, with an emphasis on critical metals; Fe, Cu, Zn, Pb, Li, Al, Cr, Mn, Co, Ni, and Cd, from BOS. Green solvents have been developed to be a more environmentally friendly (biodegradable, recyclable, non-corrosive *etc.*,) alternative to petrochemical solvents. Two types of “green”

solvents were tested – deep eutectic solvents (DES), using Choline Chloride as a hydrogen bond acceptor mixed with different hydrogen donors, Malonic acid, Ethylene glycol and Urea (Table 4). These were studied at different ratios of acceptor to donator. The second green solvents chosen were Chelating agents (CA), L-glutamic acid N N-diacetic acid tetrasodium salt (GLDA), Ethylenediamine-N,N'-disuccinic acid (EDDS), Nitrilotriacetic acid (NTA) (Table 4), which were tested and buffered to pH 4, 6 and 8.

Table 4. Chemical structure, concentration and supplier of chosen solvent.

Control		
<u>Ethylenediaminetetraacetic Acid</u>		
		
0.5 M		
Sigma Aldrich		
Deep Eutectic Solvents		
Hydrogen Bond Acceptor		
<u>Choline Chloride</u>		
		
0.1 M		
Fisher Scientific		
Hydrogen Bond Donator		
<u>Ethylene Glycol</u>	<u>Malonic Acid</u>	<u>Urea</u>
		
1 M	0.1 M	1 M
Fisher Scientific	Fisher Scientific	Fisher Scientific
Chelating Agents		
<u>L-glutamic acid N,N-diacetic acid tetrasodium salt</u>	<u>Ethylenediamine-N,N'-disuccinic acid</u>	<u>Nitrilotriacetic acid</u>
		
0.1 M	0.1 M	0.1 M
Fisher Scientific	Sigma Aldrich	Sigma Aldrich

In the static batch study, the solvents were mixed with BOS dust at a 12.5% (w/v) and in dynamic study 7.5% to aid filtration. Within the static study, the samples were agitated (150 rpm) for 15 minutes and left to settle for 2 hours, before being filtered. The leachate was collected and stored for analysis (Figure 7). Within the dynamic study, the solvents were pumped through the column continuously at 80 mL/s for 2 hours at room temperature (22 °C). The leachate phase was extracted, filtered and stored for analysis (Figure 7).

Ethylenediaminetetraacetic acid (EDTA) at concentration 0.5 M, was used as a control for conventional solvometallurgical practices, which are considered unsustainable and not environmentally friendly.

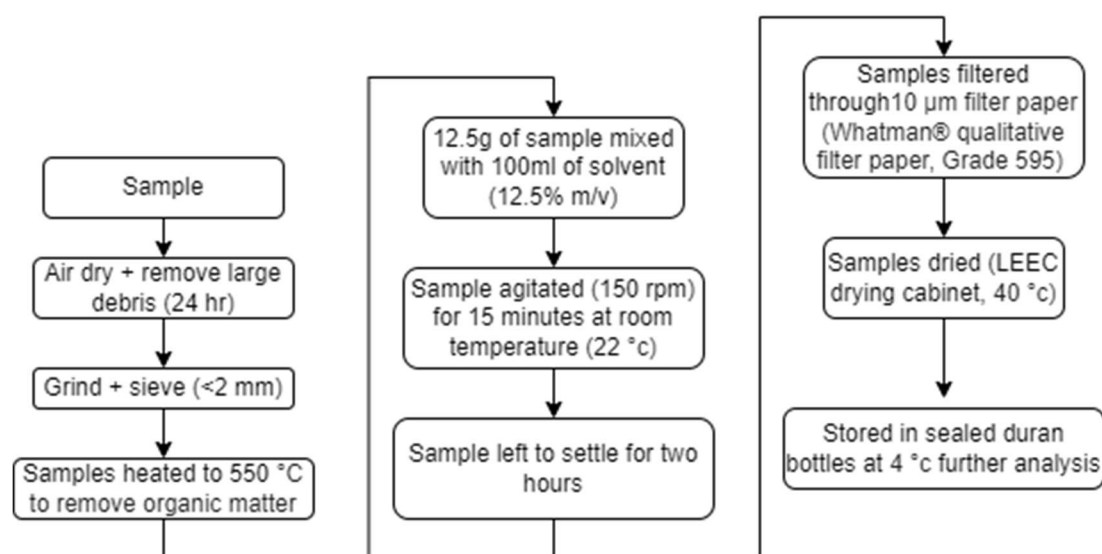


Figure 7. Experimental design of batch studies for metal extraction using green solvents.

Results

In BOS, highest total metal extracted using DES was between 47% and 57.7%. On average across the three ratios, 1:1, 1:2 and 2:1, ChCl-EG extracted 56%, ChCl-MA extracted 55% and ChCl-U extracted 48% (Figure 8). Varying the ratio in each DES ratio did vary the total metal extracted this sequence was, 1:1 > 1:2 > 2:1. This can be attributed to an imbalance in hydrogen bond acceptors, doubling the concentration of ChCl increases competition for reducing elements, this leads up to a 10% decrease in total metal extracted across all DES.

The highest metal extracted observed from DES in dynamic studies was ChCl-EG at 1:1 the individual metal extraction was; Pb (66%) > Fe (65%) > Cr, Zn, Cd (63% each) > Co (62%) > Ni, Mn (60% each) > Cu (58%) > Li (47%) (Figure 6). ChCl-U had the lowest total metal extracted, 53%, 51% and 41% at 1:1, 1:2 and 2:1 respectively. The total metal extraction using ChCl-U was 68,803.45 mg/kg, 57% less than total metal extraction using ChCl-EG, 120,675.77 mg/kg.

The EDTA pH 4 total metal extraction was 48%, a 11% decrease when compared to ChCl-EG at 1:1. Lead extraction was highest in the EDTA control batches at 77%, suggesting that DES are a more robust metal extracted option as the extracted was more homogeneous across a wider suite of metals. The results from this batch study conform to previous studies and suggest

that DES will prove to be a more effective solvent for metal extraction whilst being more sustainable than conventional EDTA solvents.

Deep Eutectic Solvents

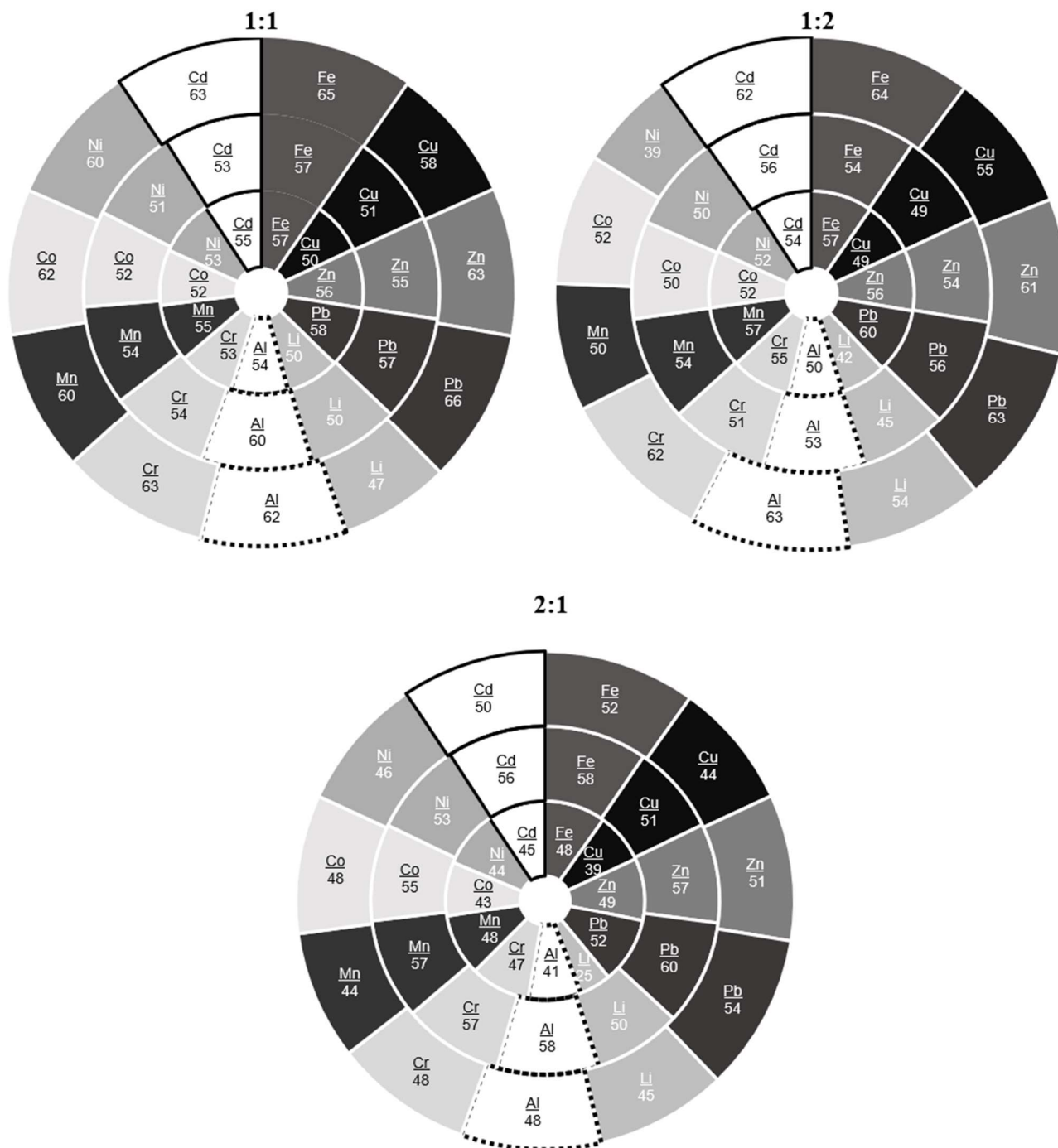


Figure 8. Metal extraction efficiencies (%) from the static study using DES in three ratios 1:1, 1:2 and 2:1 on BOS. The rings from outer to inner represent ChCl-EG, ChCl-MA and, ChCl-U, respectively.

The average total metal extracted for CA was between 32% and 34%, with EDDS extracting the highest total metal percentage. At pH 6 the lowest metal extraction percentage was observed although variations were only 2% on average. At pH 4 EDDS extracted the highest total metal

percentage, the order of critical metal extraction was Pb (62%) > Cd (56%) > Zn (53%) > Ni (48%) > Mn (46%), Cr (46%) > Co (45%) > Fe (42%), Cu (42%) > Al (34%) > Li (31%) (Figure 3).

EDTA is also a chelating agent so would be expected to perform the same as the green CA used in this batch study. On average EDTA pH 4 extracted 48% of BOS whereas CA extracted 30% on average. This suggests that there is no benefit, aside from environmental reasons, to choose CA over the use of EDTA in metal extraction.

The overall metal extraction was more effective when DES was applied. The total metal extracted using EDDS was 109,879.12 mg/kg, whereas ChCl-EG was 120,675.77 mg/kg, a 9% increase. This is due to differences in individual metal extractions and their initial concentration. However, individual metals showed similar extracted efficiencies in CA as DES including Pb, Mn, Ni and Zn depending on the CA and pH (Figure 9).

