Cranfield University

Victoria Estelle Huntington

Exploring Metal Extraction Potential from Historical Metallurgical Sites and Waste Deposits Using Solvometallurgical and Hydrometallurgical Processes

School of Water, Energy and Environment

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Academic Year 2020-2023

Supervisors: Dr. Stuart Wagland & Prof. Frederic Coulon

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Abstract

Metalliferous waste from past metallurgical sites present significant environmental risks yet provide opportunities for metal extraction and recovery to supplement global demands in the shift towards renewable technologies. Characterising site conditions, metal specificity of green solvents and chelators, and an initial assessment of operating condition are required to develop these approaches into a commercial setting. This study evaluates the efficacy of solvo- and hydro-metallurgical approaches in extracting metals from real-world metalliferous waste. Specifically, it examines the performance of green deep eutectic solvents (DES) and chelating agents (CA) on blast oxide slag dust (BOS-D) and goethite, by-products of iron smelting and zinc refinery processes, respectively. Through batch tests and column studies, the impact of varying operational conditions, including molar ratio for DES and pH for CA were assessed. The results were used to inform sequential bioleaching to solvo- or hydroleaching tests to investigate the potential of hybrid extraction processes. The extraction efficiencies across batch, column and the sequential study from BOS-D were compared against a commercial chelating agent ethylenediaminetetraacetic acid (EDTA). DES extracted 60% more of the total metal load compared to CA and EDTA from BOS-D in batch tests. When applied to goethite, CA extracted 70% more of the total metal load than DES in batch tests. There was a 1% difference in metal extraction between DES and CA from BOS-D and 2 % from goethite in the column study. EDTA extracted the same or up to 15% more of the total metal load than DES and up to 18% than CA in the column study. The sequential study demonstrated that DES and CA have minimal influence in metal extraction under the operational conditions used in earlier batch tests, when applied to the residue after bioleaching extraction using Acidithiobacillus ferrooxidans. The extraction of the total metal load was improved by 4% using CA. The findings of this study demonstrate that CA and DES can extract a robust suite of metals from

real metalliferous wastes. In BOS-D batch and column tests, analysis of metal group selectivity showed that DES had greater extraction than EDTA across all metal groups except rare earth lanthanides. In BOS-D batch studies, EDTA had greater extraction than CA across all metal groups except alkaline metals, but column studies showed that CA had greater extraction than EDTA across all metal groups except alkaline metals. This provides evidence for a robust metal extraction process and could improve the suite of extractable metals, providing sustainable alternatives in metal supply chains. The understanding of these extraction processes will be improved through, optimisation of more physical controls *e.g.*, temperature, agitation, and further optimisation of the initial chemical conditions to improve metal extraction efficiencies, metal selection and potential revenue generation.

Key Words: Resource recovery; critical metals; deep eutectic solvents; chelating agents, solvometallurgy

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Roberto and Ruby, thank you. The last three years have been a rough old time but without my team, it would not have been half as fun. Your patience, competitiveness, audacity, and undoubted belief have been a driving force, thank you.

To me; well done pal, give yourself a pat on the back and a toot of your own trumpet.

And Dad, thank you for everything. Fortunate or not, I have now become a mini you. I definitely win now…

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List of abbreviations

DES	Deep eutectic solvent
CA	Chelating agent
BOS-D	Blast oxide slag dust
ChCl	Choline chloride
EG	Ethylene Glycol
MA	Malonic Acid
U	Urea
GLDA	L-glutamic acid N N-diacetic acid tetrasodium salt
EDDS	Ethylenediamine-N,N'-disuccinic acid
NTA	Nitrilotriacetic acid
EDTA	Ethylenediaminetetraacetic acid
HBA	Hydrogen bond acceptor
HBD	Hydrogen bond donator
PV	Photo voltaic
CE	Circular economy
ELFM	enhanced landfill mining
AMD	Acid mine drainage
ICP-MS	Inductively coupled plasma mass spectrometry

1. Introduction

1. Background and Motivations

The European Green Deals Net Zero Strategy intends to reduce greenhouse gas emissions by 100% by 2050 (Hainsch et al., 2022). To fulfil this goal, a substantial society shift from fossil fuels to renewable energies such as solar photovoltaic and wind power, along with energy storage solutions is non-negotiable. As a result, the demand for critical metals are increased exponentially whilst metal reserves are diminishing (Grandell et al., 2016). Critical metals are irreplaceable in renewable technology and are metals with supply chain risks (Le et al., 2022). Through governmental subsidies, intervention and established infrastructure, the USA, Russia, China, and Australia were the top four critical metal producing countries in 2022 (International Energy Agency, 2023). To improve the security of critical metal supply within the UK, the UK Critical Mineral Strategy aims to accelerate domestic supplies to enhance international markets and bolster the UKs position within the critical metal market through innovation and novel metal extraction methods *e.g.*, solvometallurgy of metalliferous waste (Department for Business and Trade & Department for Business, 2023).

Of the 2.5 million contaminated sites in Europe, 13% are now redefined as past metallurgical site deposits and could provide a novel opportunity for resource extraction to supplement the UK Critical Mineral Strategy (Panagos et al., 2013). Exploring novel extraction opportunities like past metallurgical site deposits, where the infrastructure and accessibility to extract metals is already established could reduce the environmental impact posed from such sites whilst providing additional economic savings, contributions to a circular economy and reduced pressure on conventional extractive mining processes (Watari et al., 2021). It has been noted that one single system alone will be unable to replace conventional extraction methods, however, a combination could retrieve up to 80% (Harris, 2022).

Conventional solvometallurgy typically uses chelating agent Ethylenediaminetetraacetic acid (EDTA), known to effectively extract metals from a range of environmental matrices (Alaboudi et al., 2020). Despite the low costs, EDTA is a persistent organic pollutant and up to 64% can persist in soil under natural conditions due to low biodegradability, resulting in impaired soil function and plant growth (Alaboudi et al., 2020; Jez & Lestan, 2016).

Solvometallurgy incorporating green chemistry *e.g.*, deep eutectic solvents and chelating agents is at the forefront of emerging "green technologies" (Santana-Mayor et al., 2021). Green chemistry encompasses sustainability goals and is underpinned by effective, efficient, and environmentally friendly chemicals and processes (Horváth, 2018).

Metal extraction using deep eutectic solvents contributes to the bulk of research in green solvometallurgy. Notable for their unique composition and properties, deep eutectic solvents utilise acidolysis and redoxolysis leaching mechanisms (Faraji et al., 2020). Chelating agents, employing complexolysis leaching mechanisms, are commonly used in medicine due to their strong metal binding capabilities (Faraji et al., 2020). There is limited literature exploring the efficiencies of chelating agents to facilitate metal extraction from waste, especially metalliferous waste *e.g.*, blast furnace slag dust.

In the emerging field, solvometallurgical research has principally focussed on metal extraction from printed circuit boards, waste waters and lithium-ion batteries. However, past metallurgical site deposits *e.g.*, blast oxide slag dust and goethite, have been undervalued yet contain vast quantities of critical metals previously considered uneconomically viable to extract (Riley et al., 2020). Within the UK, 30% of past metallurgical sites have been redeveloped for housing despite such sites possessing the significant metal extraction opportunity (Riley et al., 2020). Since 1985, approximately 490 to 640 million tonnes of metal rich slag will have been generated in the UK (Renforth et al., 2011).

A comparison of deep eutectic solvents and chelating agents on blast oxide slag dust and goethite is yet to be tested and is required to accelerate the development of the commercial use of green chemistries on past metallurgical sites for metal extraction.

2. Aims and Objectives

The main research of this study is to develop an analytical framework based on green chemistries for sustainable extraction of metals from past metallurgical sites and waste deposits.

The following objectives will be addressed in the completion of this study.

1. To conduct a critical review of traditional and emerging solvometallurgical methods for extracting metals from contaminated soils and various steelmaking processes.
2. To investigate the potential for metal extraction from blast oxide slag dust and goethite cake using "green solvents" through batch and column chemical leaching.
3. To provide a techno-economic assessment of the solvometallurgical process
4. To assess the efficacy of a sequential bioleaching to chemical leaching and provide recommendations for scaling up the process.

3. Thesis Plan

Each of the following chapters were produced in the format of a journal paper, published independently or currently in peer review. Figure 1.1 presents the overall structure of the thesis linking aims and objectives with the associated chapter.

Victoria Estelle Huntington completed all the planning, experimental work, and the data analysis. All chapters were written by the first author Victoria Estelle Huntington with comments from supervisors; Dr. Stuart Wagland and Prof. Frederic Coulon. Named authors in chapter 5 contributed their knowledge and data under the supervision of Dr. Stuart Wagland and Prof. Frederic Coulon.

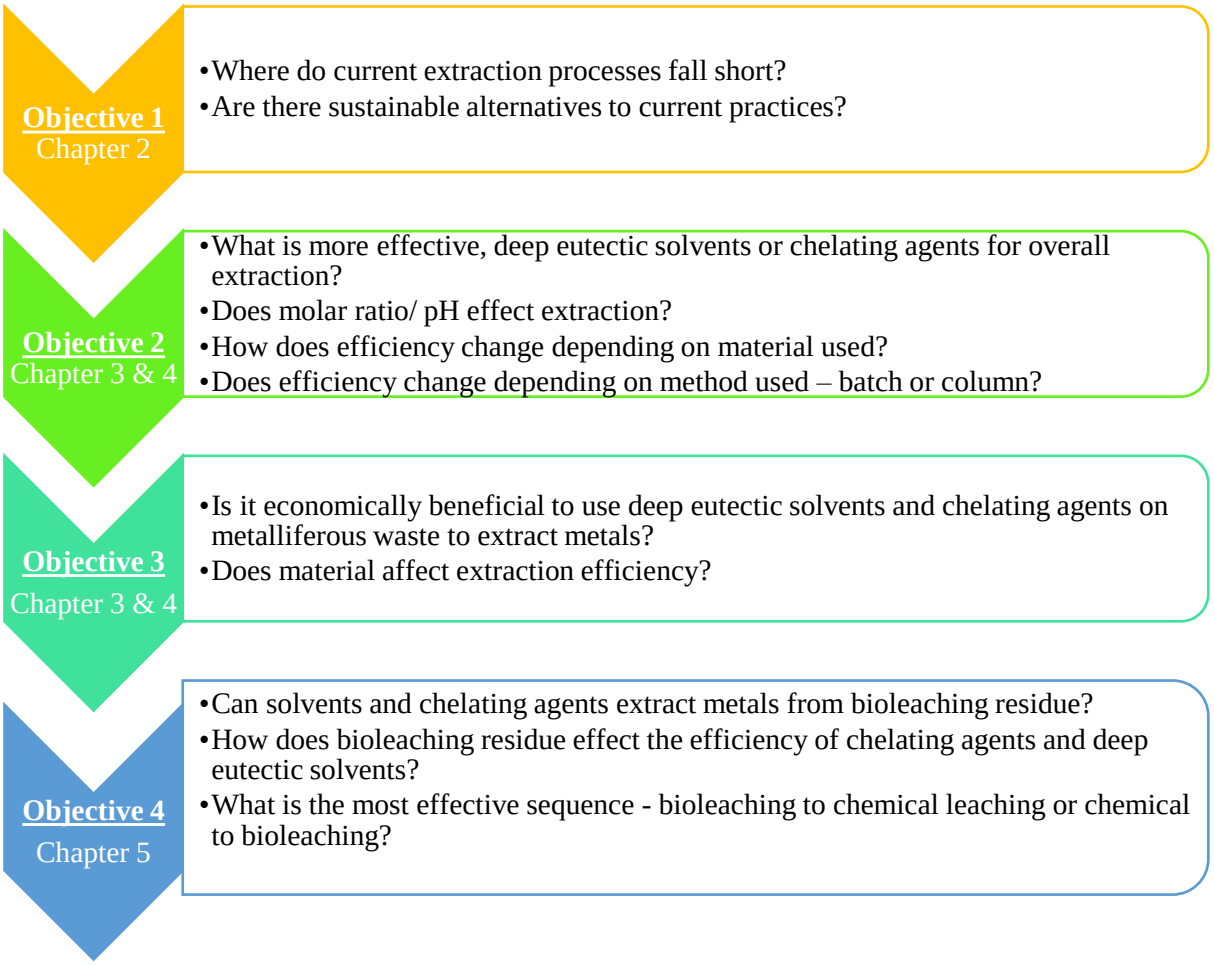


Figure 1.1 The development of the thesis objectives and the corresponding chapters addressing these aims

Chapter 2 introduces existing demand on metal, conventional metal extraction methods and critically evaluates emerging extraction processes, particularly those involving green chemistry. The outcomes from this chapter influenced the experimental designs of the subsequent chapters 3, 4, and 5. Chapter 2 was separated and published in a *Sustainability: Special Issue Sustainable Mining and Circular Economy*, entitled 'Innovative Resource Recovery from Industrial Sites: A Critical Review'.

Chapter 3 investigated the efficacy of three deep eutectic solvents (choline chloride-ethylene glycol, choline chloride-malonic acid and choline chloride-urea) and three chelating agents (L-glutamic acid N N-diacetic acid tetrasodium salt, Ethylenediamine-N,N'-disuccinic acid and Nitrilotriacetic acid) to extract metals from blast oxide slag dust and goethite in batch experiments. The blast oxide slag dust and goethite were mixed with the green chemicals in 12% (w/v). All tests were done in ambient conditions to emulate field conditions. The deep eutectic solvents were tested in three molar ratios (1:1, 1:2 and 2:1) and the chelating agents in three pH levels (4, 6, and 8). The testing conditions used on goethite was informed by results when using blast oxide slag dust. An economic assessment has been provided based upon extraction efficiencies. This paper has been submitted to the *Journal of Cleaner Production.*

Chapter 4 assessed the effectiveness of the deep eutectic solvents and chelating agents in semi-continuous columns using blast oxide slag dust and goethite. The testing conditions used on goethite was informed by results when using blast oxide slag dust. The blast oxide slag dust and goethite were fully saturated with deep eutectic solvents and chelating agents at 7.5% (w/v). The green chemicals were continuously recirculated through the column at 80 mL/s for two hours. This chapter has been submitted to *Journal of Environmental Management*.

Chapter 5 interrogated the metal extraction efficiencies of deep eutectic solvents and chelating agents on post-bioleaching blast oxide slag dust residue. The deep eutectic solvents and chelating agents choice was informed by results in chapter 3 and 4. Ipek Tezyapar Kara carried out the bioleaching phases and subsequent data analysis. The solvometallurgical phase of this sequential study reflect the methodology in chapter 3. This chapter is in preparation for the *Journal of Environmental Management*.

Chapter 6 discusses the results of this thesis and recommendations for further studies and commercial applications.

Chapter 7 collates the overall conclusions of the study in relation to the initial objectives.

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2. Innovative Resource Recovery from Industrial Sites: A Critical Review

Victoria E. Huntington [1], Frédéric Coulon[1] and Stuart T. Wagland [1, *]

[1]School of Water, Environment and Energy, Cranfield University, Cranfield, UK.
*Correspondence: s.t.wagland@cranfield.ac.uk; Tel.: +44(0)1234 750111.

Abstract: Global net-zero pledges are instigating a societal shift from a fossil-fuels based economy to renewables. The change facilitates batteries, solar PV, and wind turbines etc., all of which are underpinned by critical metals. Raw metal extraction is not renewable and environmental pledges made by government will not be met if this continues. Historic industrial sites contain vast waste stocks. These sites already have an established infrastructure for resource extraction. Applying green solvents, deep eutectic solvents (DES) to such sites for resource recovery alleviates pressure on existing raw extraction processes whilst generating more immediate stores of critical metal along with relatively insignificant environmental impacts. Existing remediation/recovery options have varying metal recovery efficiencies usually combined with high operating costs. Using novel green solvents, such as DES, on historic sites provides an opportunity to recover metals from waste that ordinarily would be looked over. Increased extraction of critical metals from waste material within the UK will reduce reliance on imported metals and improve critical metals security of supply to UK markets and the wider economy The use of these solvents provides an environmentally friendly alternative but also regenerates the legacy of waste from historic industrial sites and consequently implements a circular economy. Adopting the use of green solvents will meet EU environmental pledges, and boost the economy, by recovering metals from legacy sites to meet exponentially growing metal demand.

Keywords: Resource recovery; critical metals; deep eutectic solvents; chelating agents; renewable energy

5. Introduction

Critical metal demand has increased exponentially due to rapid industrialization and societal pressures. Reserves for critical metals are diminishing. Metals are in demand to provide services and goods which are essential to meet basic human needs [1]. European government backed policies are setting targets to reduce greenhouse gas emissions by up to 95% (compared to 1990 levels) by 2050 [2]. In order to do so a societal shift towards renewable energies (*e.g.*, solar PV, wind power, fuel cells, hydrogen storage) from fossil fuels is imperative. This change will be underpinned by critical metal supply which is already under pressure [2].

A small portion of end-of-life lithium batteries are disposed of through inappropriate waste streams, the majority are stored in landfills or collected in households [3]. The EU Battery Directive 2006/66/EC has inadequacies as there are no defined recycling efficiencies for specific elements or components nor does it reflect the CE concept [3]. Recent predictions highlight that lithium stores will deplete between 2060 and the end of the century [4]. Not only will this limit electric vehicle capacity but also solar PV, LED, electric vehicle, and nuclear power production [5]. The CE concept incorporating urban waste streams transforms industrial sites from a cost to society (contributes to global warming, occupation of valuable land and water contamination) to a resource recovery opportunity [6]. Solar PV relies on a supply of other critical metals; copper, cadmium, and aluminum [7]. In the last 30 years, the mining output for aluminum has grown 256% which is beneficial for solar PV outputs, copper output has been much slower, increasing by less than 2% since 2013[8]. As a result of increased raw extraction costs and falling copper prices discouraging investments into new mines and ore extraction [9]. This provides an encouraging platform to invest and explore novel metal resource streams *e.g.*, metal recovery from past industrial sites. Solar power is expected to reach a global capacity of 8519 GW by 2050[7]. Using historic production and consumption as a reference, the demand for indium, selenium and tellurium could limit PV panel production

by 2030[10]. This will limit the potential for mass PV panel production, reducing the potential for energy generation. Wind turbines have a strong potential for CE. Recycling pre-consumer products such as steel and post-consumer products to recover rare earth metals and metalloids from waste electrical and electronic equipment could provide vast quantities of metals for turbine generators [11].

Physical, economic, social, or environmental factors can limit critical metal supply [12]. 27 of 70 studies stated that physical factors will be the main limiting concern regarding metal supply [1]. To supplement the physical supply of metals, secondary production avenues should be explored for the recovery of metals from historic mines and other industrial sites. Studies suggest that even with recycling rates of 99% the supply of materials recovered from recycling will not meet the ever-increasing demand due to dissipative losses and long product lifetimes [13]. Therefore, resource recovery needs to be implemented to diversify critical metal sources from raw materials to secondary materials i.e., wastes from past metallurgical sites [1].

To achieve metal recovery from waste to meet net zero targets, novel metal extraction techniques are crucial. Bioleaching, green chemistry, urban mining and enhanced landfill mining are all emerging trends with novel metal extraction processes [14]. Green chemistry, including deep eutectic solvents (DES), are at the forefront of emerging “green technologies” to recover metals [15]. It has been suggested that one single system alone will be unable to replace conventional extraction methods, however, a combination could retrieve up to 80% [16]. Using alternative extraction methods from historic metalliferous sites reduces dependency upon conventional mining processes. Historic metalliferous sites already have existing infrastructure and accessibility for resource recovery, providing additional economic and carbon savings.

For example, the lithium battery industry is predicted to grow from an annual production of 100 GWh in 2018 to 800 GWh in 2027 due to a trend shift from fossil fuel to electric vehicles [17,18]. Currently it takes six years to commission a mine, this runs the risk of demand quickly outstripping the supply from raw metal reserves [9]. Metals, like lithium, are required immediately to meet the demand from renewable and energy saving technologies. There is the opportunity to find alternative lithium stores in past metalliferous sites which can be commissioned quicker than traditional mining processes. Up to 20,000 tonnes of lithium hydroxide could be sourced from historic mines in the southwest of England [19]. Applying novel green technologies *e.g.*, green solvents, to a historic site to recover metals in waste slag, relieves the need to commission traditional extraction mines. Reduced dependency on conventional mining processes alleviates all associated environmental impacts; soil, groundwater, and surface water contamination, land-use change resulting in a permanent scar in the environment, loss of biodiversity and habitat fragmentation. Using historic metalliferous sites minimizes environmental degradation yet enhances opportunities for the circular economy (CE) whilst meeting growing metal demands.

This article critically appraises traditional remediation techniques, recent and emerging recovery opportunities, and the engineering and scientific aspects which require further development. Presently there has been limited research comparing chelating agents to DES concerning recovering metals from historic blast furnace oxide slag. If high yields (>80%) of metals locked in these slags can be recovered using green solvents, it provides a feasible option for metal recovery. Green solvent recovery will implement a circular economy, meet national and international decarbonization strategies, redevelop past metallurgical site deposits, and minimize the environmental impacts of recovery processes.

6. Contaminated sites from past metallurgical activity

2.1.1 Industrial sites

The legacy of the industrial revolution has resulted in over 400,000 hectares of contaminated land in the UK [20]. The sites, contaminated with economically viable resources, situated in locations with high demand for development, are prioritized for new buildings and housing without consideration of the benefits the sites offer now or in the future [21]. Nearly 30% of the former iron and steelwork sites in the UK have been redeveloped for housing despite these sites possessing significant opportunities for resource recovery that can be coupled with site restoration and regeneration efforts [22]. Since 1985, predictions show that between 490 to 640 million tonnes of slag will have been generated in the UK [23]. The slags then produce oxyanion-rich leachates, which provide a prime opportunity for mineral and metal resource recovery [22]. The increasingly demanding European regulations and disposal costs are encouraging innovation within the manufacturing industries, past and present moving towards a circular economy [22,24].

Studies have been limited on resource recovery from industrial sites, however, Rare Earth Element (REE) recovery through solvent extraction has been proven [25]. It is not economically feasible to use ex-situ processes (soil removal) on legacy industrial waste due to low target metal concentrations however, using in-situ (heap leaching, bioremediation) has proven a successful tool [22]. A key benefit of in-situ recovery processes is the minimal disturbance to overlying environments as well as low capital costs [26].

2.1.2 Disused mines

Historic mines are one of the biggest sources of water pollution in the UK without any party being legally liable for the effluent [27]. In England and Wales, there are approximately 5,500 non-ferrous abandoned metal mines, and the 2008 Directory of Mines and Quarries identified

2,455 active mineral mines in the UK [28]. As of 1998, no metal mines remain functioning however, the Mining Waste Directive does not cover mining sites closed before 1999 thus making it difficult to find the responsible organization and attribute liability for associated pollution [27,28]. There is a perception that abandoned or unrestored mine sites have no inherent value but, conversely can provide vast quantities of resources that can be recycled and recovered back into the economy [21]. Estimates in 2014 several thousand million tonnes of metal waste is generated per annum from disused and active mine sites [29]. Acid mine drainage (AMD) has been described as the most significant environmental issue facing the mining industry and can create a legacy of long-term damage to the ecosystem and humans [29,30]. Acid mine drainage contains high concentrations of Fe, Ni, Cu, Pb [30]. Resource recovery is an opportunity to alleviate the adverse environmental effects of mineral extraction processes [21]. As previously stated, many mines have no active remediation treatment processes thus creating large stocks of highly concentrated critical metals with the potential for vast resource recovery.

