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Circular Economy Opportunities – Raw Materials Ireland Project

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EPA RESEARCH PROGRAMME 2021–2030

Circular Economy Opportunities – Raw Materials Ireland Project

(2017-RE-MS-8)

EPA Research Report

Prepared for the Environmental Protection Agency

by

University of Limerick

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Box 1.1. The 2020 list of critical raw materials

Executive Summary

Ireland is home to primary industries in mining, materials processing and power generation. Today, the majority of waste outputs associated with these industries are either sent to landfill or exported. There is potential to assess these wastes as secondary raw materials, recover any valuable metals and find alternative applications for the end waste that can contribute to a circular economy.

Objectives

In the light of the above, the high-level objectives of the Raw Materials Ireland Project are defined as follows:

- to unlock the value of various metals from mining and industrial residues;
- to push Ireland to the forefront in the area of raw materials processing technologies;
- to improve the economic viability and investment security of processing operations.

The specific objectives to achieve these are to:

- undertake characterisation of Irish wastes;
- investigate synergies between the different wastes regarding composition;
- investigate the critical raw material (CRM) content of the wastes and synergies that exist;
- develop strategies for the recovery of valuable materials;
- investigate separation techniques to recover any valuable metals and CRMs.

Waste Inventory and Synergies

- A detailed characterisation study of 24 waste samples from 12 different industrial sites across Ireland was undertaken as follows:
 - mine waste rock and tailings: Lisheen Mine, Tara Mines Silvermines, Avoca Mines, Galmoy Mine, Two Valleys Mines and Tynagh Mine;
 - power plant fly ash and bottom ash: Electricity Supply Board (ESB) Moneypoint, ESB Lough Ree, ESB West Offaly, Covanta Dublin Waste to Energy and Indaver waste to energy;
 - refinery residue: Aughinish Alumina.

- The results of the analysis revealed commonalities among a group of metals and CRMs that were present in the majority of the wastes as follows:
 - metals iron (~50–200 g/kg), zinc
 (~10–300 g/kg), aluminium (~10–50 g/kg) and calcium (~100–270 g/kg);
 - CRMs gallium, indium and phosphorus (typically ~0.1–0.2 g/kg).

Recovery Strategy and Testing

- The recovery strategy developed focused on separating the wastes into the following concentrated fractions:
 - base metals to separate iron, zinc and aluminium phases from the main fraction;
 - calcium-rich phase to concentrate the remaining calcium-rich fraction, which may have applications in the construction sector;
 - CRMs to track the locations of the CRMs within the separated fractions and any potential for downstream concentration of these elements.
- The techniques selected for investigation were mechanical and physical separation processes such as ball milling and filtration (sieving), magnetic separation, dissolution studies and gravity separation processes, including the Mozley superpanner and the multi-gravity separator (MGS).
- The test results showed that the gravity separation techniques gave the best results where individual wastes demonstrated enhanced responses for either the Mozley superpanner or the MGS, based on their specific characteristics. The MGS was more suitable for the majority of the wastes, as the Mozley technique cannot process samples with particle sizes less than 20 µm, which was very limiting for certain wastes (some mine tailings and fly ashes). Generally, the heavier metal phases (aluminium, iron, zinc) concentrated at an early stage of the process, whereas the lighter phases (calcium carbonate) passed through to the end.
- In addition, consideration of the potential market applications highlighted that gravity separation

processes may have added benefits in terms of removing unwanted elements (magnesium, sulfur and sodium) that can act as impurities in construction sector applications.

Process Flows and Circular Economy

- Process flows based on the results reported here were considered for specific market applications for the wastes, including cement clinker replacement, cement filler, aggregates and geopolymer applications.
- In addition, a process flow for multiple wastes was developed to showcase a circular economy approach at scale. In the example, wastes from

Tara Mines, Tynagh Mine, Covanta Dublin Waste to Energy, Indaver waste to energy and ESB West Offaly, which have similarities in composition, are treated together to recover iron and zinc and produce a highly concentrated calcium carbonate fraction with minor impurities for construction sector applications.

 In order to realise a circular economy for Irish secondary raw materials, such as the one outlined, strategic collaboration across the value chain from the waste producer to the end user is required. The driver for the end user to adopt the new product is key to achieving the financial and technical investments required for a circular economy.

1 Introduction

Ireland is home to primary industries in mining, materials processing and power generation. Ireland is a major exporter of zinc to the European Union (EU); Irish mining also produces significant quantities of lead, and a large-scale refinery produces large quantities of alumina. Other key sectors include power generation from coal, peat and waste-to-energy facilities. Individual plants produce significant annual tonnages of waste rock, mine tailings, fly ashes, bottom ashes and industrial residues. Today, the majority of these wastes are either sent to landfill or exported. The Raw Materials Ireland Project is focused on reviewing these Irish waste materials to understand their composition and any valuable metals or materials they contain. There is potential to assess these wastes as secondary raw materials, recover any valuable materials and find alternative applications for the end waste that can contribute to the circular economy.

1.1 Policy Context

The European Commission's Circular Economy Action Plan (EC, 2015) is focused on transitioning Europe to a circular economy in which the value of products, materials and resources is maintained in the economy for as long as possible and the generation of waste is minimised. This plan identified a number of measures across the life cycle of products, including production, consumption, waste management and production of secondary raw materials. One of the priority areas identified in the plan is critical raw materials (CRMs). CRMs are both of high economic importance to the EU and at a high risk of supply disruption (EC, 2017). The plan identified several potential sources of secondary CRMs, including electronic waste, landfills and extractive waste. The updated 2020 list of CRMs is shown in Box 1.1 (EC, 2020). The European Commission published the Staff Working Document "Report on Critical Raw Materials and Circular Economy" in 2018 (EC, 2018), highlighting key actions to manage CRMs at the end of life by following best practice procedures identified in eight sectors, including landfill and extractive wastes. Another key driver is the Extractive Waste Directive (2006/21/EC), which sets specific requirements for minimisation and recovery of extractive waste.

1.2 Research and Development

In 2019, the European Commission Joint Research Centre (JRC) reported the state of play on existing practices regarding the recovery of critical and

Box 1.1. The 2020 list of	critical raw materials	
2020 critical raw materials	s (materials added since 2017 in bold)	
Antimony	Hafnium	Dhosphorus
Barvte	Heavy rare earth elements	Scandium
Beryllium	Light rare earth elements	Silicon metal
Bismuth	Indium	Tantalum
Borate	Magnesium	Tungsten
Cobalt	Natural graphite	Vanadium
Coking coal	Natural rubber	Bauxite
Fluorspar	Niobium	Lithium
Gallium	Platinum group metals	Titanium
Germanium	Phosphate rock	Strontium
Source: EC (2020).		

other raw materials from mining waste and landfills (Blengini et al., 2019). Lessons learned, as detailed in the report, include awareness that it is unlikely that recovery processes can target one or just a few specific materials of great interest and disregard other elements or bulk matrices. This is especially true in cases where the target materials are at very low concentrations and the bulk of the waste in which they are embedded must be valorised to increase the processes' economic viability and minimise waste disposal. The authors report that, because recovery processes can be very energy intensive, environmental and land use-related aspects are particularly relevant in that environmental gains may be achieved, and, moreover, land space can be liberated and reused. They also highlight the lack of data and information on secondary materials, which are crucial for the viability of any large-scale deployment of recovery practices.

1.3 Raw Materials Ireland Objectives

In the light of the above, the high-level objectives of the Raw Materials Ireland Project are to:

- unlock the volume of various metals from mining and industrial residue and increase the range and yields of recovered raw materials;
- push Ireland to the forefront in the area of raw materials processing technologies;
- increase the economic viability and investment security of processing operations.

The specific objectives to achieve this are to:

- undertake characterisation of Irish wastes;
- investigate any synergies between the different wastes regarding composition;
- investigate the CRM content of the wastes;
- develop strategies for the recovery of valuable materials, including CRMs, where appropriate;
- investigate separation and recovery methodologies and techniques to recover any materials of value.

2 Methodology

The research approach taken to achieve the objectives is outlined as follows:

- Engage industry to request samples of wastes.
- Undertake characterisation of the wastes to understand the composition and physical properties.
- Analyse the results to identify any synergies between the different wastes.
- Identify materials of interest for recovery (Chapter 3).
- Develop a recovery strategy for these target materials (Chapter 6).
- Investigate and test potential processes and techniques to achieve materials recovery. This involved both in-house research and outsourced testing (Chapter 6):
 - Three in-house recovery techniques are reported: filtration and ball milling, magnetic separation and dissolution studies.
 - Two outsourced tests were conducted using the Mozley superpanner and the multi-gravity separator (MGS).
- Develop process flows based on the findings (Chapter 7).

2.1 Inventory

Samples of wastes were collected from three industrial sectors: mining, power and alumina. The details of the inventory are given in Chapter 3.

The wastes received were in powder form and were stored in a dry and temperature-controlled room. These wastes were mixed to achieve homogeneity and sampled from different parts to ensure a representative sample for testing. Samples were dried in an oven at 60°C overnight to remove moisture. Dried samples were then sealed to avoid moisture absorption.

2.2 Characterisation

The dried samples were subjected to leaching in aqua regia. The wastes were weighed to 1g each and dissolved in 10 mL of aqua regia at 50°C for 2 hours

while being shaken at 240 revolutions per minute (rpm). Dissolution was followed by 24 hours' cooling in an undisturbed state. The samples were then diluted 2000 times before analysis in an Agilent Technologies 5100 inductively coupled plasma optical emission spectrometer (ICP-OES or abbreviated to ICP). Each result is an average of three measurements.

The selected control samples from the inventory were observed under a scanning electron microscope (SEM) and an energy-dispersive X-ray spectroscope (EDS) to analyse the particle size range and the main elements present in the waste. The samples were transferred onto carbon tape and sputtered with a gold coating to achieve conductivity. These samples were transferred into a Hitachi SU-70 microscope at 20 kV. If the samples were non-conducting or charging, the SEM energy was reduced to 10kV. Scanning and point EDS were performed on the samples to display the major constituents of the wastes. The SEM images were analysed using ImageJ software (open source) to measure the particle size range of the samples. The samples were also analysed for average particle size using a Horiba LA-920 scattering particle size distribution analyser. The control samples were then subjected to 40 kV, copper target X-ray diffraction (XRD). The XRD patterns were analysed for crystalline phase identification using HighScore software.

The samples were tested for moisture content by taking 5g of each of the wastes and heating them to 60°C overnight. After heating, the sample was covered with a polymer until it cooled and was then transferred into the weighing machine. The difference in the sample weight was considered to be the moisture content of the sample. One gram of dried powder was then added to a measuring bottle and tapped until no further change in volume was observed. The bulk density (g/cm³) of the samples was calculated by dividing the volume by the initial sample weight.

In addition, the samples were dissolved in distilled water at 60°C and shaken at 240 rpm for 2 hours. The solution was left to cool to room temperature and the pH and electrical conductivity (mS/cm) were measured.

2.3 In-house Testing

2.3.1 Filtration (sequential sieving)

The filtration process was performed using a sequence of sieves with different porosity. These sieves were set up with the largest pore size $(500 \,\mu\text{m})$ at the top and the finest pore size $(25 \,\mu\text{m})$ at the bottom. The sequence of sieves was as follows: $500 \,\mu\text{m}$, $100 \,\mu\text{m}$, $90 \,\mu\text{m}$, $53 \,\mu\text{m}$ and $25 \,\mu\text{m}$ (Figure 2.1). The filtered powder was then analysed by ICP.

2.3.2 Ball milling

Powders were ball milled in distilled water using zirconia balls of 1 cm, 0.5 cm and 0.2 cm diameter in a plastic container. The speed of the ball milling operation was 60 rpm for 8 hours at room temperature. After ball milling, the suspension was left to settle into a clear liquid and solid deposit. The clear liquid was then decanted and the deposit was dried until all the moisture was removed. The powders were then ground to disperse any agglomeration. Finally, the filtered fractions were analysed by ICP.

2.3.3 Dry and wet magnetic separation

Dry magnetic separation was performed on dried waste powders using a 32-kg pull force neodymium magnet. The magnet was covered in a removable polymer jacket and placed into the dry waste powders repeatedly until it was saturated with the powder that it attracted (i.e. the magnetic fraction).

Wet magnetic separation was performed using the same 32-kg pull force magnet. The waste powder was mixed thoroughly with distilled water in a plastic container and the magnet was placed outside the container to attract the magnetic particles, which were collected for ICP analysis.

Following both wet and dry magnetic separation, the collected magnetic and non-magnetic powders were dried at 60°C for 2 hours and weighed. The filtered and ball-milled wastes were also subjected to wet magnetic separation as detailed in Figure 2.2. The resulting fractions were then analysed by ICP.

2.3.4 Dissolution

The individual waste powders were mixed with distilled water and agitated using the ball milling technique to achieve dissolution of the soluble elements. The mixture was then left to settle and separate. The solution was then separated carefully from the solid deposit and boiled until all the water had evaporated and a residue of the previously dissolved material was left at the bottom of the container (Figure 2.3). The dried residue was then recovered and weighed. The dried residue and solid deposit fractions were analysed by ICP.



Figure 2.1. The sequence of sieve sizes used for the filtration of the waste samples.

L. O'Donoghue et al. (2017-RE-MS-8)



Figure 2.2. Flow sheets for filtration and wet magnetic separation (left) and ball milling, filtration and wet magnetic separation of the wastes (right).



Figure 2.3. The process followed to dissolve soluble material from the waste samples.

2.4 Outsourced Testing

2.4.1 Mozley superpanner

Initial inspection

On inspection, it was noted that the waste-to-energy bottom ash samples contained large particles, up to 10 cm in width, which were not amenable to gravity separation. These particles were removed by screening the samples at 8 mm, with assay-by-size carried out on the <8 mm fraction.

Particle size analysis

Particle size analysis was carried out by wet screening on a standard $\sqrt{2}$ series of sieves.

Head assay and assay-by-size

The head assay of each size band fraction generated during particle screening was analysed by a portable X-ray fluorescence (pXRF) analyser to determine its main components.

Gravity separation testing

The Mozley superpanner is a batch version of a traditional shaking table. Where possible, the samples were split into a number of size band fractions (dependent on the particle size distribution), with the $<20 \,\mu m$ size band fraction removed. During each Mozley test, five concentrates and a tailings sample were produced, each of which was analysed by pXRF.

The heavier materials discharge at the top table exit, while the lighter materials discharge at the bottom of the table as can be seen in Figure 2.4. On completion of the test work, the samples were returned to the University of Limerick for a more accurate chemical analysis. On completion of the ICP analysis, additional analyses, including EDS and XRD, were carried out to complement the original pXRF data. The Mozley superpanner parameters are detailed as follows:

- set-up:
 - V deck for >45-µm-diameter material with a stroke length of 2.5 inches;
 - flat deck for <45-µm-diameter material with a stroke length of 3.5–4 inches;
- feed charge: 100 g material;
- wash and feed water rate: adjusted by hand in real time;
- deck angle: adjusted by hand in real time.

2.4.2 Multi-gravity separator

The micro-MGS operates on a similar principle to a shaker table to separate and upgrade very fine materials. The MGS's subtle centrifugal force simulates enhanced gravity, pinning heaver materials to the wall of the drum, while lighter tailings are agitated by the shaking motion and washed away (Figure 2.5). The micro-MGS generates one concentrate fraction and one tailings fraction for each test. Scoping tests were performed using a 10-kg sample size. The MGS parameters were as follows:

- set-up: rotating drum 100-280 rpm;
- feed charge: 10-25 kg
- wash and feed water rate: 0–10 L/min;
- deck angle: 0–9°.