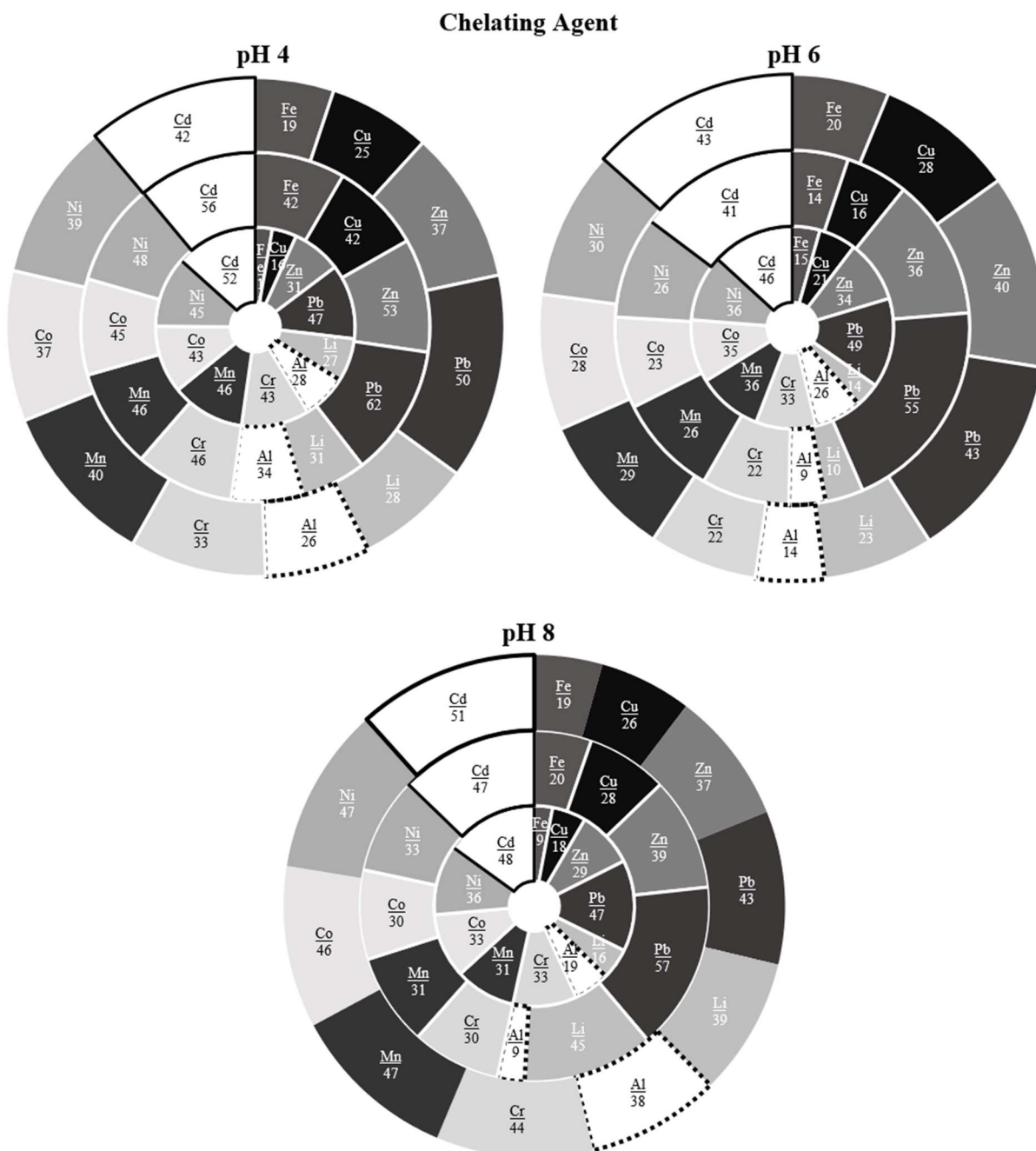


Figure 9. Metal extraction efficiencies (%) from the static study using CA in three pH levels 4,6, and 8 on BOS. The rings from outer to inner represent GLDA, EDDS and NTA respectively.

3.4.2 Continuous flow column tests

3.4.2.1 Bioleaching

According to Taguchi statistical analysis the joint optimum condition was defined as 1% solid concentration, 1% energy source concentration, 1% inoculum concentration and pH 1.75 for Y, Ce, Nd, Li, Co, Cu, Zn, Mn, Al elements. Column bioleaching was performed to evaluate the effect of the irrigation rate, 40 mL/min and 80 mL/min, to the bioleaching yield. The column used in bioleaching study was made from PVC with a 5 cm diameter × 30 cm height. A total of 10 g, 1% (v/v), of air-dried and autoclaved BOF dust was filled in between two glass wool layers in the column having PVC support plate with multiple holes at the base (Figure 10). Two-step bioleaching approach were performed for column bioleaching study [4]. First, 1000 ml of growth medium contains 1.11% of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at pH 2 was prepared and placed in a 2 litres plastic container. 10 ml of medium was discarded, and then inoculated with 1% (v/v) of log phase (≥ 600 mV) *A. ferrooxidans* culture (Day 0). After it reached the log phase, first step was completed. As second step, columns were fed from the bottom from the reservoir at a flow rate of 40 mL/min and 80 mL/min, which was controlled by a peristaltic pump (Watson-Marlow), and bioleaching started (Day 2). Sample was in submerged condition during experiment. For control experiments 1000 growth medium without inoculum were used with same conditions with 40 mL/min irrigation rate. Reservoirs were kept in a water bath at 30°C.

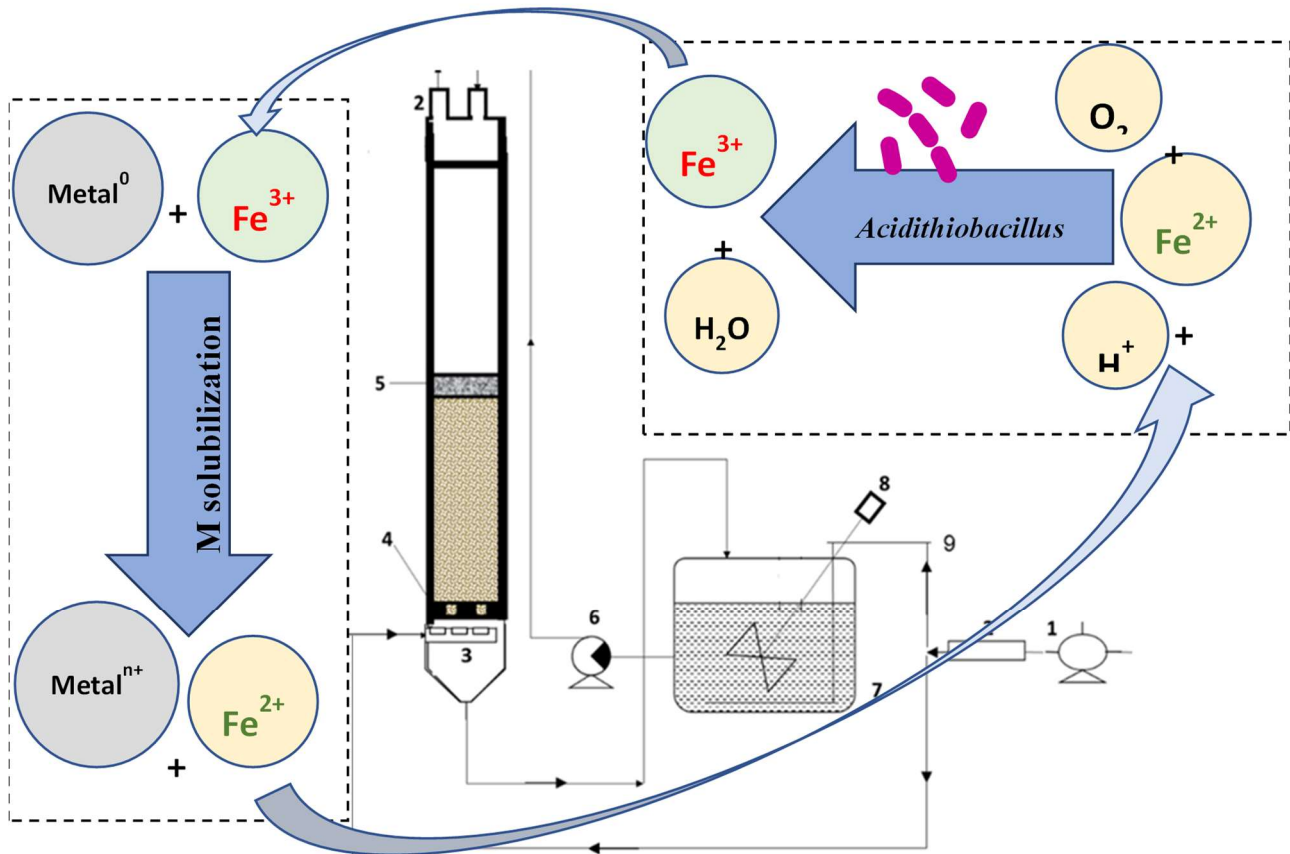


Figure 10. Column setup for bioleaching trials.

Results

To compare bioleaching efficiency on column scale Y, Ce, Nd, Li, Co, Cu, Zn Mn and Al were selected. Results indicated that 69% Y, 48% Ce, 53% Nd, 37% Li, 32% Co, 40% Cu, 36% Zn, 41% Mn and 39% Al were dissolved under 40 ml/min irrigation rate. Under 80 ml/min irrigation rate 66% Y, 48% Ce, 52% Nd, 43% Li, 31% Co, 47% Cu, 35% Zn, 41% Mn and 40% Al were leached. Overall, 0.04 mg of REE, 0.6 mg of critical metals, 66.4 mg of heavy metals and 35.4 mg other metals were extracted under 40 ml/min irrigation rate and 0.04 mg of REE, 0.6 mg of critical metals, 65.6 mg of heavy metals and 36 mg other metals were extracted under 80 ml/min irrigation rate from 10 g of BOS dust (Table 5). Leaching results from column experiment were lower than shake flask experiments and control experiments (results not shown). This may have been caused by several things for example the heat lost and insufficient solid-liquid-gas interaction in the column or pH adjustment in long intervals comparing to shake flask. More study and controlled environment are needed to use percolation method as industrial application (vat leaching)

Table 5. Bioleaching yield (%) and amounts of recovered elements from BOS-D on column scale using different irrigation rates.