2.1.3 Landfills

Using landfills as a potential avenue for resource recovery will transform landfills from a major cost to society from global warming contributions, groundwater pollution, and occupation of valuable land into a valuable resource recovery site [15]. Traditional landfill mining is the process of extracting materials from previously landfill resources [31]. As a result, landfill mining has been limited to methane extraction, possible land reclamation and partial recovery of critical metals [32,33].Unlike landfill mining, enhanced landfill mining (ELFM) is defined as the safe exploration, conditioning, excavation, and integrated valorization of landfilled waste streams (historic, present and/or future) as materials and energy using innovative transformation technologies and respecting the most stringent social and ecological criteria

[15]. ELFM reduces CO_2 by 1 million tonnes over 20 years due to fewer materials needed to be produced [15]. Estimates show that in the EU there are between 350,000 and 500,000 historic and active landfill sites with appropriate streams for secondary metal recovery [34]. Research believes that a significant stream of secondary materials and energy can be derived from ELFM [15]. However, there is little experience with ELFM on old and abandoned landfill sites. The current costs of ELFM exceed revenues of recovered resources making the concept unfeasible without funding or government-funded incentives [35]. Additionally, ELFM is associated with noise and dust pollution, habitat loss and disturbances to animals [36]. Excavated waste characteristics depend on the waste retrieved from landfill i.e., municipal solid waste, industrial waste etc., climate, location, landfill type, age of waste and leachate pH[37]. Table 2.1 combines the recovery option with the type of landfill with their associated limitations, common limitations are high content of soil-like fines, moisture, and critical metal contamination [36]. For ELFM to succeed, technology and processes should be considered on a site-by-site basis with tailored pre-treatment (*e.g.*, sorting, screening, shredding, pelletizing, drying). The quality and composition of waste within the landfills reflect the country's different economic structures, consumption patterns and waste policies of the member state [38]. Desired materials can be intermingled with other undesirable fractions and bound within larger articles *e.g.*, spring mattresses contain ~ 27 kg of steel but are locked in with natural and synthetic fabric, foam, and wood [35] necessitating pre-treatment processes (shredding, grinding, etc.,) to liberate the desirable fraction adding further cost to the process.

Table 2.1 Limitations of resource recovery processes from various types of landfill material.

Type of Landfill	Recovery Option	Limitations	Reference
Soils	Soil Removal	Limited to small working areas High initial costs Extensive machinery required	[39]
Leachate	Coagulation/ flocculation Adsorption Membrane process	High operating costs Pollutant transfer between phases Low pollutant removal efficiency Low process performance	[40,41]
Waste Electrical and Electronic Equipment	Incineration Acid leaching Hydraulic shaking bed separation	Secondary pollutants production Non-metals materials cannot be recycled. High operating costs Hard to recover metals except copper. Toxic to the environment	[42]
Construction Waste	Landfill	High cost to recycle. Lack of enthusiasm to recover resources. Minimal communication between contractors	[43]
Wastewater	Membrane filtration Chemical precipitation Biosorption	High operational costs Not selective Toxic sludge generated. Disposal limits application (biosorption)	[44,45]
Hazardous Waste	Pyrolysis	Inefficient metal recovery Energy intensive High operation costs Toxic dioxins and furans produced	[46]

When considering resource recovery from landfills, economic feasibility alone cannot demonstrate the economic value of landfill resource recovery [47]. Improved emerging extraction and separation processes, resources becoming scarcer and increase demand for land development increases landfill mining feasibility.

7. Remediation of contaminated sites

The need to apply integrated environmental strategies to include appropriate decontamination technologies to remediate contaminated sites has been highlighted [48]. The traditional remediation methods, chemical, biological, and physical, have become established over

decades but have shortcomings (Figure 2.1). When used independently of each other, chemical and physical methods generate pollutant by-products (*e.g.*, toxic sludge) and are not cost-effective, also biological processes are very time-consuming (can take several months to years) [49]. These methods have been used in conjunction to overcome these drawbacks. Typically, these techniques are used to remove contaminants from soil with little to no resources recovered. Whereas the applications for metal recovery require a critical appraisal. The use of green chemistry is becoming a promising emerging technology regarding contaminated site remediation and recovery.

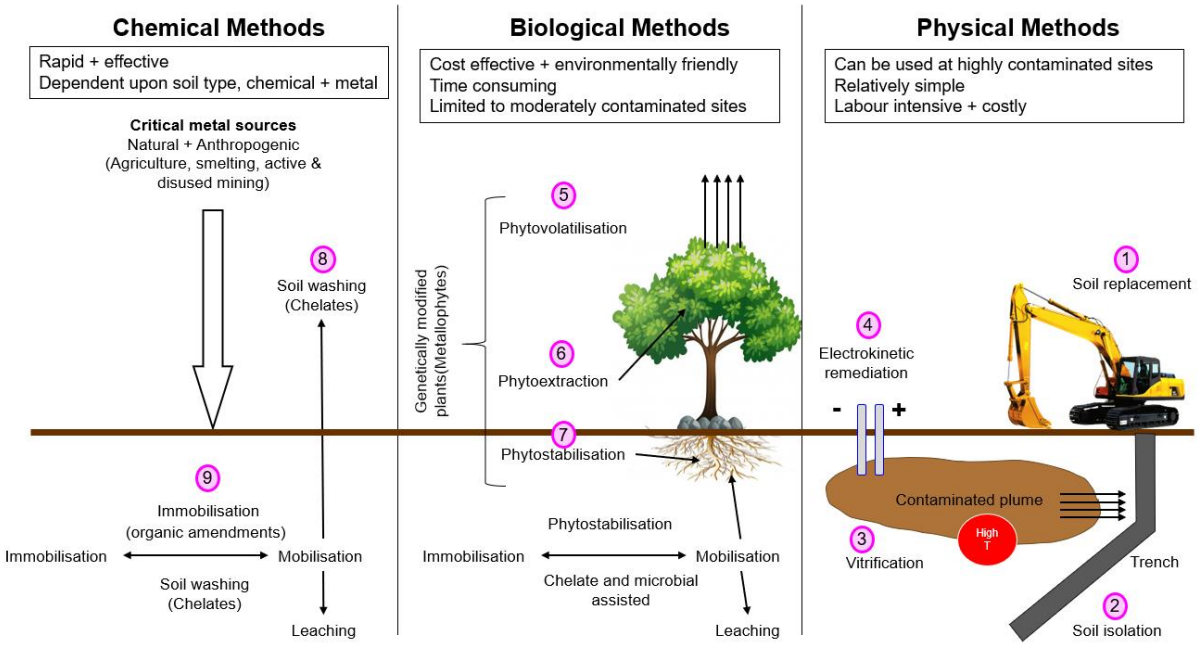


Figure 2.1 Different soil remediation techniques; physical, biological, and chemical.

8. Management of contaminated soil

2.1.4 Physical

Soil replacement involves either replacing or partly replacing contaminated soil with non-contaminated soil [50]. Replacing contaminated soil dilutes the concentration of metals in the soil, increasing soil functionality [51]. This method is costly due to large working volumes and extensive machinery required so is most effective for remediating small sites with heavy metal contamination [51]. However, it is proven to increase soil environmental capacity and dilute

pollutant concentration [52]. Removed soil is still heavily contaminated and should be processed correctly to avoid secondary pollution [51].Soil isolation is the separation of contaminated soil using subsurface barriers to avoid removal of contaminated soil [53]. Vertical barriers are used to restrict the lateral movement of groundwater, materials used include sheet piles, grout curtains and slurry walls [50]. Soil isolation does reduce the trace metal pathway into groundwater; however, it is not a direct active remediation process [54].

Stabilization of critical metals in soil can be achieved by applying high-temperature treatment (1400°C – 2000°C) [50,52,44] with two main interactions: chemical bonding and encapsulation. Vitrification of industrial waste showed immobilization of Cr, Cu, Fe, Mn, Ni, and Zn on the glass matrix [52,55]. The use of additives (clay, native soil, or sand)can improve the encapsulation of contaminants and leaching capacity [50,56]. Studies show small leaching ratios for Ag, Cr, and Cu (1.35, 0.02 and <0.01% respectively) while Cd, Pb and Zn leaching ratios were higher (3.83, 2.46 and 0.36% respectively) [58]. Temperature plays a vital role in metal recovery, showing low metal mobility at elevated temperatures [57]. Vitrification up to 1850 °C has been proven to efficiently stabilize critical metals (Cr, Cu, Ni, Pb, Zn, Al2O3, Fe2O3, MnO, MgO) from Pb and Zn-rich ceramic waste [55]. Using solar technology on waste from Ag-Pb mines in Spain, Fe, Mn, Ni, Cu and Zn were immobilized at 1350 °C whereas Zn, Ni, Mn, and Cu were immobilized at 1050 °C. Vitrification is ideal when working with small volumes but under field conditions where the soil has already lost its environmental function, or large scale (on-site) this approach is highly expensive [50,52].

Electrokinetic remediation operates on two established electric field gradients on either side of an electrolytic tank filled with contaminated soil [50]. Metals are removed through a combination of mechanisms; electromigration, electroosmosis, electrophoresis and electrolysis [50,54]. Remediation performs well in soils with low permeability achieving low soil function disturbance [52]. Applying chelators such as Ethylenediaminetetraacetic acid (EDTA),

ethylenediamine succinic acid (EDDS), nitrilotriacetic acid (NTA), and citric acid to metal-contaminated soils (As, Cd, Cr, Cu, Ni, Pb, and Zn) to enhance electrokinetic efficiency [59]. Results show that EDTA is more suited for enhanced Ni, Pb, and Zn removal in order of Pb > Ni > Zn with about 60% Pb recovered [59]. EDDs recovered 51% Cu and 26% Zn in the following order Cu > Ni > Cr > Cd ≈ Pb > As > Zn [59]. However, other research has shown that removal efficiencies are dependent upon catalysts used and the metal remediated [50]. Additionally, the main limiting factor of electrokinetic remediation is soil pH fluctuations, as soil pH cannot be maintained thus an anionic complex cannot be formed [50,59]. Adding a buffer by using a complexant or ion-exchange membrane has been shown to control soil pH [60].

2.1.5 Biological

Phytoextraction uses the capability of plant roots to uptake, translocate and concentrate metals from soil into the plant biomass [50]. Phytoextraction has been shown to be the best approach to remove contaminants from the soil without destroying soil structure and fertility [61]. Festuca Rubra L. is a commonly used grass, with recent research enhancing stabilization through various soil additives (*e.g.*, inherent mineral sorbents). Phytoextraction is suited to large quantities of low levels of contamination as most plants or hyperaccumulators cannot withstand heavily polluted sites [62]. Hyperaccumulator plant biomass is relatively easier to recycle, dispose of, treat, and oxidized than contaminated soil. The main limitation is that most hyperaccumulators are specialized to accumulate or tolerate only one metal at elevated levels with variable efficiency [62]. There are >320 Ni, 30 Co, 14 Pb, and 1 Cd hyperaccumulator species [61]. Subsequently, when trying to use phytoextraction as a remediation tool it is highly specific to the contaminating metal, with low efficiency resulting in a time-consuming approach. Though, one of the best multi-metal accumulators is *Thlaspi Caerulescens* which

can efficiently hyper accumulate Ni, Cd, Pb, and Zn. Even with multi-accumulators, for this approach to be economically feasible the plants must be able to extract, translocate and produce large quantities of plant biomass [61,63]. Like any biomass production, it is limited by the growth rate, element sensitivity, disease resistance and harvesting method. Phytoextraction is only applicable to shallow contamination (up to 60 cm), and while there are low costs associated it is a time-consuming process [52]. Phytoextraction may remove contaminants from the soil, but the contamination remains in the plant biomass which must be disposed of correctly, this is the main limitation for commercial implementation [61].

Phytostabilisation aims to minimize metal mobilization in soil and contaminants by using plants to enable stabilization [52,64]. Phytostabilisation does not remove the metal contaminants but accumulates them within the root and precipitation into the rhizosphere [62]. The isolated and adapted arbuscular mycorrhizal fungi are more adapted for phytostabilisation and are proven to be better than laboratory strains of fungi resulting in a promising avenue biotechnological remediation tool [65]. Additionally, phytostabilisation methods can be used on contaminated sites with regulatory restrictions as it limits off-site removal of contaminated soil [62]. However, because the metals remain onsite locked in plant roots, regular monitoring is necessary to ensure optimized stabilized conditions [66]. There is high public acceptance for phytostabilisation, but the method is time-consuming and limited efficiency so is better suited for large volumes of low contaminated soil [52].

Phytovolatilization is a highly specialized mechanism. Subsequently, phytovolatilization exploits genetically modified plants to assimilate metal into volatile forms which are then released into the atmosphere through plant transpiration as biomolecules [50,52]. Phytovolatilization by Pteris vittate is the preferred biological remediation approach for As [67]. Phytovolatilization focuses on Hg remediation as the gaseous form of Hg is significantly less toxic [61]. Once volatile compounds are released into the atmosphere, they become diluted

and dispersed subsequently posing negligible environmental impact [62]. However, once in the atmosphere, the volatiles are likely to be recycled by precipitation and redeposited into the aquatic environment increasing the boundaries of environmental impacts past the contaminated site [68]. This technology is only applicable to volatile contaminants (Pb, Hg, As, etc.,) thus application is limited [51].

2.1.6 Chemical Remediation

Soil washing uses extractants (*e.g.*, surfactants and co-solvents) to leach metals out of the soil [62]. Soil washing is particularly effective at removing bioavailable and total concentrations of metals to be reused in horticulture and arboriculture [56]. Soil washing is considered to be one of the most cost-effective and powerful remediation technologies for ex-situ remediation of contaminated soils [62]. Yet, previous studies have reported that remediated soil was not fit for reuse in horticulture or arboriculture and suggests that soil washing should be used in conjunction with other remediation approaches *e.g.*, phytoextraction and phytostabilisation [56]. The efficiency of soil washing is dependent on the ability of the extractant to dissolve the metal contaminants, therefore repeated rinsing of soils and targeted reagents for metal extraction improves is most efficient [62]. EDTA is known to be the most effective reagent for cationic metals (Cd, Pb, Co, Li, Hg, etc.,) [69]. While iron chloride ($FeCl_3$) is a highly effective extractant for soil washing Cd contaminated paddy soils as it has high extraction efficiency (<70%) and low environmental impact making it highly cost-effective [70]. To further increase efficiency combining different reagents with multi-metal contaminated soils [56]. Using phosphoric-oxalic acid-Na_2EDTA for soil washing heavy with removal efficiencies of 41.9 % for As and 89.6 % for Cd [71]. Metals are immobilized in the soil through three different reactions: complexation, precipitation, and adsorption [62]. This is done by the addition of immobilizing agents (clays, metallic oxides, biomaterials, etc.,) to contaminated soil to limit

metal transport and bioavailability in soil [51,62]. The use of lime-based agents, calcined oyster shells, eggshells and waste mussel shells are efficient at absorbing metals with minimal environmental impact and also improves the soil quality and function making it a highly cost-effective treatment method [52,72].

After initial application, the effect of the amendment of metal bioavailability varies due to differences in the decomposition of organic matter [62]. Residual by-products of immobilization contain metalliferous matter so must be processed appropriately to meet regulatory requirements. Such as, through advanced sewage treatment works which are successful in reducing metal concentrations in biosolids [62]. Although immobilization processes are easy to implement with high initial results contaminants remain in the soil so long-term the effectiveness of this approach is relatively poor when compared to other remediation techniques [52].

9. Remediation Vs. Recovery

Resource recovery is a more promising option for the sustainable management of contaminated sites rather than traditional remediation [38]. A shift from traditional remediation techniques could reclaim valuable urban land and recover minerals and metals to implement a circular economy [38].

Enhanced landfill mining (ELFM) can be defined as an "innovative transformation technology" and is a promising emerging technology [73]. In the first instance, ELFM concentrates materials (metals, combustibles, and inert materials) that can be used as secondary raw materials [73]. These materials are then reused to produce valuable products *e.g.*, inorganic polymers. Pyrometallurgical recycling avenues are well established, thus the metalliferous concentration can be sold at market value [74]. This makes it a key economic driver for ELFM. Numerous studies found that the recycling avenues for inorganic-non-metallic fractions are

more challenging with low application aggregate as the preferred route[75,76]. Additionally, the combustible fraction is predominantly disposed of through traditional methods *e.g.*, incineration, which the supplier must pay for rather than obtaining revenue [77,78].

The absence of the appropriate and sufficient recycling infrastructure has been highlighted as the main barrier to achieving a circular economy [79]. Using emerging green technologies for resource recovery will both improve sustainability and reduce the environmental impacts of processes involved in raw material extraction [80].

10. Emerging extraction techniques

Zeolites are a naturally occurring, crystalline, hydrous silicates that can be modified depending upon the application [81]. The isomorphous substitution of silicon (Si^{4+}) by aluminum (Al^{3+}) results in a negative charge. The net negative charge within the zeolite is balanced by sodium (Na^{+}), cadmium (Ca^{+}) and potassium (K^{+}) ions. These cations are exchangeable with critical metals cadmium (Cd^{2+}), lead (Pb^{2+}), copper (Cu^{2+}) and magnesium (Mg^{2+}) in solution [82]. Zeolites are highly suited to critical metal recovery due to; high porosity, high sorption capacity, high ion exchange capacity, and exchangeable ions and are relatively innocuous [81]. Clinoptilolite has been proven to be a good absorbent to remove metals from wastewater to below drinking water standards [83]. The ion exchange capacity of the zeolite is dependent upon the Si/Al ratio, where a higher Al content results in a higher number of charge-balancing cations, this subsequently increases the ion-exchange capacity of the zeolite [84]. Yet studies show that zeolites are unable to perform direct ion exchange as negatively charged ions limit permeability to anions [85]. Similar limitations in both natural and synthetic zeolites have been found in other studies [86,87].

Zeolites have been applied in the recovery of lithium; studies have successfully recovered critical metals from spent lithium iron phosphate (LiFePO4) batteries using zeolites [88]. This

demonstrates a novel approach for reutilizing spent batteries, further increasing resource efficiency, implementing a CE, and limiting environmental impact. The demand for $LiFePO_4$ batteries has increased exponentially since their first use in 1980. Subsequently, the number of decommissioned batteries has increased concurrently. The valuable metals and materials within the decommissioned battery are trapped in solid waste after expiration out of the material loop [89]. Resulting in diminishing stocks of such materials, including lithium [90].

Microbial technology shows promise to recover critical metals whilst producing electricity as microbial fuel cells [91]. Microbial fuel cells are bio-electrochemical systems that convert chemical energy within organic matter into electrical energy using the metabolic activity of microorganisms and are considered to be relatively low cost and sustainable [92,93]. Metal removal using microbial fuel cells was through; bio-reduction, bioaccumulation, biosorption and biomineralization [94].

Although promising, microbial fuel cells cannot treat all metal ions [95]. Reduction is only done when thermodynamically favorable i.e., the target metal has a high standard potential [96]. If metals have comparable or lower redox potentials such as Ni, Pb, Cd and Zn [97] an external power supply is required for reduction. To overcome this, was successfully used in reducing Cr to power another reactor to reduce Cd simultaneously [98]. Other studies used either a Cr or Cu microbial fuel cell to successfully drive Cd reduction using no external energy supply [95,99]. Drawbacks for the recovery of critical metals using microbial fuel cells are the high impact and inhibitory effects of metal biotoxicity on microbes reducing removal efficiencies [95]. It has been found that all metals were proven to be toxic to S. Oneidensis and at certain concentrations show inhibition of voltage [100]. Critical metals reduce anodic performance by inhibiting microbes due to metal toxicity [101]. Although <100 ug/L for Cu and <1 mg/L for Cd, voltage output was improved [100]. This is due to improved microbe attachment on the electrode increasing extracellular electron transfer.

Three of the twelve green chemistry principles are prevention, less hazardous chemical syntheses, and the use of renewable feedstocks. Microbial fuel cells not only treat chemical wastes but recover critical metals whilst generating electrical energy [95]. The scaling up of microbial fuel cells is limited due to wastewater capacity and the fuel cell architecture [95].

11. Green solvent leaching

Established commercial processes for chemical leaching for metal resource recovery, such as from coal fly ash [102], electronic wastes [103], and sewage sludge [104] amongst other avenues. There are varying degrees of success dependent upon metal type (89% of rare earth metals (*e.g.*, neodymium, cerium) [102], 90% for Au [103], and 46% of heavy metals [104]. Though differing yields, the three research papers identify that chemical leaching provides a promising technology for more sustainable metal recovery from varying wastes.

Green solvents are defined as "environmentally friendly solvents, or biosolvents, which are derived from the processing of agricultural crops" [105]. Environmentally friendly in terms of minimal or no environmental impact associated with the relevant solvents. Neither sulphuric (H_2SO_4) nor nitric acid (HNO_3) are green solvents yet are extensively used to recover metals from industrial waste with varying efficiency. Table 2.2 is a summary of recovery yields dependent upon waste material with varying solvents applied. The application of sodium hydroxide (NaOH), hydrochloric acid (HCl) and H_2SO_4 through combination batch leaching strategies are very selective for Al but proved to be inefficient [106]. This is attributed to the type of waste used for metal recovery i.e., welding slags. Submerged-arc welding slags contain distinct acid and neutral phases increasing metal recovery to 80% recovery yield [106]. More than 85% of Zn, Mg, Cu, and Al was recovered from municipal waste *e.g.*, bottom and fly ash (Table 2.2) [107]. Bottom and fly ash represent the most hazardous residue from municipal waste thus providing the largest concentration for secondary resource recovery [107]. It has been shown that H_2SO_4 changes the pH function leading to leaching performance in certain

528 elements; Ca and Al respond well to the change, but Zn and Cr react with amphoteric behavior
529 [107]. When NaOH is used as a reagent for the simultaneous extraction of Zn and Mg from
530 Zn-C alkaline. The Zn had a recovery yield of 82% and Mg 96% [109]. Sodium hydroxide
531 works in acidic conditions which are appropriate for the metals concerned, however, Mn
532 recovery could be further improved using H_2SO_4 to reduce insoluble Mn^{4+} to soluble Mn^{2+}
533 [109]. The use of NaOH and H_2SO_4 can leave a legacy of pollution when used in situ, which
534 can manifest in acid rain and high toxicity to the aquatic ecosystem [109].

Table 2.2 Critical metals and the recovery yield dependent upon extraction process.

Metal	Extraction Process	Source of Waste	Recovery Yield (%)	Reference
Al	Chemical Leaching (NaOH, HCl, H_2SO_4)	Welding Slags	80.00	[106]
	Chemical Leaching (H_2SO_4)	Spent hydrodesulphurization catalyst	11.03	[108]
	Chemical Leaching (NaOH)	Calcined spent catalyst	89.00	[109]
	Chemical Leaching (H_2SO_4)	Municipal solid waste	>85.00	[107]
Cu	Chemical Leaching (H_2SO_4)	Municipal solid waste	>85.00	[107]
	Bioleaching	Steel slag	27.00	[109]
	Chemical Leaching (EDTA)	Artificially contaminated soil	93.90	[111]
	Chemical Leaching (HNO_3)	Sulfide tailing	85.00	[112]
Co	Chemical Leaching (H_2SO_4)	Spent hydrodesulphurization catalyst	96.25	[108
	Chemical Leaching (HNO_3)	Sulfide tailing	54.60	[112]
Mn	Chemical Leaching (NaOH)	Spent batteries	96.00	[113]
	Chemical Leaching (H_2SO_4)	Municipal solid waste	>85.00	[107]
Zn	Chemical Leaching (NaOH)	Spent batteries	82.00	[113]
	Chemical Leaching (H_2SO_4)	Municipal solid waste	>85.00	[107]
	Bioleaching	Steel slag	60.00	[110]

Deep eutectic solvents (DESs) are novel ionic liquids which obey the green chemistry principles and have been described as the most promising discoveries in green chemistry as an alternative solvent [111]. A DES is a combination of two or more solids (a hydrogen bond donator and hydrogen bond acceptor) through hydrogen bonds forming a eutectic liquid mixture at a temperature lower than the melting point of the component parts [111]. As a result, DESs are 100% atom economy and due to hydrogen bonds, reactivity is limited reducing environmental impacts [112]. DESs can be infinitely reused, renewed, are biodegradable and are non-toxic. The solvents have very low vapor pressure, low flammability, and high thermal stability [113]. Currently the applicability of DESs is limited to liquid-liquid extraction as DESs are predominantly hydrophilic and is highly basic with low water content [114]. Studies are biased toward hydrophilic DESs rather than hydrophobic DESs. Hydrophobic DESs are an emerging novel concept, developed in 2015 [115]. When water is added to hydrophobic DESs, electrical conductivity and viscosity is improved as a result [116]. When the water content is above 2% w/w in hydrophobic DESs enhances mass transfer allowing free flow of ions in the medium [117]. Like the hydrophilic counterparts, hydrophobic DESs are considered 'green solvents' but there has been little research to monitor their toxicity, vapor pressure, or bioavailability [118]. Of the DESs, the so-called natural DES *e.g.*, ChCl: citric acid imposes high environmental impact as a result of water consumption and carbon dioxide emission from the fermentation phase to synthesize citric acid [116]. When comparing global warming potential, natural DES like ChCl: citric acid, produced 4.3 kg CO_2-eq per kg which is 58% higher than ChCl: ethylene glycol [109]. DESs are categorized under the umbrella term of ionic liquids which are considered a strong alternative to conventional solvents [110]. The difference between ionic liquids and DES's is the chemical formation and the source of their starting materials [120]. Most ionic liquids meet the green chemistry principles (deep eutectic solvents) however, some ionic liquids have poor biodegradability and are hazardous and toxic (sulfonium

salts) [111]. Additionally, ionic liquids are usually 5 – 10 times more expensive than conventional solvents so have not met expectations as an alternative option [122]. Despite the exponential increase in papers looking at DESs, the long-term stability of DESs remains largely unknown and needs further studies into overall greenness to corroborate existing findings for potential industrial use [117,121]. However, despite the considerable research into green technology and chemistry it is becoming clear that not one single system will replace all conventional solvents as a true environmentally friendly alternative [123]. The ideal, universal "green" solvent, applicable to all situations does not exist due to limitations regarding instability, applicability, and sustainability [123].