Figure 2.4. Mozley superpanner shaker table illustration. Reproduced from Shariati *et al.* (2015); licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).



Figure 2.5. Operation of the multi-gravity separator. Source: Gravity Mining Ltd (https://www. gravitymining.com/micro-multi-gravity-separator; accessed 2 April 2021).

3 Irish Waste Inventory and Characterisation

3.1 Selection of Samples

A review of the waste generated by industry in Ireland was undertaken. Companies in the mining, power and alumina production sectors were listed and samples of waste were requested from each company. Table 3.1 lists the samples received, the sample codes, the source of the samples and additional relevant sample information.

A full characterisation analysis of the mining, power and alumina sector waste samples was undertaken, which included assessment by SEM, energy dispersive X-ray analysis (EDX), XRD, ICP, particle size, electrical conductivity, pH, and moisture content. Sections 3.2–3.4 summarise the characterisation results for each sample.

3.2 Mining Sector Samples

Initial characterisation of the nine mining sector samples was undertaken. All the mines are zinc-lead mines with the exception of Avoca, which is a copper mine. Lisheen Mine and Tara Mines samples displayed larger particle sizes (range 2–500 µm), lower electrical conductivity (1.2 mS/cm) and higher pH (~9-10) than the other mine samples. This may be related primarily to their geology and to the facts that these are modern mines with recent mining activities and the samples were provided directly from the sites, whereas the other samples were supplied by indirect routes and, in some cases, the samples were from spoil heaps and storage facilities. The other samples exhibited a finer particle size range (~10-20 µm), lower pH (6-8) and a wider variation in electrical conductivity [the Garryard, Gortmore and Ballygown (Silvermines) and Galmoy sample values were between 2 and 5 mS/cm, while the Avoca and Two Valleys Mines samples were approximately 0.5 mS/cm].

Figure 3.1 displays the SEM and EDX analysis of the Tara Mines waste sample, in which it can be seen that the tailings sample comprised a wide range of particle sizes up to approximately $125 \,\mu$ m. The elemental map reveals the significant presence of calcium and silicon

in the bulk of these samples, and iron, sulfur and aluminium were also detected.

A similar analysis was performed for all the samples and combined with an ICP analysis, giving the quantitative elemental amounts present in the sample, as shown in Table 3.2. The major trends identified from the characterisation study are listed below according to the key elements that presented in the mining sector waste samples.

3.2.1 Calcium

Tara Mines and Tynagh Mine samples contained high concentrations of calcium ~270 g/kg; the XRD analysis showed that it was the calcium carbonate phase.

3.2.2 Iron

High concentrations of iron were detected in the samples from Lisheen Mine, Garryard, Gortmore and Ballygown sites at 139, 194, 238 and 127 g/kg, respectively. XRD analysis showed an iron sulfide phase present in the Lisheen Mine and Gortmore samples.

3.2.3 Magnesium and zinc

High levels of magnesium were detected in the Lisheen, Gortmore and Galmoy Mines samples (~40– 50 g/kg), while zinc was present in high concentrations in some samples from the Garryard and Ballygown sites (~180–270 g/kg).

3.2.4 Critical raw materials

CRMs were detected in the mining sector samples, with gallium (0.1-0.3 g/kg), indium (0.1-0.2 g/kg) and phosphorus (0.1-0.6 g/kg) present in the majority of the samples.

3.3 Power Sector Samples

Samples of fly ash and bottom ash from one coalpowered plant [Electricity Supply Board (ESB)

Site name	Sample code	Source of samples	Supplier sample code	Provider of samples	Comments
Mining sector					
Lisheen Mine	Lisheen 01	Tipperary	Lisheen Mine	Lisheen Mine	Lead-zinc mine. The received sample was wet
Tara Mines	Tara 2012	Meath	2012 sample	Tara Mines	Zinc mine. The received sample was dry and labelled 2012
	Tara 2018	Meath	2018 sample	Tara Mines	Zinc mine. The received sample was dry and labelled 2018
Silvermines Garryard	Garryard 07 SP01.2 1/2 rem	Garryard, Tipperary	07 SP01.2 1/2 rem	GSI	Lead-zinc mine. Samples were waste rock (received dry)
	Garryard 01.1 1/2 rem	Garryard, Tipperary	01.1 1/2 rem	GSI	1
	Garryard 07 SP01.7	Garryard, Tipperary	07 SP01.7	GSI	1
Silvermines Gortmore	Gortmore 1.2	Gortmore, Tipperary	1.2	GSI	Gortmore is a tailings facility for Silvermines area. Sample received dry
Silvermines Ballygown	Ballygown SIL 08 SP 03.5	Ballygown, Tipperary	SIL 08 SP 03.5	GSI	Lead mine. Samples were waste rock. The received sample was dry
	Ballygown SIL 08 SP02.1	Ballygown, Tipperary	SIL 08 SP02.1	GSI	1
	Ballygown SIL SP 15 2-inch deep	Ballygown, Tipperary	SIL SP 15 2-inch deep	GSI	1
Avoca Mines	Avoca TM4056	Avoca Mines, Wicklow	LR18114809 TM 4056	Trove Metal	Copper mine. The received sample was dry
Galmoy Mine	Galmoy M003	Galmoy Mine, Kilkenny	LR 18089369M003	Trove Metal	Lead-zinc mine. The received sample was dry
Two Valleys Mines	Two Valleys M001	Wicklow	LR 180839320M001	Trove Metal	Lead mine. The received sample was dry
Tynagh Mine	Tynagh TA 04	Galway	07 TA 04.8 1/2 mill	GSI	Lead-zinc mine. The received sample was dry

Table 3.1. List of the waste samples received from the Irish mining, power and alumina sectors

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Site name	Sample code	Source of samples	Supplier sample code	Provider of samples	Comments
Power sector					
ESB Moneypoint	EFA-MP Fly Ash	Clare	Fly Ash	ESB Moneypoint	Coal-powered plant. The received sample was dry fly ash
	EBA-MP Bottom Ash	Clare	Bottom Ash	ESB Moneypoint	Coal-powered plant. The received sample was dry bottom ash
ESB Lough Ree	ESB-LL Fly Ash	Longford	Fly Ash	ESB Lough Ree	Peat-powered plant. The received sample was dry fly ash
	ESB-LL Bottom Ash	Longford	Bottom Ash	ESB Lough Ree	Peat-powered plant. The received sample was dry bottom ash
ESB West Offaly	ESB-WO Fly Ash	Offaly	Fly Ash	ESB West Offaly	Peat-powered plant. The received sample was a dry fly ash
	ESB-WO Bottom Ash	Offaly	Bottom Ash	ESB West Offaly	Peat-powered plant. The received sample was a dry bottom ash
Covanta Dublin Waste to Energy	Cov-FA Fly Ash	Dublin	Fly Ash	Dublin Waste to Energy	Dublin waste-to-energy power plant. The samples received were flue gas-treated residues, treated with lime and activated carbon in a 3-phase treatment process.
	Cov-BA Bottom Ash	Dublin	Bottom Ash	Dublin Waste to Energy	Waste-to-energy power plant. The received sample was dry bottom ash
Indaver	In-FA Fly Ash	Meath	Fly Ash	Indaver	Waste-to-energy power plant. The received sample was dry fly ash post treatment with lime/clays.
	Ind-BA Bottom Ash	Meath	Bottom Ash	Indaver	Waste-to-energy power plant. The received sample was dry bottom ash
Alumina sector					
Aughinish Alumina	Bauxite residue 05	Limerick	Bauxite residue 05	Aughinish Alumina	Alumina refinery. The received bauxite residue was dry

-, no additional information; ESB, Electricity Supply Board; GSI, Geological Survey of Ireland.



Figure 3.1. SEM and EDX analysis of the Tara Mines waste sample (Tara 2018 control sample).

Moneypoint], two peat-powered plants (ESB Lough Ree and ESB West Offaly) and two waste-to-energy facilities [Covanta Dublin Waste to Energy (DWTE) and Indaver] were characterised.

Samples from the coal-powered ESB Moneypoint plant, shown in Figures 3.2 and 3.3, were composed of fine spherical particles that were typically $\sim 5 \,\mu$ m in size for the fly ash samples and $\sim 20 \,\mu$ m in size for the bottom ash samples. In contrast, the peat-powered plant and waste-to-energy plant samples exhibited larger ranges of particle size: from 1 to 100 μ m for fly ash and from 10 to 3000 μ m for the bottom ash samples. It was noted that, in general, the bottom ashes comprised a mixture of fine powder (which was analysed above), larger agglomerates and rock-like inclusions up to 10 cm in diameter that had been screened out.

A detailed analysis of all the samples was undertaken, and Table 3.3 displays the quantitative results of the ICP analysis of the elements present in the waste samples. The major trends identified from these characterisation studies are discussed below, according to the key elements present in the power sector waste samples.

3.3.1 Calcium

The ICP analysis showed significant calcium concentrations for the majority of the samples. Waste-to-energy samples showed the highest calcium concentrations of ~192–249g/kg for fly ash and 122–144g/kg for bottom ash. This was followed by the peat-powered plant samples, which exhibited calcium concentrations of 96–182g/kg for fly ash and 63–166g/kg for bottom ash, while the coal-powered plant samples displayed the lowest calcium

concentrations of 31 g/kg for fly ash and 4.3 g/kg for bottom ash. XRD analysis revealed the presence of calcium sulfide and calcium carbonate phases for the peat-powered plant and waste-to-energy plant samples.

3.3.2 Iron

Iron was present in all of the samples, with the peat-powered West Offaly plant samples (47 and 42 g/kg for fly ash and bottom ash, respectively) and the Covanta DWTE plant samples (92 g/kg for bottom ash) displaying the highest values. Only iron oxide phases were detected in the XRD analysis for the coalpowered Moneypoint plant samples, while calcium-iron silicates were detected in the peat-powered Lough Ree samples.

3.3.3 Magnesium and zinc

Magnesium was detected in all of the samples in the range 0.9–23 g/kg, and the peat-powered West Offaly plant and Indaver waste-to-energy plant samples showed the highest values. High zinc concentrations were detected in the Covanta DWTE samples (6–9 g/kg) and Indaver waste-to-energy samples (2–4 g/kg).

3.3.4 Critical raw materials

Gallium and indium were again constant across the samples in the range 0.1–0.2 g/kg. Phosphorus was also present in the majority of samples, typically at a level of 0.1 g/kg, but the Covanta DWTE samples showed the highest concentration (4.7 g/kg) in the fly ash. It is evident from the above that the composition of the waste samples from different plants varies significantly even within power plant sub-categories.

Table 3.2. Results of ICP elemental analysis of mining sector samples (g/kg)

	Site nam	e and sar	nple cod	0										
				Silvermines	10									
	Lisheen	Tara Min	sər	Garryard			Gortmore	Ballygown			Avoca	Galmoy	Two Valleys	Tynagh
	Mine	c 100	0 000	07 SP01.2	01.1 1/2	r 1003 ro	с т	SIL 08 SP	SIL 08	SIL SP 15	Mines	Mine	Mines	Mine
степлени	5	2012	2010			1.1076 10	7 :	0.0.0	0L02.1	z-Incii deep	0C04M1	CUUM	INUU	5
A	0.20	1.05	1.11	1.24	1.51	0.47	0.57	6.94	6.59	0.18	3.93	0.53	7.25	1.62
Ca	31.03	272.82	261.68	3.35	4.77	0.88	4.69	0.88	9.24	0.69	0.06	60.42	1.99	275.39
Cd	I	0.02	I	0.68	0.09	0.04	0.07	0.06	1.37	I	I	0.04	0.07	0.16
S	0.12	0.04	0.02	0.02	I	0.02	0.04	0.05	0.04	0.01	I	0.16	I	0.04
ŗ	0.02	0.01	0.03	0.01	0.01	0.02	0.02	0.02	0.02	I	I	I	0.02	I
Cu	0.07	0.13	0.13	0.48	0.09	0.06	0.18	0.09	0.04	0.05	0.45	0.12	0.59	1.25
Fe	139.93	32.89	41.23	88.36	93.31	194.34	238.14	127.91	140.89	12.69	47.55	52.47	17.59	19.96
Mg	44.25	0.03	0.05	18.29	2.63	0.05	42.09	0.01	4.39	0.07	1.30	54.93	3.02	5.43
ЧN	0.73	0.18	0.12	1.09	0.30	0.28	4.29	4.54	8.03	0.15	0.16	0.51	0.43	3.22
Na	0.57	24.58	29.99	0.51	0.08	0.20	0.35	0.34	0.31	0.30	0.19	0.39	0.29	0.40
ī	0.37	1.83	1.60	0.13	0.03	0.03	0.11	0.03	0.13	0.02	0.01	0.23	I	0.09
Zn	13.05	0.25	0.19	186.45	20.13	9.22	18.27	34.37	270.74	0.09	0.15	17.91	19.10	12.02
Ga	0.14	0.09	0.09	0.07	0.10	0.33	0.35	0.14	0.13	0.10	0.05	0.06	0.02	0.11
드	0.05	0.05	0.04	0.03	0.03	0.01	0.11	0.12	0.22	0.01	0.07	0.11	0.14	0.06
Ce	I	I	0.01	0.01	0.02	0.01	0.02	0.04	0.03	0.01	0.03	0.01	0.03	0.06
La	I	0.01	I	I	I	I	0.00	0.02	0.03	I	0.00	0.00	I	0.01
pN	Ι	I	0.11	0.02	0.03	0.01	0.05	0.02	0.03	0.02	0.01	0.05	0.01	0.02
Pr	Ι	I	Ι	0.02	0.02	0.01	0.03	0.03	0.05	0.03	0.01	0.03	0.02	0.17
Sc	I	I	I	I	I	I	I	I	I	I	I	I	I	0.08
≻	Ι	0.01	0.02	I	I	I	I	0.02	0.05	I	I	I	I	0.02
д.	0.02	0.56	0.53	0.12	0.09	0.07	0.02	0.01	0.03	0.02	0.16	0.37	0.99	0.30
Sb	I	0.25	0.19	I	I	I	I	0.01	0.02	0.03	0.10	0.05	0.07	0.01
Si	0.40	0.07	0.05	0.30	0.12	0.19	0.15	0.05	0.06	0.07	0.13	0.10	0.12	0.16
F	0.04	0.02	0.02	0.02	0.02	0.03	0.02	0.04	0.05	0.03	0.03	I	0.19	0.01
>	0.02	0.02	0.02	0.02	0.03	0.03	0.02	0.03	0.03	0.02	0.02	0.01	0.02	0.02

not detected.



Figure 3.2. SEM and EDX analysis of fly ash samples from the ESB Moneypoint coal-powered plant.



Figure 3.3. SEM and EDX analysis of bottom ash samples from the ESB Moneypoint coal-powered plant.

3.4 Alumina Sector Samples

The bauxite residue samples exhibited a particle size range of 1–10 µm, as shown in Figure 3.4, accompanied by electrical conductivity of 2.46 mS/cm and high pH of 10.5. The ICP analysis indicated high concentrations of aluminium (27.8 g/kg) and iron (44.7 g/kg), whereas the calcium concentration was low (0.6 g/kg) (Table 3.4). The CRMs found included gallium and indium, which were present in similar concentrations (0.1 g/kg) to those found in the mining and power sector samples. XRD analysis confirmed that these elements were present and combined in the following phases: iron hydroxides, aluminium iron oxides, iron oxides, silicon oxides and aluminium oxides.