	40 ml/min		80 ml/min	
Element	Bioleaching yield (%)	Amounts of recovered element (mg)	Bioleaching yield (%)	Amounts of recovered element (mg)
REE				
Yttrium	69	0.0089	66	0.0086
Cerium	48	0.0186	48	0.0185
Praseodymium	35	0.0016	38	0.0017
Neodymium	53	0.0095	51	0.0093
Samarium	41	0.0014	43	0.0015
Europium	0	0.0000	0	0.0000
Gadolinium	46	0.0013	40	0.0011
Terbium	0	0.0000	0	0.0000
Dysprosium	35	0.0009	42	0.0010
Holmium	0	0.0000	0	0.0000
Erbium	10	0.0001	19	0.0002
Thulium	0	0.0000	0	0.0000
Ytterbium	9	0.0001	8	0.0001
Lutetium	0	0.0000	0	0.0000
Total REE		0.04		0.04
Critical metals				
Lithium	37	0.02	43	0.02
Cobalt	32	0.03	31	0.03
Antimony	0	0.00	0	0.00
Copper	40	0.51	47	0.59
Total critical metals		0.6	0.56	0.6
Heavy metals				
Chromium	13	0.2	10	0.2
Nickel	24	0.1	25	0.1
Zinc	36	65.6	35	64.9
Cadmium	74	0.5	77	0.5
Mercury	0	0.0	0	0.0
Lead	0	0.0	0	0.0
Total heavy metals		66.4	66.4	65.6
Others				
Beryllium	17	0.0	0	0.0
Boron	485	1.2	434	1.0
Aluminium	39	10.4	40	10.6
Vanadium	0	0.0	0	0.0
Manganese	41	23.9	41	24.3
Gallium	0	0.0	0	0.0
Barium	0	0.0	0	0.0
Rhenium	0	0.0	0	0.0
Total other metals		35.4		36.0
Total elements		102.4		102.3

The highest metal recovery from BOS dust was achieved at 1% solid concentration, 1% energy source concentration, 1% inoculum concentration, and pH 1.5. Solid concentration emerged as the most influential parameter, followed by pH. Regular monitoring and adjustment of pH can effectively prevent the formation of jarosite and enhance the bioleaching yield.

According to Taguchi statistical analysis the joint optimum condition for recovery of Y, Ce, Nd, Li, Co, Cu, Zn Mn and Al from BOS dust was defined as 1% solid concentration, 1% energy source concentration, 1% inoculum concentration, and pH 1.75. When the effect of different irrigation rate was tested on bioleaching rate on column scale, it was observed that all the metal dissolution was lower than shake flask experiments as well as control. This may have been caused by several things for example the heat lost and inefficient microorganism-leaching agent-material interaction when volume increased, or pH adjustment was in long intervals comparing to shake flask. More study and controlled environment are needed to use percolation method as industrial application. As a scale-up alternative, at this stage, stirred tank reactor can be suggested for an industrial application of bioleaching for BOS dust. More study is needed to recover metals from the leachate.

3.4.2.2 Chemical leaching

The column study ran at 7.5% m:v ratio compared to batch studies which were ran at 12.5%. This was to improve filtration of the solvent through the column but may hinder potential metal extraction as a result (Figure 11). The column study investigated the impact continuation infiltration and recirculation (at 80 mL/min) has on the extraction efficiency of solvents, compared to agitation and settlement investigated in the batch study.

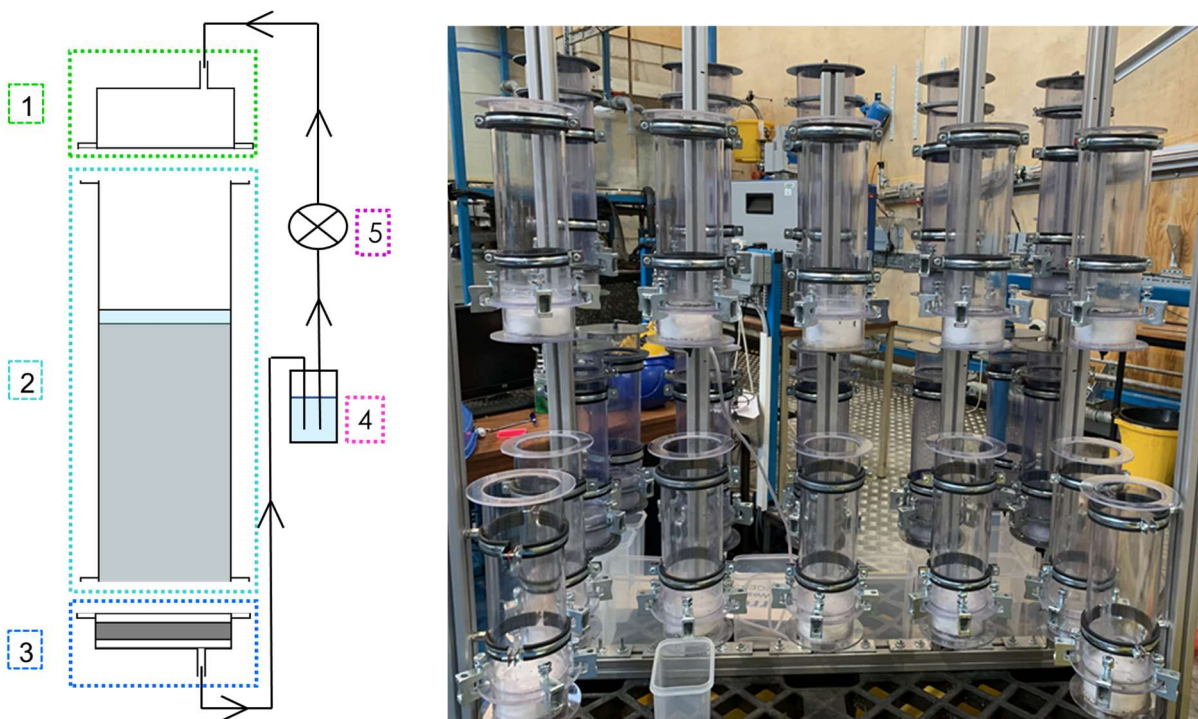


Figure 11. Column setup for chemical extraction trials.

Results

Total metal extraction from BOS was 29%, 28% and 25% for ChCl-EG, ChCl-U and ChCl-MA respectively. The total metal extraction decreased in the order of, 1:1 > 2:1 > 1:2. This can be attributed to changes in viscosity, where less viscous mixtures had the higher extraction percentages.

The average metal extraction from BOS using ChCl-EG at 1:1, 1:2 and 2:1 was 32%, 27% and 31% respectively (Figure 12). The highest total metal extraction was measured after ChCl-EG at 1:1, the breakdown in metal extraction was; Fe, (89.46%) > Pb (64.07%) > Cu (62.85%) > Cr (60.68%) > Li (49.19%) > Co (46.47%) > Ni (42.43%) > Cd (39.63%) > Zn (38.72%) > Al (18.49%) > Mn (16.39%) (Figure 3). It can be noted that Fe, Cu and Li extraction is improved, for Fe this was up to 100% improvement, through dynamic leaching.

Although ChCl-EG has the highest average total metal extraction efficiency (30%), total metal extracted was greatest using ChCl-MA, 212,686.8 mg/kg compared to 181,078.45 mg/kg using ChCl-EG, a difference of 31,608.35 mg/kg. This is due to differences in individual metal extractions and their initial concentration.

The static study had increased extraction efficiency when using DES compared to the dynamic study. This could be attributed increase m/v ratio, an increased contact time between particles and solvent due to the agitation stage, further promoting the complexing of metal oxides in BOS.

In the dynamic study, the extraction efficiency of EDTA pH 4 was higher than DES at 34%. The operational conditions of the dynamic study may have hindered the extraction capabilities of DES, which were superior in the static batches, see recommendations for to see future work suggestions.

Deep Eutectic Solvents

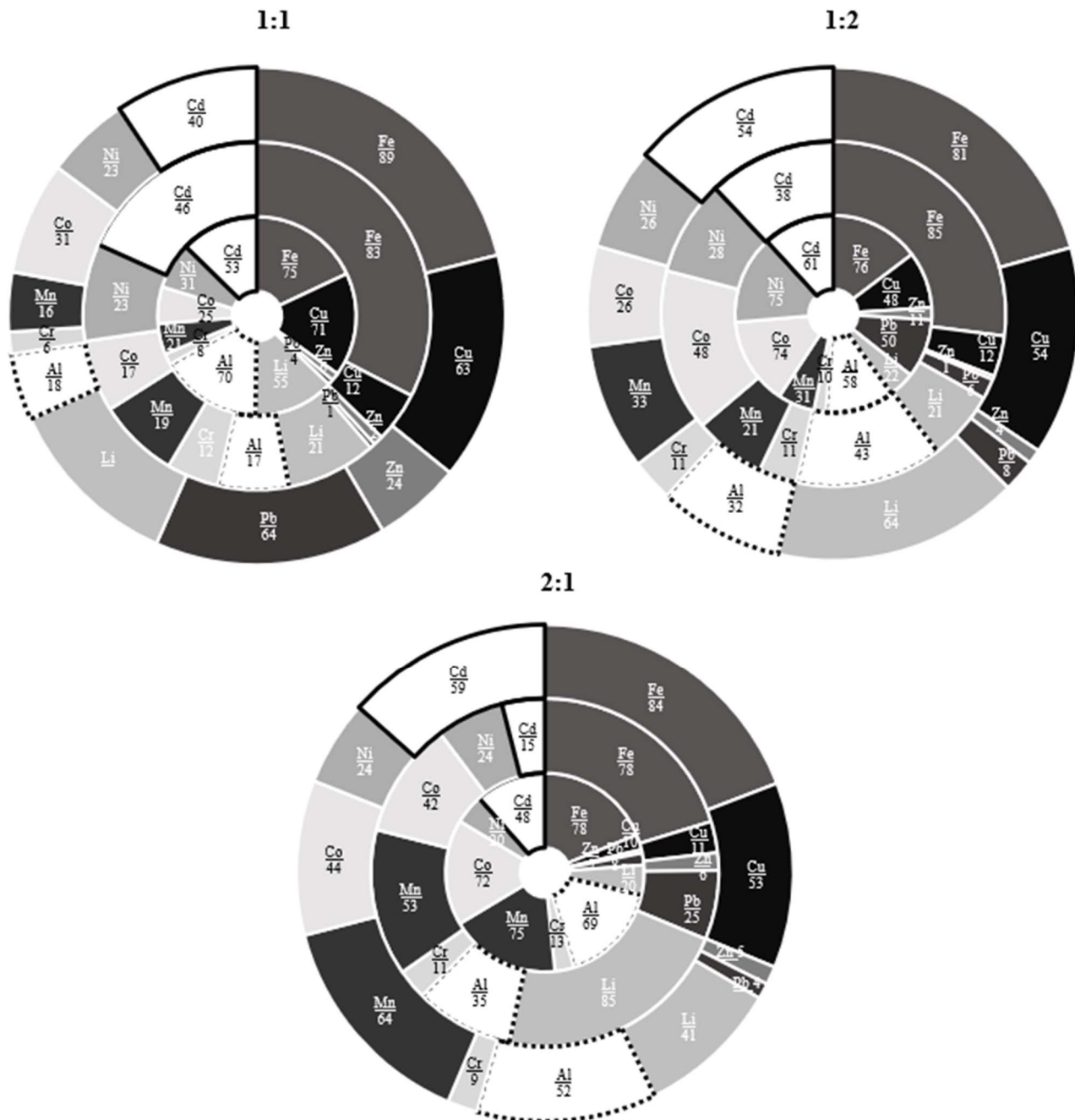


Figure 12. Metal extraction efficiencies (%) from the dynamic study using DES in three ratios 1:1, 1:2 and 2:1 on BOS. The rings from outer to inner represent ChCl-EG, ChCl-MA and, ChCl-U, respectively.