Batch tests have been advantageous as redox conditions can be controlled, the simple laboratory set-up required, and fast yielding results [124]. When compared to continuous column leaching, batch tests have a higher standard deviation, this is attributed to artefacts resulting from secondary compound mobilization or cross-contamination [124]. Initially, the batch approach underpredicts effluent concentrations during percolation, yet long-term over-estimate concentrations [124].

Packed column studies are relatively simple to operate - low initial and operational costs, no moving parts and limited facility footprint [125]. Column leaching has been found to be suitable for both organic and inorganic compounds [126]. Though, pulsed columns applying mechanical energy, enhanced mass transfer from the generation of dispersed droplets [125]. This is supported by the German Institute for Standardization. Using EDTA as a chelator in a continuous leaching process had a recovery yield of 93.9% and recycled the solvent to achieve saturated conditions [127]. High recovery yield can be attributed to the use of EDTA and its strong chelating properties. Additionally, a saturated column achieves pre-equilibrium which reduces the likelihood of artefact generation [124]. Limited studies explore the potential for

584 using DESs to recover high yields (>85%) of critical metals from industrial slags, particularly
585 blast oxide furnace slags.

586 Of the limited metal extraction using solvents in extraction column models, there is a focus on
587 hydrodynamics and the prediction of mass transfer coefficients [125]. When modelling pack
588 column extraction, there are two key models: the axial dispersion model and the population
589 balance model (PBM) [125]. The axial dispersion model can be used to predict the overall mass
590 transfer coefficient for samarium and gadolinium in an extraction column [128]. However, the
591 axial dispersion model does not consider the change in the interfacial area due to droplet
592 breakage and coalescence [125]. The PBM considers droplet dynamics due to coalescence and
593 breakage [125]. Previous literature has highlighted extraction column modelling, but more
594 consideration is necessary regarding droplet breakage, coalescence, and metal ion mass
595 transfer.

596 **12. Development challenges and growing demand**

597 2.1.7 Recovery of metals to meet sustainable development goals.

598 Sustainable development is at the core of resource resilience and management [129]. A CE
599 business model that falls into two groups; one that fosters reuse, extended service life through
600 repair, remanufacture and upgrades, and the other as turning old resources into new resources
601 by recycling [130]. Both models close the loop on resources and minimize waste (Figure 2.2).
602 The current CE model extends conventional waste and by-product service life and recycles
603 materials in applications where most of the economic value of the product has been lost [131].
604 The longer products remain in the inner circles of Figure 2.2, the more sustainable they become
605 due to the reduced demand for energy and less resources in these stages. The inner circles
606 demand less resources and energy. The time resources are kept in the inner circles should be
607 maximized.

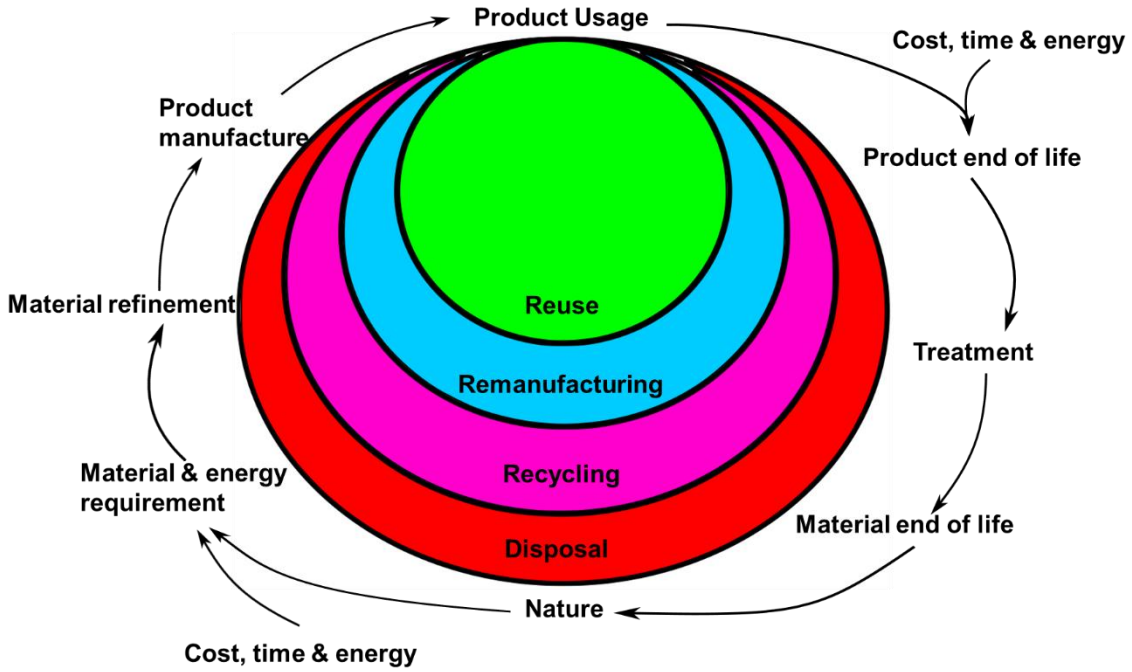


Figure 2.2 Current concept for the circular economy model, adapted from [130].

The European 'Green Deal' is a roadmap of key policies for the EU's climate agenda, the commission will continue to develop legislative proposals and strategies from 2020 onwards [132]. The main aim of the 'Green Deal' is the complete reduction in net emissions of greenhouse gases by 2050 in the whole Union [129]. Both the 'Green Deal' and the CE model provide a pathway for sustainable development but are yet to provide a systematic scope of strategic direction regarding environmental, economic, and social matters [129]. The emphasis is on mineral resource management and decoupling economic growth from resource usage [133]. Ensuring the security of raw materials depends on the country, due to the lack of native deposits, imports of materials are necessary [129]. Imports are not always secure due to both political and economic instability [134]. The European Institute of Innovation and Technology on the Raw Materials was established in 2014 with three strategic goals: securing the supply of raw materials, designing innovative solutions, and closing material cycles [130]. A global shift towards a CE is crucial in the implementation of a resource-efficient and environmentally friendly approach to future material management [125]. By definition, primary extraction processes lie outside the boundaries of a CE. It is unrealistic to assume that society will not

need new resources [3]. Expanding current CE boundaries to include closed, abandoned and currently operating mines would reduce the requirement for new mines and create value from mining waste. Expanding the CE boundaries aligns with the CE goals of "keeping resources in use for as long as possible, extracting the maximum value from them whilst in use, then recovering and regenerating products and materials at the end of each service life" [136].

2.1.8 Political Perceptions

Access to critical metals is restricted by political, environmental, economic, legal, and social factors [137]. The high risk of supply disruption is not always implied from actual physical resources [138]. Additionally, there is an imbalance of exploitation and production on increased supply risk [139]. Globally, China is the main producer of 31 of the 44 critical metals in 2017, furthermore 67% of the EU's supply of critical metals is supplied by Russia [140]. In 2017, only three critical metals (tin, tungsten, and lead) were mined in the UK [131]. As there is a limited number of producers, this means that suppliers can intentionally limit supply and drive-up prices [138]. The supply risk is also a direct consequence of illegal mining and exploitation of raw materials [139]. Illegal mining and exploitation are derived from a lack of regulation and a result of government corruption in developing countries [52]. To secure European access to raw critical materials the European Commission adopted a Raw Materials Initiative which supports over 70 projects to manage and secure metals stocks [142].

Political and social perceptions may drive recovery habits, which can be inappropriate by following ideologies based on negative public opinions, for example, metal recovery from sewage [143]. Implementing extended producer responsibility schemes to ensure manufacturers are responsible for the product's entire life cycle, including disposal [137]. However, the EU has various schemes regarding extended producer responsibility, most are

targeted toward the mass of material recovered which may make current schemes redundant with regard to critical metal recovery [144].

13. Conclusions

Global critical metal stores are depleting whilst societal metal demand is increasing exponentially. Raw lithium, a fundamental resource for renewable energy (solar PV and electric vehicles), is set to be diminished within the next 80 years [12]. Renewable energy is not renewable if the component parts are not renewable. A commercial shift from contaminated land remediation to resource recovery is crucial. Established traditional remediation removes critical metals but, in the process, generates pollutants. Using emerging novel extraction technologies *e.g.*, DES, on past metalliferous sites (*e.g.*, industrial sites, abandoned mines, brownfield sites etc.) will remove significant pressure from extractive metal processes such as open-cast ore mining, alleviating all associated environmental impacts. Green solvents, particularly DESs are a promising emerging recovery technique that can yield high yields of critical metals whilst minimizing environmental impacts as well as being infinitely renewal and recyclable. This underpins the renewable in renewable energy. From previous studies, it is evident not one single system will replace conventional methods, especially if considering traditional commercial recovery practices. Exploiting novel green solvents to recover metals will eliminate pollutant by-products and generate an alternative source of critical metals. Finding alternative sources of critical metals will restore sites with a legacy of pollution that cannot be pinpointed for liability. Alternative sources will also generate significant quantities of critical metals which can be exploited for renewable energies and reintroduce resources into a circular economy.

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3. Assessing the ability of 'green chemistry' to extract metals and assess their recovery opportunities from past metallurgical sites

Victoria E. Huntington [1], Frederic Coulon[1] and Stuart T. Wagland [1, *]

[1] School of Water, Environment and Energy, Cranfield University, Cranfield, UK;
* Correspondence: s.t.wagland@cranfield.ac.uk; Tel.: +44(0)1234 750111.

Abstract: There are numerous sites of metalliferous waste, which could provide a significant opportunity for metal extraction to relieve global demand on raw materials for technologies whilst remediating a contaminated site. 'Green chemistries' are a sustainable solution to intensify the removal of metals from these sites. The extraction efficiencies of known green chemical compounds; deep eutectic solvents (DES) and chelating agents (CA) were tested on metalliferous wastes from two sites, representing two different metalliferous wastes (blast oxide slag dust (BOS-D), UK, and goethite France). The impact of varying molar ratio (DES) and pH (CA) were assessed. The metal extraction from BOS-D was 60% greater when DES were applied compared to CA. In goethite, CA metal extraction was 70% greater than DES. In goethite, Glutamic acid diacetic acid (GLDA) at pH 8 extracted 31% of metals, the most effective condition across chelators and DES. Choline chloride (ChCl-EG) had the most consistent performance across an array of metals, attributable to low viscosity and increased oxidation/reduction potential. These 'green chemistries' were compared to the extraction efficiencies of Ethylenediaminetetraacetic acid (EDTA), an industrial chelating agent and known persistent organic pollutant, DES and 'green' CA were superior. The findings of this study highlight the promising potential of metal extraction from historic metalliferous waste.

Keywords: resource recovery; critical metals; deep eutectic solvents; chelating agents

15. Introduction

The stress on raw resources is growing as the world shifts towards renewable technologies. To ensure resource security it is crucial to look for alternative sources of these metals to supplement supply from mining imports which are subject to socio-economic instability. There are a number green initiatives such as, the European Green Deal, and the internal combustion engine ban by 2035, a sustainable supply of critical metals is essential. Predictions suggest that up to 90% of all passenger car sales will contain a Li-ion battery. In 2022, Li-ion battery demand was 700 GWh but will increase to 4.7 TWh by 2030, this requires at least 150 new Li-ion battery factories globally (Fleischmann et al., 2023).

To supplement depleting raw resources alternative sources must be explored. Historic mine and industrial sites, contain significant quantities of key metals previously uneconomically viable to extract which are now poses a serious threat to the environment (Prior et al., 2013). Innovative extraction processes *e.g.*, green solvometallurgy, could be used to utilise these former 'waste' sites into sites of metal extraction opportunities whilst minimising environmental impact (Watari et al., 2021).

Deep eutectic solvents (DES) use acidolysis and redoxolysis and chelating agents (CA) use complexolysis (Faraji et al., 2020). Leaching mechanisms associated solvometallurgy within commercial metal extraction is predominantly acidolysis rather than complexolysis (Attia et al., 2022). Acidolysis is more aggressive and faster than complexolysis than so it is expected that DES will be more effective than CA for metal extraction (Faraji et al., 2020).

There is little understanding of the applicability of green solvents and green CA on real world metalliferous wastes and how they compare directly with two wastes of differing composition. This study aims to develop and improve the understanding of metal extraction from metalliferous waste whilst comparing the extraction efficiencies of green DES and green

chelators. DES have been described as a promising discovery as an alternative solvent and categorised as environmentally friendly ionic liquids (Xie et al., 2005). CA are multidentate organic molecules that can form two or more co-ordination bonds with a central metal ion (Almubarak et al., 2022). Denticity refers to the number of atoms with which a ligand can bind with a metal ion (Aaseth et al., 2016). Increased denticity increases the number of binding sites available for adsorption of metals increasing extraction (Sahoo et al., 2018).

Three Type III DES; Choline Chloride-Ethylene Glycol (ChCl-EG) and Choline Chloride-Malonic Acid (ChCl-MA) and Choline Chloride-Urea (ChCl-U) (Abbott et al., 2009; Huang et al., 2022; Dwamena, 2019). And three aminopolycarboxylic acid based green CA; glutamic acid diacetic acid (GLDA), Ethylenediamine-N,N'-disuccinic acid (EDDS) and, Nitrilotriacetic Acid (NTA) (Liu et al., 2020; Song et al., 2016; Begum et al., 2012). The order of denticity across CA is as follows: EDDS > GLDA> NTA from hexadentate, pentadentate and tetradentate, respectively (Almubarak et al., 2022). These green chemical compounds were chosen as they have shown promise dissolving metals in earlier studies. The selectivity of these green compounds has not been fully assessed, studies have shown hydrophobic DES using menthol as a hydrogen bond acceptor and octanoic acid, decanoic acid, and lauric acid as hydrogen bond donators, extracted up to 81% of Li (Ke et al., 2023).

16. Materials and Methods

3.1.1 Characterisation of materials

The samples of blast oxide slag were collected randomly from the top 10cm layer of a stockpile of ~8000t in autumn, 2021. The goethite samples were obtained as an 8 kg goethite filter cake pre-neutralisation with lime. Both materials were heated to 550°C for two hours to remove biodegradable material and characterised before batch studies and are summarised in Table 3.1. The results from blast oxide dust informed the solvent and chelating agent used on the goethite samples.

A control of Ethylenediaminetetraacetic acid (EDTA) was used, to compare these green solvents and green CA with an industry used solvent. The metal extraction efficiencies of these compounds were tested on two materials, blast oxide slag dust (BOS-D) and goethite. The BOS-D is a by-product of the blast oxide slag process in the Northeast of England, in an area with a legacy of steel industry and manufacture. Goethite is a by-product of zinc refinery processes in the North of France.

Table 3.1 Characterisation of BOS-D (n = 2) and Goethite (n = 2). RSD: Relative standard deviation

	BOS-D		**Goethite**	
pH	9		4.6	
Electrical Conductivity (S/m)	215.54		0.48	
	mg/kg	RSD	mg/kg	RSD
Fe (mg/kg)	589156	6	305333	7
Cu (mg/kg)	168	1	30614	6
Zn (mg/kg)	25747	8	112942	7
Pb (mg/kg)	2666	9	35273	7
Li (mg/kg)	6	4	4	10
Al (mg/kg)	3136	3	16449	7
Cr (mg/kg)	205	4	330	7
Mn (mg/kg)	8515	4	2204	6
Co (mg/kg)	13	3	14	1
Ni (mg/kg)	77	2	51	6
Cd (mg/kg)	83	10	608	7

3.1.2 Deep Eutectic Solvent and Chelating Agent Conditions

The DES were applied in three molar ratios 1:1, 1:2 and 2:1, between the hydrogen bond acceptor and hydrogen bond donators. Choline chloride was used as the hydrogen bond acceptor and ethylene glycol, malonic acid, and urea as the hydrogen bond donators. Ratios were chosen based on effective results found in literature (Ghazali *et al*., 2020, Parmentier *et al*., 2015, Pateli *et al*., 2020 & Qin *et al*., 2020).

The pH of the CA; GLDA, EDDS and NTA was adjusted using sodium hydroxide (NaOH) to pH 4, 6 and 8 prior to mixing with samples. All solvents were purchased from Fisher Scientific and Sigma Aldrich.

3.1.3 Batch Experimental Design

Prior to heating, metalliferous waste samples were screened sieved to < 2mm and mixed at 12.5% weight to volume (w/v), in accordance with previous studies (Cao et al., 2018). The samples were agitated at 150 rpm for 15 minutes at room temperature (22°c) and left to settle for two hours. To ensure equal mixing and contact time between the material and tested solution in each batch. The samples were filtered through 10μm filter paper (Whatman® qualitative filter paper, Grade 595). The leachate was retained for analysis and the solid residue was left to dry (LEEC Drying Cabinet, 40°C) and stored (4°C) for further analysis. Each green solvent was conducted in duplicate for validity (Figure 3.1).

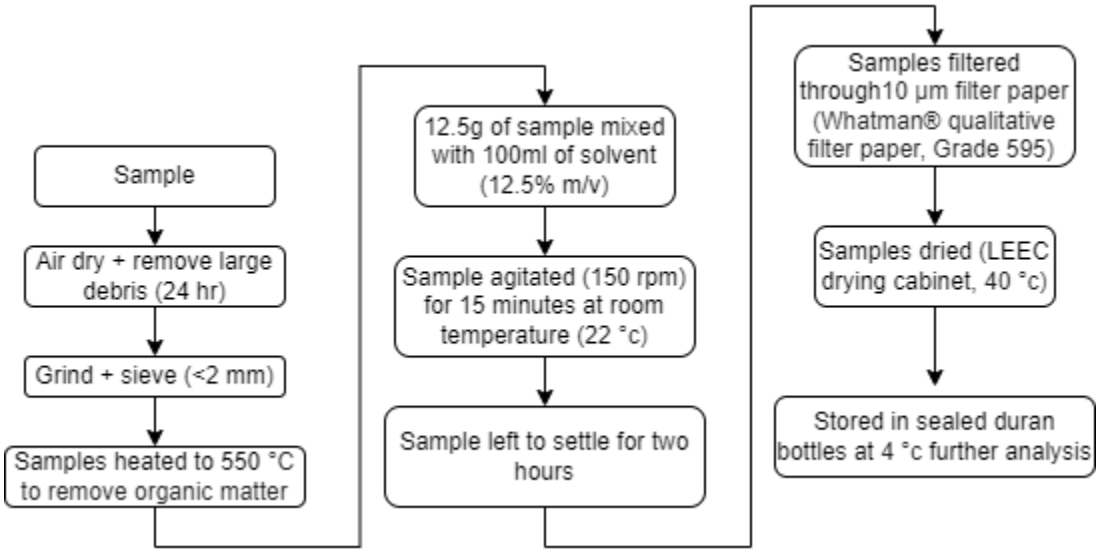


Figure 3.1 Flow chart of the experimental design of batch studies for metal extraction using green solvents.

3.1.4 Analytical Methods

The elemental composition of the BOS-D was determined using aqua regia digestion (HNO_3 and HCl in a ratio of 1:3) followed by microwave digestion (45 minutes, 800W) (Guiterrez-Guiterrez et al., 2015). The solution was filtered (Fisher, Syringe filter, 0.45µm), diluted 100%. The metal content of this and the leachate recovered from batch tests were analysed using inductively coupled plasma mass spectrometry (ICP-MS) (Elan 9000 Perkin-Elmer SCIEX). All leachate samples were diluted 100-fold prior to analysis. The ICP-MS was calibrated using certified standard solutions, including the Rare Earth Elements ICP-MS standard (CMS-1, Inorganic Ventures) and single ICP standards (analyte concentration of 1000 µm ml^{-1}, SCP SCIENCE). These standards covered both major (Ca, Fe, K, Mg, Mn, Na, S, Si) and trace metals (Al, As, Ba, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Sb, V, Zn). For the major elements, the concentration ranges were 1, 5, 15, 20, and 40 µg ml^{-1}. For trace and rare earth elements, concentrations ranges were 0.01, 0.1, 0.5, 1, 2 µg ml^{-1}. To ensure analytical accuracy and control for potential contamination, a programmed rinse time was implemented between the analysis of samples, and procedural blanks were analysed every eight samples. These measures

were in place to monitor blank contamination, assess sensitivity, verify operating conditions, and maintain accuracy. The results are presented as mean values along with standard error, based on duplicate samples.

3.1.5 Statistical Analysis

A One-way ANOVA (SPSS version 28) was used to establish significant differences in metal extraction, statistical significance (P value <0.05). Descriptive statistics (minimum, maximum, mean, and standard deviation) were calculated using Excel (Windows 11) to provide further analysis of the possible interactions between solvents, solvent condition, extraction efficiencies and selectivity.

17. Results and discussion

3.1.6 BOS-D

Overall metal extraction was 20% more effective with DES compared to CA. ChCl-EG and ChCl-MA extracted 53% of metal composition of the wastes. ChCl-U extracted 47% of metals (Figure 3.2). The most effective chelating agent was GLDA, which extracted 39% of metals. NTA and EDDS extracted 36% and 35% of metals, respectively. This indicates that, within BOS-D, redoxolysis and acidolysis are more effective than complexolysis. When redoxolysis and acidolysis conditions are optimised, extraction efficiencies can be improved, for example once optimised extraction of nickel increased to 97.7% from 61% using sulphuric acid (Van Yken et al., 2020).

Metal extraction using DES was greatest using a 1:1 molar ratio and lowest in 2:1. This is likely due to an imbalance in hydrogen bond acceptors, where 2:1 has double the concentration of choline chloride than 1:1. This increases the competition between the hydrogen bond donators *e.g.*, malonic acid and the target metals which could decrease metals extraction. The order of

extraction yields using DES reflects their relative viscosities; the lower the viscosity, the greater the extraction. In 1:1, ChCl-U 1:1 is 0.66 mPa.s and 1:2 is 0.5 mPa.s (Bakhtyari et al., 2020). ChCl-EG 1:1 32.6 mPa.s (Bakhtyari et al., 2020). ChCl-EG extracted 54% of metals whereas ChCl-U extracted 48%. This suggests that viscosity is a driving force for metal extraction. This corroborates the models in Bakhtyari et al., (2020) and findings in Pateli et al., (2020) on metalliferous dust using choline chloride–ethylene glycol.

A key parameter in metal speciation is pH. In acidic conditions there is a greater concentration of H^+ leading to the potential of greater metal complexes through redoxolysis, acidolysis (J. Huang et al., 2017). However, there was no significant difference in extraction between pH levels tested in the CA (Figure 3.2).

The influence of oxidation state and coordination number of the metal ion, and the electronic structure and character of the chelate, determine the nature and stability of the bond between the metal and chelator (Begum et al., 2012). NTA contains three carboxyl groups, the greatest within the chosen CA (Waters et al., 2020), however there was no statistically significant difference between this, and the other green CA used in batch tests.