3.5 Analysis of Compositional Variation within the Samples

To investigate the level of variation within the samples, a second batch of selected samples was requested as follows:

- Tara Mines tailings samples;
- coal-powered ESB fly ash samples;

- Covanta DWTE fly ash samples;
- Aughinish Alumina bauxite residue samples.

A comparison of the physical characteristics of the first and second batches was undertaken, in which some variation in density, pH, electrical conductivity and particle size was observed. Bulk density exhibited the least variation, with values differing by 0.02–0.08 g/cm³, while true density was more variable, with values deviating by 0.02–0.78 g/cm³. ESB and Covanta DWTE samples showed the greatest consistency between batches, whereas Tara Mines and Aughinish Alumina samples showed the most variation.

The batch 1 and batch 2 samples from each mine or site had consistent pH measurements – the maximum variation seen was a decrease in pH of 0.35 for the batch 2 ESB samples. Electrical conductivity was also consistent between batch 1 and 2 samples, with the Covanta DWTE samples showing the largest deviation of 2.82 mS/cm.

Particle size showed the largest variation of all the physical characteristics. The Covanta DWTE samples were the most consistent, with particle size measurements of $10.53 \,\mu$ m and $11.61 \,\mu$ m for the first

	Site name and	sample codes								
	ESB Moneypo power plant	int – coal-fired	ESB Lough Re power plant	e – peat-fired	ESB West Offaly power plant	y – peat-fired	Covanta – DWT	TE plant	Indaver – was plant	te-to-energy
Element	Fly ash	Bottom ash	Fly ash	Bottom ash	Fly ash	Bottom ash	Fly ash	Bottom ash	Fly ash	Bottom ash
A	11.22	2.63	28.77	6.51	11.89	11.01	19.14	38.10	53.51	36.17
Са	31.13	4.34	96.52	63.85	182.34	166.92	249.04	122.09	192.51	144.81
Dd	I	I	I	I	1	I	0.16	I	0.04	0.15
ů	I	I	I	I	1	I	I	0.04	0.06	0.03
ŗ	0.04	0.00	0.10	0.00	0.11	0.10	0.06	0.18	0.12	0.07
Cu	1	I	0.03	I	0.03	0.02	0.57	2.54	0.61	0.79
Fe	16.29	3.94	31.98	10.17	47.81	42.83	9.42	92.72	28.34	35.13
Mg	7.28	0.87	17.36	9.45	23.23	21.35	9.06	8.00	18.38	11.26
Mn	0.13	0.06	0.57	0.21	1.72	1.59	0.66	1.36	1.51	0.87
Na	0.22	0.42	3.28	0.14	4.47	3.57	36.29	8.75	24.36	12.18
Ņ	1		0.06	I	0.09	0.09	0.03	0.15	0.16	0.11
Zn	1	I	0.08	I	0.07	0.11	9.22	6.64	4.62	2.79
Ga	0.12	0.11	0.13	0.13	0.09	0.08	0.16	0.08	0.22	0.23
드	0.13	0.13	0.16	0.12	0.12	0.09	0.15	0.12	0.05	0.03
Ce	0.03	0.04	0.06	0.02	0.05	0.05	0.04	0.02	0.05	0.03
La	1	0.00	0.02	0.00	0.02	0.02	0.01	0.00	0.02	0.01
Nd	0.04	0.01	0.02	0.04	0.03	0.01	0.02	0.03	0.05	0.04
Pr	0.03	0.04	0.04	0.04	0.05	0.06	0.04	0.04	0.12	0.09
Sc	1	I	0.02	I	0.04	0.04	I	I	0.06	0.04
~	I	I	0.02	I	0.02	0.02	I	I	0.02	I
٩	0.15	0.44	1.56	0.44	2.83	2.56	4.70	1.35	1.50	0.50
Sb	0.03	I	0.02	0.02	I	I	0.21	0.03	I	I
Si	0.35	0.27	0.31	0.35	0.35	0.35	0.31	0.36	0.20	0.30
Ħ	I	0.08	0.32	0.04	0.34	0.31	1.25	0.37	0.02	0.25
>	0.00	0.01	0.04	0.00	0.03	0.03	0.10	0.02	0.05	I

Table 3.3. Results of ICP elemental analysis of the power sector waste samples (g/kg)

not detected.



Figure 3.4. SEM and EDX analysis of bauxite residue from Aughinish Alumina plant (control sample: Bauxite residue 05).

and second batch samples, respectively. Tara Mines samples showed the most variation, with the particle size ranging from $0.35\,\mu m$ for batch 1 samples to

Table 3.4. ICP elemental analysis of the bauxiteresidue 05 sample from the Aughinish Aluminarefinery plant

Element	Content in sample (g/kg)
AI	27.76
Са	0.64
Cd	-
Со	0.01
Cr	0.29
Cu	0.07
Fe	44.68
Mg	1.60
Mn	0.98
Na	0.16
Ni	-
Zn	1.02
Ga	0.06
In	0.10
Се	0.02
La	0.01
Nd	-
Pr	0.02
Sc	-
Y	-
Р	0.02
Sb	-
Si	0.39
Ti	1.65
V	-

-, not detected.

 $6.86\,\mu m$ for batch 2 samples. In contrast, the ESB and Aughinish Alumina samples showed a variation of ~3 μm between the batch 1 and 2 samples.

ICP analysis of batch 1 and 2 samples investigated the variation in the concentration of key elements within the samples (Table 3.5). Aluminium concentrations were high in the Covanta DWTE and Aughinish Alumina samples. A small difference in aluminium concentration was found in the Covanta DWTE samples (19.4 g/kg in batch 1 vs 24.9 g/kg in batch 2), whereas the Aughinish Alumina samples showed a large difference in concentration (27.8 g/kg in batch 1 vs 45.9 g/kg in batch 2).

Iron values varied significantly for all samples with the exception of the Covanta DWTE samples. Iron concentrations in the Aughinish Alumina samples ranged from 44.7 to 147.8 g/kg, and the ESB and Tara Mines samples also showed considerable variation in the levels of iron present (16.3 g/kg in batch 1 vs 4.4 g/kg in batch 2 for the ESB samples and 41.2 g/kg in batch 1 vs 25.2 g/kg in batch 2 for the Tara Mines samples).

Although the calcium concentrations were high in the Tara Mines and Covanta DWTE batch 1 samples and remained so in the batch 2 samples, variations were observed; the concentrations in the Tara Mines samples ranged from 261.7 g/kg in batch 1 to 168.3 g/kg in batch 2 and in the Covanta DWTE samples from 249.0 g/kg in batch 1 to 265.4 g/kg in batch 2.

CRM concentrations generally stayed within their expected range of 0.1–0.2 g/kg for the majority of samples; however, variations between batch 1 and

	Sample code and batch												
	Tara Mines 2018		ESB Mone fly ash	ypoint coal	Covanta D	WTE fly ash	Aughinish Alumina refinery plant bauxite residue 05						
Element	Batch 1	Batch 2	Batch 1	Batch 2	Batch 1	Batch 2	Batch 1	Batch 2					
AI	1.11	0.45	11.22	2.95	19.14	24.90	27.76	45.89					
Са	261.68	168.30	31.13	5.00	249.04	265.40	0.64	25.50					
Fe	41.23	25.18	16.29	4.44	9.42	9.64	44.68	147.78					
Ga	0.09	0.08	0.12	0.06	0.16	0.21	0.06	0.98					
Mg	0.08	17.53	7.28	1.55	9.06	10.07	0.16	0.33					
Na	29.98	0.19	0.22	0.36	36.29	17.43	0.16	30.13					
Р	0.53	0.33	0.15	0.26	4.70	5.92	0.02	0.94					
S	4.30	2.50	9.10	0.91	4.60	6.22	-	1.27					
Si	0.05	0.10	0.35	0.49	0.31	0.56	0.39	1.35					
In	0.04	0.22	0.13	0.23	0.15	0.27	0.10	0.13					

Table 3.5. Results of ICP elemental analysis of the selected batch 1 and batch 2 samples (g/kg)

-, not detected.

batch 2 samples were evident. ESB batch 2 samples for the bottom ash showed the lowest concentration of gallium at 0.06 g/kg, and Aughinish Alumina samples showed the highest at 1.6 g/kg. The Tara Mines batch 1 samples exhibited the lowest indium concentration at 0.04 g/kg.

XRD and SEM analysis of both batches of samples produced similar results. The morphology of the

particles as examined under the SEM was very consistent between the two batches of samples, and XRD analysis of the samples produced near-identical patterns. This indicates that the bulk of the individual samples are relatively consistent between batches with respect to the phases that are predominant. However, variation in the concentrations of particular elements and metals remains large from sample to sample.

4 Synergies between Wastes from Different Sectors

Table 4.1 summarises the key elements that were present in waste samples from the different sectors according to the results of the ICP analysis. Common base metals such as iron, aluminium, zinc and magnesium were present in the majority of samples and, although calcium was present in all samples, some power plant and mining sector samples contained very high concentrations of over 200 g/kg. There was also good consistency regarding the presence of three CRMs, namely gallium, indium and phosphorus, and these elements were present in similar concentrations in most of the waste samples. Figure 4.1 groups the different wastes according to their main compositional synergies for key metals present. *Calcium* concentrations in the Tara Mines and Tynagh Mine samples were very high, at greater than 270 g/kg, and the waste-to-energy samples also contained similar calcium levels. Samples from the peat-powered plants had calcium concentrations of \sim 100 g/kg.

The high concentration of calcium in these samples may represent a potential opportunity to treat these wastes together to separate and concentrate the

Element	Mining sector	Power sector	Alumina sector
Base metals			
Fe	12–238	3–92	44
Al	2.6–53	0.5–6.9	27
Zn	0.2–270	0–9.2	1
Mg	0–54	0.9–23	1.6
Cementitious material			
Са	0.9–275	4–249	0.6
CRMs			
Ga	0.1–0.3	0.1–0.2	0.1
In	0–0.2	0–0.2	0.1
Р	0-0.5	0 1-4 7	0

Table 4.1. Summary of the key elements present in the different waste sector samples (g/kg)



Figure 4.1. The three most abundant metals and the highest values of these metals measured in the various waste samples.

calcium phase. A concentrated calcium fraction such as this would help to reduce the bulk of the waste and could potentially have reuse applications in the construction sector.

The Garryard and Ballygown site samples displayed very high concentrations of *zinc* at ~180 g/kg. These samples are waste rock samples rather than post-processing samples (i.e. not tailings), which is assumed to account for the high zinc concentration. However, they may represent an opportunity for zinc recovery now that more advanced recovery techniques are standard in industry (Wang, 2016). The waste-toenergy samples displayed elevated quantities of zinc in both the bottom ash and fly ash samples, which could also represent an opportunity for recovery either before or after any processing of the samples to separate the calcium phase.

Finally, *iron* in concentrations greater than 100g/kg was found in the group of Silvermines samples and in the Lisheen Mine samples, while the waste-toenergy and West Offaly peat-powered plant samples typically contained ~50 g/kg iron. Iron phases can be removed by magnetic separation if the magnetic phase is present in the samples (magnetite), and this represents an opportunity to reduce the bulk quantity of these wastes. However, the XRD analysis highlighted a mixture of magnetic and non-magnetic iron phases present in the samples.

Table 4.2. List of calcium phases detected in thewaste samples

Samples	Calcium phase detected in XRD analysis
Tara Mines	Calcium carbonate
	Calcium iron magnesium carbonate
Tynagh Mine	Calcium carbonate
	Calcium sulfate hydrate
Covanta DWTE	Calcium carbonate
Indaver	Calcium aluminium silicate
	Calcium hydroxide aluminium silicate hydrate
ESB Lough Ree	Calcium sulfate
	Calcium iron silicate
ESB West Offaly	Calcium carbonate
	Calcium sulfate hydrate
	Calcium sulfate

XRD analysis revealed the presence of calcium in different phases, as shown in Table 4.2. Calcium carbonate was the predominant phase in the samples from the Tara and Tynagh Mines, although it was accompanied by other calcium mixed oxide phases. Calcium carbonate was the main calcium-bearing phase in the Covanta DWTE samples, while Indaver samples showed a preponderance of mixed oxide silicates and both peat-powered plant samples showed a preponderance of calcium in sulfate phases. The separation of calcium from the bulk of these waste materials may be made more difficult by the presence of calcium in mixed oxide phases.

XRD analysis of the samples revealed the presence of zinc in different phases, as shown in Table 4.3. Zinc was detected in the Garryard samples as zinc gallium sulfide, whereas analysis of the Ballygown samples showed no zinc phase. This is in contrast to the high zinc concentration detected in the ICP analysis and points to a potentially large variation in zinc concentrations in the waste samples. Covanta DWTE waste samples contained a complex zinc oxide, correlating with the ICP result in which a concentration of approximately 9g/kg of zinc was detected. A zinc phase was not detected in Indaver samples, and this could simply be due to a lower concentration of zinc in these samples.

XRD analysis revealed the presence of iron in these wastes in the phases shown in Table 4.4. It can be seen that iron was detected in the majority of the samples as both magnetite and haematite. The mine samples also showed the tendency of iron to form sulfide phases. The presence of magnetite would lend itself well to magnetic separation; however, non-magnetic haematite is also present.

These compositional trends represent a potential synergy whereby these different wastes could be treated together by using separation techniques based

Table 4.3. List of zinc phases detected in the wastesamples

Samples	Zinc phase detected in XRD analysis
Garryard Mine	Zinc gallium sulfide
Ballygown Mine	Zinc phase not detected in XRD
Covanta DWTE	Barium lanthanum zinc ruthenium oxide
Indaver	Zinc phase not detected in XRD

Table 4.4. List of iron phases detected in the wastesamples

Samples	Iron phase detected in XRD analysis
Silvermines	
Garryard	Iron oxide sulfate hydrate
	Iron oxide magnetite
Gortmore	Iron oxide haematite
	Iron sulfide
Ballygown	No iron phase detected in the XRD
Lisheen Mine	Iron sulfide
	Calcium iron magnesium carbonate
	Iron oxide haematite
	Iron oxide magnetite
ESB West Offaly	Iron oxide haematite
	Iron oxide magnetite
Covanta DWTE	Iron oxide haematite
	Iron oxide magnetite
Indaver	Iron oxide haematite
	Iron oxide magnetite

on the calcium, zinc and iron phases present. The potential to process different wastes together could offer an economy of scale to any recovery process and improve the economic feasibility of such processes. In addition, all of these samples contained similar quantities of indium, gallium and phosphorus, which may offer opportunities for combined recovery of these elements from the different wastes.

5 Development of a Recovery Strategy

The characterisation and synergy analyses of the wastes revealed that calcium, iron and zinc were the dominant elements present. The CRMs indium, gallium and phosphorus were present in the majority of the wastes in low concentrations. A holistic recovery strategy based on the materials identified would need to address the entirety of the waste and not just the perceived higher-value elements such as CRMs, as recovery of only CRMs would leave the bulk of the waste still requiring waste management. Therefore, the approach involves the investigation of potential processes that may generate three fractions: (1) a base metal-rich fraction (iron, zinc); (2) a calcium-rich fraction; and (3) a CRM-rich fraction (Figure 5.1).

The approach, therefore, is to achieve bulk separation of these materials in one or multiple steps. The fractions containing concentrated levels of metals could be processed by traditional recovery and purification methods, and the high metal concentrations and economies of scale could potentially make the recovery economically feasible (Figure 5.2).