The order of extraction efficiency for all metals when using CA in the dynamic study was; NTA (34%) > EDDS (34%) > GLDA (25%) with pH 4 as the most effective pH level (Figure 13). There was no significant difference in average CA for critical metal extraction; EDDS 42%, NTA 41% and GLDA 44%. The most efficient CA for critical metals was GLDA pH 8 with 54% of critical metals extracted. The order of extraction of critical metals from GLDA pH 8 was; Cd (98.72%) > Cu (83.76%) > Zn (73.79%) > Fe (71.06%) > Mn (62.56%) > Co (60.36%) > Al (52.06%) > Li (47.45%) > Ni (18.57%) > Pb (13.42%) > Cr (12.08%) (Figure 13). The most extracted critical metals were Cd using NTA pH 4 82.2%, attributable to acidic conditions and specificity of NTA, and Pb using EDDS pH 6 at 82.5%, potentially due to higher complexation constants between GLDA and Pb.

Both EDDS and NTA pH 6 had superior average total metal extraction compared to EDTA, 36%, 35% and 30% respectively. The extraction efficiency of GLDA pH 4 was 23%, not sufficient to outcompete EDTA. Again, the enhanced extraction efficiency of CA in dynamic conditions could be derivable from changes in m/v ratio, contact time and agitation. If the dynamic study is scaled, the extraction efficiency of EDDS and NTA could present as a sustainable alternative to EDTA for industrial applications.

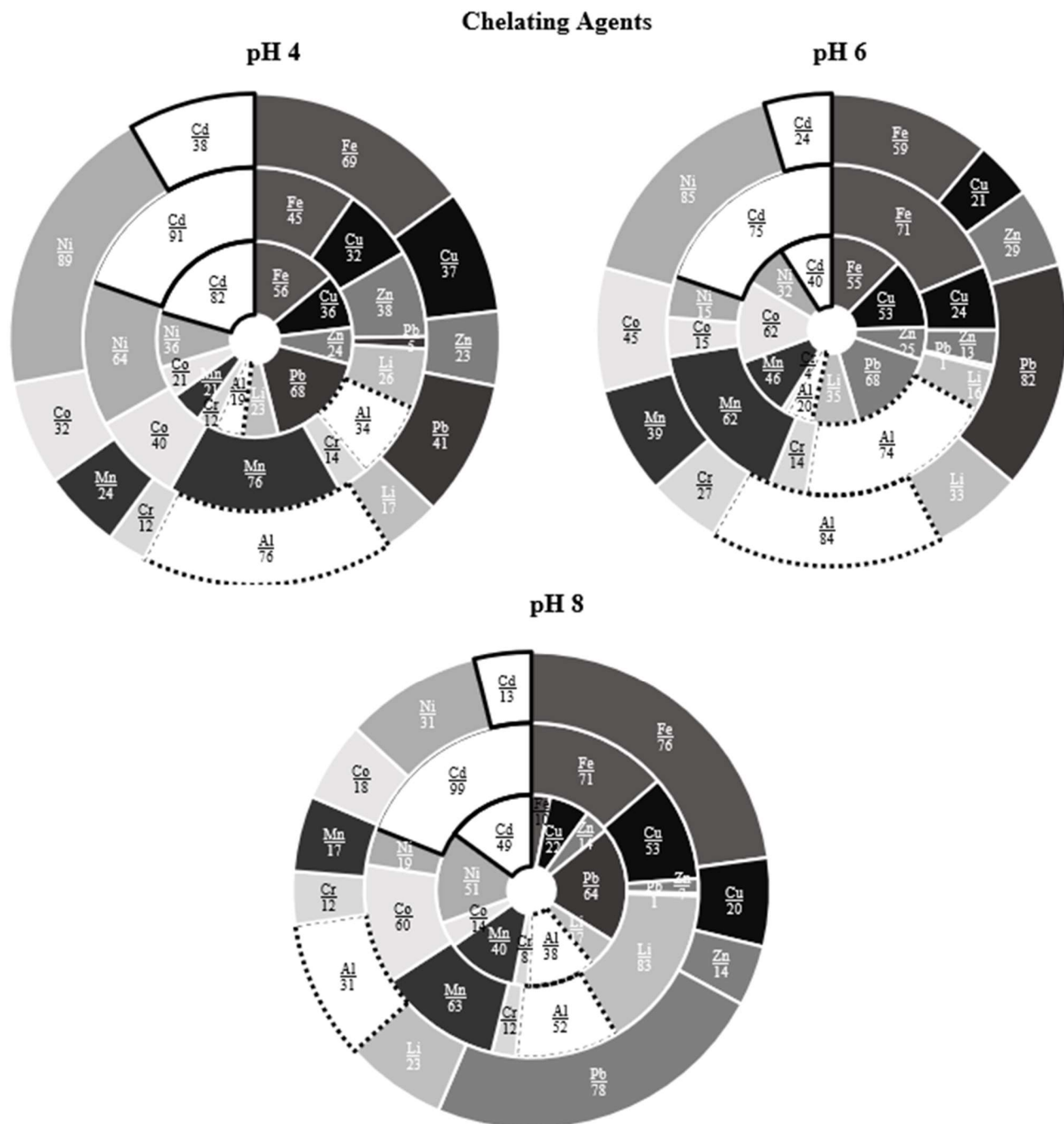


Figure 13. Metal extraction efficiencies (%) from the dynamic study using CA in three pH levels 4,6, and 8 on BOS. The rings from outer to inner represent GLDA, EDDS and NTA.

A comparison between batch and column extraction is provided in Figure 14.

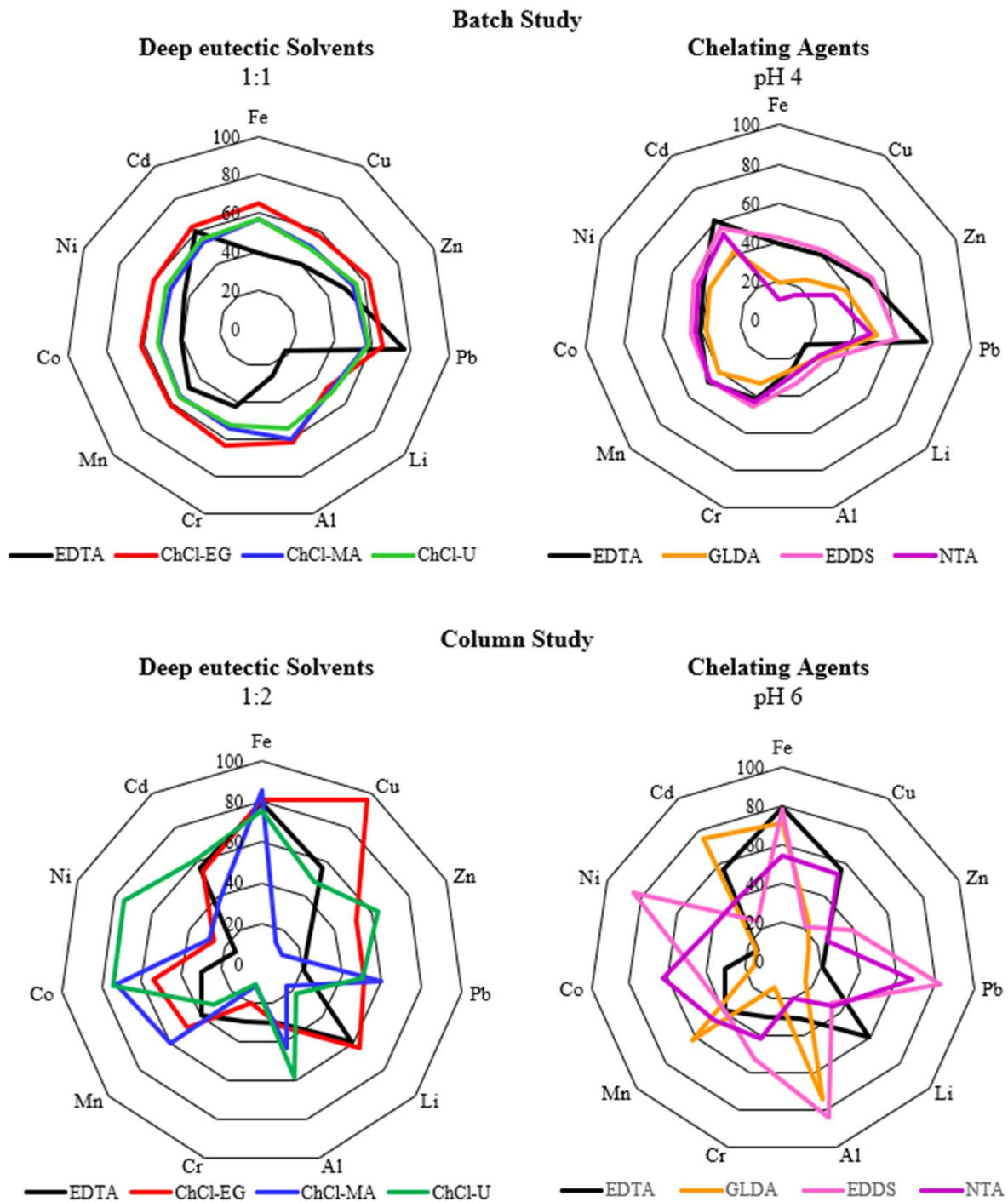


Figure 14. Comparison of extraction efficiencies between the most efficient solvent conditions for DES and CA against EDTA in static and dynamic conditions

The results from these static and dynamic studies have been used to develop an initial criterion for green solvent selection (Table 6).

Table 6. Recommendations of green solvents for dynamic leaching columns based on metal type.

Metal Type	Solvent Recommendation
Alkaline Metals (Li)	ChCl-EG (1:2) ChCl-U (1:1)
Alkaline Earth Metals (Mg, Ba)	ChCl-U (1:1) NTA (pH 6)
Transition Metals (Fe, Cu, Sc, V, Cr, Mn, Co, Ni, Y, Mo, Ir)	ChCl-EG (2:1) EDDS (pH 4)
Other Metals (Zn, Pb, Al, Ga, Cd)	EDDS (pH 4 & 6) NTA (pH 4)
Rare Earth Lanthanides (La, Ce, Nd)	NTA (pH 6 & 8)

A suggestion to maximise metal extracted based on Table 6 is as follows; contaminated soil should then be washed with NTA at pH 4 followed by NTA at pH 6. This should be followed sequentially by ChCl-EG and ChCl-U at a ratio of 1:1 increasing the ratio of the hydrogen bond donator and then hydrogen bond acceptor over time.

Wherever timely extraction is essential, the application of chelating agents, (either acidic EDDS or NTA) should be followed by deep eutectic solvents (combination of ChCl-EG or ChCl-U) increasing the ratio of the hydrogen bond donator and then hydrogen bond acceptor over time.

3.4.3 Leachate analysis

Recovered leachate samples were analysed using inductively coupled plasma mass spectrometry (ICP-MS). The use of ICP-MS provides a robust form of analysis for the whole suite of metals in this study. A comparison between the extraction efficiencies between bioleaching and chemical extraction is provided in Figure 15. Bioleaching significantly out-performed chemical extraction for Mg, Li, Ce and Y, whilst chemical extraction was comparable for other metals. Extraction of Zn was greatest in chemical extraction trials. This highlights opportunities to selectively recover metals in sequential processes, using optimum conditions to target specific metals.