EDDS extracted 35% of metals across all tested pH levels, despite containing two carboxyl groups. NTA extracted 32%. EDDS is hexadentate, providing the largest number of binding sites for potential metal-chelator complexes. The results suggest denticity has a greater influence on metal extraction than functional groups present within the CA. This disagrees with findings in Aaseth et al., (2016) which suggests that hexadentate chelators can form only one metal-chelator complex whereas lower dentate chelators can form multiple complexes. However, the findings in Botelho et al., (2022) demonstrate the enhanced metal extraction capacity of EDDS due to denticity resulting in reduced competition for cations and H^+ supporting the results in this study.

EDTA pH 4 was used as a control. Overall, the application of the DES was superior in comparison to the control, 51% and 48% respectively. Whilst the green CA extracted less, at 37% of metals. The accepted chelation affinity hierarchy of EDTA is; Cr > Fe > Zn > Cd, (Corsello et al., 2009). The results in this study did not conform with this as Cd extraction was greater than Cr, 61% and 42% respectively. This suggests that the binding or structure of the host material plays some control on the efficiency of metal extraction.

Both ChCl-EG 1:1 and EDDS pH 4 had superior extraction efficiencies of Fe compared to EDTA, at 65% and 42%, respectively (Figure 3.2 and 3.3) in comparison to 39%. The extraction of Cr using ChCl-EG 1:1 was 63% compared to 46% when using EDTA. This is despite EDTA having the strongest affinity to Cr and Fe. The superior extraction of EDDS pH 4 and ChCl-EG 1:1 could be attributed to improved mass transport, denticity and proticity (Pańczuk-Figura & Kołodyńska, 2016; Yuan et al., 2022). Results demonstrate that CA can selectively extract metals and DES can extract a wider suite of metals compared to EDTA.

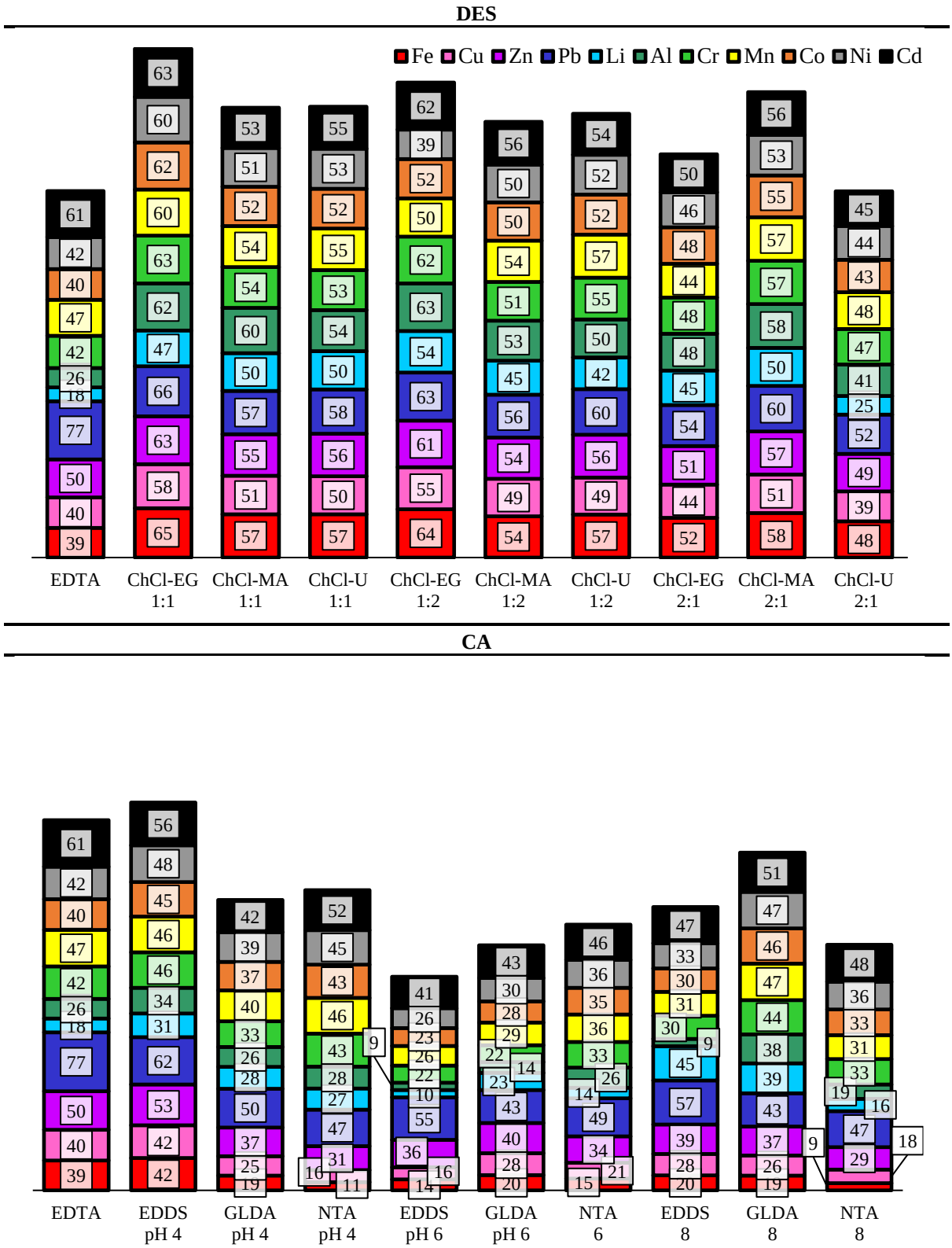


Figure 3.2 Metal extraction efficiencies (%) from BOS-D using DES and CA. The from outer to inner represent; ChCl-EG, ChCl-MA and ChCl-U.

18. Comparison between metals groups

A comparison has been made between the varying metal/metalloid groups to better distinguish the selectivity of the green compounds tested as well as identify particular metals that certain compounds have an affinity for. ChCl-EG 1:1 had the greatest extraction efficiency amongst the DES for alkaline earth metals 75% (Mg, Ba), other metals 66% (Zn, Pb, Al, Ga, Cd), transition metals 62% (Fe, Cu, Sc, V, Cr, Mn, Co, Ni, Y, Mo) and rare earth lanthanides 42% (La, Ce, Nd). EDDS pH 4 had the greatest extraction efficiency amongst the CA for alkaline earth metals 54%, transition metals 45%, other metals 52% and rare earth lanthanides 49%.

ChCl-EG 1:1, removed the highest percentage of Fe. This is to be expected as ChCl-EG is an aliphatic compound and studies have demonstrated Fe exhibits high affinity for aliphatic compounds (Spathariotis et al., 2020). The most effective ratio for Fe extraction was 1:1 (65%) > 1:2 (64%) > 2:1 (52%) (Figure 3.2). ANOVA analysis showed this relationship is statistically significant, $p < 0.001$, this indicates that for Fe extraction should be utilise a ChCl-EG at 1:1. ChCl-EG had a high extraction efficiency for Li and B. The extraction of Li between solvents showed significant relationships ($p = 0.013$). This indicates that for selective Li extraction, the DES needs to be specific, ChCl-EG 1:2 showed the highest extraction of lithium further to this, increasing the ratio of ethylene glycol to choline chloride, increased Li extraction from 13% to 54%.

There is little evidence within literature proving that Li can be chelated. The results show that GLDA pH 8 extracted 39%, the most effective chelating agent for Li extraction thus providing potential evidence for the chelation of Li (Figure 3.2). Studies suggest that Li ions form strong chemisorption with soil particles thus preventing large quantities from being leached (Zhou et al., 2020). Literature states that the low extraction of Li should be expected based on the extraction of metal salts with ionic liquids (Parmentier et al., 2015).

DES extracted 65% of metalloids compared to 41% by CA. DES extracted 98% of B compared to 19% by CA. Oppositely, CA extracted 82% of Si compared to 55% by DES. Specifically, GLDA pH 6 extracted 90% Si. This can be attributed to improved solubility and stabilisation associated with GLDA (Ni et al., 2024). The extraction of Si using DES found that 1:1 was the most effective deep eutectic solvent condition. ChCl-MA 1:1 extracted the most Si of the DES with 71% extraction, this supports the notion that malonic acid will improve metal extraction due to efficient protons (Qin et al., 2020).

Like metalloids, other metals were extracted more effectively with DES rather than CA, 58% and 41% respectively. The greatest extraction of Zn was with the addition of ChCl-EG 58% followed by ChCl-MA 55%. The most effective chelating agent was EDDS at 43% extracted. A one-way ANOVA statistical test showed there was significant difference in Zn extraction (p 0.003), indicating that the solvent or chelator has a significant control on the extraction of zinc. The results are supported by Kalhor et al., (2021), who found when Zn and ChCl-EG were mixed, the H-bonding network of ethylene glycol was destroyed to the largest extent. This increased length in the Zn-Cl bond and increased the strength of the coordination bond Zn-O thus implying the strongest intermolecular interactions and high solvation of Zn. A similar study corroborates the results found in these batch tests, Zn was extracted at 56% on average using DES on electric furnace dust (Youcai & Stanforth, 2000). The composition of electric furnace dust is comparable to BOS-D, 83% of particles are < 5.5μm and is comprised of predominantly Fe and Zn with Cr, Cd and Pb (Chirila & Luca, 2011).

The extraction of Cd was greatest in DES at 57% on average, CA averaged 47%. The extraction mechanism of Cd is complexolysis and is enhanced with the number of coordination groups donated by the ligand (Aaseth et al., 2016). Therefore, it would be expected that chelators would have the greatest extraction efficiency, specifically EDDS due to having the greatest denticity. However, DES extracted more and there was not significant difference between CA.

All CA at pHs between 4 and 8 extracted between 41% and 51% of Cd (Figure 3.2). A study using NTA to extract Cd from charcoal power, a similar material to the BOS-D, extracted 99.9% of Cd attributed to increased presence of carboxyl groups (Saini et al., 2019). Other studies extracted >95% of Cd using NTA (Y. Huang et al., 2015). This suggests that carboxyl groups have a greater influence on metal extraction compared to denticity, which in terms of Cd extraction, however the same extraction efficiencies were not seen in this study suggesting that other variables not characterised play larger influence on Cd extraction.

ChCl-EG 1:1 extracted 66% of Pb and EDDS pH 4 extracted 62% (Figure 3.2). Significance testing suggest the deep eutectic solvent ratio have a significant impact ($p<0.001$) on Pb extraction. The effectiveness of ChCl-EG 1:1 can be attributed to optimised mass transfer due to improved viscosity (Yuan et al., 2022). Additionally, the atomic solvation of the Cl within the choline chloride hydrogen bond acceptor could explain the enhanced extraction of Pb using DES (Yuan et al., 2022).

Rare earth lanthanides make up 0.002 % of the BOS-D sample. Ce and Nd were extracted greater when DES were applied. ChCl-EG 1:1 had the greatest extraction of Ce 59%, and Nd 58%. Entezari-Zarandi & Larachi, (2018) found the order of metal oxides extracted decreases with increasing atomic number inferring that La would be the most extracted. La was the least extracted rare earth lanthanide using DES (7%) but the most using chelating agent (76%). EDDS pH 4, a hexadentate chelating agent, extracted 88% of La. Emerging studies have found that using multidentate chelators promote complexes otherwise unobtainable using electrostatic interactions *e.g.*, La (Tsiouri et al., 2010). Rare earth lanthanides use redoxolysis and can be related to proton availability in DES (Entezari-Zarandi & Larachi, 2018). The low viscosity can be attributable for the effective extraction efficiencies of Ce and Nd using ChCl-EG (Bakhtyari et al., 2020).

The high extraction of all the DES across the three ratios may be a combination of reduced viscosity, alcohol functional groups but predominantly the low pH conditions increasing oxidation potential.

3.1.7 Goethite

ChCl-EG and ChCl-MA at all earlier ratios were continued into goethite batch tests of the DES. Alongside GLDA pH 8, NTA pH 6 and, EDDS pH 4 out of the CA.

Overall extraction of metals from goethite was lower than in BOS-D. The overall metal extraction was greater using CA rather than DES, 28% and 20% respectively (Figure 3.3). This demonstrates that the mechanism may control metal extraction efficiency and that complexolysis, facilitated by CA is the more robust mechanism for extracting metals from goethite.

GLDA pH 8 extracted 31% of metals followed by NTA pH 6 at 28% and EDDS pH 4 26%. ChCl-MA 1:1 extracted 22%, and at 2:1 extracted 20%. ChCl-EG 1:1 extracted 20% and at 1:2 18%. This further supports the influence of stability through complexation provided by CA, in particular GLDA for metal extraction (Ni et al., 2024). Results also show a preference for more neutral conditions. A study by (Liu et al., 2014) found, at higher pH values (>pH 7) the surface precipitation of goethite increased and subsequent metal extraction. This is supported by the results, as metal extraction decreased with decreasing pH.

Common assumption is as H^+ ions increase, desorption of metal ions increases promoting metal extraction (Begum et al., 2012). However, in this study, GLDA pH 8 had the highest extraction of Cu 55%, Zn 32%, and Cd 43%. Literature suggests that GLDA has a strong affinity to chelate Cu, Ni, Zn and Cd due to coordination preferences (G. Wang et al., 2016). Further literature states that if the ratio of GLDA to metal ions increases, the pH dependency of extraction is less prominent (Wu et al., 2015). However, in (G. Wang et al., 2016), the extraction efficiencies of

Cd, Pb, and Zn increased concurrently with pH. This study supports this, where CA with the highest pH had the highest metal extraction.

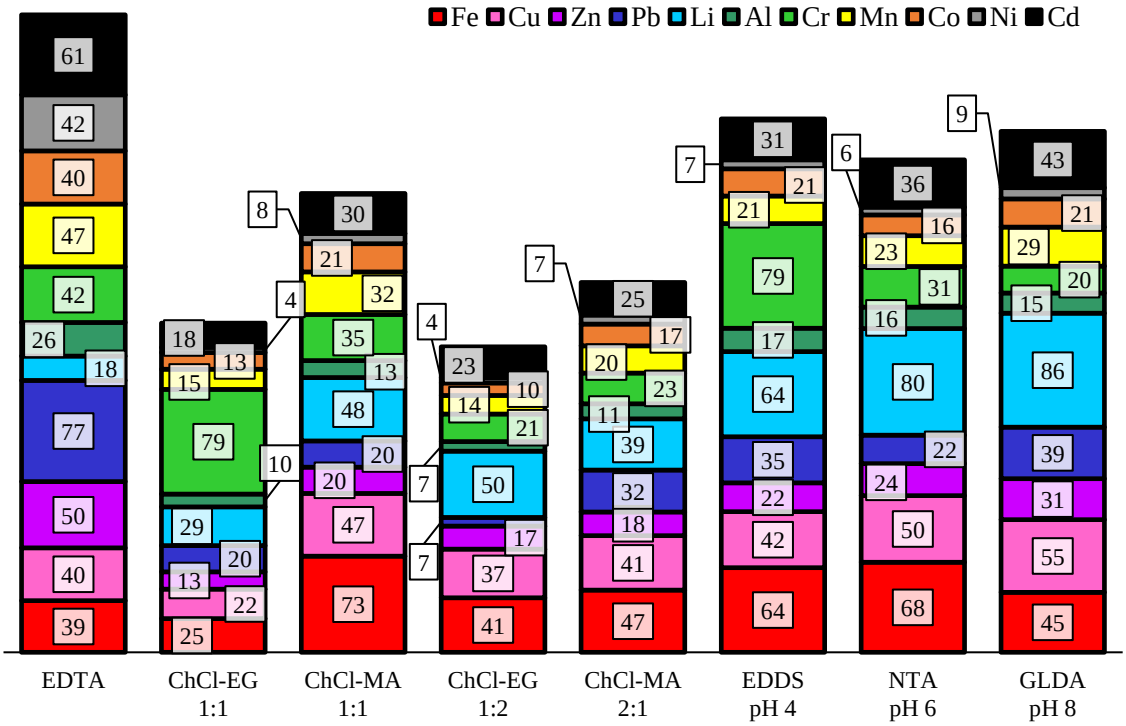


Figure 3.3 Metal extraction efficiencies (%) from goethite using DES and CA.

3.1.8 Metal groups

GLDA pH 8 had the greatest extraction efficiencies for alkaline metals 86%, alkaline earth metals 71% and, other metals 28% (Figure 3.4). NTA pH 6 had the greatest extraction of metalloids 24%. EDDS pH 4 had the greatest extraction of transition metals 34%. The extraction of rare earth lanthanides was less than 5% for all CA. The error bars indicate significant error. This is attributed to the small data set as each test was done in duplicate. A larger data set would provide more reliable results. Additionally, the total of metals per metal group is not consistent which is not reflected in the error bars. Both of these factors must be considered before interpretation of the error bars. The error bars are presented to provide insight into the results but should not be used to justify any significant or non-significant statistical difference.

The order of extraction using CA for transition metals was between 30% and 34%. The average extraction of transition metals from goethite was lowest using NTA, yet it had the highest extraction efficiency of CA used on BOS-D.

Iron extraction using NTA pH 6 was 68%, the most efficient chelating agent for Fe extraction. Goethite has an orthorhombic crystal structure which is made up of iron oxide-hydroxide (Fe(III)O(OH)). Iron accounts for 59% metals present in the goethite sample compared to 94% in BOS-D. Despite this, extraction efficiency from goethite is higher than BOS-D, 68% and 49% respectively. Studies suggest that increasing pH levels to more basic conditions enhances Fe extraction as acidic conditions increases the concentration of insoluble ferric Fe (Vandevivere et al., 2001). However, a study applying EDDS found acidic conditions enhance Fe solubility; pH 3 extracted 94% and pH 7 extracted 78% (Ye et al., 2020). This is attributed to the increased OH^- production from Fenton-like reactions from uncomplexed ferric Fe. These have contradictory optimum conditions for Fe extraction, and in this batch test on goethite neither proved to be more effective with conditions at pH 6 extracting the highest percentage of Fe. This suggests other factors have a greater control than these pH changes, as discussed earlier this includes mass transfer, functional carboxyl groups.

Both EDDS pH 4 and ChCl-EG 1:1 extracted 79% of Cr. This could be attributed to optimised mass transfer through viscosity and denticity. Transition metals can act as Lewis acids in metal-ligand interactions and can decrease the acid dissociation constant of the ligand which determines the optimal pH range for metal extraction (Shanahan & Szymczak, 2020). This is supported by Rodrigues et al., (2001) in which Cr formed stable complexes in acidic chloride-based ligand solutions and attributed improved Cr extraction to the presence of chloride ions acting as a ligand. Results support this as pH 4 was the most effective condition for metal extraction by CA and comparable to the most effective deep eutectic solvent.

For alkaline metal extraction, GLDA pH 8 was the most effective green solvent with 86% extraction. This is consistent with alkaline metal extraction from BOS-D. Studies using CA to extract Li from end-of-life lithium-ion batteries suggest that the extraction of Li can be enhanced when Co is extracted (Gupta et al., 2022), this is due to both typically occurring as $LiCoO_2$. The extraction of Co causes the crystal lattice to breakdown, enabling the extraction of Li (Gupta et al., 2022). However, Co extraction from goethite was 21% or less in using CA and Li extraction was between 64% and 86% suggesting that the findings from Gupta et al., (2022) is not true for all occurrences of Li and Co and the two metals are not associated with one another in goethite.

GLDA pH 8 extracted the greatest yield of Zn, 31% extraction ChCl-MA 1:1 extracted 20% of Zn, the most effective deep eutectic solvent condition. EDDS pH 4 extracted 54% of Zn in BOS-D but reduced 22% in goethite despite goethite containing four times as much Zn. Goethite has the capacity to absorb metal cations, the order of absorption is Cu > Pb > Zn > Cd > Co > Ni > Mn (H. Liu et al., 2014). It is therefore possible the observed decreased extraction efficiency was due to dissolved metals being sorbed to goethite particles.

The most effective chelating agent, GLDA pH 8 extracted 39% of Pb, the most effective deep eutectic solvent was ChCl-MA 2:1 with 32% extraction of Pb, again supporting the extraction of Pb from contaminated red soils in (Liu, 2020).

3.1.9 Extraction efficiencies from BOS-D versus goethite

Figure 3.4 Comparison of extraction efficiencies (%) for DES and CA grouped by metal type on BOS-D and Goethite (bars represent standard deviation).2 compares the most effective deep eutectic solvent with the most effective chelating agent for both BOS-D and goethite. Metalloid extraction was poorest from goethite, 19% and 9% were extracted using CA and DES,

respectively. The extraction of metalloids from BOS-D, was much greater with DES achieving up to 66%. The extraction efficiency of CA on BOS-D was poorer than DES.

The improved extraction of Li from goethite compared to BOS-D may be attributed to the decomposition of goethite increasing availability of Fe ions which enhances nucleation of Li potentially increasing extraction (Skurikhina et al., 2020). CA extracted 51% of Li compared to 29% by DES. Alkaline metal extraction is driven by physical adsorption rather than ion exchange (Baldermann et al., 2018). This could explain the enhanced extraction using CA rather than DES. Li is not known to chelate and there have been few studies showing the effect of EDDS, GLDA and NTA on Li extraction.

The reduced Pb extraction from goethite relative to extraction from BOS-D, could again be attributed the adsorption mechanism in goethite (H. Liu et al., 2014). Literature states that Pb extraction has a strong correlation with pH, favouring acidic conditions due to increased H^+ present (Mukhopadhyay et al., 2016) yet GLDA pH 8 was the most effective solvent condition for Pb extraction. Further studies suggest that pH 7-10 using CA have improved extraction efficiencies for Pb (Niinae et al., 2008). Enhanced Pb extraction using GLDA could be related to a higher complexation constant between GLDA and Pb increasing the stability of Pb complex across a wider pH range (pH 2-10) (Thinh et al., 2021).

Rare earth lanthanide extraction was greatest from BOS-D in both CA and DES compared to extraction efficiencies from goethite (Figure 3.4). On average CA extracted 42% of the rare earth lanthanides present in BOS-D, whereas extraction from goethite was less than 5% for DES and CA. Extraction of rare earth lanthanides may be limited in goethite due to Fe precipitates from goethite, sorbing rare earth lanthanides rather than being completely leached (Dutrizac & Soriano, 2018). There are two potential explanations; physical adsorption to complex with the goethite surface or substitution of trivalent rare earth elements for the

trivalent Fe^{3+} present (Dutrizac & Soriano, 2018). The high extraction efficiency of Fe and minimal extraction of rare earth lanthanides would suggest that substitution of rare earth lanthanides may be occurring in goethite batch tests. A study using a cascade of reactions involving saponification with lipids, increased agitation and washing with phosphorus-based chelators effectively and economically separates rare earth lanthanides (Lyon et al., 2016). Goethite has the ability to bind anions and cations due to the ionic structure of the FeO(OH) octahedra that share edges and corners to form 2:1 octahedra tunnels bonded partially by H bonds (Cornell & Schwertmann, 1997). It is commonly used as a system for metal adsorption and is stable in ambient conditions (Dash et al., 2020). A study found that within 20 minutes 55% of Ni, Cd and Zn had been adsorbed by goethite (Dash et al., 2020). The results of this study suggest that the reabsorption of metals to goethite particle surfaces may be occurring leading to the observed reduction in extraction efficiency across most metal/metalloid groups.