As the objective of the research was to generate material fractions from the waste samples that have increased concentrations of base metals, calcium and CRMs, a review of potential techniques was undertaken. Figure 5.3 summarises the main extractive metallurgical techniques available for materials recovery. The goal is to recover valuable materials, reduce the quantity of waste materials to be sent to landfill and minimise the environmental impact of the waste. With this goal in mind, it was



Figure 5.1. The materials of interest for the recovery strategy.

decided to avoid techniques that use large volumes of concentrated acids and/or generate acidic by-products. Typically, hydrometallurgy and electrometallurgy use concentrated acids to dissolve metals, whereas pyrometallurgy uses high-temperature processing. These techniques can have a considerable environmental impact because of their energy and acid use, which is exacerbated in cases where the target materials are present in low concentrations, making these processes uneconomical and unsustainable. Therefore, these techniques are more appropriate for processing the downstream fractions of the wastes once higher target material concentrations have been achieved. Consequently, mineral processing operations that typically rely on mechanical and physical separation techniques were selected as being most appropriate for the separation of target metals from the wastes.

Figure 5.4 summarises the key mineral processing techniques used in the mineral processing industry. *Comminution* is the action of reducing a material, especially a mineral ore, to small particles or fragments using grinding and crushing techniques. This is typically followed by a *sizing operation*, which is the general term for separating minerals according to their particle size. The simplest mineral-sizing process is screening or passing particles to be sized through a screen, although more advanced, automated processes such as trommels and sorters are available.

Other processes, such as *concentration techniques*, involve the separation of valuable materials from the bulk material or mineral ore, typically following grinding. In large-scale operations this is accomplished by taking advantage of the different properties of the minerals such as specific gravity or density properties.

Froth flotation is a process for separating minerals from gangue by taking advantage of differences in their hydrophobicity. Such differences between valuable minerals and waste gangue are increased through the use of surfactants and wetting agents. The flotation process is used to separate a range of sulfides, carbonates and oxides before further refinement.

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Figure 5.2. The main steps to achieving final recovery of materials of interest.

EXTRACTIVE METALLURGY
Mineral processing
Hydrometallurgy
Pyrometallurgy
Electrometallurgy
Geometallurgy

Figure 5.3. Summary of the key processing technologies for metals extraction and recovery.

Separation of minerals using differences in their electrical properties may be carried out using an *electrostatic separator*. It separates electrical conductors (minerals such as cassiterite and rutile) from those that are electrical non-conductors (minerals such as zircon and siderite). The principle of separation is based on a process in which the particles to be treated are passed through an intense electric field and each particle acquires a charge. The conductors lose their charge when emerging from the field, while the non-conductors retain theirs momentarily. This difference is used to separate the materials.

Magnetic separation is the process of separating components of mixtures by using magnets to attract magnetic fractions, thereby detaching them from non-magnetic materials.

Sensor-based sorting is an umbrella term for all applications in which particles are singularly detected by a sensor technique and rejected by an amplified mechanical, hydraulic or pneumatic process. The technique is generally applied in three industries – mining, recycling and food processing – and to particle sizes between 0.5 and 300 mm.



Figure 5.4. Summary of the key mineral processing techniques for materials separation.

Based on the above, *comminution and sizing operations* were selected to investigate whether there is any relationship between particle size and concentration of particular metals in the waste materials. As comminution can also be used as a preprocessing step for other operations, understanding the relationship between particle size and composition, if any, for these wastes is key. In-house techniques available for such a study include ball milling, screen filtration, chemical analysis and characterisation to determine any concentration effects in the different particle size bands generated.

In addition, as iron is one of the key base metals present in the majority of wastes and magnetite was detected in some of the waste materials by XRD analysis, *magnetic separation* was also chosen for in-house testing.

Although electrostatic separation may offer potential for separation, it depends on the contrast between the conducting and non-conducting minerals within each waste mixture and would require further investigation. Although froth flotation techniques involve targeting particular particles based on hydrophobicity, they may not be suitable for initial bulk separation but might be considered, depending on the response of materials to the bulk separation processes, for targeting carbonate fractions in particular. To explore potential options in wet chemistry recovery techniques, preliminary *dissolution studies* of the wastes were generally selected to investigate the slurry behaviour of the wastes.

In addition, as mechanical and physical processing of the wastes has benefits in terms of minimising the number of processing steps, energy consumption and chemical use, gravity/density separation techniques were selected for study. To study the amenability of the samples to gravity separation, gravity release analysis using a *Mozley superpanner*, which is effectively a batch version of a shaker table (an industrial standard), was chosen for study. The study was intended to gauge the general response of the waste samples to gravity separation. In addition, the multigravity concentrator technique was also selected for study, because of its advantages regarding processing fine particle size materials. As these techniques are not available in-house, these studies were outsourced to specialised consultant laboratories with the relevant equipment.

Table 5.1. Samples selected for testing recoverytechniques for bulk metal separation (controlsamples)

Sector	Control sample selected
Mining	Tara Mines
Power	ESB Moneypoint coal-powered plant
	Covanta DWTE plant
Alumina	Aughinish Alumina

As a large number of samples were analysed under the waste inventory, representative samples of each of the three sectors were chosen to act as control samples for testing the metal recovery techniques with the best potential for recovery. The selected samples are listed in Table 5.1.

Tara Mines samples were selected to represent the mining sector, as these samples are from the only live mine in Ireland with an ongoing need to manage tailings. These samples were particularly high in calcium and contained significant concentrations of iron, gallium, indium and phosphorus.

ESB Moneypoint samples were selected to represent coal power plants, as a sufficient volume of samples was available. These samples contained low concentrations of calcium and iron, as well as the CRMs gallium, indium and phosphorus. Samples from the peat-powered plants had similar compositions to the coal-powered plant samples but exhibited higher concentrations of calcium and iron. However, insufficient quantities of the peat-powered plant samples were available for further testing.

Covanta DWTE samples were selected to represent the waste-to-energy sector, as they have high concentrations of calcium and iron. These samples also contained elevated zinc concentrations, as well as the CRMs gallium, indium and phosphorus.

The bauxite residue samples were provided by Aughinish Alumina and contained high concentrations of aluminium and iron along with low concentrations of zinc, gallium, indium and phosphorus.

The selected control samples then underwent individual testing of the following recovery techniques: comminution, sizing operations, magnetic separation, dissolution studies, Mozley superpanner separation and multi-gravity separation.

6 Testing Separation Techniques

6.1 Comminution and Sizing Tests

The process of filtration and separation of the samples into size band fractions was investigated to establish whether there is any concentration effect on key metals or elements in the different size band fractions. The control samples were filtered through a series of sieves of different mesh grades to achieve five size band fractions with diameters of: 500-100 µm, <100–90 µm, <90–53 µm, <53–25 µm and <25 µm (Figure 6.1). As Tara Mines, ESB fly ash, Covanta DWTE fly ash and bauxite residue have fine particle sizes (typically $< 25 \,\mu$ m), it was expected that these samples would pass through the sieves and any agglomerations of the particles would be broken up. On testing, this was found to be the case, with 100 g of the samples passing through the sieves, resulting in a single particle size band of <25 µm, with negligible loss of material in the process.

However, the bauxite residue samples, which previously showed a particle size of between 4 and $8\,\mu$ m, separated into different particle size bands. It was found that almost 47% of the weight (wt%)



Figure 6.1. Diagram illustrating the screening sieves for the sizing operation.

of the sample filtered into the 500–100 μ m size band, 2.6 wt% into the 100–90 size band, 27 wt% into the 90–53 μ m size band and 20 wt% into the 53–25 μ m size band, with less than 2 wt% of the sample in the <25 μ m size band. It is suspected that this result may be due to persistent agglomeration of the particles, which is supported by the finding that there was no significant compositional variation in these different size bands.

The bottom ash samples from the coal and wasteto-energy plants separated into five different size bands, and each of these was analysed by ICP. The fine fractions of the ESB bottom ash samples showed slightly higher aluminium, calcium and iron concentrations; however, no significant trends were identified for any other elements. The fine size band fractions of the Covanta DWTE bottom ash also displayed higher concentrations of aluminium and calcium, but there was no trend in the concentration of iron or other elements in these fractions.

To further investigate whether comminution would have an effect on the distribution of particle sizes, the samples were ball milled and then filtered into the different particle size bands. There was no effect on the Tara Mines, ESB fly ash and Covanta DWTE fly ash wastes, which again did not separate into size bands because the particle size was already finer than $25 \,\mu$ m.

However, ball milling and filtration of the ESB bottom ash, Covanta DWTE bottom ash and bauxite residue samples resulted in a larger proportion of the sample (~57 wt%) in the fine particle size bands. The ICP analysis of the different size band fractions for these samples showed a slight increase in aluminium and calcium in the fine particle size band in the ESB bottom ash samples, but no other major trends were identified for the other elements or samples.

6.2 Magnetic Separation

Wet and dry magnetic separation were performed on the control samples to investigate an optimised approach to maximise iron separation from the main fraction. Wet and dry magnetic separation performed on the Tara Mines samples did not provide a magnetic fraction. Characterisation analysis revealed that iron was present in non-magnetic phases (haematite and calcium iron magnesium carbonate), which accounts for the lack of response to magnetic separation in these particular samples.

ESB coal-powered plant samples responded to magnetic separation. Dry magnetic separation of the fly ash resulted in a fraction (3 wt%) with the concentration of iron increased to ~40 g/kg. The fly ash responded similarly to wet magnetic separation, with a separated fraction (4.6 wt%) containing ~50 g/kg iron. Bottom ash samples responded in a similar fashion to both wet and dry separation but with slightly smaller volumes of iron separation and lower iron concentrations observed, which correlates with the lower iron concentrations in the original samples.

Dry magnetic separation of the Covanta DWTE fly ash resulted in a fraction (1 wt%) being generated with an iron concentration of 26 g/kg. Calcium, magnesium and phosphorous concentrations were also increased in this fraction to 208, 33 and 12 g/kg, respectively. However, wet magnetic separation of the Covanta DWTE fly ash resulted in a fraction (3 wt%) being generated that had a higher iron concentration of 78 g/kg and a similar trend towards increased concentrations of calcium, magnesium and phosphorus.

It may be the case that iron oxide is converted to magnetite (Fe_3O_4) in the high-temperature processing of the ESB and Covanta DWTE materials, hence generating wastes with higher concentrations of this magnetic phase.

Dry magnetic separation of Covanta DWTE bottom ash gave a fraction (8wt%) with an iron concentration of 92 g/kg, and no other major trends in metal concentrations were observed. Wet magnetic separation resulted in the highest weight fraction separated, 12.5 wt%, with the highest iron concentration of 160 g/kg (Figure 6.2). No other trends in the redistribution of metals were observed.

Dry magnetic separation of the *bauxite residue* resulted in a very low weight per cent fraction (0.4 wt%) with an iron concentration of 27 g/kg. Wet magnetic separation performed marginally better. This corresponded with the XRD analysis, which showed



Figure 6.2. Wet magnetic separation of the Covanta DWTE bottom ash samples that gave the highest iron separation.

that iron is predominantly present in non-magnetic phases such as haematite, aluminium iron oxide and iron hydroxides.

Wet magnetic separation in general performed better than dry magnetic separation across the range of samples, giving higher weight per cent separation and typically higher iron concentrations.

6.3 Ball Milling, Filtration and Magnetic Separation

Combining the processes of ball milling, filtration and wet magnetic separation had a positive effect on the amount of iron separated. As expected from previous results, the Tara Mines samples again did not separate into size bands or generate a magnetic fraction. Although ball milling and filtration of the ESB and Covanta DWTE fly ashes did not generate size band fractions, the samples contained higher concentrations of iron in the magnetically separated fraction. The ESB fly ash generated a magnetic fraction with an iron concentration of 290 g/kg and a high concentration (33 g/kg) of magnesium. The Covanta DWTE fly ash samples responded similarly but also exhibited high calcium concentrations, reaching 232 g/kg in the separated magnetic fraction.

Ball milling and filtration of the ESB bottom ash samples resulted in five size band fractions, each of which produced a magnetic fraction with a higher iron concentration than in the main sample. This trend was exaggerated in the Covanta DWTE bottom ash sample, in which ball milling and magnetic separation resulted in a separated magnetic fraction with concentrations of iron as high as 460 g/kg in particular <25 µm size band fractions.

Table 6.1 summarises the calculations of iron recovery, comparing the results for the techniques tested. It can be seen that ball milling and filtration results in a significant increase in the quantities of iron collected through an increase in the volume of the fraction separated and/or an increase in the concentration of iron within the volume separated. The ESB fly ash and Covanta DWTE bottom ash samples displayed this trend strongly, and separated magnetic fractions have iron concentrations of ~30 wt%. In these samples a significant proportion of iron is present as magnetic iron in magnetite, while iron is also present in the ESB bottom ash and Covanta DWTE fly ash in nonmagnetic forms such as haematite, iron magnesium sulfide and zinc indium iron oxide. It is clear that ball milling is a beneficial pre-processing step to enhance iron recovery by wet magnetic separation where

a considerable weight per cent iron separation is achievable for magnetic fractions.

6.4 Dissolution of Wastes in Slurry Solution

To investigate the behaviour of the material in a slurry form, the waste control samples were mixed with distilled water and agitated using the ball milling technique. Some of the material dissolved on mixing and ball milling, while insoluble material remained as a deposit at the bottom of the slurry after it settled (termed the deposit). The dissolved material was further investigated by separating the solution by vaporising the water content to leave the residue. Both of these fractions, the residue and the deposit, were dried and filtered into narrow size band fractions.

Table 6.2 summarises the calcium content found in the deposit and residue fractions in the dissolution experiments. It can be seen that the majority of the calcium remained in the deposit in the Tara Mines,

		Wet magnetic	separation		Combination separation			
Waste sample	Infeed weight (g)	Weight ofMagneticthe ironfractionmagneticweight (g)fraction (g)		Percentage of iron in the magnetic fraction	Magnetic fraction weight (g)	Weight of the iron magnetic fraction (g)	Percentage of iron in the magnetic fraction	
ESB fly ash	100	4.63	0.18	3.95	4.77	1.36	28.58	
ESB bottom ash	100	5.12	0.17	3.24	4.94	0.32	6.49	
Covanta DWTE fly ash	100	3.21	0.26	7.99	3.30	0.26	7.99	
Covanta DWTE bottom ash	100	12.56	2.01	16	30.70	10.43	33.96	
Bauxite residue	100	0.9	0.05	6.02	3.06	0.19	6.46	

Table 6.1. Results for iron recovery from industrial waste samples using wet magnetic separation alone and combined ball milling, filtration and wet magnetic separation

Table 6.2. Summary of the calcium content of the deposit and residue fractions generated in the dissolution experiments on the industrial waste samples

	Tara Mines		ESB Moneypoint fly ash		ESB Moneypoint bottom ash		Covanta DWTE fly ash		Covanta DWTE bottom ash	
	Deposit	Residue	Deposit	Residue	Deposit	Residue	Deposit	Residue	Deposit	Residue
Weight (g)	9.88	0.12	9.57	0.43	9.58	0.42	9.65	0.35	9.85	0.15
Calcium (g/kg)	76	336	28	535	3.50	76	179	175	172	91
Calcium/sample wt (g)	0.75	0.04	0.27	0.23	0.03	0.03	1.73	0.06	1.69	0.01
Wt% calcium	94.90	5.10	53.81	46.19	51.23	48.77	96.58	3.42	99.20	0.80

Covanta DWTE fly ash and Covanta DWTE bottom ash samples (approx. 94, 96 and 99 wt% calcium, respectively). Although high concentrations of calcium are seen in the residue fractions of these samples, the amount of residue generated was low. These samples also had dominant calcium carbonate phases, according to the XRD analysis, whereas the Tara Mines samples, which had the highest level of calcium dissolution, contained a calcium iron magnesium carbonate phase that may have facilitated greater calcium dissolution.