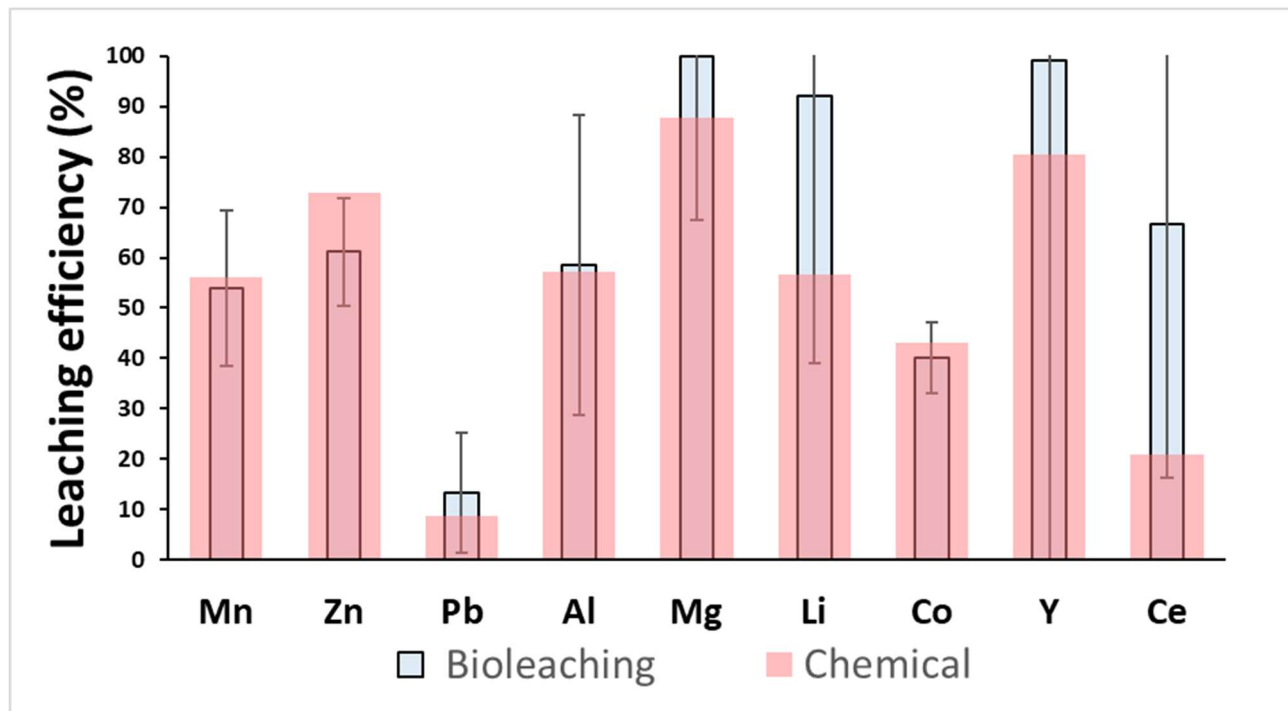


Figure 15. Comparison of bioleaching to chemical extraction for selected metals.

4 POST SAMPLING - CLE31

Geophysical investigations were carried out on CLE31. During the measurement campaign samples were collected from the surface and sub-surface (~20cm depth) of 17 locations and selected to overlap with geophysical measurements and capture the full range of conditions observed on-site and through initial geophysical measurements. 3 replicates were taken at each location, and these were split and taken by Cranfield University, BRGM and Materials Processing Institute. Deliverable I1.2.3 presents the correlation of rapid assessment methods with conventional techniques.

Samples underwent 5 sample treatment steps; sieving to <2mm; drying at 105°C for 24 hours (ISO 11465:1993); transfer to portable X-ray fluorescence spectrometry (pXRF) sample cups; grinding with a disk mill for 18 seconds to produce a fine powder; and ignition at 450°C for 4 hours to remove organic matter (BS EN 13039:2000).

Before and after each sample treatment step replicate pXRF measurements were taken using a Delta Premium (Olympus USA) with Rh X-ray tubes in soil mode using the steal suitcase accessory.

Following pXRF measurements, all samples underwent microwave-assisted acid digestion following (ISO 11047:1998). Briefly, 0.5 g of sample was dissolved in Aqua regia (HCl: NHO₄, 6 ml:2 ml Fisher Brand, UK) followed by the standard microwaving program. after cooling digestate was filtered and diluted in deionised water in volumetric flasks (100ml) and stored at room temperature until analysis by induction coupled plasma-mass spectrometry (ICP-MS) (PerkinElmer NexION 350D).

An overview of the metals analysis following ICP-MS and portable XRF are shown in Figure 16.

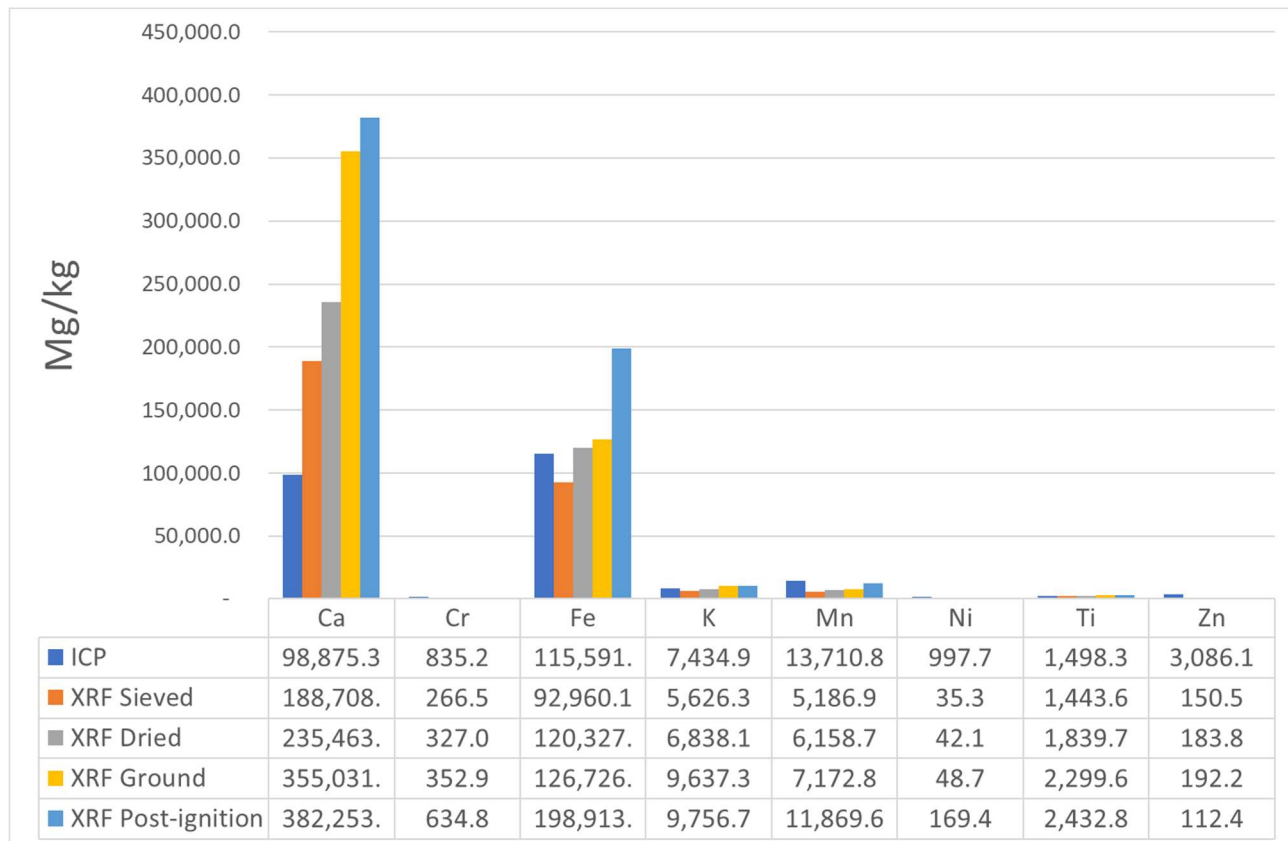


Figure 16. Metals analysis of CME31 samples using ICP-MS and pXRF.

There was significant variation between ICP-MS and pXRF results, particularly for Ca and Fe. Further analysis of the ICP-MS, pXRF and geophysical datasets is provided in Deliverable I1.2.3.

A plan was produced to follow up the surface samples with bore holes targeted to corroborate the results of the geophysical investigation.

Meetings were held with the site representatives to discuss the logistics of performing the sampling exercise. The CLE31 is classed as “Closed” and the site remains in “Aftercare” which means that it is still managed under an active waste management licence. Any works undertaken to the landfill such as drilling boreholes must be managed under CQA (Construction Quality Assurance) regulations to gain approvals from the UK Environment Agency to drill into a permitted landfill. This will require a specialist consultant to submit a plan/method statement (outlining the works and how the boreholes would be reinstated); verification report (detailing the outcome of the works); and supervision of the site work to ensure that it is carried out in accordance with the agreed plan.

In addition, a specialist drilling company would be required to perform the core drilling exercise.

Quotations were obtained for the costs and timescales required to perform the sampling. The combined costs of supervision and excavation were a minimum of 70,200 Euros and with a lead time of at least a month. It was decided that it would not be possible to perform the work both in terms of timescales and financially within the remaining project.

5 SUMMARY OF RESULTS

5.1 HISTORICAL DATA

SLEMS Material

- Chemical analysis from reference material

5.2 PRE SAMPLING

SLEMS Material

- Elemental analysis of samples
- Metal concentrations was determined using a portable X-Ray fluorescence spectrometer
- Mineral separation data
 - CTP
 - Buntings
- Hydrometallurgy
 - Bioleaching
 - Batch testing
 - Continuous Column tests
 - Chemical (Solvent) leaching
 - Batch testing
 - Continuous Column tests

5.3 POST SAMPLING

CLE 31 Material

- Metal concentrations was determined using a portable X-Ray fluorescence spectrometer
- Elemental analysis of samples

6 REFERENCES

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bioleaching from past metallurgical sites and waste deposits: UK case study, *Detritus*, 21: 62-71. <https://doi.org/10.31025/2611-4135/2022.17232>