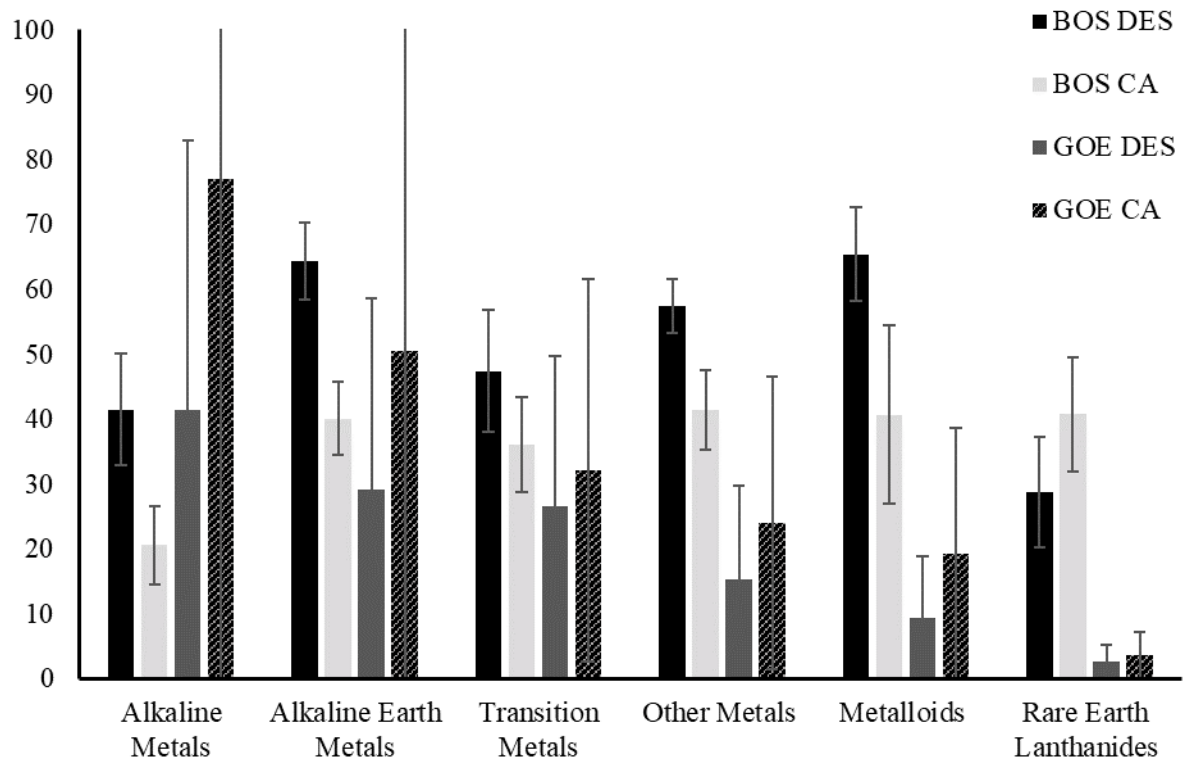


Figure 3.4 Comparison of extraction efficiencies (%) for DES and CA grouped by metal type on BOS-D and Goethite (bars represent standard deviation).

19. Economic assessment

The batch study results provide the beginning of a decision framework to utilise green chemistries to extract metals from contaminated sites. Solvometallurgical decisions are site dependent and to enhance efficiency can be tailored to extract specific metals. Additionally, the economic opportunities are site dependent.

A comparison in potential revenue generated in principle from material used in metal extraction studies is indicated in Table 3.2. The potential revenue generated is in principle as it is not possible to quantify the process costs of the studies referenced.

The study using electrolysis to extract Pb from electric arc furnace slag (EAF) could generate £1.26 /mt based on the mass of material used (Abbott *et al*., 2009). Electrolysis is a highly efficient and pure extraction processes the operational costs are vast. The associated capital and operational costs are significant. Electrolysis is significantly energy intensive which is likely to be provided by burning fossil fuels. This diminishes the possibility of making metal extraction sustainable using electrolysis. The costs associated with the electricity input will be dependent on current energy prices and scale of operation. Both BOS-D and EAF are by-products of the steel making process; BOS-D is generated by the reduction of iron ore, and EAF by the refining of recycled steel (Lee *et al*., 2019). BOS-D typically contains higher concentrations of critical metals when compared to EAF (Lee *et al*., 2019). This could suggest that if BOS-D was processed in the process outlined by Abbott *et al*., (2009) but powered by green energy, metal extraction could be significant with minimal operational costs generated high potential revenue.

The revenue generated by the methods used in this study are comparable and better when compared to the methods presented in Table 3.2. The CA and DES chosen in this study are relatively cheap when compared to energy costs required for electrolysis and are an

environmentally friendly alternative to known toxic chemicals e.g., HCl or HNO_3. It was out of the scope of this study to provide a life cycle assessment or carbon accounting. In doing so, it will provide a comprehensive assessment of how sustainable the process outlined in this study is, the feasibility and can inform process design improvement to further enhance metal extraction.

Establishing a sustainable yet cost effective process to extract metals from metallurgical waste could improve socio-economic standards, alleviating pressure on existing raw extraction processes whilst generating more immediate stores (Huntington *et al*., 2023).

Table 1.2 A techno-economic assessment of potential commercial revenue (£/mt) generated from this study using DES or CA and comparison with other metal extraction processes (commodity prices accurate at time of writing - 06/01/2023 (Trading Economics, 2023)).

	Method	Treatment	Material	Mass of Material	Extraction Efficiency	Commodity Value (£/mt)	Potential revenue (in principle)	Reference
Al	Batch leaching	HCl leaching	Coal fly ash	2 g	12%	£17,901.81	£0.00	(Pan *et al*., 2021)
	Batch leaching	HNO_3	Coal fly ash	2 g	8%		£0.00	(Pan *et al*., 2021)
Co	Sequential chemical batch leaching	HNO_3 - H_2SO_4	Low grade Ni-Cu sulphide tailings	20 g	55%	£41,096.53	£0.45	(Xie *et al*., 2005)
	Batch leaching	ChCl-EG 1:1	BOS-D	12.5 g	62%		£0.32	
	Batch leaching	EDDS pH 4	Goethite	12.5 g	62%		£0.32	
Cu	Electrolysis	-	Wastewater	600 mg/L	92%	£6,569.64	£0.00	(Wang *et al*., 2014)
	Sequential chemical batch leaching	HNO_3 - H_2SO_4	Low grade Ni-Cu sulphide tailings	20 g	85%		£0.11	(Xie *et al*., 2005)
Fe	Microbial fuel cell	-	Acid mine drainage	500 mg/L	99%	£83.84	£0.00	(Wang *et al*., 2014)
	Batch leaching	HCl	Coal fly ash	2 g	30%		£0.00	(Pan *et al*., 2021)
	Batch leaching	HNO3	Coal fly ash	2 g	5%		£0.00	(Pan *et al*., 2021)
Li	Batch leaching	ChCl-EG 1:2	BOS-D	12.5 g	54%	£33,460.26	£0.23	
	Batch leaching	EDDS pH 4	Goethite	12.5 g	80%		£0.33	
Ni	Sequential chemical batch leaching	HNO_3 - H_2SO_4	Low grade Ni-Cu sulphide tailings	20 g	92%	£20,411.82	£0.38	(Xie *et al*., 2005)
Pb	Batch leaching	ChCl-EG 1:1	BOS-D	12.5 g	66%	£1,683.63	£0.01	
	Batch leaching	EDDS pH 4	Goethite	12.5 g	39%		£0.01	
	Electrolysis	ChCl-EG 1:2	Electric arc furnace slag	5 kg	15%		£1.26	(Abbott *et al*., 2009)

Zn	Batch leaching	ChCl-EG 1:1	BOS-D	12.5 g	63%	£2,400.17	£0.02	
	Batch leaching	EDDS pH 4	Goethite	12.5 g	31%		£0.01	
	Electrolysis	ChCl-EG 1:2	Electric arc furnace slag	5 kg	70%		£8.40	(Abbott *et al.*, 2009)

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20. Conclusions

The need to relieve demand for raw critical metals as renewable technologies develop has been identified and a solution is to diversify sources such as exploring innovative opportunities for metal extraction from past metalliferous sites. This study has demonstrated that green CA and green DES can extract metals/metalloids non-discriminately or selectively from different metalliferous wastes. This study demonstrates that solvents should be chosen based the metal or metals required to be extracted and characteristics of the material. DES had higher extraction efficiencies in 23 of the 25 metals/metalloids analysed from BOS-D compared to CA. DES at 1:1 was the greatest condition for critical metal extraction from BOS-D, 58%. ChCl-EG 1:1 was the most robust solvent and had the greatest extraction efficiency from BOS-D. This can be attributed to the decreased competition for hydrogen bond donators further increases reduction potential and reduced viscosity. DES extraction was superior across all conditions relative to EDTA. Thus, demonstrating that DES could provide a sustainable alternative. pH had little effect for metal speciation between CA. An increase in ligand exchange complexes facilitated on the surface of the goethite material meant that chelating agent extraction was greater than DES from goethite. EDTA had superior metal extraction compared to CA when used on BOS-D however CA extracted more critical metals from goethite. Further optimisation of green solvents and green chelators is required to find optimum conditions where agitation, temperature and residence time could improve the extraction efficiencies of the chemicals studied so far. This study also demonstrates that metal extraction can be achieved with green solvents and chelators can recover significant quantities of certain critical metals that could be recovered for resource recovery and substitute into the supply chain relieving raw metal reserves.

21. References

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4. Assessing metal extraction from metalliferous waste: a study using deep eutectic solvents and chelating agents Vs. ethylenediaminetetraacetic acid

Victoria E. Huntington [1], Frederic Coulon[1] and Stuart T. Wagland [1, *]

[1] School of Water, Environment and Energy, Cranfield University, Cranfield, UK

* Corresponding author: s.t.wagland@cranfield.ac.uk; Tel.: +44(0)1234 750111.

Abstract: Conventional methods of metal recovery involving solvents have raised environmental concerns. To address these concerns and promote sustainable resource recovery, we explored the use of deep eutectic solvents (DES) and chelating agents (CA) as more environmentally friendly alternatives. Goethite and blast oxide slag dust (BOS-D) were collected from heap piles at their respective sites, the material was characterised via ICP-MS. the study was unable to determine if the metals present were oxides, sulphides or fluorides and subsequently no assumptions were made. The greatest extraction of critical metals was from goethite, removing 38% of all metals compared to 21% from the blast oxide slag. Among the tested CA, nitrilotriacetic acid (NTA) was the most effective, while for DES, choline chloride ethylene glycol (ChCl-EG) demonstrated superior performance in extracting metals from both blast oxide slag dust and goethite. The study further highlighted the selectivity for transition metals and metalloids was influenced by the carboxyl groups of DES. Alkaline metals and rare earth lanthanides extractions were favoured with DES due to improved mass transfer and increased denticity, respectively. In comparison to ethylenediaminetetraacetic acid (EDTA), typically used for metal extraction, CA and DES showed comparable extraction efficiency for Fe, Cu, Pb, Li, Al, Mn, and Ni. Using these greener chelators and solvents for metal extraction show significant promise in enhancing the sustainability of solvometallurgy. Additional parameters *e.g.*, temperature and agitation combined with a cascading leaching process could further enhance metal extraction potential

Keywords: resource recovery; critical metals; rare earth elements; deep eutectic solvent; chelating agent.

22. Introduction

Since 1992, the European Union (EU) has been actively addressing climate change through various policies (Siddi, 2020). The ambitious Net Zero strategy of the European Green Deal aims to reduce greenhouse gas emissions by 100% by 2050 (Hainsch et al., 2022). Achieving this goal necessitates a substantial shift from fossil fuels to renewable energies such as solar photovoltaic and wind power, along with energy storage solutions. However, this transition places increased demand on metal resources (Grandell et al., 2016). To alleviate pressure on natural ore reserves, it is crucial to explore alternative sources, particularly historic mining sites and industrial wastes. These sources contain significant quantities of critical metals that are essential for renewable energy technologies but are often lost through disposal or waste deposits (Prior et al., 2013; Shuya et al., 2020). Developing novel extraction technologies for these secondary sources can reduce the environmental impact compared to traditional mining operations and contribute to a circular economy (Watari et al., 2021).

Conventional metal recovery options using ethylenediaminetetraacetic acid (EDTA), an example of an environmentally persistent chelating agents (CA) and citric acid, amongst others are well established methods of metal extraction (Gluhar et al., 2020).Despite the low costs, EDTA is a persistent organic pollutant and up to 64% can persist in soil under natural conditions due to low biodegradability, resulting in impaired soil function and plant growth (Alaboudi et al., 2020; Jez & Lestan, 2016). CA are employed in metal leaching due to their strong metal-binding capabilities and they are effective in extracting a wide range of metals from various sources (Faraji et al., 2020). However, they have inherent limitations such as the generation of toxic by-products, high costs and time-consuming processes (Sharma et al., 2018). Recently, the emergence of deep eutectic solvents (DES) offers a promising solution to address the limitations encountered when using CAs. DES represent a specialised subset within the green solvents category. They are notable for their unique composition and properties,

setting them apart from traditional solvents. Their mechanisms typically involve processes like acidolysis and redoxolysis. They can be tailored to specific applications by selecting appropriate combinations of hydrogen bond acceptors (HBAs) such as Choline Chloride (ChCl) or Malonic Acid (MA) and hydrogen bond donors (HBDs) such as Urea, glycerol or ethylene glycol. DES are known for their potential to dissolve a wide range of metal oxides and salts, but a comprehensive understanding of their mechanisms is still required (Morina et al., 2022; Smith et al., 2014).

In this study, the extraction efficiencies of three DES including Choline Chloride-Ethylene Glycol (DES1) and Choline Chloride-Malonic Acid (DES2) and Choline Chloride-Urea (DES3) and 4 chelating agents (CA) including Glutamic acid diacetic acid (CA1), Ethylenediamine-N,N'-disuccinic acid (CA2), Nitrilotriacetic Acid (CA3), and EDTA were evaluated on two metalliferous waste materials: goethite, a product of Fe precipitation during zinc refinery processes, and blast oxide slag (BOS-D), a residue generated during pig iron production in blast furnaces. A semi-continuous batch column system was chosen as it offers a controlled and dynamic environment in which the interaction between the solvents and the metalliferous waste materials could be thoroughly examined. Furthermore, the semi-continuous batch column system provided a valuable advantage by enabling a more controlled experimental setup compared to field studies. It allowed us to manipulate critical variables such as solvent concentration, pH, and flow rates, providing insights into how these parameters influenced the extraction efficiency of the solvents.

In the emerging field, solvometallurgical research has principally focused on metal extraction printed circuit boards, waste waters and lithium-ion batteries. However, past metallurgical site deposits *e.g.*, blast oxide slag dust and goethite, have been undervalued yet contain vast quantities of critical metals previously considered uneconomically viable to extract (Riley et al., 2020). At present, the capacity of UK domestic critical metal supply is not fully understood.

Additionally, there are limited studies comparing DES to CA and their applications for metal extraction from historic metalliferous site deposits. as a result, the commercial benefits are unknown. If critical metals can be extracted at high yields (>80%) using green functional chemistries, this provides an environmentally feasible whilst sustainable opportunity for metal extraction. After subsequent green recovery processes, these methods could redevelop historic metalliferous sites which could aid in the implementation of a circular economy and help meet national and international decarbonisation strategies.

This study compared traditionally environmentally hazardous metal extraction processes *e.g.*, EDTA, to emerging extraction opportunities *e.g.*, DES and CA. Blast oxide slag dust, a by-product generated from blast furnaces, and goethite, a by-product generated during zinc refinery processes were used as material for metal extraction. Both materials, though heterogenous, represent the vast quantities of resources that could be harnessed in order to fulfil national and internation targets for net zero.

23. Materials and Methods

4.1.1 Metalliferous waste collection and characterisation

The BOS-D samples were collected manually by sampling randomly the top 10 cm layer of a stockpile of ~8000 tonnes.

Goethite samples were collected manually from 8 kg goethite filter cake, pre-neutralised with lime. Prior to the characterisation of BOS-D and goethite samples (

Characterisation was done in duplicate and the values in Table 4.1 represent the average concentration (Table 4.1), the samples were furnaced for 550°C for two hours to remove biodegradable material (Cao et al., 2018). Characterisation was done in duplicate and the values in represent the average concentration.

Table 4.1. Characterisation of blast oxide slags dust (BOS-D) and Goethite sample.

	BOS-D		**Goethite**	
pH	9		4.6	
Electrical Conductivity (S/m)	215.54		0.48	
	mg/kg	RSD	mg/kg	RSD
Fe (mg/kg)	589156	6	305333	7
Cu (mg/kg)	168	1	30614	6
Zn (mg/kg)	25747	8	112942	7
Pb (mg/kg)	2666	9	35273	7
Li (mg/kg)	6	4	4	10
Al (mg/kg)	3136	3	16449	7
Cr (mg/kg)	205	4	330	7
Mn (mg/kg)	8515	4	2204	6
Co (mg/kg)	13	3	14	1
Ni (mg/kg)	77	2	51	6
Cd (mg/kg)	83	10	608	7

4.1.2 Chelating agents and Deep Eutectic Solvents Conditions

The chelating agents (CA) are all multidentate organic molecules. The order of denticity across the CA is Ethylenediamine-N,N'-disuccinic acid (CA2) > L-glutamic acid N,N-diacetic acid tetrasodium salt (CA1) > Nitrilotriacetic acid (CA3) from hexadentate, pentadentate and tetradentate, respectively (Almubarak et al., 2022). The pH of the CA was adjusted to pH 4, 6,

and 8 using sodium hydroxide before addition to samples. The DES mixtures had the molar ratio of HBA; choline chloride, to HBD; ethylene glycol, malonic acid and urea, adjusted to 1:1, 1:2, and 2:1. The molar ratio and viscosity of DES underpin potential metal removal. All CA and DES conditions were tested in duplicates (Table 4.2). To provide a baseline comparison for the DES and CA, Ethylenediaminetetraacetic acid (EDTA) was used as a control as it is used in conventional solvometallurgical practices (Gluhar et al., 2020). Deionised water was used to provide an indication of the benefits of applying the DES and CA mixtures. Initial batch test results from BOS-D column studies informed the solvents used for the goethite samples.

Table 4.2 Summary of chelating agents and deep eutectic solvents with relevant experimental conditions and abbreviations.

		Condition	Material		Description
Chelating agents	GLDA	pH 4	BOS-D	-	CA1-4-B
		pH 6	BOS-D	-	CA1-6-B
		pH 8	BOS-D	Goethite	CA1-8-B or G
	EDDS	pH 4	BOS-D	Goethite	CA2-4-B or G
		pH 6	BOS-D		CA2-6-B
		pH 8	BOS-D		CA2-8-B
	NTA	pH 4	BOS-D		CA3-A
		pH 6	BOS-D	Goethite	CA3-B
		pH 8	BOS-D	Goethite	CA3-C-B or G
	EDTA	pH 4	BOS-D	Goethite	Control-B or G
Deep Eutectic Solvents	ChCl-EG	1:1	BOS-D	Goethite	DES1-A-B or G
		1:2	BOS-D		DES1-B
		2:1	BOS-D		DES1-C
	ChCl-MA	1:1	BOS-D	Goethite	DES2-A-B or G

		1:2	BOS-D		DES2-B
		2:1	BOS-D	Goethite	DES2-C-B or G
	ChCl-U	1:1	BOS-D		DES3-A
		1:2	BOS-D		DES3-B
		2:1	BOS-D		DES3-C

24. Experimental Design

Polycarbonate and PVC columns were used to ensure resistance to chemical interactions, with an internal diameter of 10 cm (Figure 4.1). The top lid (1) was equipped with an inflow connected to the reservoir and a perforated sheet (2 mm) to ensure uniform distribution of solvent, so that no channelling occurred by-passing the waste material (Figure 4.1). The working column (2) was 30 cm tall and contained the sample and the infiltrating solvent. To minimise the risk of clogging, a layer of 20 mm gravel (200 g) and 1.5 mm sand (150 g) was placed at the bottom of the column. The removeable bottom section of the column housed two removable filters (2 mm) sandwiching glass wool, to prevent suspended solids entering the reservoir. The reservoir (4) contained the solvent, and a peristaltic pump (Watson Marlow 505s) continuously circulated the solvent back to the top of the column (Figure 4.1).

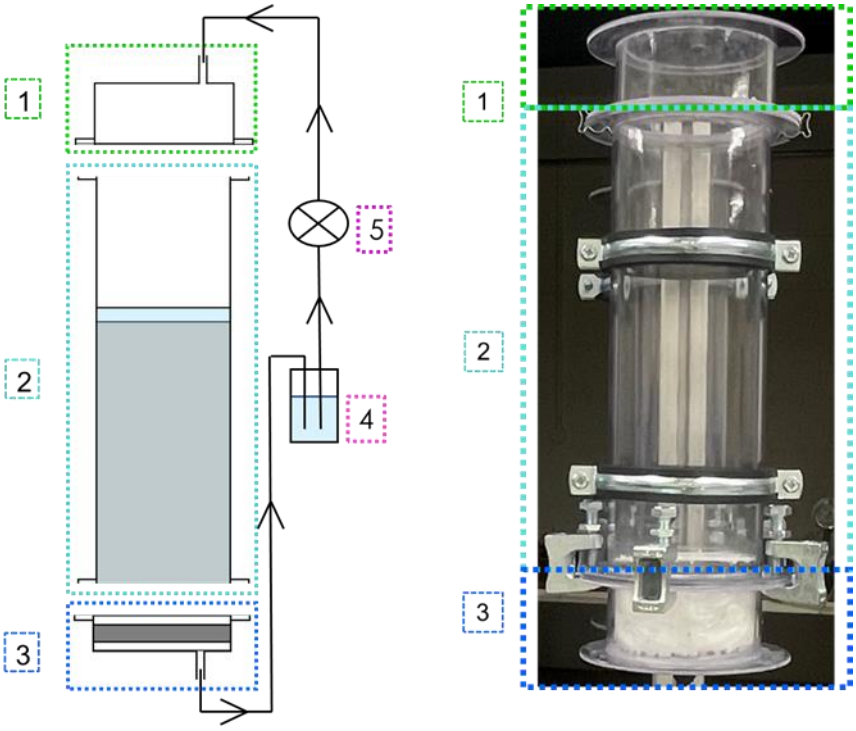


Figure 4.1 Continuous column design. 1 - Top lid, 2 - working column, 3 - bottom lid, 4 - reservoir, 5 - peristaltic pump.

Each column was loaded with 150 g of BOS-D or goethite followed by the addition of 2 L of DES or CA. The weight/volume ratio (w/v) was set at 7.5% after pilot tests to facilitate filtration. The solvent was continuously recirculated within the column at room temperature (22°C) with a flow rate of 80 mL/s for 2 hours using a peristaltic pump to maintain sample saturation. Each solvent condition was tested in duplicate. After 2 hours, 50 mL of leachate as

collected and filtered using 0.45 μm syringe filter (Fisher) and stored at 4°C for analysis. An overview of the sampling process is provided in Figure 4.2.

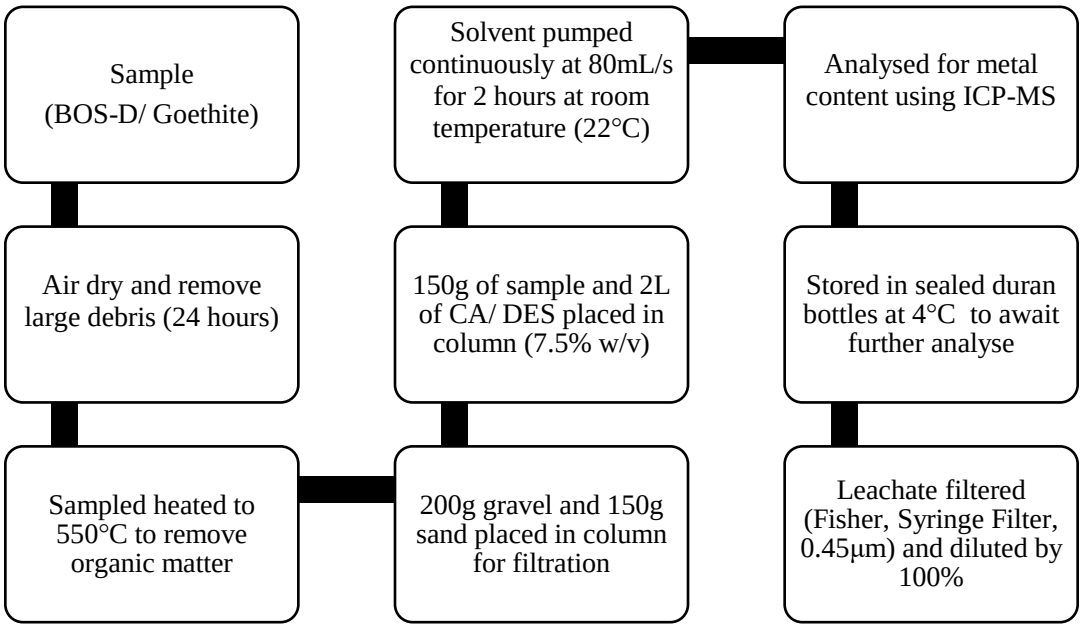


Figure 4.2 Experimental design for the continuous column leaching study to extract metals using green solvents from past metallurgical site deposits.