ESB fly ash and bottom ash samples displayed the highest levels of calcium dissolution, with 46 and 48 wt% calcium, respectively, in the residue fraction. Nonetheless, this means that a significant amount of calcium still remained in the deposit fraction (Table 6.2). XRD analysis revealed the presence of calcium chlorate in the fly ash, which may have facilitated greater calcium dissolution, as it is extremely water soluble. No dominant peak for a calcium phase was seen in the bottom ash samples, and this correlates well with the low calcium concentrations seen in these samples.

As bauxite residue samples contain minimal amounts of calcium, no major trends were seen for these samples on dissolution. In conclusion, the dissolution experiments illustrated that the phases present in the wastes are generally stable in slurry form. Dissolution of calcium-bearing phases mainly occurred when calcium iron magnesium carbonate and calcium chlorate showed higher dissolution and associated elements moved into the residue fraction.

6.5 Mozley Superpanner Testing

The Mozley superpanner, as can be seen in Figure 6.3, is a shaker table that operates on sample batches of 100g and shakes at an angle while adjusting wash water flow feed. The table has collection zones for different fractions segregating during its operation, numbered concentrate fractions (concs.) 1–5, where conc. 1 is near the top of the table and conc. 5 is near the bottom of the table, followed by a tailings collection point. Denser elements are expected to collect at the top of the table at concs. 1–3, whereas lighter elements are expected to move towards concs. 4 and 5 and the tailings fraction. The technique is not suitable for very fine particle sizes, and fractions below 20-µm particle size are typically removed.



Figure 6.3. Image of the Mozley superpanner (courtesy of Grinding Solutions Ltd).

6.5.1 Tara Mines samples

The samples were filtered through a series of sieves to generate different size band fractions (-355 to $+63 \mu m$, -63 to $+20 \mu m$ and $-20 \mu m$). Filtration of the Tara Mines samples resulted in 63 wt% of the sample in the $<20 \mu m$ size band, with the balance being more heavily distributed in the $32 \mu m$ and $20 \mu m$ size bands.

The size band fractions selected for testing were $-355/+63 \,\mu\text{m}$ (band 1) and $-63/+20 \,\mu\text{m}$ (band 2), and each of these size bands was presented to the superpanner table, generating five concentrate fractions and one tailing fraction for each band.

For both size bands most of the sample processed through the table and into the tailings fraction (>80 g). However, small fractions were found in concs. 1-3 (~1- to 3-g fractions) at the top of the table, which contained most of the iron, whereas most of the calcium was found in concs. 4 and 5 and the tailings fraction, which comprised the finer particle sizes (Table 6.3).

The band 2 fraction generated ~1 g of conc. 1 with an iron concentration of 22 wt%. Combining concs. 1–3 would yield an even higher volume of the iron-rich fraction, while combining concs. 4 and 5 would yield a higher volume of calcium-rich fraction. Although the Tara Mines samples did not contain high iron concentrations to begin with (~40 g/kg), the technique showed potential for significantly improving the separation of calcium and iron phases in these wastes. Previous XRD analysis showed the presence of calcium carbonate, calcium iron magnesium

	Fraction	Elemental analysis (wt%)									
Fraction	weight (g)	AI	Са	Fe	Ga	In	Mg	Na	Р	S	Si
Conc. 1	0.8	0.01	0.45	22.28	0	0.02	0.17	0.04	0.02	22.8	0.02
Conc. 2	1.1	0.03	0.46	18.91	0	0.02	1.21	0.03	0.08	16.21	0.04
Conc. 3	2.2	0.06	4.31	14.26	0	0.02	5.44	0.03	0.13	1.6	0.03
Conc. 4	8.3	0.01	24.97	2.11	0	0	2.77	0.01	0.05	0.13	0
Conc. 5	23.5	0.01	29.72	0.31	0	0	0.71	0	0.01	0.04	0
Tailings 1	82.4	0.08	19.93	3.4	0	0.03	2.74	0.04	0.05	0.45	0

Table 6.3. Results of ICP elemental analysis of the concentrates generated from the $-63/+20 \,\mu$ m size band fraction of the Tara Mines tailings sample by the Mozley superpanner

carbonate and iron oxide phases. It is expected that individual iron and calcium oxide phases are effectively separated during the process. However, calcium was still widely dispersed among concentrates and tailings fractions. In addition, one particular drawback of the technique for these samples remains its inability to process samples with <20 μ m particle sizes, which represent a large portion of the samples.

6.5.2 ESB Moneypoint samples

ESB fly ash was filtered into 10 size band fractions, with 78% of the sample found in the $< 20 \,\mu$ m size band. As the majority of the sample was $< 20 \,\mu$ m, the remainder of the sample was processed as one size band fraction through the Mozley superpanner, where the majority of the sample collected in the tailings. Only small amounts of material separated into different concentrate fractions, ~ 0.3 g to ~ 1 g in each. Iron and calcium did concentrate in concs. 3 and 4, with conc. 3 having the highest levels (approx. 14 wt% iron and 3wt% calcium). The result can be viewed in the light of the previous characterisation analysis, in which generally low concentrations of iron (16 g/kg) and calcium (30 g/kg) were initially seen in the fly ash samples. However, the calcium and iron elements moved together into the concentrate fractions, which is not desirable.

ESB bottom ash was filtered into 22 particle size bands and the sample was relatively evenly distributed across the different bands. Four bands, namely $-2000/+1000 \,\mu\text{m}, -1000/+355 \,\mu\text{m}, -355/+90 \,\mu\text{m}$ and $-90/+20 \,\mu\text{m}$, were selected for testing. Only 6.9 wt% of the sample was found in the <20 μ m size band.

Processing of the individual size bands generated larger amounts of concentrate fractions than previously seen, and up to 8 g in one individual concentrate fraction was among the highest recorded. Table 6.4 displays a summary of the ICP results for the calcium and iron concentrations in the different fractions collected. For the four different particle size bands tested, iron was significantly concentrated in concs. 1 and 2 but sometimes also in conc. 3. The concentration effect was enhanced for the fine particle

	ESB Moneypoint bottom ash size bands												
	–2000/+1000μm			–1000/+355µm			–355/+90μm			–90/+20μm			
Fraction	Fraction weight (g)	Wt% Ca	Wt% Fe	Fraction weight (g)	Wt% Ca	Wt% Fe	Fraction weight (g)	Wt% Ca	Wt% Fe	Fraction weight (g)	Wt% Ca	Wt% Fe	
Conc. 1	2.8	0.38	2.24	1.7	1.01	4.33	2.7	1.53	9.65	0.5	1.56	18.37	
Conc. 2	5.7	2.35	1.85	2.5	0.5	1.1	4.1	1.09	2.61	2.8	1.6	23.92	
Conc. 3	6.4	0.15	0.21	2.7	0.7	0.91	4.3	0.8	1.23	2	1.79	11.92	
Conc. 4	8	0.10	0.12	2.9	0.51	1.26	2.7	0.86	0.83	2.6	1.28	3	
Conc. 5	6.3	0.12	0.09	2.5	0.31	0.55	1.9	0.76	0.76	4.1	0.75	1.44	
Tailings 1	82.4	0.13	0.11	99.9	0.33	0.28	108.4	0.65	0.5	98.4	0.7	0.63	

Table 6.4. Results of ICP elemental analysis of the concentrates and tailings generated from four size band fractions of the ESB Moneypoint bottom ash samples by the Mozley superpanner

size bands, where fractions with up to 23 wt% iron were generated.

As the bottom ash samples generally contained low iron (3g/kg) and calcium (4g/kg) concentrations, which were present as iron oxide and calcium chlorate, respectively, the results show effective iron separation using this technique.

6.5.3 Covanta Dublin Waste to Energy control samples

The Covanta DWTE fly ash was filtered into nine size band fractions with relatively even distribution across the different size bands and 56 wt% of the sample located in the <20 µm size band. Therefore, the remainder of the sample was tested as one size band (+355/-20 µm) and most of the sample passed down the Mozley superpanner table and entered the tailings fraction. Individual concentrate fractions (concs. 1, 2, 3, 4 and 5) of approximately 2g each were generated for the fly ash, which each contained aluminium (between 11 and 15 wt% aluminium in concs. 1-5), but lower concentrations were found in the tailings fraction (~2wt% aluminium). Iron tended to be prevalent in the concentrate fractions in general, and calcium in the tailings; however, the weights per cent calcium per fraction were not especially high. Previously XRD analysis had shown the presence of calcium carbonate, iron oxide and aluminium oxide in the fly ash samples, and it is clear that aluminium and iron occurred predominantly in the concentrate fractions. Therefore, there is potential for a light comminution or de-agglomeration pre-processing step to improve the separation performance.

Covanta DWTE bottom ash was filtered into 19 size band fractions, with approximately 5 wt% of the sample in the <20 µm size band. The three size bands selected for testing are shown in Table 6.5. It can be seen that processing generated significant weights of individual concentrate fractions (up to ~10g). Iron was concentrated in concs. 1-3 and calcium in concs. 4 and 5 and in the tailings. The trend is most clearly displayed for the largest particle size band fraction of -2000/+1000 µm, where approximately 10 g of a concentrate fraction generated 58 wt% iron concentration; this represents the highest and most concentrated iron separation achieved in the tests. Trends regarding aluminium concentrations in the bottom ash were less noticeable than the trends for the fly ash samples. XRD analysis of the bottom ash had previously revealed the presence of calcium carbonate, iron oxide, aluminium oxide and aluminium phosphate. It was noted that zinc was not detected in the fly ash or bottom ash in the XRD analysis of the concentrate or tailings fractions. The results illustrate a significant potential for the Mozley superpanner technique to separate iron and calcium fractions on a large scale in these samples and that it could be applied to the majority of the wastes while noting the particle size limitations.

6.5.4 Bauxite residue control samples

The bauxite residue sample was filtered into 11 size band fractions, and 77 wt% of the sample was located in the <20 μ m size band. Three size bands (-355/+90 μ m, -90/+45 μ m and -45/+20 μ m) were selected for testing and the ICP analysis showed that, although significant quantities of concentrate

	Covanta D\	NTE bottom	ash size bar	nds						
	-2000/+100	0 µm		-1000/+355	μm		–355/+20μm			
Fraction	Fraction weight (g)	Wt% Ca	Wt% Fe	Fraction weight (g)	Wt% Ca	Wt% Fe	Fraction weight (g)	Wt% Ca	Wt% Fe	
Conc. 1	9.9	3.58	58.11	3.30	3.98	50.82	3.00	11.72	24.75	
Conc. 2	5.8	7.38	33.44	3.60	5.87	30.15	10.30	15.72	12.32	
Conc. 3	5.3	12.24	24.49	2.40	9.39	30.89	2.80	11.98	22.04	
Conc. 4	8.3	14.77	14.91	3.10	12.1	24.33	3.70	20.87	6.71	
Conc. 5	4.9	16.71	9.65	2.30	15	21.72	1.70	22.95	3.77	
Tailings 1	82.9	17.74	5.83	96.00	19.7	3.61	66.70	26.89	2.50	

Table 6.5. Results of ICP elemental analysis of the concentrates and tailings generated from three size band fractions of the Covanta DWTE bottom ash samples by the Mozley superpanner

fractions were generated that were high in iron and aluminium, significant amounts of iron and aluminium made their way into the tailings fraction. XRD analysis had previously shown the presence of aluminium iron oxides, as well as individual iron oxides, iron hydroxides and aluminium oxides. The combined aluminium iron oxide phase, if dominant, would present a challenge to the physical separation process; the results of the Mozley superpanner confirmed this, as aluminium and iron moved together into both the concentrate and the tailing fractions. In addition, 77 wt% of the sample was below 20 µm particle size and was therefore not processed through the Mozley superpanner, making this technique not particularly suitable for the bauxite residue samples.

6.6 Multi-gravity Separator Testing

The micro-MGS (Figure 6.4) is a miniaturised version of the industrial MGS method and operates on a similar principle to a shaking table to separate and upgrade materials with a particular focus on very fine particles. The MGS's subtle centrifugal force stimulates enhanced gravity, pinning heavier materials to the wall of a rotating drum while lighter tailings are agitated by the shaking motion and washed away. The system is capable of working with 10-kg sample sizes and delivering high-grade recovery from fine and ultrafine materials in the range of 1–500 µm. The waste control samples (excluding the bottom ash samples owing to their larger particle sizes) were tested as a single size band for this technique.



Figure 6.4. A micro-multi-gravity separator (image courtesy of Gravity Mining Ltd).

6.6.1 Tara Mines samples

A number of experimental runs were undertaken to establish the best conditions for the separation of phases for the Tara Mines samples, which were found to be a drum rotational speed of 300 rpm and 1 L/min wash water. The results can be seen in Table 6.6. The ICP analysis for this run revealed that iron accumulated in the conc. 8 fraction at ~14 wt% iron, while calcium accumulated in the tailings fraction at ~22 wt% calcium.

The XRD analysis of these samples showed that the concentrates generally contained calcium carbonate, silicon oxide, and zinc and lead phases such as lead niobium oxide, lead zirconium oxide and zinc lead oxide. Because XRD analysis did not detect an iron phase, it is supposed that the lead and zinc phases dominated the reading. These lead or zinc phases were not seen in the tailings samples, and it can be seen that the technique has merit for the separation of the zinc–lead phases. In conclusion, this technique has shown a clear potential for segregating zinc and iron phases to the concentrate and calcium to the tailings. There is also potential for optimisation of the process to yield further weight per cent increases.

6.6.2 ESB fly ash samples

The MGS results for the ESB fly ash samples showed that almost equal weights of the sample were distributed to the concentrate and the tailing fractions. There was a preference for calcium, iron and magnesium to locate in the concentrate fraction. Table 6.7 shows the results from an experimental run that gave the best results using a drum rotational speed of 231 rpm and 1 L/min wash water feed. Calcium, iron and magnesium were higher in the concentrate, showing the movement of these elements together into the concentrate phase. In general, the weight per cent concentration of these elements in the concentrate fraction was low, being approximately ~1.4 wt% calcium, ~2 wt% iron and ~0.5 wt% magnesium. XRD analysis of the concentrates showed silicon oxide was a dominant phase throughout. This was similar for the tailings fraction but with the additional presence of aluminium phosphate. The movement of the elements together and low weight per cent achieved from the process means this technique is not particularly appropriate for the ESB fly ash samples.

	Fraction	Elemer	nt (wt%)									
Fraction	weight (g)	AI	Са	Fe	Ga	Mg	Na	Р	S	Si	In	
Conc. 8	1	0.09	0.39	14.83	0.01	0.88	0.02	0.03	11.48	0.009	0.03	
Tailings 8	16.55	0.06	22.01	1.81	0.001	1.94	0.01	0.04	0.38	0.002	0.02	

Table 6.6. Results of ICP elemental analysis of the concentrate and tailing fractions generated by theTara Mines tailings samples by the MGS separator (control sample: C8)

 Table 6.7. Results of ICP elemental analysis of the concentrate and tailing fractions generated by the

 ESB Moneypoint fly ash samples by the MGS separator (control sample: C3)

	Fraction	Element	(wt%)								
Fraction	weight (g)	AI	Са	Fe	Ga	Mg	Na	Р	S	Si	In
Conc. 3	16.1	0.34	1.38	1.97	0.007	0.46	0.01	0.06	0.12	0.04	0.03
Tailings 3	18.75	0.32	0.45	0.34	0.005	0.14	0.02	0.02	0.11	0.05	0.02

6.6.3 Covanta Dublin Waste to Energy fly ash samples

Testing of the Covanta DWTE fly ash samples generated a series of concentrates and tailings where a drum rotational speed of 410 rpm and 1.4 L/min wash water gave the best results (Table 6.8). Although calcium was high in both the concentrate and the tailings fractions, it occurred predominantly in the concentrate fraction. Calcium in the concentrate fraction reached ~43 wt%, but the volume of the concentrate generated was low (3.6g). Iron and aluminium also displayed a preference for the concentrate fractions at ~6 wt% and ~7 wt%, respectively.