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7 APPENDIX A – HISTORICAL ANALYSIS OF SLEMS MATERIAL

Sample ID			TP101	TP102	TP103	TP104	TP105	TP106	TP107	TP108	TP109	TP110
Depth	MDL	Units	2	2.5	1	1	3	2.5	1	5	3.8	4.5
Sampling Date			26/03/18	26/03/18	26/03/18	27/03/18	26/03/18	27/03/18	26/03/18	27/03/18	27/03/18	26/03/18
Metals												
Aluminium	1	mg/kg	14000	8400	2900	2100	1800	5200	1800	8200	920	6400
Antimony	1	mg/kg	6.1	4.6	15	15	14	6.7	13	11	14	9.2
Arsenic	0.2	mg/kg	2	6.6	7.8	14	11	26	11	43	13	2.1
Barium	1.5	mg/kg	460	120	86	68	50	120	51	72	44	110
Beryllium	0.2	mg/kg	0.6	1	< 0.2	< 0.2	< 0.2	0.7	< 0.2	0.9	< 0.2	< 0.2
Boron, Water Soluble	0.2	mg/kg	0.9	7	0.9	1.6	2.6	1.6	1.2	6	2.9	3.2
Cadmium	0.1	mg/kg	0.4	26	25	94	58	28	31	75	37	3.1
Chromium	0.15	mg/kg	390	40	110	120	140	40	130	34	170	610
Chromium, Hexavalent	1	mg/kg	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Copper	0.2	mg/kg	20	20	94	140	170	42	130	26	160	22
Iron	25	mg/kg	130000	270000	470000	21000	620000	220000	520000	240000	560000	200000
Lead	0.3	mg/kg	36	1500	1000	1600	1200	2500	1100	3100	830	93
Magnesium	1	mg/kg	31000	11000	5300	4700	4900	6500	4600	7300	6700	31000
Manganese	20	mg/kg	33000	1200	5900	4500	6600	830	5800	1600	9300	18000
Mercury	0.05	mg/kg	< 0.05	0.42	0.13	0.35	0.1	0.54	0.15	0.29	0.1	< 0.05
Molybdenum	0.4	mg/kg	3	1.4	5.7	6.3	11	3.9	9	2.7	6.8	4.6
Nickel	1	mg/kg	8.8	23	34	27	54	23	47	44	46	60
Silicon	10	mg/kg	30000	36000	22000	50000	9200	25000	12000	34000	3200	45000
Vanadium	0.8	mg/kg	400	46	61	51	60	33	56	55	250	530
Zinc	1	mg/kg	190	9300	8700	21000	5500	17000	5800	23000	3800	440
Inorganics												
pH			12.6	8.5	9.2	9.1	10.6	8.4	9.3	8.8	9.6	12.6
Cyanide, Total	0.1	mg/kg	0.2	75	2	3.1	< 0.1	140	1.5	10	5	0.5
Organic matter	0.1	%	0.7	5.2	5.2	4.4	1	8.3	4.3	4.6	5	1.5
Sulphate Aqueous Extract as SO4	10	mg/l	15	1100	660	310	650	400	290	720	440	17
Sulphur Free	0.75	mg/kg										
Petroleum Hydrocarbons												
Aliphatic C5-C6	0.01	mg/kg	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.10	< 0.01
Aliphatic C8-C8	0.01	mg/kg	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.10	< 0.01
Aliphatic C8-C10	0.01	mg/kg	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.11	< 0.01	< 0.01	0.26	< 0.01
Aliphatic C10-C12	1.5	mg/kg	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
Aliphatic C12-C16	1.2	mg/kg	< 1.2	< 1.2	< 1.2	< 1.2	< 1.2	< 1.2	< 1.2	< 1.2	< 1.2	2.7
Aliphatic C16-C21	1.5	mg/kg	2.2	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	5.6
Aliphatic C21-C35	3.4	mg/kg	14	< 3.4	< 3.4	< 3.4	< 3.4	58	< 3.4	< 3.4	< 3.4	29
Aliphatic C5-C35	10	mg/kg	17	< 10	< 10	< 10	< 10	59	< 10	< 10	< 76.3	38
Aromatic C5-C7	0.01	mg/kg	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.10	< 0.01
Aromatic C7-C8	0.01	mg/kg	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.10	< 0.01
Aromatic C8-C10	0.01	mg/kg	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.10	< 0.01
Aromatic C10-C12	0.9	mg/kg	< 0.9	< 0.9	< 0.9	< 0.9	< 0.9	< 0.9	< 0.9	< 0.9	< 0.9	< 0.9
Aromatic C12-C16	0.5	mg/kg	< 0.5	< 0.5	< 0.5	1.6	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	9.8
Aromatic C16-C21	0.6	mg/kg	1.3	< 0.6	< 0.6	15	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	25
Aromatic C21-C35	1.4	mg/kg	5.7	< 1.4	< 1.4	52	< 1.4	< 1.4	< 1.4	< 1.4	< 1.4	80
Aromatic C5-C35	10	mg/kg	< 10	< 10	< 10	70	< 10	< 10	< 10	< 10	< 34.3	120
TPH AliAro Total	10	mg/kg	25	< 10	< 10	70	< 10	59	< 10	< 10	110	150
PAHs												
Naphthalene	0.03	mg/kg	< 0.03	0.22	0.07	0.17	< 0.03	0.37	< 0.03	0.39	1.4	< 0.03
Acenaphthylene	0.03	mg/kg	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.07
Acenaphthene	0.03	mg/kg	< 0.03	0.1	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	1.1	0.51
Fluorene	0.03	mg/kg	< 0.03	0.38	< 0.03	< 0.03	< 0.03	0.11	< 0.03	0.13	0.38	0.22
Phenanthrene	0.03	mg/kg	0.13	1.3	0.16	0.2	< 0.03	0.55	0.05	0.59	0.36	0.97
Anthracene	0.03	mg/kg	< 0.03	0.12	< 0.03	0.06	< 0.03	< 0.03	< 0.03	< 0.03	0.06	0.15
Fluoranthene	0.03	mg/kg	0.14	0.37	0.11	0.15	< 0.03	0.14	0.05	0.14	0.23	1.3
Pyrene	0.03	mg/kg	0.1	0.44	0.16	0.19	< 0.03	0.23	0.11	0.24	0.21	1.2
Benzo(a)anthracene	0.03	mg/kg	0.04	< 0.03	< 0.03	0.08	< 0.03	< 0.03	< 0.03	< 0.03	0.06	0.48
Chrysene	0.03	mg/kg	0.05	< 0.03	< 0.03	0.14	< 0.03	< 0.03	< 0.03	< 0.03	0.11	0.54
Benzo(b)fluoranthene	0.03	mg/kg	0.03	< 0.03	< 0.03	0.06	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.59
Benzo(k)fluoranthene	0.03	mg/kg	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.21
Benzo(a)pyrene	0.03	mg/kg	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.41
Indeno(1,2,3-c,d)pyrene	0.03	mg/kg	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.29
Dibenzo(a,h)anthracene	0.03	mg/kg	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.04
Benzo(g,h,i)perylene	0.03	mg/kg	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.31
PAH - USEPA 16, Total	0.1	mg/kg	0.49	2.9	0.5	1.1	< 0.10	1.4	0.21	1.5	3.9	7.2

Sample ID	MDL	Units	DH63TP	DH63TP	DH64TP	DH64TP	DH65TP	TP61	TP61	TP62	TP62	TP65	TP65
Depth			2	5	2	3.5	4.5	6.5	2.5	1.5	2.5	2.5	0.00-1.50
Sampling Date			26/12/17	26/12/17	26/12/17	26/12/17	26/12/17	26/12/17	26/12/17	26/12/17	26/12/17	26/12/17	26/12/17
Metals													
Aluminium	1	mg/kg	8300	9800	3900	5500	10000	540	3100	1100	10000	8400	11000
Antimony	1	mg/kg	3.9	3.5	5	5.2	3.5	7.2	6	19	10	16	8.1
Arsenic	0.2	mg/kg	3.1	7	0.7	0.9	1.9	5.7	0.6	19	46	54	9.6
Barium	1.5	mg/kg	140	230	38	65	210	18	58	250	390	140	
Beryllium	0.2	mg/kg	0.5	0.6	< 0.2	0.3	0.2	< 0.2	< 0.2	< 0.2	1.6	0.9	0.4
Boron, Water Soluble	0.2	mg/kg	13	14	5	4.8	11	1.3	5.2	1.7	15	11	6.5
Cadmium	0.1	mg/kg	0.5	0.5	0.6	2.8	1.4	12	< 0.1	76	19	43	7.3
Chromium	0.15	mg/kg	240	200	330	330	200	71	460	130	140	130	370
Chromium, Hexavalent	1	mg/kg	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Copper	0.2	mg/kg	13	220	17	14	16	45	7.4	160	92	190	51
Iron	25	mg/kg	55000	45000	83000	100000	81000	180000	74000	400000	170000	230000	160000
Lead	0.3	mg/kg	41	50	25	52	100	720	6.2	1700	3600	2100	720
Magnesium	1	mg/kg											
Manganese	20	mg/kg	14000	21000	7400	7300	10000	3400	7400	6600	6100	13000	9500
Mercury	0.05	mg/kg	< 0.05	0.05	< 0.05	< 0.05	0.1	< 0.05	< 0.05	0.29	3.1	1.2	0.58
Molybdenum	0.4	mg/kg	1.8	2	2.2	2	2.4	5.2	1.7	8.3	2.4	5.6	3.2
Nickel	1	mg/kg	7.2	9.3	9.7	6.4	6.8	23	17	33	32	42	19
Silicon	10	mg/kg											
Vanadium	0.8	mg/kg	460	960	210	240	180	27	260	47	180	160	240
Zinc	1	mg/kg	170	160	150	640	440	4800	27	18000	8400	11000	2500
Inorganics													
pH			12.6	12.6	12.7	12.7	12.5	10.4	12.7	9.2	9.7	8.7	12.5
Cyanide, Total	0.1	mg/kg											
Organic matter	0.1	%											
Sulphate Aqueous Extract as SO4	10	mg/l											
Sulphur Free	0.75	mg/kg	< 0.75	1.6	< 0.75	1.4	< 0.75	< 0.75	< 0.75	< 0.75	< 0.75	100	< 0.75
Petroleum Hydrocarbons													
Aliphatic C5-C8	0.01	mg/kg											
Aliphatic C9-C10	0.01	mg/kg											
Aliphatic C11-C12	0.01	mg/kg											
Aliphatic C13-C16	1.5	mg/kg											
Aliphatic C17-C21	1.2	mg/kg											
Aliphatic C22-C25	1.5	mg/kg											
Aliphatic C26-C35	3.4	mg/kg											
Aliphatic C36-C38	10	mg/kg											
Aromatic C5-C7	0.01	mg/kg											
Aromatic C7-C8	0.01	mg/kg											
Aromatic C8-C10	0.01	mg/kg											
Aromatic C10-C12	0.9	mg/kg											
Aromatic C12-C16	0.5	mg/kg											
Aromatic C16-C21	0.6	mg/kg											
Aromatic C21-C35	1.4	mg/kg											
Aromatic C36-C38	10	mg/kg											
TPH All/As Total	10	mg/kg											
PAHs													
Naphthalene	0.03	mg/kg	0.11	0.14	< 0.03	0.05	< 0.03	0.19	0.04	0.12	97	0.93	0.06
Acenaphthylene	0.03	mg/kg	0.08	0.13	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	11	0.25	< 0.03
Acenaphthene	0.03	mg/kg	0.04	0.08	< 0.03	< 0.03	< 0.03	< 0.03	0.08	< 0.03	120	2.4	0.06
Fluorene	0.03	mg/kg	< 0.03	0.08	< 0.03	< 0.03	< 0.03	< 0.03	0.4	< 0.03	68	1.3	0.03
Phenanthrene	0.03	mg/kg	1.7	3.3	0.07	0.19	0.24	0.16	7.7	0.29	100	1.3	0.16
Anthracene	0.03	mg/kg	0.18	0.32	< 0.03	0.03	< 0.03	0.04	3.7	0.12	24	0.51	0.03
Fluoranthene	0.03	mg/kg	2.4	3.5	0.12	0.27	0.2	0.19	3.9	0.18	48	1.9	0.11
Pyrene	0.03	mg/kg	1.6	2.3	0.13	0.28	0.24	0.31	2.3	0.22	36	1.2	0.12
Benzo(a)anthracene	0.03	mg/kg	0.66	0.93	0.03	0.08	0.12	< 0.03	0.66	0.17	14	0.44	0.04
Chrysene	0.03	mg/kg	0.85	1.2	0.05	0.15	0.16	0.04	0.73	0.18	15	0.51	0.05
Benzo(b)fluoranthene	0.03	mg/kg	0.97	1.3	0.04	0.1	0.27	< 0.03	0.47	0.59	13	0.35	0.08
Benzo(k)fluoranthene	0.03	mg/kg	0.34	0.5	< 0.03	0.03	0.1	< 0.03	0.18	0.15	4.3	0.1	< 0.03
Benzo(a)pyrene	0.03	mg/kg	0.41	0.55	< 0.03	0.03	0.16	< 0.03	0.18	0.28	7.7	0.19	< 0.03
Indeno(1,2,3-c,d)pyrene	0.03	mg/kg	0.29	0.44	< 0.03	< 0.03	0.14	< 0.03	0.1	0.14	2.7	0.07	< 0.03
Dibenzo(a,h)anthracene	0.03	mg/kg	0.1	0.14	< 0.03	< 0.03	0.04	< 0.03	0.04	0.06	0.83	< 0.03	< 0.03
Benzo(g,h,i)perylene	0.03	mg/kg	0.36	0.52	< 0.03	< 0.03	0.19	< 0.03	0.12	0.22	3.6	0.09	< 0.03
PAH - USEPA 16, Total	0.1	mg/kg	10	15	0.44	1.2	1.9	0.92	21	2.7	570	11	0.75