4.1.3 Metals analysis

The metal content of the 50 leachate samples was determined using inductively coupled plasma mass spectrometry (ICP-MS) (Elan 9000 Perkin-Elmer SCIEX). The 50 leachate samples were diluted 100-fold prior to analysis. The ICP-MS was calibrated using certified standard solutions, including the Rare Earth Elements ICP-MS standard (CMS-1, Inorganic Ventures) and single ICP standards (analyte concentration of 1000 μm ml-1, SCP SCIENCE). These standards covered both major (Ca, Fe, K, Mg, Mn, Na, S, Si) and trace metals (Al, As, Ba, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Sb, V, Zn). For the major elements, the concentration ranges were 1, 5, 15, 20, and 40 μg ml-1. For the trace element and RRE concentrations ranges were 0.01, 0.1, 0.5, 1, 2 μg ml-1. To ensure analytical accuracy and control for potential contamination, a programmed rinse time was implemented between the analysis of samples, and procedural blanks were analysed every eight samples. These measures were in place to monitor blank

contamination, assess sensitivity, verify operating conditions, and maintain accuracy. The results are presented as mean values along with standard error, based on duplicate samples.

4.1.4 Statistical Analysis

To evaluate the significance and efficiency of the solvents used for metal extractions, statistical analyses were carried out using SPSS (version 28). These analyses included one-way ANOVA and independent t-tests to determine whether the observed extraction efficiencies were statistically significant (indicated by P value <0.05). Additionally, descriptive statistics for the key parameters such as minimum and maximum values, means, and standard deviations were used to assess the variability of the dataset. Scatter plots and factorial statistical design were both employed to explore potential relationships and interactions among solvents, their conditions of use, and resulting metal yields.

25. Results and discussion

4.1.5 Evaluating the efficiency of DES vs CAs for metal extraction from BOS-D

The comparison between CA and DES for metal extraction from BOS-D indicated that CA2-B exhibited the highest extraction efficiency at 34%, followed by CA3-B at 33% > DES1-B at 31% > CA1-B at 30%> DES3-B at 27%, and DES2-B at 21% (averaged across conditions). Notably, DES1-A-B was the most effective. (Figure 4.3). The best metal extraction measured was Pb at 83% using CA2-6-B. DES1-A-B was the most effective DES. The order of critical metal extraction was (Figure 4.3).

The extraction of Fe, Al, Cr and Ni were the same when water was used in the column study as CA, indicative that CA leaching is comparable to water. Research has focussed on the less polar phase of extraction processes (Li et al., 2019). Extensive studies have shown the success of CAs for metal extraction from metalliferous waste; contaminated marine sediment (Song et al., 2016), contaminated soils (Leštan et al., 2008) and industrial sludge (Wu et al., 2015). There is little research for metal extraction from BOS-D or associated wastes by CA and water. It is known that CAs can form unstable metal-ligand complexes (Nyamato, 2023). Polarity has shown to significantly enhance Ni, Li, Co, and Mn extraction (Li et al., 2019). Water is highly polar (Pauling electronegativity = 3.44) driving metal extraction (Duan et al., 2022) further supporting results from (Li et al., 2019). The leachate was analysed rather than solid samples. CA may have had greater extraction, but the complexes may be ‘trapped’ within the solid material which would require further metal recovery. Metal recovery is out of the scope of this study.

Lower pH improves redox potential thus metal extraction and it is a key parameter in metal ion speciation (Huang et al., 2017). DES1-B was pH 4, DES2-B was pH 1 and DES3-B was pH 8, acidic DES can improve mass transfer in metal extraction (Panić et al., 2022). Across all

conditions, DES2-B had the lowest metal extraction efficiency from all DES and CA with 26% metal extraction despite being the most acidic DES.

The most effective condition regarding metal extraction was pH 4; DES1-B extracted 30%, CA1-4-B 22%, CA2-4-B 31% and CA3-4-B 37% (Figure 4.3). However, a statistical test showed that there was no significant difference between pH levels. CA2-B is polyprotic, CA1-B and CA3-B are both tetraprotic (Pańczuk-Figura & Kołodyńska, 2016; Scheglova & Popova, 2023). Increased acidity gives rise to protons which can increase proticity, the donation of hydrogen bonds improving potential metal extraction and should be optimised in order to maximise metal extraction efficiencies (Scheglova & Popova, 2023). CA3-B contains one more carboxyl group than CA2-B and CA1-B and is proven to be the most efficient function group for metal extraction, specifically for Pb (Rosillo-Lopez & Salzmann, 2018). CA2-6-B extracted 82% of Pb, CA3-4-B extracted 68% (Figure 4.3). This supports the influence of proticity, specifically for Pb extraction (Scheglova & Popova, 2023).

Denticity refers to the number of groups donator from the ligand to a metal ion (Sahoo et al., 2018). With greater denticity, there is an increased number of available binding sites resulting in a more stable ligand complex which can be used across a wider pH range for optimal metal extraction (Sahoo et al., 2018; Scheglova & Popova, 2023). CA2 is hexadentate, CA1 is pentadentate and CA3 is tetradentate (Sahoo et al., 2018). CA2 has the greatest denticity and proticity and would be expected to have significantly greater metal extraction efficiencies. This is not the case across metals analysed. Across the conditions tested, CA3-B extracted 35% of metals compared to 32% by CA2-B. This suggests that the carboxyl group is more effective and have more influence in metal extraction than proticity and denticity (Rosillo-Lopez & Salzmann, 2018).

Changes in the molar ratio of DES impacts viscosity which drives mass transfer and metal extraction (Abbott et al., 2009; Yuan et al., 2022). The viscosity of DES1-A is 32.6 mPa.s, DES2-A is 1650 mPa.s and DES3-A is 660 mPa.s (Bakhtyari et al., 2020; Kumar Jangir et al., 2021). Metal extraction using DES was greatest in molar ratio 1:1 with 31%, 1:2 and 2:1 both extracted 29% (across all DES). There was no significant different in metal extraction between molar ratios. The increase in HBD increases competition for reducing elements leading to decreased in metal extraction. This can be seen in Cu extraction. DES1-A-B extracted 63% of Cu but DES1-B-B extracted 54% (Figure 4.3). Results are supported by (Qin et al., 2020). The HBD:HBA ratio can affect the strength of the DES hydrogen bond (Yin et al., 2018). Studies found that DES with shorter chains are more stable thus better hydrogen bonds increasing extraction potential (Basil et al., 2022). DES1 and DES3 have the shortest chain and DES2 the longest. Both DES1-A-B and DES3-A-B extracted 32% of metals. DES3 is the most viscous DES. This suggests that chain length has more influence than viscosity, as found in Basil et al., (2019) and Basil et al., (2022). However, studies suggest that the protons in DES2 act as good oxygen acceptors improving metal solubility to form metal-solvent complexes (Qin et al., 2020).

Wei et al., (2016) report that removal efficiencies are improved when there is repeated washing. The green solvents were continuously recirculated through the column for 2 hours and maintained at 7.5% (w/v) (Figure 4.2). The lower extraction yields of DES2-B could be attributable to saturation, viscosity or length of the HBD chain (Abbott et al., 2009; Basil et al., 2019).

Studies comparing the efficiencies of CA to DES are scarce. This study found that the least effective CA condition (pH 8) extracted 30% which is more than the most effective DES condition (1:1) extracted 29%. This indicates that metal extraction in BOS-D is favourable to

chelation rather than solvation. Further work, optimising leaching conditions could provide advantageous mechanisms to enhance metal extraction from BOS-D.

EDTA, the control extracted 38% of metals. DES3-A-B, CA2-B-B, CA3-A-B and CA3-B-B extracted 37% of metals. EDTA is a multidentate ligand providing further binding sites (Touti et al., 2009). Potential Cd complexes increase with coordination groups offered by the ligand (Andersen, 1984). The widely accepted EDTA chelation affinity hierarchy was reported as follows by Corsello et al. (2009): Cr > Fe > Zn > Cd and is based on stability constants. From BOS-D, EDTA extracted 30% of Cr, 80% Fe, 20% of Zn and 56% of Cd. This would make the affinity hierarchy Fe > Cd > Cr > Zn, rather than the hierarchy proposed by Corsello et al., (2009). The pH, metal concentrations and reaction time will have influenced the efficiency of EDTA *e.g.*, if EDTA was circulated through the column for longer than two hours the potential for greater metal extraction increases. The greatest extraction of Cr was CA3-8 with 39%, Fe was DES1-A with 89%, Zn was CA1-4 with 38% and CA3-4 had the greatest extraction of Cd with 82%. Extraction is dominated by CAs and is superior to the control, further supporting metal ion affinity for chelation rather than solvation. Results show that CA and selected DES (DES1-B) can rival extraction efficiencies of EDTA across an array of metals (Table 4.3). This could provide an economically viable and sustainable alternative to EDTA for metal extraction from metalliferous waste. Leaching parameters such as time, degradability and life-cycle assessment of solvents should be investigated when choosing a green solvent to leach.

Table 4.3 Comparison of the most efficient DES or CA for critical metal extraction from BOS-D.

Metal	DES1 (molar ratio)	DES2 (molar ratio)	DES3 (molar ratio)	CA1 (pH)	CA2 (pH)	CA3 (pH)
Li	1:2	EDTA	EDTA	EDTA	EDTA	EDTA
Fe	1:1	1:2	EDTA	EDTA	EDTA	EDTA
Cu	1:1	EDTA	1:2	8	EDTA	EDTA
Mn	2:1	2:1	2:1	4	EDTA & 6	6
Co	EDTA	EDTA	EDTA	4	6	6
Ni	1:2	1:2	2:1	8	4	8
Zn	1:1	EDTA	EDTA	4	6	6
Pb	1:1	EDTA	1:2	EDTA	6	4
Al	1:2	1:2	2:1	6	4	8
Cr	EDTA	EDTA	EDTA	EDTA	EDTA	8
Cd	EDTA	EDTA	EDTA	EDTA	EDTA	4

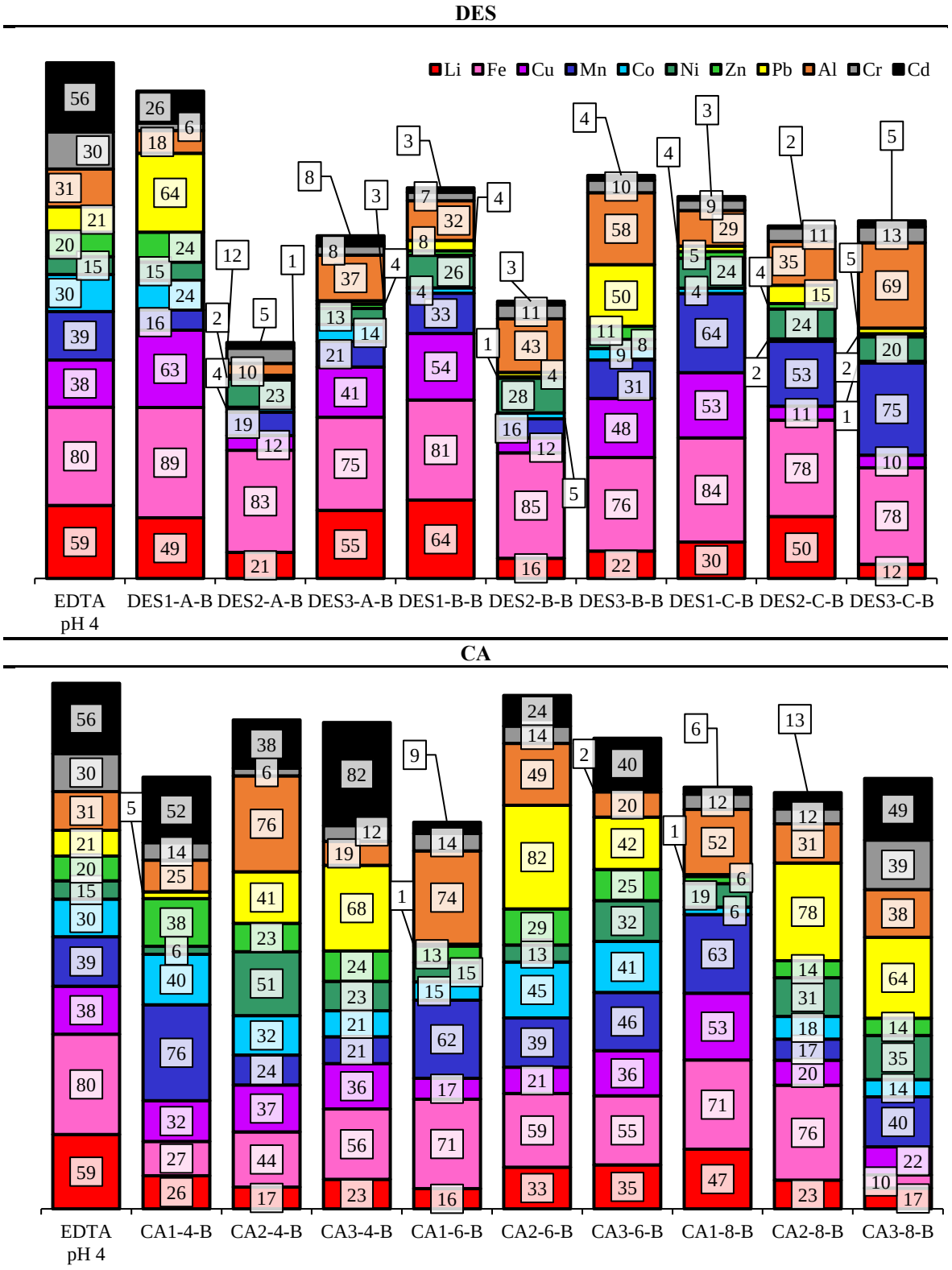


Figure 4.3 Metal extraction efficiencies (%) as proportions using DES in molar ratios 1:1. 1:2 and 2:1 and CA in pHs 4, 6, and 8 on blast oxide slag dust.

26. Evaluating the efficiency of DES and CAs for metal extraction from goethite

The solvent selection was informed from by extraction efficiencies from BOS-D. The order of solvent extraction efficiency for critical metals is CA3-B-G 28% > DES1-B-G = DES2-C-G 26% > DES1-A-G = CA2-A-G 24% > DES2-A-G 22% > CA1-8-G, 19% (Figure 4.4). There is no significant difference in extraction between DES and CA. The extraction of Cu, Zn, Li, Mn, Ni and Cd using water was greater or equal to CA extractions. As previously mentioned, Ni, Li, Co, and Mn extraction is enhanced with polar solvents (Li et al., 2019). Water is a highly polar solvent and would be expected to enhance Ni, Li, Co and Mn extraction (Duan et al., 2022). The extraction of Pb and Li with DES were minimal and when normalised to water, extraction was not enhanced with the addition of DES. The conditions DES were tested in was not optimised for Pb or Li extraction. When leaching conditions are optimised (40℃, continuous agitation for 30 minutes) 92% of Pb can be extracted (Huang et al., 2022). The extraction Pb and Li will not be discussed here. It should be noted generally, extraction of critical metals that weren't enhanced with DES from goethite were enhanced with CA and vice versa *e.g.*, Fe, Cu, Zn. This could be attributed to the preferred solvolysis mechanisms of the metals and goethite material *e.g.*, Pb favours complexolysis used by chelators and Ni favours acidolysis and redoxolysis used by DES.

CA3-6-G is tetradentate and tetraprotic. The lowest denticity and proticity of CAs tested yet the most effective CA with 23% metal extraction. CA1-8-G extracted 22% of metals and CA2-4-G 18% of metals. Elevated extraction using CA3-6-G could be attributed to the additional carboxyl group (Rosillo-Lopez & Salzmann, 2018). The extraction of Fe was greatest with CA3-6-G (Figure 4.3). Neubauer et al., (2000) found that when CA3 is applied to goethite in pH metals are mobilised more than at higher pH and using other ligands *e.g.*, citrate, further supporting results found in this study. The superior extraction of Fe by CA3 may have left

zones of structural weakness in the goethite orthorhombic crystal structure which are then prone to acid penetration thus improving metal extraction (Barrow et al., 2012). At higher pH levels (>7) metals are adsorbed by goethite removing the potential for extraction by CA1-8 and promoting potential reducing the potential extraction when using CA2-4-G (Barrow et al., 2012). Neither DES nor CA extraction efficiencies do not support this. DES1-A-G and DES1-B-G are pH 4 and extracted 21% and 19% respectively. DES2-A-G and DES2-C-G is pH 1 and extracted 19% and 21% respectively (Figure 4.3). CA2-4-G extracted 18%. This further supports the influence of additional carboxyl groups for improved metal extraction (Rosillo-Lopez and Salzmann, 2018).

DES1-A-G and DES2-C were the most effective DES on goethite. DES1-A was also the most effective DES from BOS-D. This suggests that the viscosity and chain length of the HBD has more influence on extraction in goethite than BOS-D. A shorter HBD chain and viscosity could justify the efficiency of DES1-A. DES2 is suggested to have greater solubility than DES1 due to oxygen acceptor abilities and is assumed to form halo-metalate anions with lower oxidation states (Qin et al., 2020; Abbott et al., 2004). The extraction efficiencies of DES2-A and DES-C were greater from BOS-D compared to goethite, 23%, 32%, 19% and 21%, respectively (Figure 4.3). This suggests that metals are more available for extraction in BOS-D than goethite.

In BOS-D, Al extraction was not enhanced with DES addition. In goethite, Al extraction was improved with DES additions with high specificity for DES1-A 70% (Figure 4.3). The concentration of aluminium is 5 times higher in goethite than in BOS-D. Therefore, the increased availability of cation adsorption sites could enable elevated extraction efficiencies (Qin et al., 2023).

Goethite is an Fe oxyhydroxide containing Fe(III) which facilitates partial H+ to bind to anions and cations to form 2:1 octahedra tunnels (Cornell & Schwertmann, 1997). Studies suggests that the Fe(III) has selectivity for Cr extraction (Han et al., 2016). Like Al, the concentration of Cr is 1.5 times higher in goethite than BOS-D. The greatest extraction of Cr in goethite was 64% (DES1-B-B) but in BOS-D it was 39% (CA3-8-B). This could be attributed to greater concentration of Cr or a preference towards complexolysis under testing conditions.

Results may not represent the true extraction of metals from goethite. The adsorptive nature of goethite may result in metal complexes that were once extracted once again becoming absorbed into the goethite structure due to hysteresis (Barrow et al., 2012). This may result in perceived lower extraction of metals from goethite compared to BOS-D. When the temperature of goethite is increase, the desorption process can be accelerated, this could overcome hysteresis in goethite improving the potential for metal extraction (Fischer et al., 2007).

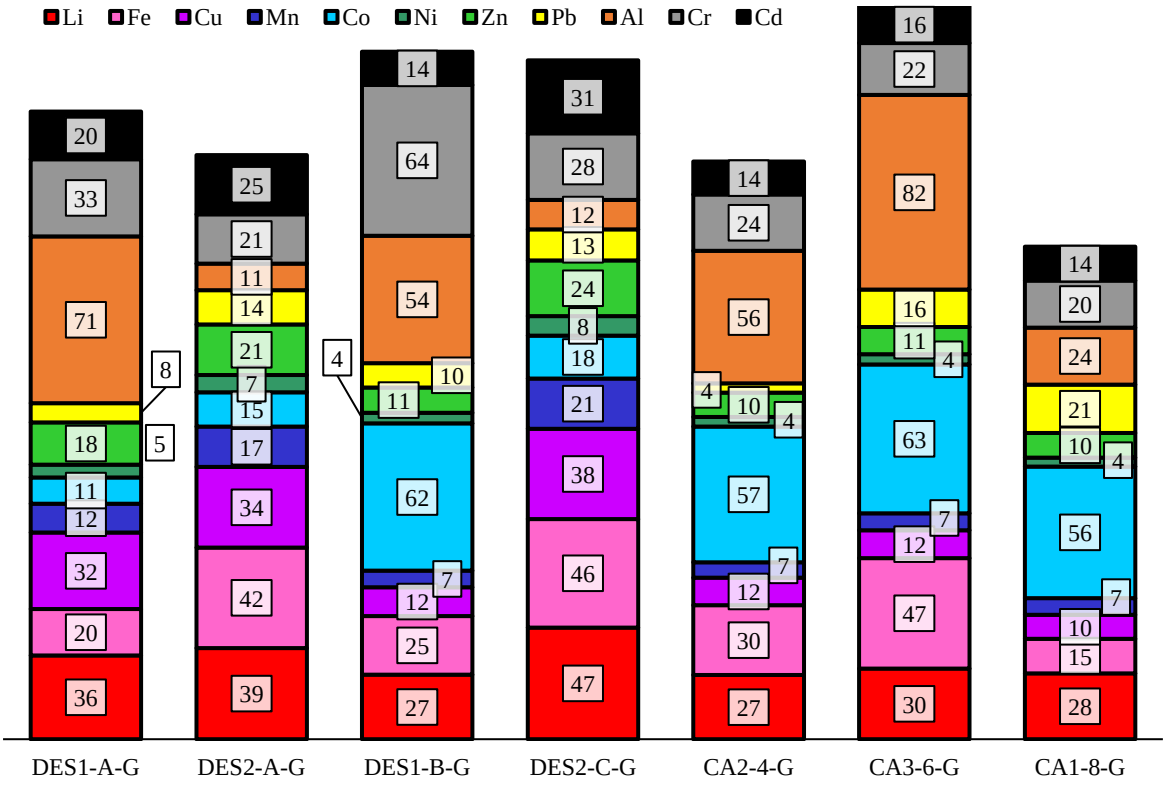


Figure 4.4 Metal extraction efficiencies (%) by proportion, using deep eutectic solvents and chelating agents on goethite.

27. Comparison of metal groups

4.1.6 Blast oxide slag dust

Alkaline metals (Li) were the least extracted metal group using CA but the second most when DES were applied (Figure 4.5). The most effective CA for Li extraction was CA1-C-B with 47%. Results align with (Zing & Srinivasan, 2023) where it is stated that the addition of CA improves Li extraction. A study using DES extracted 95% of Li owing the success to the improved hydrogen bonding between DES and Li due to decreased viscosity and improved mass transport (Hanada & Goto, 2023). There was no significant difference in Li extraction between DES and CA.

DES1-A-B extracted 49% of Li, whereas DES1-B-B extracted 64% of Li (Figure 4.5). Li is strongly hydrophobic and once complexed with chloride is highly soluble in ethylene glycol (Peeters et al., 2022; Zante et al., 2020). The change in molar ratio, increasing the ratio of ethylene glycol to chloride could be attributed to the increase in Li extraction. As previously mentioned, mass transfer within DES is driven by chain length and viscosity. DES1 is the least viscous and has the shortest chain out of the DES. The efficiency of DES is said to be DES2 > DES3 > DES1, owing to favourable oxygen acceptors from the DES2 protons (Abbott et al., 2006). The results in this study do not support this as the efficiency of Li extraction using DES was DES1 47% > DES3 30% > DES2 29% (averaged across molar ratios) (Figure 4.5). Results are supported by Chen et al., (2021) who extracted 62% of Li using ethylene glycol-based DES.

Other metals (Zn, Pb, Al, Ga, Cd) make up 5% of the BOS-D sample providing increased availability of cation adsorption sites which could enable elevated extraction efficiencies (Qin et al., 2023). Other metals were the least extracted group when DES were applied with 18%, but the second most extracted group with the addition of CA 35%. CA2-6-B extracted 82% of Pb (Figure 4.5). The extraction of Pb was greater using CA then DES. A one-way ANOVA

statistical test shows a significant difference in Pb extraction between solvents (p=0.005). Again, the denticity and proticity of CA2-6-B can be attributed to elevated Pb extraction (Wang et al., 2019). When normalised to water, Pb extraction was improved with the addition of DES. DES1-A-B extracted 64%. Results are supported by Omar et al., (2016). This study found that the superior extraction by DES1 is owed to its aliphatic qualities increasing the hydrophilic tendencies of Pb. This, like Li improves adsorption thus increasing metal extraction (Omar et al., 2016). Other metal extraction results further support the notion that carboxyl groups are the most effective functional group for metal extraction (Rosillo-Lopez & Salzmann, 2018).