XRD analysis of the concentrate showed the presence of aluminium fluoride, calcium carbonate, calcium sulfate, iron oxide and silicon oxide phases, while the tailings fraction showed sodium iron sulfate, calcium carbonate, calcium sulfate, silicon oxide and iron oxide phases. The fractions share similar dominant phases, corresponding to high concentrations of similar metals and phases seen in both the concentrate and the tailings. Previous analysis of the Covanta DWTE control samples showed the presence of zinc phases; however, these were not detected in any of the concentrate or tailings fractions. Again, because metals of interest moved together into the concentrate fraction and the concentration weight per cent achieved was not high, this technique is not appropriate for the Covanta DWTE fly ash samples.

6.6.4 Bauxite residue samples

Testing of the bauxite residue samples revealed that a drum rotational speed of 330 rpm and 1 L/min wash water gave the best results (Table 6.9). Iron was slightly more likely to be located in the concentrate (~20 wt%) than in the tailings fraction and calcium was most likely to occur in the tailings fraction (~2 wt%). However, as the volume of concentrate generated was low and because of the low calcium content in the samples, the results were negligible for the bauxite residue samples. XRD analysis supported this, showing that the concentrate fraction contained iron oxide, silicon oxide and aluminium oxide, as well as a combined phase of calcium aluminium silicate, while the tailings fraction displayed the same phase with the addition of potassium aluminium silicate.

Table 6.8. Results of ICP elemental analysis of the concentrate and tailing fractions generated by the
Covanta DWTE fly ash samples by the MGS separator (control sample: C7)

	Fraction	Element	: (wt%)								
Fraction	weight (g)	AI	Ca	Fe	Ga	Mg	Na	Р	S	Si	In
Conc. 7	3.6	6.78	43.57	6.49	0.09	3.81	1.33	2.06	1.78	0.12	0.02
Tailings 7	17.57	2.13	24.76	0.70	0.02	0.93	1.38	0.51	0.37	0.06	0.03

Table 6.9. Results of ICP elemental analysis of the concentrate and tailing fractions generated by thebauxite residue samples by the MGS separator (control sample: C5)

	Fraction	Elemen	t (wt%)								
Fraction	weight (g)	AI	Са	Fe	Ga	Mg	Na	Р	S	Si	In
Conc. 5	6.41	0.91	0.69	20.41	0.07	0.03	0.24	0.02	0.00	0.05	0.02
Tailings 5	25.77	4.64	2.28	14.32	0.1	0.03	2.63	0.10	0.14	0.13	0.01

One significant result was the presence of sodium mainly in the tailings fraction, which was evident in the majority of the test runs. The technique appears to have the potential to reduce the sodium content of the bauxite residue (from ~3.0 to 0.2 wt% sodium), which would render the materials more suitable for application in the construction sector. However, optimisation is required to increase the yield of the sodium-reduced fraction.

6.7 Summary and Key Findings

Table 6.10 summaries the key findings and shows the following:

- Ball milling has an effect on the waste materials that have a large range of particle sizes, increasing the distribution of material into the fine particle size band fractions.
- The combination of ball milling and magnetic separation gave the largest fraction and highest concentration of iron. The ESB fly ash and Covanta DWTE bottom ash samples gave the best results, generating a magnetic iron-rich fraction of ~30 wt% iron.
- The Mozley superpanner performed well for specific wastes, showing potential for processing Tara Mines and bottom ash samples. In general, significant amounts of iron were segregated to the concentrate fraction and calcium to the tailings fraction, achieving up to ~58 wt% iron in some cases (bottom ash samples). The process also appeared to perform better on fine particle sizes (to a limit of 20 µm), suggesting that a preprocessing ball milling step would enhance the results. The technique also showed potential for segregating aluminium in the Covanta DWTE fly ash samples.

The MGS performed well for specific wastes. Treatment of the Tara Mines samples led to zinc and iron locating in the concentrate (~14 wt% iron) and calcium in the tailings (~22 wt% calcium). Although bottom ash samples were not tested owing to the larger particle sizes of these materials, there is potential that comminution of these samples (rod grinding) and processing via the MGS may yield good results, based on the known levels of zinc, iron and calcium in these samples. In addition, the MGS has shown significant potential to reduce the sodium content of bauxite residue.

	Tara Mines	ESB fly ash	ESB bottom ash	Covanta DWTE fly ash	Covanta DWTE bottom ash	Bauxite residu
Key metal composition	Ca 261 g/kg; Fe 41 g/kg; Zn 0.19g/kg	Ca 31 g/kg; Fe 16g/kg; Zn – ND	Ca 4.3g/kg; Fe 3.9g/kg; Zn – ND	Ca 249g/kg; Fe 9.42g/kg; Zn 9.22g/kg	Ca 122 g/kg; Fe 92.72 g/kg; Zn 6.64 g/kg	Ca 0.64 g/kg; Fe Zn 1.02g/kg
XRD phases detected	CaCO ₃ ; CaFeMgCO ₃ ; SiO ₂ ,AIMn; Fe2O ₃ ; Al ₂ O ₃	Al ₂ SiO ₅ ; SiO ₂ , Fe ₂ O ₃ , Ca(ClO ₃) ₂ ; Al ₂ O ₃	SiO_2 , Fe_2O_3 , $FeMgSH_2O$; InFeZn ₈ O ₁₁ ; Fe_2O_3	CaCO ₃ ; Al ₂ O ₃ ; Fe ₂ O ₃ ; Na ₂ Mn ₆ Si ₇ O ₂₁ ;	CaCO ₃ ; SiO ₂ ; AIPO ₄ ; CIO ₂ ; Fe ₂ O ₃ ;Fe ₃ O ₄ ; AI ₂ O ₃	Iron hydroxide; A SiO ₂ , AI ₂ O ₃ and F
Ball milling and filtration	No effect	No effect	Increased distribution of particles to the fine size bands (wt%):	No effect	Increased distribution of particles to the fine size bands (wt%):	Increased distribu particles to the fir bands (wt%):
			-500+100 µm 0%		-500+100 µm 0%	-500+100 µm 3.8
			-100+90 µm 8.38%		-100+90 µm 8.65%	—100+90µm 6.97°
			-90+53μm 21.67%		-90+53μm 20.31%	-90+53 μm 23.19 ^c
			–53+25μm 57.76%		-53+25μm 46.26%	-53+25μm 38.229
			–25 μm 10.57%		–25μm 22.50%	–25μm 25.5%
Combined ball milling, filtration and magnetic separation	No effect – magnetic Fe not present	Achieved 28.5wt% Fe magnetic fraction (4.7g)	Achieved 6.5wt% Fe magnetic fraction (4.9g)	Achieved 7.98 wt% Fe magnetic fraction (3.3g)	Achieved 33.9 wt% Fe magnetic fraction (30.7 g)	Achieved 6.45wt% magnetic fraction (
Mozley superpanner	Processed 37% of sample	Processed 22% of sample	Processed 93.1% of sample	Processed 44% of sample	Processed 95% of sample	Processed 23% of
	Achieved ~20 wt% Fe(~4g) in concentrates; achieved ~25 wt% Ca (~110g) in tailings; enhanced effect for fine particle sizes -63 +20 µm	Achieved ~2 wt% Ca and ~14 wt% Fe (~6g each) concentrated together in concentrates; tested as one size band	Achieved ~23 wt% Fe (~3g) in concentrates; enhanced effect for fine particle sizes –355+90 µm; –90 +20 µm size	Achieved ~15 wt% (1.4g) Al in concentrates; some Fe up-concentration; tested as one size band; Zn not detected in XRD	Achieved ~58 wt% Fe (~10g) in concentrates; achieved ~17 wt% Ca (~82g) in tallings; Zn not detected in XRD	Movement of Fe ar together
MGS	Achieved ~14 wt% Fe (1 g) and Zn in concentrate; achieved ~22 wt% Ca in tailings	No significant effect	Not performed	Ca (~43 wt%), Fe (~6 wt%) and AI (~7 wt%) concentrated together in concentrate (~4 g); Zn not detected in XRD	Not performed	No significant effe metals of interest; Na in concentrate

Table 6.10. Summary of the key findings from the separation testing of the different Irish wastes

Red text indicates a positive effect for separation. ND, not detected.

7 Process Flows

7.1 Tara Mines

The key elements and phases present in the Tara Mines waste were:

- 261 g/kg calcium, 41 g/kg iron and 0.2 g/kg zinc;
- silicon oxide; calcium carbonate; calcium iron magnesium carbonate; zinc chloride; lead zinc fluoride; alumina; iron oxide.

Calcium, iron and zinc are present as materials in significant quantities and have potential value. However, the iron and zinc concentrations (4.1 wt% iron and 0.002 wt% zinc) in these samples are low compared with typical ore grades (~65wt% iron and 5-15 wt% zinc). The investigations to date have focused on concentrating these materials in separate fractions. The Tara Mines samples showed an effect for both the Mozley superpanner and the MGS separation techniques, but the MGS is deemed to be more suitable as it can process the entire sample, unlike the Mozley technique, which could process only 37% of the sample owing to particle size limitations. The MGS produced 1g of 14 wt% iron concentrate, which is still comparatively low in terms of economic recovery of significant volumes of iron. The tailings fraction registered 22 wt% calcium, showing some loss of calcium to the concentrate fraction as a result of the movement of the calcium iron magnesium carbonate phase into the iron-rich concentrate. Regarding the concentration of zinc, XRD analysis detected a significant presence of zinc in the concentrate fraction, but unfortunately ICP data were unavailable to guantify the levels of zinc, although it is evident that zinc was concentrated in the iron fraction. In addition, it was noted that significant volumes of sulfur relocated into the concentrate fraction (12wt% sulfur) and the concentration was much reduced in the tailings fraction (0.4 wt%).

To assess potentially beneficial process flows for the Tara Mines samples, it is necessary to consider the end use applications of the target materials. The iron and zinc fractions could be processed to recover the key metals once the concentrations become economically viable, but the calcium-rich fraction, which accounts for the bulk of the waste material, still requires a suitable application. As this fraction is composed of calcium carbonate, potentially suitable applications include uses for limestone in its powdered form (which contains ≥50% calcium carbonate). Limestone is used as a raw material in the manufacture of quicklime, slaked lime, cement and mortar, and as a soil conditioner to neutralise acidic soils.

The manufacture of cement involves the production of clinker by heat treatment of limestone and clays, followed by blending the clinker, gypsum and additives to generate the final cement product. European Standard EN 197-1 (CEN, 2011) outlines the criteria for the composition of the different cements and their ingredients. Potential uses for the calcium carbonaterich waste materials are as:

- an ingredient for the production of the clinker;
- replacement for the clinker (i.e. filler 35 wt% max.);
- a minor constituent (5 wt% max.);
- an addition (0.5–1 wt% max.).

The use of Tara Mines tailings as a raw material for clinker production merits investigation if the combination of infeed raw materials can be balanced to achieve the required clinker composition. Table 7.1 gives an example of a typical cement clinker composition (Vaiciukynienė *et al*., 2016), while Table 7.2 displays the elemental composition achieved for the MGS tailings fraction for the Tara Mines samples. It can be seen that the iron, magnesium

Table 7.1. Example of the composition of cement clinker

Oxides	Wt%	
CaO	63.42	
SiO ₂	20.61	
Al ₂ O ₃	5.45	
Fe ₂ O ₃	3.36	
MgO	3.84	
K ₂ O	1.00	
Na ₂ O	0.20	
SO3	0.80	

Source: Vaiciukynienė et al. (2016).

	Element	(wt%)								
Sample code	Са	Si	AI	Fe	Mg	Na	S	Ga	Р	In
Control sample: T8	22.00	0.002	0.06	1.81	1.94	0.014	0.38	0.01	0.043	0.02

Table 7.2. Composition of MGS tailings fraction separated from the Tara Mines waste (control sample: T8)

and sulfur concentrations of the samples are generally in an acceptable range of the composition of cement clinker shown in Table 7.1. The EN 197-1 standard (CEN, 2011) specifies that magnesium oxide concentration should be kept below 5 wt% and sulfur as SO₃ should be below 3.5-4 wt%, depending on the particular type of cement. A major benefit observed is the reduction of sulfur achieved using the MGS technique. The separation of zinc and iron are additional benefits.

The calcium, silicon and aluminium concentrations of the Tara Mines samples were lower than those typically seen in clinker but could be amended with further concentration steps for calcium and the use of additives typical in the sector, such as fly ash for silicon oxide concentrations and bauxite for alumina concentrations. This also points to opportunities for blending other Irish wastes such as fly ashes and bauxite residues.

Another challenge for the use of Tara Mines tailings as raw materials for the cement sector is the uniformity and homogeneity of the tailings, which would need to be addressed. Furthermore, the market and legal acceptance of the use of the tailings waste as a secondary raw material also need to be addressed.

The EN 197-1 standard (CEN, 2011) currently stipulates the compositional parameters for clinker (CaO/SiO₂ ratio, MgO and SO₃ limits) but not the infeed raw materials for the manufacture of the clinker. However, it is probable that clarification regarding the use of tailings and/or other wastes would be required within the standard. Another potential option for the tailings is using them as a replacement for the clinker directly (i.e. as a filler); however, currently this is prohibited by the EN 197-1 standard (CEN, 2011), which specifies the permitted list of main constituents (clinker, pozzolanic materials, blast furnace slag, fly ash, etc.). There is potential in the future for amendments to the standard based on evidence and the drive to achieve the circular economy objectives laid out in the European Green Deal.¹

Figure 7.1 displays a potential process flow for Tara Mines waste based on the above, with options for comminution and mixing steps to address uniformity, followed by an MGS step to remove iron, zinc and sulfur concentrations and finally a blending step to increase the calcium carbonate weight per cent, which may include blending other wastes with a high calcium concentration.

7.2 ESB Moneypoint

The key elements and phases present in the ESB Moneypoint waste were:

- Fly ash: 31 g/kg calcium, 16 g/kg iron and 0 g/kg zinc. Phases: Al₂SiO₃, SiO₂, Fe₂O₃, CaClO₃, Al₂O₃.
- Bottom ash: 4.3 g/kg calcium, 3.9 g/kg iron, 0 g/kg zinc. Phases: SiO₂, Fe₂O₃, FeMg₅(H₂O), InFeZn₈O₁₁, Fe₃O₄.

The fly ash contains an array of different elements and phases but none with particularly high individual concentrations. Therefore, these materials pose a challenge to any separation process because insufficient contrasting volumes of phases are present. The Mozley and MGS separation techniques did not produce any significant results for these fly ash samples.

However, based on its composition, fly ash already has accepted market applications for use as a main constituent in cement, where it can be included up to 25 wt% under the EN 197-1 standard. According to the composition obtained from the ICP analysis, the ESB Moneypoint fly ash falls under the calcareous category, which requires a minimum of 10 wt% calcium oxide. Other reported applications for fly ash include its use as an ingredient for soil cement applications (Federal Highway Administration, 2003). In addition, the authors are participating in an EU-funded large-scale

¹ https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal_en (accessed 6 April 2021).