Sample ID			BH01TP	BH01TP	BH04	BH05	BH05	BH06	BH06	BH06	BH06	BH06	BH06
Depth	MDL	Units	1	2	1.2	1	4	1	2.5	5.5	2.2	5.4	8.2
Sampling Date			18/12/17	18/12/17	18/12/17	18/12/17	18/12/17	18/12/17	18/12/17	18/12/17	18/12/17	18/12/17	18/12/17
Metals													
Aluminium	1	mg/kg	9600	8000	1600	14000	16000	2000	6000	8600	14000	5500	11000
Arsimony	1	mg/kg	8.1	6.5	14	1.5	5.4	15	6.5	7.3	5.6	6.1	6.1
Arsenic	0.2	mg/kg	3.7	15	13	8.6	1.3	13	1.6	7.7	2.9	3.7	4.6
Barium	1.5	mg/kg	290	170	110	250	130	62	91	230	600	160	360
Beryllium	0.2	mg/kg	0.4	0.4	< 0.2	1	0.4	< 0.2	< 0.2	0.6	0.6	0.5	0.7
Boron, Water Soluble	0.2	mg/kg	5.4	3.4	1.7	2.5	7.8	1.8	4.8	7.2	43	9	6.6
Cadmium	0.1	mg/kg	3.9	9.7	86	1.3	3.6	52	0.6	4.3	0.6	5.7	1.1
Chromium	0.15	mg/kg	530	200	100	33	320	120	640	320	420	340	450
Chromium, Hexavalent	1	mg/kg	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Copper	0.2	mg/kg	35	150	120	36	23	140	16	100	18	33	28
Iron	25	mg/kg	160000	130000	460000	55000	120000	450000	170000	170000	110000	160000	150000
Lead	0.3	mg/kg	140	920	1200	100	110	1200	17	210	28	400	64
Magnesium	1	mg/kg											
Manganese	20	mg/kg	18000	6900	3600	840	11000	7100	16000	17000	42000	22000	38000
Mercury	0.05	mg/kg	< 0.05	0.94	0.27	0.07	< 0.05	0.19	< 0.05	< 0.05	< 0.05	0.07	< 0.05
Molybdenum	0.4	mg/kg	4.4	6	5.4	1.2	2.6	8	2.9	6.9	2.6	3.1	2.7
Nickel	1	mg/kg	16	90	25	36	8.1	38	3.7	22	8.8	8.2	10
Silicon	10	mg/kg											
Vanadium	0.8	mg/kg	460	200	66	34	270	61	500	780	390	2600	3300
Zinc	1	mg/kg	1000	2400	17000	310	780	14000	110	1400	180	2300	280
Inorganics													
pH			12.4	11.9	10	9.2	12.6	9.7	12.6	12.5	12.6	12.5	12.5
Cyanide, Total	0.1	mg/kg		170									
Organic matter	0.1	%		13									
Sulphate Aqueous Extract as SO4	10	mg/l		740									
Sulphur Free	0.75	mg/kg	< 0.75	870	6.9	< 0.75	< 0.75	< 0.75	< 0.75	< 0.75	1.7	< 0.75	2.4
Petroleum Hydrocarbons													
Aliphatic C5-C6	0.01	mg/kg		< 0.01									
Aliphatic C6-C8	0.01	mg/kg		< 0.01									
Aliphatic C8-C10	0.01	mg/kg		2.2									
Aliphatic C10-C12	1.5	mg/kg		220									
Aliphatic C12-C16	1.2	mg/kg		1700									
Aliphatic C16-C21	1.5	mg/kg		4700									
Aliphatic C21-C35	3.4	mg/kg		22000									
Aliphatic C5-C35	10	mg/kg		28000									
Aromatic C5-C7	0.01	mg/kg		14									
Aromatic C7-C8	0.01	mg/kg		7.9									
Aromatic C8-C10	0.01	mg/kg		6.6									
Aromatic C10-C12	0.9	mg/kg		3400									
Aromatic C12-C16	0.5	mg/kg		12000									
Aromatic C16-C21	0.6	mg/kg		6200									
Aromatic C21-C35	1.4	mg/kg		11000									
Aromatic C5-C35	10	mg/kg		33000									
TPH All/Aro Total	10	mg/kg		61000									
PAHs													
Naphthalene	0.03	mg/kg	< 0.03	3600	0.06	0.05	< 0.03	0.07	0.03	35	< 0.03	< 0.03	< 0.03
Acenaphthylene	0.03	mg/kg	< 0.03	370	0.05	< 0.03	< 0.03	< 0.03	< 0.03	10	< 0.03	< 0.03	< 0.03
Acenaphthene	0.03	mg/kg	0.04	3400	0.06	0.05	< 0.03	< 0.03	< 0.03	1	< 0.03	< 0.03	0.07
Fluorene	0.03	mg/kg	< 0.03	2100	0.1	0.07	< 0.03	< 0.03	< 0.03	8.9	< 0.03	< 0.03	0.11
Phenanthrene	0.03	mg/kg	0.14	1300	0.16	0.06	0.07	0.12	0.04	28	< 0.03	< 0.03	0.54
Anthracene	0.03	mg/kg	0.03	330	0.04	< 0.03	< 0.03	< 0.03	< 0.03	6.4	< 0.03	< 0.03	0.06
Fluoranthene	0.03	mg/kg	0.19	570	0.27	< 0.03	0.04	0.1	0.12	18	0.03	< 0.03	0.51
Pyrene	0.03	mg/kg	0.17	400	0.24	< 0.03	0.07	0.19	0.11	14	0.03	< 0.03	0.36
Benzo(a)anthracene	0.03	mg/kg	0.09	180	0.12	< 0.03	< 0.03	0.04	0.04	5.2	< 0.03	< 0.03	0.15
Chrysene	0.03	mg/kg	0.11	160	0.39	< 0.03	< 0.03	0.05	0.04	4.8	< 0.03	< 0.03	0.16
Benzo(b)fluoranthene	0.03	mg/kg	0.1	200	0.06	< 0.03	< 0.03	0.04	0.04	4.9	< 0.03	< 0.03	0.15
Benzo(k)fluoranthene	0.03	mg/kg	0.03	76	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	1.8	< 0.03	< 0.03	0.05
Benzo(a)pyrene	0.03	mg/kg	0.04	150	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	3.7	< 0.03	< 0.03	0.06
Indeno(1,2,3-c,d)pyrene	0.03	mg/kg	0.06	83	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	1.7	< 0.03	< 0.03	0.05
Dibenzo(a,h)anthracene	0.03	mg/kg	< 0.03	20	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.57	< 0.03	< 0.03	< 0.03
Benzo(g,h,i)perylene	0.03	mg/kg	0.08	110	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	2.1	< 0.03	< 0.03	0.06
PAH - USEPA 16, Total	0.1	mg/kg	1.1	13000	1.5	0.23	0.18	0.61	0.43	150	< 0.10	< 0.10	2.4