The extraction of Cd was greatest using CA3-4-B, 82%. The least effective CA was CA1-8-B with 6% Cd extraction (ANOVA shows a significant difference in Cd extraction p= 0.15). It is known that potential Cd complexes increase concurrently with proticity (Andersen, 1984). CA2-4-B would be expected to be the most effective for Cd extraction, yet CA3-4-B extracted 82% extraction. There have been no studies using CA3 to extract Cd from BOS-D. Saini et al., (2019) used CA3 on charcoal powder, simulating industrial effluent, extracted 90% of Cd. Further studies using CAS on toxic metal contaminated soil found that CA3 was the most effective for Cd extraction (Liu et al., 2020; Mai et al., 2019). Acidic conditions and functional groups could explain the extraction attained by CA3.

Metalloid (Si, B, As, Sb) extraction is greatest with CA3-4-B, 49% (Figure 4.5). The extraction of Si was greatest with CA2-4-B 84%, B with CA3-4-B 92%, As with CA1-4-B and Sb with CA3-6-B. Results show that metalloid extraction is preferential to acidic conditions. DES2 is the most acidic DES used at pH 1 but extracted 27% of metalloids, the same as DES3 which is pH 8 (Figure 4.5). Again, it can be inferred from the DES metalloid extraction that more than pH conditions influence potential metal extraction with favourable extraction with increased denticity, proticity and carboxyl containing CAs (Rosillo-Lopez & Salzmann, 2018; Sahoo et al., 2018).

Transition metals (Fe, Cu, Sc, V, Cr, Mn, Co, Ni, Y, Mo) represents 93% of the metals in BOS-D sample providing an abundance of binding sites for metal extraction. Fe alone represents 92% of all metals present within BOS-D and is assumed to be Fe(II) (Kurunov, 2010). Fe extraction favoured DES rather than CA. DES1-A-B extracted the most Fe at 89%. Ferrous metal salts are generally more readily soluble and mobile than ferric salts which dissolve slower (Alıcılar et al., 2008). The testing conditions were aerobic, and studies show that in the presence of oxygen, Fe can form a ferrous chelating agent with DES1 which further increases metal removal (Dou et al., 2021). Like Pb, Fe exhibits a high affinity for aliphatic compounds (Spathariotis et al., 2020). Results support both Dou et al., (2021) and Spathariotis et al., (2020) that DES1 extraction of Fe was greater than DES2 and DES3 across all molar ratios. Elevated Fe extraction may be a result of improved solubility due to decreased viscosity improving mass transport increasing redoxolysis supporting (Abbott et al., 2009). Caution regarding Fe removal must be taken. The initial concentration of Fe was the highest and subsequently, the availability of cation adsorption sites could show elevated extraction efficiencies compared to other metals.

In this study, Cu extraction was greatest when DES1-A was applied, 63%. An ANOVA displays a significant difference in Cu extraction between solvents ($p = 0.019$). Other studies have had greater extraction of Cu using DES2 and DES3 rather than DES1 (Abbott et al., 2006). It was found that Cu forms chlorometalate complexes due to the hydrogen bond donators acting as good oxygen acceptors (Abbott et al., 2006). The best CA for Cu extraction was CA1-C, 53%. Literature states this should be expected (Parmentier et al., 2015). A study found that the dissolution of Cu is controlled by mass transport (Carlesi et al., 2022). The enhanced extraction is attributable to decreased viscosity and a smaller hydrogen bond chain of DES1.

Ni and Cr extraction was only enhanced with the addition of CA, not DES. Ni was greatest extracted by CA2-A 51%, and Cr with CA3-C 39%. Both Ni and Cr show significant differences in extraction between solvents through ANOVA ($p=0.047$ and $p=0.027$,

respectively). CA2, CA3 and CA1 are aminopolycarboxylic acids. The amine groups have a particular affinity to Cr and Ni cations due to the donor ability of the nitrogen atoms acting as a target point for metal ions to bind (Lakshmi & Rangasamy, 2021). Basic conditions were favourable for Cd extraction from basic oxygen furnace slag and acidic conditions for Zn extraction from blast furnace sludge (Han et al., 2016; Vereš et al., 2012). Song et al., (2016) applied distilled water, EDTA, CA2, CA3 and CA to contaminated sediment and found that CA2 enhanced Ni extraction and CA3 enhanced Cr extraction. This further supports the notion of amine affinity for Ni and Cr extraction.

The average extraction of rare earth lanthanide (La, Ce, Nd) was <24% from BOS-D (Figure 4.5). Lanthanides are known to be preferentially chelated in basic conditions and are known the be difficult to separate due to lanthanide contraction (Bart, 2023; Moldoveanu & Papangelakis, 2021). Yet in this study, acidic conditions were superior. CA3-8-B extraction efficiency was the greatest for La and Nd, 27% and 76% respectively. CA2-6-B was the most effective CA for Ce extraction, 61%. Due to increased denticity, proticity and carboxyl functional groups increasing the possibility of multiple metal-oxygen bonds and high stability constants CA2 and CA3 have been described as the most efficient chelating agents for lanthanides (Moldoveanu & Papangelakis, 2021). This finding is in good agreement with Tsiouri et al., (2010) where multidentate chelators extraction previously unobtainable complexes *e.g.,* La which interactions. Moldoveanu & Papangelakis, (2021) back results found in this study and Tsiouri et al., (2010). Using a cascade of reactions with differing agitation and pH levels could enhance lanthanide extraction (Lyon et al., 2016).

4.1.7 Goethite

Metal extraction from goethite starts with metal sorption followed by the desorption from external binding sites leading to back diffusion from binding sites to solvents (Barrow et al.,

2012). Fe extraction creates zones of weakness could facilitating the incorporation of Cr and Co (Barrow et al., 2012). Cr sorption by goethite is suggested to be through physical adsorption *e.g*., mass transport (Salami & Adekola, 2002). DES1-B-G extracted 64% of Cr attributable to efficient mass transport conditions *e.g*., viscosity and chain length (Abbott et al., 2009) which confirms that mass transport underpins Cr sorption (Salami & Adekola, 2002).

Studies have outlined two pathways of penetration into the goethite structure; mesopores and the spaces between pores or, penetration of the crystal structure via exchanges with metal ions and Fe ions within the micropores or sub-micropores (Barrow et al., 2012). For Co, isomorphous substitution of Fe is preferred (Barrow et al., 2012). CA3-6-G extracted the greatest amount of Co and Fe, 63% and 47% respectively confirming Barrow et al., (2012). Fischer et al., (2007) further supports this, stating that metal ionic radius impacts the sorption and subsequent desorption of metals in goethite. Co and Cr have similar ionic radii to Fe (Barrow et al., 2012)

Transition metal extraction increased concurrently with acidity (Figure 4.5). Goethite has shown a high affinity for Cr at low pH (Zhong et al., 2015). CA3-4 and DES1-B-G extracted the more Cr than DES2 despite DES2 being pH 1. This further confirms that efficient mass transport and functional groups influence metal extraction greater than pH (Abbott et al., 2009; Rosillo-Lopez & Salzmann, 2018; Salami & Adekola, 2002).

Unlike transition metals, alkalkine earth metal extraction decreased with increased acidity *e.g*., DES2-A-G which is pH 1 extracted 23% of alkaline earth metals (Figure 4.5). Baldermann et al., (2020) found that Ba extraction is governed by surface complexations and is most effective in pH 8 and may be caused by the degradation of goethite decreasing surface area for adsorption (Arthur et al., 1999). Other studies suggest that alkaline earth metal extraction is inhibited in the prescence of CA (Shende, 2012). Results reject this as CA were more effective than DES but confirm the influence of pH for alkaline earth metal extraction as CA1-8-G extracted 49%

(Figure 4.5). Superior CA1-8-G metal extraction in goethite rather than BOS-D can be attributed to superior alkaline earth metal extraction. There are a limited number of studies comparing the extraction efficiency of DES and CA for alkaline metals from goethite meaning the comparison of results is difficult.

As is the trend, CA3-6-G and DES1-A-G were most effective for other metal (Zn, Pb, Al, Ga and Cd) extraction 26% and 23% respectively with high selectivity for Al. CA3-6-G extracted 82% of Al, the greatest extraction of all metals analysed from goethite. Unlike Cr and Co, the radius of Al is large and not a suitable substitute for Fe within goethite (Fischer et al., 2007). As a result penetration into goethite will be slower (Barrow et al., 2012). If Al is unable to penetrated within the goethite, DES and CA could extract before adsorption and desorption which could explain elevated extraction efficiencies.As previously stated, the goethite contains 5 times as much Al than BOS-D increasing the liklihood of extraction. CA1-6-B and CA2-4-B were most effective for Al with 76% extraction compared to 82% and 71% by CA3-6-G and DES1-A-G in goethite. High extractions in both BOS-D and goethite were in acidic conditions, supporting Scheglova & Popova, (2023). Studies have shown that Al can form stable complexes with CA3-6 from goethite due to the additional carboxyl group and the negative charge (Cardiano et al., 2018). This further corroborates results and Rosillo-Lopez & Salzmann, (2018).

Again, DES1-A-G and CA3-6-G were the most effective for rare earth lanthanides (La, Ce and Nd) extraction despite the average extraction being <6% (Figure 4.5). As previously mentioned lanthanide contraction makes lanthanide separation difficult (Bart, 2023). Though low comparable to other metals, the 10% extraction La using DES1-A-G can be attributed the preference of La to redoxolysis, a mechanism used by DES1 (Entezari-Zarandi & Larachi, 2018). Studies have found that rare earth lanthanides can substitute for Fe3+ within the goethite structure (Dutrizac & Soriano, 2018). CA3-6-G extracted 11% of Nd and 47% of Fe, the

greatest extraction of Fe from goethite. The elevated extraction of Fe using CA3-6-G supports the substitution mechanism. A study using a cascade of reactions with increased agitation which would add additional contact points for dissolution and washing with phosphorus-based chelators effectively and economically separates rare earth lanthanides (Lyon et al., 2016).

Metalloids (Si, B, As, Sb) extraction favoured more basic CA than the more acidic DES (Figure 4.5).. CA1-8-G was the most efficient across all metalloids extracting 26%. The extraction of Sb was negligable due to high affinity to goethite (Burton et al., 2020). CA1 is known to have an affinity to B (Pańczuk-Figura & Kołodyńska, 2016). Additionally, the adsorption, desorption of B in goethite is most efficient in pH 6-8 (Goldberg et al., 1993). B was extracted with CA3-8-G by 66% showing great affinity to CA3 and more neutral/ basic conditions, supporting Pańczuk-Figura & Kołodyńska, (2016) and Goldberg et al., (1993).

Si is known to adsorb onto goethite through bidentate surface complexes with an affinity towards CA (Hiemstra et al., 2007). Results in this study do not support this. DES2-B-G had the greatest efficiency for Si extraction which would suggest under experimental conditions the preferred solvolysis mechanism of Si redoxlysis or acidolysis. DES2, has previously stated had the most efficient mass transport properites out of the DES owing to improved extraction efficiencies (Abbott et al., 2009).

Hysterisis can occur in the desorption of metals from goethite (Fischer et al., 2007). This study was conducted over two hours. If the study was completed over a longer course of time, metal extractions could have improved to account for the hysterisis.

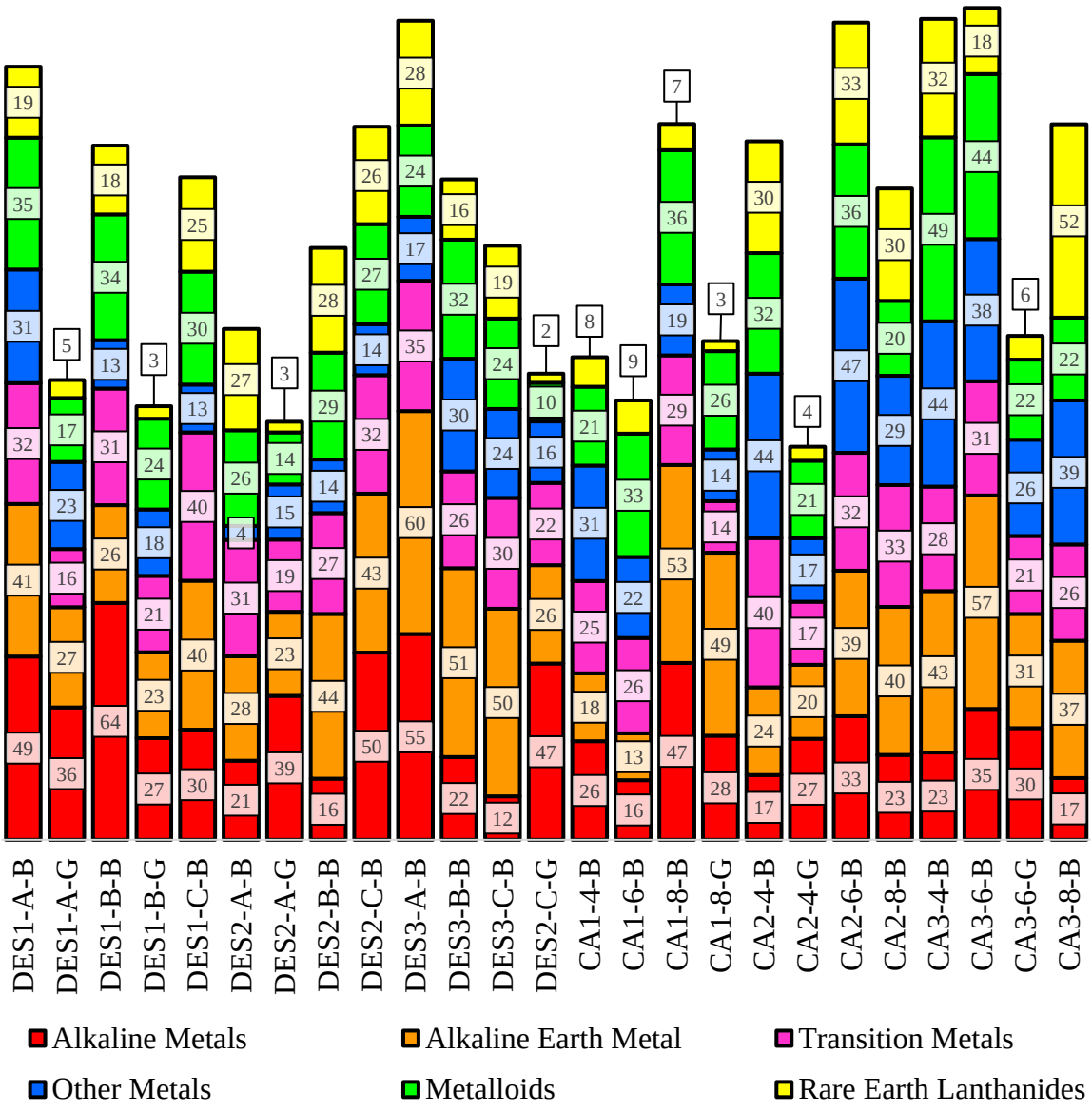


Figure 4.5 Comparison of extraction efficiencies (%) for deep eutectic solvents (DES) and chelating agents (CA) grouped by metal type on blast oxide slag dust and Goethite.

28. Economic assessment

The column study results highlight the possibilities and the opportunities for sustainable alternative metal extraction processes from contaminated site. To optimise metal extraction, the site specifics e.g., material, metal concentrations etc., should be considered and tailored to desired outcomes.

A comparison in potential revenue generated in principle from material used in metal extraction studies is indicated in Table 4.4. The values presented are in principle as it is not possible to quantify the process costs of the studies referenced. electrolysis is the most lucrative process as £7.08 /mt could be generated from the process outlined in Abbott et al., (2009). The revenue calculated does not account for the process costs. Electrolysis is underpinned by the constant supply of electricity which will mostly likely be provided by the combustion of fossil fuels. Not only is this non-environmentally friendly practice but is also significantly expensive and energy intensive. The material used in Abbott et al., (2009) is comprised of electric area furnace slag (EAF) which is similar in composition to BOS-D however more refined (Lee et al., 2019). There are limited studies assessing the feasibility of extraction metals from BOS-D has not been done but when relating to the extraction of metals from EAF, electrolysis could be an effective alternative in terms of purity and economic gain. In order for electrolysis to be a more sustainable alternative to the processes set out in this study, the energy used in electrolysis must be from a sustainable source e.g., solar PV. against processes using EAF.

A study by Sahoo et al., (2017) used Fe3O 4–APTES–EDTA (FAE) on contaminated water to extract metals. Sahoo et al., (2017) obtained very high extraction efficiencies (>95%) using FAE based on EDTA. The methodology aforementioned in this study used EDTA as a control to compare the efficiency of DES and CA, typically environmentally friendly alternatives to EDTA. The potentially generated revenue from the processes in Sahoo et al., (2017) is higher than the other processes highlighted in Table 4.4. However, the environmental cost has not

been defined. EDTA, is a known environmentally persistent organic pollutant. The potentially generated revenue may be higher than revenue generated from processes outlined from this study but the environmental impact of applying FAE is vast and comes with associated environmental and waste management costs.

It was outside of the scope to undertake a life cycle assessment and carbon accounting for the process in this study and other studies referenced. If completed, a life cycle assessment and/ or carbon accounting would provide a comprehensive assessment of how sustainable the process outlined in this study is, the feasibility and can inform process design improvement to further enhance metal extraction.

This study, though not obviously economically lucrative, has limited associated operational costs and environmental costs as the components are classified as environmentally friendly and easily disposed of. Promoting sustainable metal extraction methods, like this study, could generate alternative sources of resources e.g., critical metals. Consequently, this could improve socio-economic standards, alleviating pressure on existing raw extraction processes whilst generating more immediate stores (Huntington et al., 2023).

Table 4.4 A techno-economic assessment of potential commercial revenue generated from this study using DES or CA and comparison with other metal extraction processes (commodity prices accurate at time of writing – 20/08/2023 (Focus Economics, 2023)).

	Method	Treatment	Material	Mass of Material	Extraction Efficiency (%)	Commodity Value (£/mt)	Potential revenue (in principle)	Reference
Al	Column leaching	ChCl-EG 1:1	BOS-D	150 g	89%	£1,806.51	£0.24	
	Column leaching	NTA pH 6	Goethite	150 g	82%		£0.22	
Co	Column leaching	EDDS pH 6	BOS-D	150 g	45%	£26,666.78	£1.80	
	Batch leaching (five cycles)	Fe3O 4–APTES–EDTA	Contaminated water	200 ml	97%		£5.17	(Sahoo *et al.*, 2017)
Cu	Column leaching	ChCl-MA 1:2	Goethite	150 g	38%	£6,757.66	£0.39	
	Co-transport in columns	-	Polyaluminium chloride and anionic polyacrylamide water treatment residuals	25 g	75%		£0.13	(Duan *et al.*, 2022)
	Batch leaching (five cycles)	Fe3O 4–APTES–EDTA	Contaminated water	200 ml	97%		£1.31	(Sahoo *et al.*, 2017)
Fe	Column leaching	NTA pH 6	Goethite	150 g	47%	£89.21	£0.01	
	Microbial fuel cell	-	Acid mine drainage	500 mg/L	99%		£0.04	(Wang *et al.*, 2014)
Li	Column leaching	ChCl-EG 1:2	BOS-D	150 g	64%	£25,698.65	£2.47	
	Electrolysis	-	Spent Li batteries	0.002 g	41%		£0.00	(Morina *et al.*, 2022)
Ni	Batch leaching (five cycles)	Fe3O 4–APTES–EDTA	Contaminated water	200 ml	96%	£17,820.15	£3.42	(Sahoo *et al.*, 2017)
Zn	Column leaching	ChCl-MA 1:2	Goethite	150 g	24%	£2,023.55	£0.07	
	Electrolysis	ChCl-EG 1:2	Electric arc furnace slag	5 kg	70%		£7.08	(Abbott *et al.*, 2009)
	Co-transport in columns	-	Polyaluminium chloride and anionic polyacrylamide water treatment residuals	25 g	58%		£0.03	(Duan *et al.*, 2022)

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29. Conclusions

This study compared the extraction efficiencies of DES and CA from metallurgical deposits in order to contribute to scientific knowledge and explore sustainable alternative opportunities for metal extraction. Critical metal extraction from goethite was almost double that of BOS-D potentially due to enhanced Fe extraction leading to increase penetration of the goethite structure. Additionally, the extraction efficiencies of CA and DES rivalled EDTA across a suite of critical metals; lithium, nickel, aluminium and cobalt, with the scope to develop more selective DES and CA through optimisation.

The outcome of this study demonstrates that it is possible to extract metals from otherwise polluting metallurgical deposits, enabling a transition in managing these sites. The basic economic feasibility assessment presented demonstrates the financial benefits of using CA and DES on metallurgical deposit material which supports previous studies. The evidence from this study helps to demonstrate the significant opportunity to redefine metallurgical deposits whilst extracting metals to meet demand for renewable energy whilst also offsetting remediation costs. Not only does this meet sustainable development goals *e.g.*, affordable and clean energy, remove potential sources of metal pollution, but also helps to bolster the UK Critical Minerals Strategy.

To further optimise extraction efficiencies additional studies are required to optimise conditions *e.g.*, temperature, agitation and contact time. There is opportunities to combine green extraction processes in sequence or cascading processes *e.g.*, bioleaching. The results in this study show the promise of this emerging research domain and results support the benefits of metal extraction from metallurgical deposits whilst meeting sustainable development goals and promoting circular economy opportunities and green legislation.

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5. A sequential bio-solvoleaching investigation into the ability of deep eutectic solvents and chelating agents to extract metals from past metallurgical sites.

Victoria E. Huntington[1], Ipek Tezyapar Kara[1],Frédéric Coulon[1] and Stuart T. Wagland [1,*]

[1] School of Water, Environment and Energy, Cranfield University, Cranfield, UK;
v.e.huntington@cranfield.ac.uk(V.E.H.); f.coulon@cranfield.ac.uk(F.C.)
* Correspondence: s.t.wagland@cranfield.ac.uk; Tel.: +44(0)1234 750111.

Abstract: Independently, bioleaching and solvoleaching are not sufficient to achieve high efficiencies for all metal extraction. Sequential leaching experiments were carried out to extract critical metals including zinc, copper, iron, chromium, lithium, manganese, cobalt, aluminium, and nickel, present in blast oxide furnace dust. Bioleaching with *Acidithiobacillus ferrooxidans* was completed first as a batch approach followed by a static batch study using green chelating agents and deep eutectic solvents. The optimized bioleaching conditions had an initial pH of 1.75, pulp density of 1% (w/v), and a temperature of 30°C. A second step of solvoleaching was applied to bioleaching residue. In which the efficacy choline chloride – ethylene glycol and ethylenediamine-N, N'-disuccinic acid, were compared to one another and against the environmentally hazardous, but commercially used solvent, ethylenediaminetetraacetic acid. This study has demonstrated the promise of sequential treatment to extract critical metals from metalliferous waste and provide a sustainable alternative to ethylenediaminetetraacetic acid and could promote circular economic opportunities from mine wastes**.**

Keywords: resource recovery; critical metals; chelating agents; deep eutectic solvents; bioleaching.

31. Introduction

The Net-Zero Act, a pillar of the European Union Green Deal, aims to decarbonise all sectors by 2050 (European Commission, 2023). The transition to clean energy is underpinned by critical metal supply. The demand for lithium outstripped supply in 2022 (International Energy Agency, 2023). The demand for copper, zinc and lithium is expected to be greater than supply in 2023 (Clark & Clarry, 2023; ILZSG, 2023). This could be exacerbated further because of the time taken to find new resources to extract and commission before mining activity can take place; it can take up to 20 years to commission a copper mine (Energy Transitions Commission, 2023). Secondary supply opportunities *e.g.*, historic past metallurgical sites, are crucial to supplement naturally occurring supplies. Tailings perceived as waste at the time of mining , are now sources for critical metals *e.g.*, cobalt and lithium (Rodriguez Rodriguez et al., 2022). Critical metals are essential for renewable technologies, often supply of these metals are subject to socio-economic issues with supply (Department for Business and Trade, 2023). Furthermore, critical metals are removed from material cycles through disposal or waste deposits diminishing (Prior et al., 2013).