Figure 7.1. Potential process flow for Tara Mines tailings waste.

demonstration project called RemovAL (Removing Waste from Alumina Production), which is testing six technologies for valorising wastes, and one pilot study is focused on building a demonstration road in Ireland using a soil cement based on fly ash and bauxite residue.² In the light of the results presented here and these established market applications, there is likely to be little benefit in further processing these fly ash wastes.

The ESB Moneypoint bottom ash samples also contained an array of elements in mixed concentrations. Although the ICP analysis indicated low iron concentrations and no presence of zinc, XRD analysis highlighted that significant phases of iron and zinc were present. The lower concentrations in the results of the ICP analysis are believed to be due to the nature of the sampling for ICP and the non-uniformity of the samples. As the bottom ash samples have a much larger particle size, reaching the ~2000 µm limit (larger agglomerates and rocks up to 10-cm diameter were screened from the fraction before testing), the Mozley superpanner was the most appropriate technique for separation, achieving iron separation of up to ~23 wt% iron for specific concentrate fractions.

Potential applications for the bottom ash are similar to the fly ash, including its use in cement clinker production; however, it is not specifically catered for in the EN 197-1 standard. Other options include its use as an alternative raw material, replacing earth or sand or aggregates, for example in road construction.

Reviewing the results of the Mozley superpanner technique in the light of the applications for bottom ash wastes in the cement/construction sector, it can be seen that the original samples were not high in sulfur or magnesium and the iron levels are not considered excessive for cement applications. Table 7.3 displays the results of the four output tailings fractions of the Mozley superpanner process, and it can be seen that the elemental concentrations of individual metals are very low. There is no obvious benefit to justify the cost of processing these bottom ashes.

In the light of the above, the suggested process flows for the ESB Moneypoint bottom ash point solely to strategies to use the material in its "as is" condition, taking advantage of its particle size for applications such as construction aggregates, or undertaking homogenisation of the bottom ash to increase the uniformity of the sample and further investigating

² RemovAL project: https://www.removal-project.com/pilot-plants/ (accessed 6 April 2021).

		Eleme	nt (g/kg)								
Tailing fractions (µm)	Weight (g)	AI	Са	Fe	Ga	In	Mg	Na	Р	S	Si
-2000/+1000	82.4	0.09	0.13	0.11	0	0.02	0.03	0.03	0.01	0.05	0
-1000/+355	99.9	0.26	0.33	0.28	0	0.02	0.07	0.03	0.02	0.04	0
-355/+90	108.4	0.46	0.65	0.5	0	0.02	0.14	0.03	0.04	0.09	0.02
-90/+20	98.4	0.5	0.7	0.63	0	0.02	0.17	0.03	0.06	0.04	0.04

Table 7.3. Composition of Mozley superpanner tailing fractions as separated from the ESB Moneypointbottom ash samples for the four particle size bands tested

whether there are any benefits of using the Mozley superpanner or MGS techniques to recover metal and/or refine the composition for use in cement applications (Figure 7.2).

7.3 Covanta Dublin Waste to Energy Plant

The key elements and phases present in the Covanta DWTE wastes were:

 Fly ash: 249g/kg calcium, 9.42g/kg iron and 9.22g/kg zinc. Phases: CaCO₃; Al₂O₃; Fe₂O₃; Na₂Mn₆Si₇O₂₁. Bottom ash: 122g/kg calcium, 92.72g/kg iron and 6.64g/kg zinc. Phases: CaCO₃; SiO₂; AIPO₄; CIO₂; Fe₂O₃; Fe₃O₄; Al₂O₃.

The Covanta DWTE fly ash contains high concentrations of calcium and zinc, which were the focus of the separation studies. With calcium carbonate accounting for the bulk of the sample, the following potential applications in the cement/ construction sector were considered:

- use as a raw material in the production of clinker;
- use as a clinker replacement (i.e. similar to the coal-produced fly ash).



Figure 7.2. Potential process flow for ESB Moneypoint bottom ash. PS, particle size.

Table 7.4. Composition of the MGS tailing fractions	separated from the Covanta DWTE fly ash samples
(control sample: T7)	

	Element	(wt%)								
Sample code	AI	Са	Fe	Ga	Mg	Na	Р	S	Si	In
Control sample: T7	2.12	24.76	0.70	0.02	0.93	1.38	0.51	0.37	0.06	0.03

With these applications in mind, the composition of the Covanta DWTE samples was reviewed, and concentrations of undesirable elements such as magnesium (~9g/kg) and sodium (~36g/kg) were detected by ICP analysis, while EDS analysis detected the presence of chlorine. The processing of these samples through the separation techniques showed that the MGS was more suitable than the Mozley superpanner because the latter could process only 44 wt% of the sample. However, it was noted that the Mozley superpanner achieved high levels of aluminium separation (as well as iron, magnesium and sodium) into the concentrate fraction, leaving a large tailings fraction with 32 wt% calcium and low concentrations of the above elements. The MGS was able to process all of the sample and also separated aluminium, iron, magnesium and sulfur into the concentrate fraction, leaving a large tailings fraction with 25 wt% calcium and low concentration of these four elements. Table 7.4 shows the composition of the MGS tailings fraction in which the magnesium, sodium and sulfur levels were all low. Although zinc concentrations were not available from the ICP data and XRD analysis did not detect zinc, it is suspected that there is some potential for zinc separation. The MGS has potential as a technique for refining the composition of the fly ash, making it more suitable for applications in the cement sector. However, the use of this fly ash as a main constituent for clinker is currently prohibited under the EN 197-1 standard, which stipulates that only fly ash from furnaces fired by pulverised coal is allowed. The high calcium concentration of the waste-to-energy fly ash means that it has potential both for use in clinker production and as a replacement. Figure 7.3 outlines a process flow to homogenise and refine its composition for such uses.

The Covanta DWTE bottom ash contained high levels of calcium, iron and zinc, as well as other elements of interest such as aluminium (38g/kg). It was noted that the calcium concentration is less than half that of the fly ash and that iron concentrations were much higher (92g/kg). Applications for the bottom ash would be similar to those for the ESB Moneypoint bottom ash, for example as an aggregate owing to its larger particle size, as well as in cement applications. The lower calcium concentrations seen in the bottom ash would require concentration, as well as comminution and homogenisation steps for any application as a raw material for clinker production. With cement and construction applications in mind, a review of the compositional data of the bottom ash samples showed the presence of magnesium (8g/kg) and sodium (8g/kg) from ICP analysis, and EDS analysis highlighted the presence of chlorine and sulfur.

The results of the Mozley superpanner testing on the bottom ash samples showed that iron and sulfur tended to separate to the concentrate fraction,



Figure 7.3. Potential process flow for Covanta DWTE fly ash. Conc., concentration.

leaving a bulk tailings fraction containing high calcium concentrations and the aluminium. Table 7.5 displays the composition of the tailings fractions generated for the bottom ash samples where the low concentrations of iron and sulfur can be seen; iron in the concentrate fraction reached up to 58 wt%, making this technique suitable for the recovery of high concentrations of iron.

Figure 7.4 outlines a process flow for potential processing and use options for the Covanta DWTE bottom ash.

7.4 Bauxite Residue

The key elements and phases present in the bauxite residue were:

0.64 g/kg calcium, 44.68 g/kg iron and 1.02 g/kg zinc;

• iron hydroxide; Al₂Fe₅O₁₂; SiO₂; Al₂O₃; Fe₂O₃.

The main elements of the bauxite residue are aluminium and iron oxides. Many potential applications for bauxite residue wastes are being explored, including soil cement and geopolymer applications as alternatives to ordinary cement (i.e. ordinary Portland cement). The authors have previously undertaken a desk-based study and Irish stakeholder workshop on the potential use of Irish residues and by-products in geopolymer applications (Algeopolymer project; see Ujaczki *et al.*, 2019). The study pointed to the potential for circular economy opportunities and the need to establish adequate chemistries and address current legislative barriers to the acceptance of geopolymers. Currently, the authors are engaged in research under

Table 7.5. Composition of the Mozley superpanner tailing fractions separated from the three particle size bands of the Covanta DWTE bottom ash samples

		Element (g/kg)									
Tailings fraction (µm)	Weight (g)	AI	Са	Fe	Ga	In	Mg	Na	Р	S	Si
-2000/+1000	82.9	12.06	17.74	5.83	0	0.02	1.49	1.37	0.81	0.43	0.06
-1000/+355	96	8.15	19.69	3.61	0	0.02	1.43	0.99	0.88	0.56	0.04
-355/+20	66.7	5.58	26.89	2.5	0	0.02	1.92	0.76	1.22	0.43	0.06



Figure 7.4. Potential process flow for Covanta DWTE bottom ash. Conc., concentration.



Figure 7.5. Potential process flow for bauxite residue.

the European "RemovAL" project,³ which is focusing on:

- de-alkalinisation of the bauxite residue to reduce the Na₂O content to <0.5wt% to increase its suitability for market applications;
- the use of bauxite residue in soil cement applications as a road sub-base layer;
- the use of bauxite residue in blending applications with cement;
- the use of bauxite residue in geopolymer cement.

With these potential applications in mind, a review of the results of the Mozley superpanner and MGS testing highlights that one of the main benefits seen was the potential for the MGS to reduce the sodium concentration in the bauxite residue (Figure 7.5). Table 7.6 highlights a sample run that generated a large volume of concentrate fraction with significantly reduced sodium concentration. The MGS technique offers a benefit in terms of reducing sodium at relatively low cost, achieving separation without the use of chemicals or additives typically used in other processes.

7.5 Concluding Remarks

The potential process flows outlined above for the individual wastes are focused on:

- separating any base metals of significant concentration;
- optimising the remaining bulk fraction (typically calcium carbonate-rich) for use in a market application.

It was noted that the techniques performed on the different waste materials did not result in any concentration of the CRMs (gallium, indium and phosphorus) into either the concentrate or the tailings fraction. These elements appeared to be distributed relatively evenly throughout the tailings and the concentrate fractions for the majority of the samples. It is recommended that comminution of the samples to increase uniformity and homogeneity, and any effects on the separation of individual fractions under gravity separation, should be investigated. In addition, there may be potential for comminution to assist the release of CRMs.

Table 7.6. Composition of MGS concentrate and tailings fractions as separated from the bauxite residue samples (control sample: C1)

Fraction		Element (wt%)										
Fraction	weight (g)	AI	Ca	Fe	Ga	Mg	Na	Р	S	Si	In	
Conc.	18.52	0.62	0.91	8.18	0.05	0.02	0.29	0.01	0.01	0.08	0.02	
Tailings	25.11	4.38	2.093	11.56	0.08	0.03	2.68	0.09	0.15	0.09	0.01	

3 European RemovAL research project: https://www.removal-project.com/ (accessed 7 April 2021).

8 The Potential for an Irish Circular Economy

8.1 The Irish Waste Inventory

As it was not possible to test the techniques on all the Irish wastes, a review of the wastes likely to perform well under the separation processes was undertaken. Table 8.1 lists the metal concentrations and phases of target materials present in the remaining industrial samples of the waste inventory.

8.1.1 Iron

For the mining sector samples, it can be seen that the Lisheen Mine and Silvermines samples contain concentrations of iron greater than 100 g/kg, which would give sufficient volume of contrasting phases for separation. Although the presence of iron was detected in the Lisheen Mine and one of the Silvermines Garryard samples as magnetite, it was predominantly found as haematite in the majority of the mining sector samples and co-occurs with magnetite in the Lisheen Mine samples. This indicates that gravity separation would be better than magnetic separation for iron recovery from these wastes. The Garryard samples also contained iron in the form of iron sulfide and iron oxide sulfide phases; therefore, the recovery of iron from the bulk waste would potentially reduce the sulfur content in the remaining fraction.

8.1.2 Zinc

Many of the mining sector waste materials contain high zinc concentrations, including the Silvermines Garryard samples in the form of zinc gallium sulfide and the Galmoy Mine samples in the form of calcium zinc carbonate. There is potential for gravity separation techniques to separate these phases from the bulk of the waste material and in some cases capture CRMs such as gallium.

8.1.3 Calcium

Calcium was present in the Tynagh Mine samples as a calcium carbonate phase, which should also lend itself well to separation by gravity release processes, with iron and zinc gravitating to the concentrate fractions. The power plant samples generally display high

calcium concentrations (~150–200 g/kg), especially in the ESB West Offaly and Indaver waste samples. The ESB West Offaly samples contain calcium in the form of calcium carbonate and calcium sulfate, which again should be amenable to gravity separation. Finally, the Indaver samples contained calcium in the form of calcium sulfate and calcium magnesium aluminium sulfide. The aluminium is also present as aluminium oxide; therefore, depending on the concentration of the mixed phase, there is potential for the separation of aluminium phases and calcium phases using gravity release techniques.

8.2 Synergies between the Different Wastes

Consideration of the compositional synergies between the wastes has been undertaken previously, in which the wastes were categorised into high-concentration calcium, iron and zinc wastes as follows:

- High calcium concentrations: Tara Mines, Tynagh Mine, Covanta DWTE, Indaver, ESB Lough Ree, ESB West Offaly.
- High iron concentrations: Garryard mine, Ballygown mine, Covanta DWTE.
- High zinc concentrations: Silvermines; Lisheen Mine, Galmoy; Two Valleys Mines, Tynagh Mine, Covanta DWTE, Indaver.

In addition, consideration of the market applications for any recovered fractions can highlight further synergies among the different waste materials:

- raw materials for the production of clinker cement;
- use of fly ash for clinker replacement as a main constituent for cement;
- use as aggregates in the construction sector;
- use as a raw material for the production of geopolymers (alternative cements).