Sample ID			TP03	TP04	TP04	BH01 (TP)	BH08	BH08	BH08	BH08	BH08	BH08
Depth	MDL	Units	1	3	1.00-2.00	1.5	8	12	15	1	3	5
Sampling Date			18/12/17	18/12/17	18/12/17	18/12/17	06/12/17	13/12/17	13/12/17	30/11/17	01/12/17	01/12/17
Metals												
Aluminium	1	mg/kg	5500	790	1700		2200	6100	4900	2400	1400	890
Antimony	1	mg/kg	9.1	13	20		17	5.7	11	19	20	19
Arsenic	0.2	mg/kg	43	7.5	17	3.9	9.9	9.8	17	16	14	12
Barium	1.5	mg/kg	240	50	140		85	120	120	110	120	72
Beryllium	0.2	mg/kg	0.8	< 0.2	< 0.2		< 0.2	0.7	0.4	0.2	< 0.2	< 0.2
Boron, Water Soluble	0.2	mg/kg	2	1.2	1	5.7	2.3	2.9	2.9	1.1	1.1	1
Cadmium	0.1	mg/kg	87	21	73	3.7	34	25	27	47	48	29
Chromium	0.15	mg/kg	28	110	110	190	170	48	74	88	91	120
Chromium, Hexavalent	1	mg/kg	< 1.0	< 1.0	< 1.0		< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Copper	0.2	mg/kg	23	160	150	50	170	26	75	99	110	160
Iron	25	mg/kg	210000	420000	510000		420000	200000	260000	290000	440000	480000
Lead	0.3	mg/kg	7900	1700	1600	270	1800	2500	2400	1400	1200	1600
Magnesium	1	mg/kg										
Manganese	20	mg/kg	780	5200	4200		8000	1200	2500	3900	5600	8900
Mercury	0.05	mg/kg	1.4	0.1	0.19	0.15	0.07	0.28	0.24	0.19	0.13	0.15
Molybdenum	0.4	mg/kg	2.1	7.9	5.1		7.2	1.6	4.3	5.1	4.9	6.8
Nickel	1	mg/kg	22	39	27	38	42	18	26	23	23	43
Silicon	10	mg/kg										
Vanadium	0.8	mg/kg	58	75	47		140	43	53	49	48	49
Zinc	1	mg/kg	33000	8900	37000	960	11000	10000	12000	14000	22000	11000
Inorganics												
pH			6.9	10.2	9.1	11.8		11	10.3	10.3	9.1	9.5
Cyanide, Total	0.1	mg/kg										
Organic matter	0.1	%				47						
Sulphate Aqueous Extract as SO4	10	mg/l				110						
Sulphur Free	0.75	mg/kg	220	< 0.75	3		< 0.75	36	28	1.6	1	< 0.75
Petroleum Hydrocarbons												
Aliphatic C5-C6	0.01	mg/kg				< 0.01						
Aliphatic C6-C8	0.01	mg/kg				0.15						
Aliphatic C8-C10	0.01	mg/kg				1.1						
Aliphatic C10-C12	1.5	mg/kg				< 50.0						
Aliphatic C12-C16	1.2	mg/kg				380						
Aliphatic C16-C21	1.5	mg/kg				1100						
Aliphatic C21-C35	3.4	mg/kg				6200						
Aliphatic C5-C35	10	mg/kg				7700						
Aromatic C5-C7	0.01	mg/kg				4						
Aromatic C7-C8	0.01	mg/kg				3.8						
Aromatic C8-C10	0.01	mg/kg				4.1						
Aromatic C10-C12	0.9	mg/kg				460						
Aromatic C12-C16	0.5	mg/kg				1800						
Aromatic C16-C21	0.6	mg/kg				1300						
Aromatic C21-C35	1.4	mg/kg				2600						
Aromatic C5-C35	10	mg/kg				6200						
TPH All/Aro Total	10	mg/kg				14000						
PAHs												
Naphthalene	0.03	mg/kg	4.1	0.03	0.04	410	< 0.03	0.1	0.13	0.06	0.04	< 0.03
Acenaphthylene	0.03	mg/kg	0.07	< 0.03	< 0.03	62	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Acenaphthene	0.03	mg/kg	0.66	< 0.03	< 0.03	560	< 0.03	< 0.03	0.05	< 0.03	< 0.03	< 0.03
Fluorene	0.03	mg/kg	1.2	< 0.03	< 0.03	330	< 0.03	0.09	0.16	< 0.03	< 0.03	< 0.03
Phenanthrene	0.03	mg/kg	3.4	0.06	0.1	230	0.08	0.21	0.37	0.27	0.19	< 0.03
Anthracene	0.03	mg/kg	0.41	< 0.03	< 0.03	64	< 0.03	< 0.03	0.05	< 0.03	< 0.03	< 0.03
Fluoranthene	0.03	mg/kg	1.4	0.06	0.07	150	0.08	0.05	0.14	0.31	0.19	< 0.03
Pyrene	0.03	mg/kg	2.8	0.06	0.09	120	0.1	0.14	0.35	0.24	0.18	< 0.03
Benzo(a)anthracene	0.03	mg/kg	0.06	< 0.03	< 0.03	46	< 0.03	< 0.03	< 0.03	0.04	0.04	< 0.03
Chrysene	0.03	mg/kg	0.17	< 0.03	< 0.03	38	0.05	< 0.03	< 0.03	0.09	0.09	< 0.03
Benzo(b)fluoranthene	0.03	mg/kg	0.04	< 0.03	< 0.03	52	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Benzo(k)fluoranthene	0.03	mg/kg	< 0.03	< 0.03	< 0.03	20	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Benzo(a)pyrene	0.03	mg/kg	< 0.03	< 0.03	< 0.03	42	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Indeno(1,2,3-c,d)pyrene	0.03	mg/kg	< 0.03	< 0.03	< 0.03	20	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Dibenzo(a,h)anthracene	0.03	mg/kg	< 0.03	< 0.03	< 0.03	5.1	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Benzo(g,h,i)perylene	0.03	mg/kg	< 0.03	< 0.03	< 0.03	24	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
PAH - USEPA 16, Total	0.1	mg/kg	14	0.18	0.31	2200	0.31	0.6	1.3	1	0.72	< 0.10

8 APPENDIX B – ELECTROSTATIC AND MAGNETIC SEPARATION AT BUNTING MAGNETICS

Electrostatic separation

The sample was screened and dried into the following fractions: above 2.8mm, 2.8mm to 1mm, 1mm to 500 microns and below 500 microns.

The 3 finer fractions were chosen for electrostatic separation. The above 2.8mm was considered too coarse for electrostatic processing. The conditions: applied voltage, roll speed and splitter plate position were optimised for each run. Although little evidence of pinning was seen in the coarser fractions. A non-conductor (insulator) fraction and conductor fraction were collected and weighed. The vast majority of the material was found to be conductors on the unit. Above 500 microns only between 1 and 2% were separated as non-conductors, below 500 microns approximately 10%. The fractions were analysed using the XRF and as can be seen in Table 2 the XRF data indicates little difference in the chemistry of the conductors and non-conductors.

Table 2 – XRF Analysis of Electrostatic separation size fractions

Sample	weight	Mg	Al	Si	P	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Mo	Sn	Pb
minus 500 micron feed		1.243	0.460	1.407	0.072	0.274	2.957	0.043	0.250	0.046	1.064	60.14	0.008	0.024	2.283	0.002	0.018	0.300
minus 500 micron non conductors	30 g	0.788	0.570	1.698	0.085	0.287	3.249	0.068	0.272	0.051	1.008	59.65	0.008	0.200	2.142	0.001	0.024	0.297
minus 500 micron conductors	305 g	1.944	0.523	1.642	0.100	0.329	3.059	0.070	0.316	0.047	1.022	60.54	0.007	0.030	2.198	0.002	0.022	0.301
1mm,+500 microns feed		0.738	0.371	1.166	0.065	0.235	2.742	0.054	0.240	0.039	1.096	61.59	0.011	0.022	2.230	0.002	0.026	0.320
1mm,+500 microns non conductors	4.1 g	1.087	0.703	1.893	0.081	0.269	3.303	0.079	0.274	0.047	1.000	57.68	0.007	1.038	2.042	0.005	0.019	0.284
1mm,+500 microns conductors	333 g	0.917	0.357	1.261	0.072	0.246	2.663	0.050	0.250	0.042	1.035	61.22	0.006	0.078	2.330	0.003	0.024	0.311
2.8mm,+1mm feed		0.673	0.352	1.344	0.073	0.238	2.812	0.047	0.240	0.043	1.046	61.41	0.010	0.019	2.143	0.002	0.028	0.344
2.8mm,+1mm non conductors	5.2 g	0.736	0.603	1.619	0.066	0.248	3.095	0.065	0.252	0.045	0.935	58.66	0.000	1.509	2.023	0.003	0.017	0.286
2.8mm,+1mm conductors	802 g	0.590	0.362	1.179	0.065	0.230	2.773	0.042	0.230	0.058	1.000	61.61	0.000	0.077	2.388	0.002	0.029	0.346

Magnetic separation

The sample was screened and dried into the following fractions: above 2.8mm, 2.8mm to 1mm, 1mm to 500 microns and below 500 microns. All fractions underwent magnetic separation. Again, settings were optimised for each run. All fractions were collected and weighed. The fractions were analysed using the XRF and as can be seen in Table 3 the XRF data indicates little difference in the chemistry of the of the different size fractions Magnetic separation is of little or no benefit on the SLEMS material.

Table 3 - XRF Analysis of Magnetic separation size fractions

Name	mass	Mg	Al	Si	P	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sn	Pb
>2.8mm Feed	2200 g	0.891	0.439	1.313	0.077	0.261	2.912	0.070	0.217	0.058	0.969	60.36	0.016	0.026	1.821	0.026	0.301
>2.8mm	1994 g	1.191	0.564	1.344	0.072	0.257	2.888	0.049	0.242	0.042	1.010	60.51	0.007	0.027	2.014	0.025	0.280
>2.8mm	7.0 g	1.841	2.330	5.031	0.133	1.051	4.751	0.275	0.336	0.064	0.867	47.53	0.040	0.064	1.633	0.029	0.208
>2.8mm	96 g	2.551	1.253	2.625	0.106	0.456	5.225	0.182	0.258	0.050	1.133	52.57	0.018	0.036	1.767	0.000	0.235
>2.8mm	16 g	1.448	1.423	3.674	0.169	0.387	23.73	0.235	0.315	0.081	1.244	32.38	0.018	0.022	0.718	0.024	0.086
2.8-1mm Feed	1570 g	0.000	0.260	1.137	0.068	0.211	2.725	0.044	0.232	0.050	1.041	60.94	0.007	0.022	2.119	0.033	0.336
2.8-1mm	1340 g	0.956	0.566	1.402	0.071	0.268	2.716	0.067	0.225	0.050	1.048	61.70	0.007	0.027	2.153	0.022	0.319
2.8-1mm	192 g	1.022	0.821	1.772	0.080	0.341	3.255	0.065	0.253	0.044	1.025	59.03	0.009	0.026	2.050	0.028	0.282
2.8-1mm	14 g	0.564	2.348	4.960	0.077	0.845	2.490	0.126	0.203	0.044	0.866	52.46	0.129	0.307	1.869	0.025	0.298
2.8-1mm	0 g																
1mm-500microns Feed	572 g	0.751	0.328	1.215	0.071	0.250	2.759	0.046	0.235	0.049	1.008	60.61	0.000	0.015	2.250	0.027	0.322
1mm-500microns	501 g	0.889	0.682	1.694	0.074	0.320	2.876	0.066	0.264	0.047	1.016	62.01	0.007	0.028	2.097	0.021	0.311
1mm-500microns	59 g	0.609	0.693	1.410	0.062	0.265	2.748	0.071	0.244	0.050	0.995	60.94	0.007	0.032	2.199	0.027	0.320
1mm-500microns	3 g	1.199	2.793	3.291	0.094	0.643	3.593	0.270	0.228	0.053	0.883	52.57	0.008	0.214	1.889	0.023	0.257
1mm-500microns	0 g																
<500microns Feed	1700 g	0.410	0.398	1.327	0.069	0.248	2.846	0.062	0.260	0.055	1.046	60.58	0.011	0.018	2.237	0.024	0.321
<500microns	1265 g	0.263	0.253	1.148	0.068	0.190	2.462	0.000	0.235	0.045	1.031	62.85	0.006	0.015	2.293	0.021	0.321
<500microns	215 g	0.665	0.613	2.072	0.067	0.241	3.234	0.067	0.241	0.057	1.055	59.29	0.012	0.035	2.254	0.022	0.317
<500microns	30 g	1.382	0.939	2.519	0.116	0.418	3.187	0.176	0.269	0.037	1.035	56.72	0.014	0.024	2.276	0.033	0.325
<500microns	10 g	0.687	1.185	3.057	0.099	0.431	3.023	0.148	0.244	0.051	1.026	56.62	0.015	0.029	2.265	0.031	0.344
<500microns	5 g	0.853	1.676	4.759	0.102	0.586	2.900	0.171	0.240	0.038	0.982	52.95	0.008	0.050	2.144	0.031	0.297
<500microns	4.5 g	0.719	1.509	4.046	0.093	0.489	2.843	0.133	0.239	0.050	1.004	54.75	0.010	0.034	2.174	0.022	0.291
<500microns	11 g	1.475	6.356	16.385	0.104	2.005	2.391	0.440	0.000	0.045	0.563	26.24	0.009	0.044	1.555	0.021	0.233