Table 8.2 outlines the key materials parameters for the highlighted market applications, where it can be seen that there are tighter controls on the clinker and fly ash compositions for the cement applications, whereas the aggregate and geopolymer applications have more

 Table 8.1. Metal concentrations and phases of materials present in the industrial waste samples that were

 not tested for physical separation previously

	Metal (g/kg)				
Sample (particle size)	Fe	Са	AI	Zn	Phases present
Mining sector					
Lisheen Mine (100–500 µm)	139	31	0.2	13	Iron sulfide; calcium carbonate; calcium iron magnesium carbonate; silicon oxide; zinc sulfide; aluminium oxide; iron oxide (haematite and magnetite)
Silvermines Garryard 07 SP01.2 1/2 rem (10 µm)	88	3.55	1.24	186	Zinc gallium sulfide; aluminium silicate; silicon oxide; iron oxide sulfate; calcium aluminium silicate; calcium sulfide; calcium phosphate hydrate; magnetite
Silvermines Garryard 01.1 1/2 rem (30 µm)	93	4.77	1.51	20	Copper chloride; aluminium iodate hydrate; magnesium sulfate; aluminium phosphide; iron oxide
Silvermines Garryard 07 SP01.7 (50μm)	194	0.88	0.47	9.22	Iron sulfide; calcium magnesium carbonate; calcium silicate hydrate; aluminium oxide; iron oxide (haematite)
Silvermines Gortmore (25µm)	238	4.69	0.57	18.27	Iron sulfide; calcium magnesium carbonate; iron oxide (haematite); aluminium oxide; calcium silicate; complex zinc phase
Silvermines Ballygown (20–100 µm)	12–127	0.69– 9.24	0.18– 6.94	0.09– 270.74	XRD not available
Avoca Mines (20 µm)	47.55	0.06	3.93	0.15	Silicon oxide; beryllium fluoride; silicon sulfide; calcium magnesium oxide hydrate
Galmoy Mine (20µm)	52.47	60.42	0.53	17.91	Calcium magnesium carbonate; copper chloride; calcium zinc carbonate; calcium magnesium carbonate; iron sulfide; calcium iron magnesium carbonate
Two Valleys Mines (10–30 µm)	17.59	1.99	7.25	19.10	Silicon oxide; calcium iron oxide chloride; aluminium phosphate; copper chloride
Tynagh Mine (10 µm)	19.96	275.39	1.62	12.02	Silicon oxide; copper gallium telluride; silicon sulfide; iron oxide (haematite); calcium carbonate; aluminium oxide
Power sector					
ESB Lough Ree fly ash (100 µm)	31.98	96.52	28.77	0.08	Silicon oxide; calcium iron sulfate; magnesium silicate; iron oxide; aluminium oxide
ESB Lough Ree bottom ash (500–2000 µm)	10.17	63.85	6.51	-	Silicon oxide; calcium iron sulfate; magnesium silicate; iron oxide; aluminium oxide
ESB West Offaly fly ash (1–50 µm)	47.81	182.34	11.89	0.07	Aluminium silicate; calcium carbonate; silicon oxide; calcium sulfate; aluminium magnesium hydroxide carbonate; sodium nitrate; iron oxide (haematite and magnetite)
ESB West Offaly bottom ash (10–200 μm)	42.83	166.94	11.01	0.11	Silicon oxide; calcium carbonate; calcium sulfate; aluminium oxide; iron oxide (magnetite)
Indaver fly ash (100 µm)	28.34	192.51	53.51	4.62	Calcium sulfate; calcium magnesium aluminium sulfide; silicon oxide; aluminium oxide; iron oxide (haematite and magnetite)
Indaver bottom ash (3000 µm)	35.13	144.81	36.17	2.79	Calcium sulfate; calcium magnesium aluminium sulfide; silicon oxide; aluminium oxide; iron oxide (haematite and magnetite)

flexibility in terms of composition. Wastes containing high levels of calcium and silicon could be evaluated for clinker and cement production applications, respectively, whereas those with higher potassium and sodium concentrations may be more amenable to geopolymer applications. As can be seen in Table 8.2, generally, a reduction in magnesium, sulfur and alkali metals, and refinement using gravity release techniques, is an option to achieve this. Based on the chemistries from the waste inventory and the market applications identified above, Table 8.3 outlines the particular wastes that have synergies and potential for consideration in the various markets.

8.3 Potential Process Flows for the Circular Economy

All of the wastes highlighted in section 8.2 for each market application need specific investigation based

Production of cement clinker ^a	Fly ash – cement main constituent⁵	Aggregates – construction sector°	Geopolymer applications ^d
High calcium concentrations CaCO ₃ > 50 wt% Ideally > 75 wt% Low MgO concentrations <5 wt% CaO:SiO ₂ > 2 Contains CaO, SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃	 Siliceous fly ash: minimum SiO₂ 25 wt% contains SiO₂, Al₂O₃, Fe₂O₃ reactive calcium oxide should be less than 10 wt% free calcium oxide should not exceed 1 wt% produced from pulverised coal Calcareous fly ash: contains CaO, SiO₂, Al₂O₃, Fe₂O₃ reactive calcium oxide should not be less than 10 wt% not less than 25 wt% of reactive silicon dioxide SO₃ < 3.5–4 wt% produced from pulverised coal 	Typically uses particle sizes of 12–20 mm Can be fine or coarse grade Presence of acid-soluble sulfates <0.2% Total sulfur content <1% Controlled level of sulfides Controlled level of alkali metals (K, Na) Limit organic contaminants Fragmentation resistance	Requires an alumina silicate precursor Requires an alkali reagent (Na,K-soluble silicates) Source of calcium cations for room temperature hardening Geopolymers can be based on fly ashes Geopolymers can be rock based

Table 8.2. Key materials parameters for the four market applications highlighted as relevant for the wastes

^aVaiciukynienė et al., 2016.

^bStandard EN 197-1 Cement.

^cStandard EN 12620 Aggregates for concrete.

^dhttps://en.wikipedia.org/wiki/Geopolymer (accessed 6 April 2021).

Table 8.3. List of Irish wastes for consideration within the different market applications identified

	Application								
	Production of cement clinker	Fly ash – cement main constituent	Aggregates – construction sector	Geopolymer applications					
General characteristics	CaCO ₃ -rich materials	SiO ₂ -rich materials	Low S, Na, K content and relevant particle size	Alumino-silicate, alkali, calcium cation content					
Potential wastes for consideration	Tara Mines tailings	ESB Moneypoint fly ash	ESB Moneypoint bottom ash	Bauxite residue					
	Covanta DWTE	ESB Lough Ree fly ash	Covanta DWTE bottom ash	ESB Moneypoint fly ash					
	Indaver		Indaver bottom ash	ESB Lough Ree fly ash					
	ESB west Offaly		Silvermines Garryard waste rock	Covanta DWTE fly ash					
	Tynagh Mine		Silvermines Ballygown waste rock						

on the requirements of the particular market identified, and Figure 8.1 indicates how this could be achieved. Once the market application is selected, a specific target chemistry can be identified whereby wastes can be screened and potentially blended to achieve the required target composition. The material can then be further refined using the gravity release techniques identified in this report (Mozley superpanner and MGS among others) to remove metals and any unwanted contaminants (magnesium, sulfur, sodium, potassium, etc.). Considerable process development would be required to achieve target chemistries, blending ratios and optimisation of the selected separation techniques to achieve the final market-acceptable composition of the output fractions.

In addition, it is important to note that use of these waste materials would require legal authorisation, as well as market acceptance of the end-of-waste criteria and the industrial standards, which in many cases specify permitted raw materials for each application. Development and testing of particular scenarios, in which successful results would form the basis for requests to update relevant legislation and standards as appropriate, would also be required.

Figure 8.2 highlights an example of a process flow for the calcium-rich materials and their use in cement applications. The calcium-rich wastes, including Tara Mines tailings, Tynagh Mine tailings, Indaver waste, Covanta DWTE waste and ESB West Offaly wastes, were selected for blending to achieve further concentration of calcium carbonate in the main fraction. This fraction undergoes comminution and mixing for homogenisation, after which it is processed to remove valuable metals, such as zinc and iron, and any unwanted impurities (e.g. magnesium, sulfur, sodium). Filtration can be used to distribute the material into different particle size band fractions, which can then be selected to optimise the individual gravity separation processes. It is also proposed to use concentration techniques, depending on the specific elements to be separated, including the use of froth flotation to further concentrate the carbonate fraction. Any significant concentrations of separated valuable metals (zinc, iron) can be recovered through standard downstream recovery operations. Typically, these fractions, once at high enough concentrations and volumes, are sent to an external smelter for processing. Samples of the fraction would be assayed by the smelting house to determine the price per tonne. The main calcium carbonate-rich fraction, once sufficiently refined, would be supplied to the cement sector.

The development of any such circular recovery process would require buy-in and participation of all the sectors in the value chain, from waste suppliers and market intakers to governmental and policy authorities, and industrial sector representatives. The process development phase would require close



Figure 8.1. Potential route to develop processes for the use of waste materials in specific market applications.



Figure 8.2. Example of a potential process flow for processing calcium-rich wastes to use in the cement sector.

collaboration between the process developer and the industrial end user (i.e. cement/construction sector, smelting house, etc.).

To be financially viable an operation such as this would need to achieve a scale at which the quantities of metal recovered and secondary raw materials produced are of sufficient volumes to feed the market needs. The equipment necessary for comminution, blending and separation technologies, sampling analysis for chemistry, automated chemistry analysis and adjustment (outlined in Figure 8.3) all requires significant investment and, therefore, is only viable once a threshold processing tonnage and baseline market price for the product are achieved. For example, the scenario using waste as a clinker or filler replacement would require comparison with the current price of raw materials and also the potential CO₂ savings. Finally, the key to developing such processes lies with the market needs and any market drivers, including environmental benefits, for the acceptance of secondary raw materials.



Figure 8.3. Outline of key processes for scaling up operations for the recycling of waste materials into secondary raw materials.

9 Concluding Remarks

Progress towards developing a circular economy for secondary raw materials in Ireland involves the following key steps:

- taking a joint collaborative approach between the end user, the process developer and the supplier of the waste material;
- developing a test-bed case or pilot plant for a specific market application and the most appropriate compatible wastes, as highlighted in this research;
- developing and producing samples of the output fractions that can be analysed and assessed by the market end user;
- establishing the cost of processing and the price of the secondary raw materials;
- showcasing the results as evidence for any legislation requirements and/or amendments necessary for industrial authorisation;
- building the individual business case to attract investment to fund the process set-up.

The contribution of this research to the original objectives of the Raw Materials Ireland project is summarised as follows:

 To unlock the volume of various metals from mining and industrial residue and increase the range and yields of recovered raw materials. The research has highlighted the potential for zinc-, iron- and calcium-rich materials to be recovered from Irish wastes, achieving up to 58 wt% iron and 33 wt% calcium for specific materials and fractions with reduced levels of unwanted impurities.

- To push Ireland to the forefront of the area of raw materials processing technologies. The research has provided a foundational study on national wastes, generated an Irish Waste Inventory, provided detailed characterisation and investigated a suite of separation techniques for the different wastes, allowing the development of unique strategies for using Irish wastes in circular economy applications.
- To achieve greater economic viability and investment security of processing operations. The research has highlighted the wastes of interest and synergies among the wastes, as well as potential market applications through valorisation pathways. Potential process flows have been outlined, in addition to the steps required to further develop the use of Irish wastes in the circular economy.
- To investigate the potential for recovery of CRMs. A detailed study of the CRM content of the different wastes was undertaken in which synergies for indium, gallium and phosphorus were identified across the majority of different wastes. However, the technique that gave the best results for the separation of base metals did not result in increased concentrations of CRMs. As the separation processes would require optimisation for specific market applications, the continued monitoring of CRMs is proposed, especially regarding further comminution of infeed fractions.

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Abbreviations

Conc.	Concentrate fraction
CRM	Critical raw material
DWTE	Dublin Waste to Energy
EDS	Energy-dispersive X-ray spectroscope
EDX	Energy-dispersive X-ray analysis
ESB	Electricity Supply Board
EU	European Union
ICP	Inductively coupled plasma spectroscopy
MGS	Multi-gravity separator
pXRF	Portable X-ray fluorescence
rpm	Revolutions per minute
SEM	Scanning electron microscope
XRD	X-ray diffraction

AN GHNÍOMHAIREACHT UM CHAOMHNÚ COMHSHAOIL

Tá an Ghníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaol a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaol a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: Déanaimid córais éifeachtacha rialaithe agus comhlíonta comhshaoil a chur i bhfeidhm chun torthaí maithe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcloíonn leis na córais sin.

Eolas: Soláthraímid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spriocdhírithe agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.

Tacaíocht: Bímid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaol atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaol inbhuanaithe.

Ár bhFreagrachtaí

Ceadúnú

Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaol:

- saoráidí dramhaíola (m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistrithe dramhaíola);
- gníomhaíochtaí tionsclaíocha ar scála mór (m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta);
- an diantalmhaíocht (m.sh. muca, éanlaith);
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe (OGM);
- foinsí radaíochta ianúcháin (m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíocha);
- áiseanna móra stórála peitril;
- scardadh dramhuisce;
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdaráis áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhíriú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídíonn an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaol.

Bainistíocht Uisce

- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uiscí idirchriosacha agus cósta na hÉireann, agus screamhuiscí; leibhéil uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaol

- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil (m.sh. tuairisciú tréimhsiúil ar staid Chomhshaol na hÉireann agus Tuarascálacha ar Tháscairí).

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn

- Fardail agus réamh-mheastacháin na hÉireann maidir le gáis cheaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhair breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil

• Taighde comhshaoil a chistiú chun brúnna a shainaithint, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta

 Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaol in Éirinn (*m.sh. mórphleananna forbartha*).

Cosaint Raideolaíoch

- Monatóireacht a dhéanamh ar leibhéil radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as taismí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas

- Comhairle agus treoir a chur ar fáil d'earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaol ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinnteoireacht i ndáil leis an gcomhshaol (*m.sh. Timpeall an Tí, léarscáileanna radóin*).
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhaíl ghuaiseach a chosc agus a bhainistiú.

Múscailt Feasachta agus Athrú Iompraíochta

- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an ghníomhaíocht á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d'Oifigí:

- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- Oifig um Chosaint Radaíochta agus Monatóireachta Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltaí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair imní agus le comhairle a chur ar an mBord.

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Circular Economy Opportunities – Raw Materials Ireland Project

COOResearch

Authors: Lisa O'Donoghue, Chinnam Rama Krishna, Eva Ujaczki and John Mulcahy

Identifying Pressures

Ireland is home to primary industries in mining, materials processing and power generation. Today, the majority of waste outputs associated with these industries are either sent for disposal or exported. There is, however, potential to assess these wastes as secondary raw materials, recover any valuable metals and find alternative applications for the end waste that can contribute to a circular economy. In the light of this, the high-level objectives of the Raw Materials Ireland Project are defined as follows:

- to unlock the value of various metals from mining and industrial residues;
- to push Ireland to the forefront in the area of raw materials processing technologies;
- to improve the economic viability and investment security of processing operations.

The specific objectives to achieve these are to:

- undertake characterisation of certain waste from the mining, materials processing and power generation sectors;
- investigate synergies between the different wastes regarding composition;
- investigate the critical raw material (CRM) content of the wastes and synergies that exist;
- develop strategies for the recovery of valuable materials;
- investigate separation techniques to recover any valuable metals and CRMs.

Informing Policy

A detailed waste inventory and characterisation study of 24 waste samples from 12 different industrial sites across Ireland was undertaken as follows:

- mine waste rock and tailings: Lisheen Mine, Silvermines, Avoca Mines, Galmoy Mine, Two Valleys Mines, Tara Mines and Tynagh Mine;
- power plant fly ash and bottom ash: Electricity Supply Board (ESB) Moneypoint, ESB Lough Ree, ESB West Offaly, Covanta Dublin Waste to Energy and Indaver waste to energy;
- Refinery residue: Aughinish Alumina.

The results of the analysis revealed commonalities among a group of valuable materials and CRMs that were present in the majority of the wastes as follows:

- metals iron (~50–200 g/kg), zinc (~10–300 g/kg), aluminium (~10–50 g/kg) and calcium (~100–270 g/kg);
- CRMs gallium, indium and phosphorus (typically ~0.1–0.2 g/kg).

The development of an initial waste inventory with detailed composition of national wastes is key to informing Irish policymakers of the secondary raw materials resources available and the potential contributions they can make to circular economy.

Developing Solutions

The recovery strategy developed focused on separating the wastes into the following concentrated fractions:

- base metals to separate iron, zinc and aluminium phases from the main fraction;
- calcium-rich phase to concentrate the remaining calciumrich fraction, which may have applications in the construction sector;
- CRMs to track the locations of the CRMs within the separated fractions and any potential for downstream concentration of these elements.

The research focused on techniques for mechanical and physical separation, such as ball milling and filtration, magnetic separation, dissolution studies and gravity separation processes, including the Mozley superpanner and the multi-gravity separator (MGS). The test results showed that the gravity separation techniques gave the best results where individual wastes demonstrated enhanced responses for either the Mozley superpanner or the MGS, based on their specific characteristics.

Process flows based on the results were developed for specific market applications for the wastes, including cement clinker replacement, cement filler, aggregates and geopolymer applications.

The process flows illustrate processing steps to unlock the valuable materials including base metals and the calcium rich-fractions. In addition, a process flow for multiple wastes was developed to showcase a circular economy approach where the scaling of the process and the capability to co-process different wastes augment the economic viability of the operation.

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