Previously, critical metals were not economically viable to extract from past metallurgical sites due to unsuitable processing infrastructure or unfavourable economic conditions (Whitworth et al., 2022). Historic mine wastes pose a considerable threat to both the environment and humans (Bevandić et al., 2021). Conventional metal extraction processes comprise of pyrometallurgy and hydrometallurgy with associated costs and environmental impacts *e.g.*, high operating temperatures and the generation of toxic by-products (Whitworth et al., 2022).

There are many issues surrounding past metalliferous sites, once decommissioned, ownership, regulatory controls, and economic disruptions can result in historic metalliferous waste comingling within itself and the surrounding substrate. If no mitigation is realised, serious

environmental damage is inevitable. This compounds the costs for conventional pyrometallurgical and hydrometallurgy.

Solvometallurgy using green chelating agents (CA), deep eutectic solvents (DES) and bioleaching are emerging trends in hydrometallurgy. These green alternatives provide a sustainable alternative to benzene and EDTA, both known contaminants (Doble & Kruthiventi, 2007).

In addition, bioleaching, one of the biohydrometallurgy methods involves the use of microbes using biological solubilisation and bio-oxidation to break down minerals in low-grade ores, providing a green, cheaper, low-energy and material requirement alternative to conventional hydrometallurgical processes *e.g*., cyanidation (Tezyapar Kara et al., 2023a; Srichandan et al., 2020; Arya and Kumar, 2020). A few bioleaching studies for ferrous slags have been reported as ferrous slag contains small amounts of base metal compared to non-ferrous slag (Binnemans et al. 2020). Yet, these by-products now gain attention of researchers as recover value from by-products and wastes is one of the pillars of circular economy (Riley et al., 2020). Hocheng et al., (2014) extracted 28% to 75%, from 14% to 60% and from 11% to 27%, for Mg, Zn and Cu, respectively, using *Acidithiobacillus thiooxidans* from electric arc furnace (EAF) steel slag sample. Gomes et al. (2018) extracted 100% of Al, 84% of Cr and 8% of V from basic oxygen furnace (BOF) steel slag in 22 days by using mixed acidophilic culture. Moreover, a combined approach using deep authentic solvent leaching and bioleaching may provide an enhanced extraction efficiency (Pourhossein et al., 2021; Hao et al., 2020; Priya and Hait, 2018).

DES are the green branch of ionic liquids and align with the green chemistry principles. Their mechanisms are primarily acidolysis and redoxolysis. In this study type III DES were used; choline chloride as the hydrogen bond acceptor and ethylene glycol as the hydrogen bond donator (ChCl-EG) but combinations can be tailored to specific applications. CA are multidentate molecules which can use multiple sites simultaneously to one metal ion to form

rings (chelates) (Almubarak et al., 2022). They are employed in metallurgy due to their strong metal complexing capabilities using complexolysis and can extract a wide suite of metals (Faraji et al., 2020) This study used Ethylenediamine-N, N'-disuccinic acid (EDDS). In solvoleaching, acidolysis is the dominant extraction mechanism and is faster than complexolysis (Attia et al., 2022; Faraji et al., 2020). Reduced leaching efficiency in the solvoleaching phase could be due to changes in morphology in the BOS-D residue. The degradation of BOS-D particle surfaces as a result of *A. ferrooxidans* leaching has the potential to improve metal dissolution potential for specific metals (Chiang et al., 2013).

32. Materials and Methods

5.1.1 Blast Oxide Slag Dust

The BOS-D material was collected manually by randomly sampling the top 10cm layer from a stockpile of ~8000 tonnes and characterised (Table 5.1). The BOS-D was air-dried, grounded, and sieved using a 2 mm mesh to remove large debris. Electrical conductivity and pH were measured according (ISO 11265:1994 and ISO 10390:2005, respectively. For bioleaching study, the sample was autoclaved for 15 minutes at 121° C to remove native microorganisms and to ensure precise evaluation of the targeted microbial activity and metal leaching without interference (Faraji et al., 2018; Gomes et al., 2018). The elemental composition of the autoclaved and non-autoclaved materials was determined using aqua regia digestion, with 1:3 ratio of nitric acid (HNO_3) and hydrochloric acid (HCl), followed by microwave digestion as described by Gutiérrez-Gutiérrez et al., (2015). Extracts were analysed with a PerkinElmer's NexION® Inductively Coupled Plasma Mass spectrometer (ICP-MS) was used to analyse the extracts using uranium (U) as internal standard.

5.1.2 Microorganisms and Culture Conditions

An actively growing culture of Acidithiobacillus ferrooxidans (DSM 583), was received from Leibniz Institute (DSMZ), Braunschweig (Germany). The culture was then adapted to 5% (w/v) of BOS-D as described in Tezyapar Kara et al., (2022) and was preserved in Erlenmeyer flasks with a concentration of 10% (v/v). The culture was maintained in 90 ml of optimised 4.5 K salt medium at pH 1.75 at 30°C at 150 rpm as described by Chen et al., (2015) and Tezyapar Kara et al., (2023b). Rapid increase in oxidation-reduction potential (ORP), 300 mV to 600 mV, and rapid ferrous iron consumption in two days were assumed as a good bacterial growth indicator instead of applying microbiological method, *e.g.*, microscopy as the many bacterial cells were deposited on the precipitate that formed during the A. ferrooxidans growth as previously reported

by Roy et al., (2021) (Muddanna and Baral, 2021). The adapted culture was sequentially cultivated for 2 days on two separate occasions in order to it reach to high ORP (>600 mV), before bioleaching. Chen et al., (2015) was used to prepare the growth medium a modified basal salt medium. The optimised growth mediums consist of two parts, part A (modified basal salt medium) and part B (ferrous iron solution). The part A was prepared by adding 2.00 g of $(NH4)_2SO_4$, 0.25 g of K_2HPO_4, 0.25 g of $MgSO_4 \cdot 7H_2O$, 0.10 g of KCl and 0.01 g of $Ca(NO_3)2$ into a 700 ml of deionised water (DIW). The part B was prepared by adding 11.1 g of $FeSO_4.7H_2O$, in 300 ml DIW get 2.22 g/L Fe+2 in the medium, respectively. Both solutions were adjusted at pH 2 using 5 M H_2SO_4. After pH adjustment, part A was autoclaved at 121°C for 15 minutes. Ferrous iron solution was instead filtered using 0.2 µm Millipore filter. After that the part A and part B was mixed. The pH is then adjusted to 1.75 for bioleaching study using 5 M H_2SO_4.

5.1.3 Deep eutectic solvents and chelating agent conditions

The DES, ChCl-EG was tested in 1:1 molar ratio (HBA: HBD) due to low viscosity and acidic conditions improving redox potential and mass transfer, both key parameters in metal extraction (Huang et al., 2017; Panić et al., 2022).

The CA, EDDS, was tested at pH 4 informed. EDDS is hexadentate and polyprotic. Enhanced proticity increases hydrogen donation and subsequently potential metal extraction (Scheglova & Popova, 2023). Denticity refers to the available binding sites for potential ligand-metal complexes, as EDDS is hexadentate there are six potential binding sites (Sahoo et al., 2018). The combination of denticity and proticity should enable EDDS to be highly effective for metal extraction from BOS-D. The pH of EDDS was adjusted to pH 4 using sodium hydroxide (NaOH) before mixing with samples. Ethylenediaminetetraacetic acid (EDTA) pH 4 was used

as a control. Each solvent was tested in duplicate. All solvents were purchased from Fisher Scientific and Sigma Aldrich.

5.1.4 Bioleaching Experimental Design

First, 300 ml growth medium contains 1.11% of $FeSO_4.7H_2O$ at pH 1.75 was prepared and placed in a 500 ml shake flask. Then, 3 ml of the growth medium was discarded to add 3 ml, 1 % (v/v), of inoculum. Culture was incubated at 30°C on an orbital shaker at 150 rpm for 2 days. Then, 1% (w/v) of BOS-D was added into the flask, and bioleaching started (Day 2). A platinum electrode with an Ag/AgCl reference electrode was used for measurements of the ORP (Srichandan et al., 2014). The pH and ORP was monitored on the day 0, 2, 3, 5, 8, 11, 16, and pH was adjusted to 1.75 (results not shown). Experiment was performed as duplicate.

5.1.5 Solvo/hydrometallurgy

This study was performed as a two-step sequential study. As the first step bioleaching was performed with *A. ferrooxidans* then it was followed by solvoleaching using ChCl-EG (DES), EDDS (CA) or EDTA (control). Bioleaching residue was mixed with solvents; EDTA, ChCl-EG and EDDS in 12.5% (w/v), in accordance with previous studies (Cao et al., 2018). To guarantee equal contact time, samples were agitated, at 150 rpm, for 15 minutes in ambient conditions (22°C). Samples were then left to settle for two hours before being filtered through 10 μm filter paper (Whatman® qualitative filter paper, Grade 595). The leachate was stored (4°C) in sealed Duran bottles for further analysis.

5.1.6 Analytical Methods

The metal content of the leachate samples was determined using inductively coupled plasma mass spectrometry (ICP-MS) (Elan 9000 Perkin-Elmer SCIEX). All leachate samples were diluted 100-fold prior to analysis. The ICP-MS was calibrated using certified standard solutions, including the Rare Earth Elements (REE) ICP-MS standard (CMS-1, Inorganic Ventures) and single ICP standards (analyte concentration of 1000 μm ml-1, SCP SCIENCE). These standards covered both major (Ca, Fe, K, Mg, Mn, Na, S, Si) and trace metals (Al, As, Ba, Cd, Co, Cr, Cu, Li, Mo, Ni, Pb, Sb, V, Zn). For the major elements, the concentration ranges were 1, 5, 15, 20, and 40 μg ml-1. For the trace element and RRE concentrations ranges were 0.01, 0.1, 0.5, 1, 2 μg ml-1. To ensure analytical accuracy and control for potential contamination, a programmed rinse time was implemented between the analysis of samples, and procedural blanks were analysed every eight samples. These measures were in place to monitor blank contamination, assess sensitivity, verify operating conditions, and maintain accuracy. The results are presented as mean values along with standard error, based on duplicate samples.

5.1.7 Statistical Analysis

To evaluate the significance and efficiency of the sequential bioleaching solvoleaching for enhanced metal extraction, statistical analyses (one-way ANOVA) were carried out using SPSS (version 28) to established statistical significance ($P = <0.01$).

Additional descriptive statistics for the key parameters *e.g.*, minimum, and maximum values, means, and standard deviations were used to assess the variability of the dataset.

33. Results and discussion

5.1.8 Characterisation of BOS-D

The electrical conductivity and the pH were found as 215.54 (S/m) and 9, respectively, indicating that BOS-D was an alkaline material. Elemental composition of the autoclaved and non-autoclaved BOS-D were given in Table 5.1. BOS-D was dominated by Fe, Zn, Mn and Al. the difference between autoclaved and non-autoclaved concentrations is likely due to analytical or operator errors.

Table 5.1. Characterisation of blast oxide slags dust (BOS-D).

BOS-D	Unit	**Fe**	**Cu**	**Zn**	**Pb**	**Li**	**Al**	**Cr**	**Mn**	**Co**	**Ni**	**Cd**
Non-autoclaved	mg/kg	58,9156	168	25,747	2,666	6	3,136	205	8,515	13	77	83
Autoclaved	mg/kg	390,500	127	18,000	1738	4.5	2,660	157	5,870	10	59	62

5.1.9 Chemical leaching vs. bioleaching vs. sequential leaching

ChCl-EG leaching, conducted with a solid concentration of 12.5% (w/v), successfully dissolved over half amount of all metals (58 - 63%) within two hours (Table 5.2). After 14 days of bioleaching 82% Y, 62% Ce and 64% Nd were extracted. The extraction efficiency for rest of the elements were between 34% and 46% (Table 5.2). In attempts to further extract metals from BOS-D, ChCl-EG and EDDS were applied to the *A. ferrooxidans* BOS-D residue (Table 5.2) and compared to the extraction efficiency of EDTA. The results of the solvoleaching phase are shown in Table 5.2 below.

Overall extraction of metals from the BOS-D residue was minimal. EDDS was the most effective with 4% of analysed metals extracted. Both ChCl-EG and EDTA extracted 1% of metals (averaged over nine selected metals). The results were not statistically significantly different.

Li extraction from *A. ferrooxidans* BOS-D was effective, yet all the green CA and DES extracted <1% of the BOS-D residue Li, with the extraction from the residue observed being 11% using EDTA ChCl-EG tests. Li ions form strong complexes with BOS-D particles inhibiting leaching potential (Zhou et al., 2020). Li is hydrophilic and has been extracted when a fatty acid is applied (Zante et al., 2020). There is little literature evidence for the chelation of Li despite the greatest extraction using EDTA, a chelator. If the sequence was reversed and BOS-D was mixed with the green alternative CA and DES first, Li could be selectively extracted (Huang et al., 2022), improving potential overall extraction and process sustainability.

The extraction of Mn was insignificant. Mn has been shown to form strong complexes with EDTA (Gluhar et al., 2020). EDTA and EDDS are isomers so would be expected to behave the same *e.g*. EDDS would form strong complexes with Mn, yet extraction was <0.01% across EDDS, EDTA and ChCl-EG. The extraction of Cu and Co was minimal across all conditions with <0.5% extraction. This further supports the findings in Yue et al., (2023), where Cu and Co metal extraction is reduced when Mn concentration is reduced.

A. ferrooxidans extracted 39% of Zn from the initial sample (Table 5.2). Similar to Mn, Zn extraction was not substantial from the BOS-D, <0.01%. High solvation of Zn using ChCl-EG is attributed to the destruction of the hydrogen bond within EG promoting Zn-Cl bonding (Kalhor et al., 2021). Acidic conditions also promote the destruction of hydrogen bonds, and which enhances Zn extraction. This is similar to results found by Vereš et al., (2012), where Zn extraction from blast oxygen furnace was up to 92% in acidic conditions. As previously stated, bioleaching had lower Zn extraction due to mass transfer limitations and low reaction kinetics (Rouchalova et al., 2020). Mass transfer is underpinned by viscosity, ChCl-EG has a short hydrogen chain and low viscosity improving mass transfer potential (Abbott et al., 2009).

Though the results in this study do not align with similar literature for singular phase leaching, there has been no previous study analysing the potential for sequential bioleaching to solvoleaching on BOS-D like material using green CA and DES. A study comparing a wider array of green CA and DES is needed to find a solvent/ chelator that is more compatible with bioleached residue. Additional steps should be taken to ensure that any residual organic compounds or microbes are removed or neutralised to remove potential unnecessary reactions which would interfere with metal extraction. Optimisation of the process to include increased temperature, agitation and varying w/v ratio could improve extraction efficiencies with DES and CA.

Table 5.2 The average extraction and standard deviation of metals extracted from BOS-D

	REE					
	Extracted (%)	Standard Deviation	Extracted (%)	Standard Deviation	Extracted (%)	Standard Deviation
	Y	**Y**	**Ce**	**Ce**	**Nd**	**Nd**
EDTA	0.62	0.00	0.01	0.00	0.23	0.00
ChCl-EG	1.85	0.15	0.15	0.10	7.87	7.83
EDDS	8.87	0.57	1.59	0.76	24.80	11.44
	Critical Metals					
	Extracted (%)	Standard Deviation	Extracted (%)	Standard Deviation	Extracted (%)	Standard Deviation
	Li	**Li**	**Co**	**Co**	**Cu**	**Cu**
EDTA	11.11	0.00	0.01	0.00	0.00	0.00
ChCl-EG	0.08	0.00	0.02	0.01	0.00	0.00
EDDS	0.22	0.10	0.01	0.00	0.00	0.00
	Heavy Metal and others					
	Extracted (%)	Standard Deviation	Extracted (%)	Standard Deviation	Extracted (%)	Standard Deviation
	Al	**Al**	**Zn**	**Zn**	**Mn**	**Mn**
EDTA	0.00	0.00	0.00	0.00	0.00	0.00
ChCl-EG	0.00	0.00	0.00	0.00	0.00	0.00
EDDS	0.01	0.00	0.00	0.00	0.00	0.00

34. Conclusions

This study demonstrates the potential of sequential treatment of real-world metalliferous wastes (BOS-D) using novel bioleaching and green solvoleaching methodologies. The *A. ferrooxidans*

→ EDDS combination extracted the greatest concentration of metals 4%. The *A. ferrooxidans* → EDTA combination had superior extraction of Li compared to ChCl-EG and EDDS. Overall metal extraction using solvoleaching was insignificant and further optimisation is necessary to make the process economically viable. Additionally, scalar studies from a static batch to a continuous column is needed to emulate field conditions and optimisation of physical conditions for improved solvent extraction of metals *e.g*., varying temperature and contact time could further improve the extraction of metals from metalliferous wastes in the solvent extraction step. An optimised sequential treatment approach utilising bioleaching and green solvent extraction will improve the feasibility of treating metalliferous wastes and improve opportunities to recover metals extracted in the process.

Author Contributions

Huntington, V conducted the solvoleaching study and lead the completion of this draft contributed over 70% of the content. Tezyapar Kara, I. participated in the design, completion, and analysis of the bioleaching phase. Coulon, F. and Wagland, S. T. helped draft and review the manuscript.

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6. Discussions

36. Introduction

The aim of this PhD was to directly compare metal extraction between green deep eutectic solvents (DES) in differing molar ratios and green chelating agents (CA) in differing pH levels from real-world metalliferous wastes, blast furnace oxide dust slag (BOS-D) and goethite. Batch and column studies were done, and metal extraction efficiencies were calculated, normalised to water, and compared against extraction using EDTA. A sequential study was also performed to explore the potential of combining bioleaching with DES or CA leaching.

37. Discussion of key findings

6.1.1 The efficacy of deep eutectic solvents and chelating agents to extract metals from blast oxide furnace slags and goethite cake through batch and column chemical leaching

Overall metal extraction was greater from BOS-D than goethite in batch. The pre-treatment of both BOS-D and goethite were identical *e.g.,* ground to <2mm and placed in a furnace for two hours at 550°C. A smaller particle size means a thinner protective passive layer increasing surface area and available site for complexes and thus metal extraction. Padilla et al., (2008) presented results where there was no obvious effect on leaching kinetics when particle sizes are between showed that if particle size 49 – 89µm, indicating that outside of this range kinetics is influence by particle size.

Results between the batch and column suggest that agitation has a greater influence than initially considered for metal extraction. The initial batch study was agitated for 15 minutes prior to settling for two hours. Despite the solvent completely saturating the sample in the column, the impact of channelling may have resulted in decreased contact time. Whereas mechanical agitation further increases the contact time between the solvent or chelator and the material which enhances metal extraction. Additionally, the batch study was completed at

12.5% (w/v) whereas the column study was 7.5% (w/v). The higher solid to liquid ratio further provides more surface area for potential metal-solvent/chelator complexes. The column study results indicate that more intense mechanical processing would be required to ensure good uniform filtration of the solvent or chelator in a passive system. It can be reasonably predicted that with additional agitation and greater solid to liquid ratios, metal extraction yields from the column will match or be greater than those achieved in the batch study.

Across batch, column, and the sequential study, ChCl-EG remained the most effective DES. Results attribute the success of ChCl-EG to short HBD chains and low viscosity, as supported by Abbott et al., (2009). The most effective CA was dependent upon the study. In the batch study, GLDA was the most effective but in the column study NTA was the most effective. The notable difference between the studies is that the batch study was a closed anaerobic process whereas the column study was aerobic. This suggests the carboxyl functional group has more influence in aerobic conditions where oxygen can facilitate greater metal-chelator complexes than denticity. As seen in results in Rosillo-Lopez & Salzmann, (2018).

The metal extraction yields from goethite were lower than BOS-D in the batch and column studies. Goethite has a two-step metal extraction process; sorption followed by desorption. This can lead to hysteresis. If the study was completed over a longer course of time to account for hystersis, metal extraction may improve.

6.1.2 Sequential bioleaching to chemical leaching

The findings from chapter 3 and 4 informed the selection of DES and CA for the sequential study. Compared against EDTA as a control. Overall metal extraction on the BOS-D bioleaching residue was minimal. The maximum extracted was 4% using EDDS. The chosen DES, ChCl-EG and EDTA both extracted 1% of metals. there is no evidence that molar ratio or pH have influence on metal extraction as EDDS, ChCl-EG and EDTA are pH 4.

The bioleaching phase of this study extracted >35% of all metals with a high efficiency for rare earth lanthanides, 57% extraction. The extraction of rare earth lanthanides was 13% using EDDS despite only 4% of total metals being extracted. The residue did not undergo the same pre-treatment processes as Chapters 3 and 4. Lower extraction efficiencies could after bio-leaching could be due to no pre-treatment. For earlier batch and column studies organic matter was removed using a furnace at 550°C for two hours. This is for two reasons; organic matter can bind to metals reducing the efficiency of the DES and CA applied, and heat of BOS-D can improve the porosity and surface activity which further optimises potential metal extraction (Changalvaei et al., 2021). Therefor it is possible that organic material from the bio-leaching limited the extraction efficiency of the green solvents and chelators tested. To develop the process, treatment of the bioleaching residue before a solvometallurgical step should be introduced.

6.1.3 Techno-economic assessment of the solvometallurgical process

A business case for solvometallurgical and hydrometallurgy has been made in Table 6.1. The calculations are relevant for one cycle of experiments despite the ability of the deep eutectic solvents and chelating agents to be recycled. The economic assessment accounts for the extraction efficiencies and average commodity costs (accurate at the time of writing). The outcomes are outlined in Table 6.1.

The difference in potential revenue generated between BOS-D and goethite and batch and column studies reflect results found in chapters 3 and 4. ChCl-EG 1:1 remains the most effective and lucrative DES on BOS-D. In general, the batch study could generate more revenue across the array of DES and CA used, attributable to improved contact time and solid to liquid ratios, as previously discussed. However, in the column study, when ChCl-EG 1:1

and NTA pH 6 is applied, the potential revenue is 6 times as much as its corresponding result the batch study. This suggests efficiencies of these DES and CA in a more continuous system.

The BOS-D has more potential for-profit generation compared to goethite. If the methodology from chapter 3 was used across all available goethite on the site, the process would lose money across all DES and CA applied, with the exception of GLDA pH 8. The experimental design of chapter 4 is more effective for metal extraction from goethite and thus more revenue could be generated. However, the results from chapter 4 show that 3 times as much revenue could be generated from available BOS-D. This could be attributed to hysteresis in goethite reducing the extraction potential and the smaller particle size of BOS-D improving contact time due to increased surface area.

Based on the performance, efficiency and potential revenue generated, ChCl-EG 1:1 would be recommended for use on BOS-D like materials and GLDA pH 8 on goethite like materials if this study were to be scaled to a commercial operation.

Table 6.1 A techno-economic assessment of potential commercial revenue generated from batch and column studies using DES or CA

Average Commodity Price £/t					15,450.96
		BOS-D		**Goethite**	
DES/CA	**Condition**	**Potential Mass Extracted (t)**	**Potential extraction value (£)**	**Potential Mass Extracted (t)**	**Potential extraction value (£)**
ChCl-EG	1:1	20151520.5	5540815878	1.14057075	1364.193948
ChCl-EG	1:2	19827660	5455531851	1.707190607	1670.236916
ChCl-EG	2:1	19827660	5455531851	-	-
ChCl-MA	1:1	17675823.5	5007193104	1.134010607	1321.096148
ChCl-MA	1:2	16766634	4699757536	-	-
ChCl-MA	2:1	16766634	4699757536	2.046095464	2371.428649
ChCl-U	1:1	17680576.5	4872149718	-	-
ChCl-U	1:2	17676824	4762217352	-	-
ChCl-U	2:1	17676824	4762217352	-	-
GLDA	pH 4	6184645.5	2511663730	-	-
GLDA	pH 6	6489529	2268182776	-	-
GLDA	pH 8	6194614	2843141321	2.659988786	2480.824334
EDDS	pH 4	13196291	3844454848	2.201568964	2932.913977
EDDS	pH 6	4677489.5	1870581680	-	-
EDDS	pH 8	6487672	2133454071	-	-
NTA	pH 4	3749428.5	2179354762	-	-
NTA	pH 6	4965873.5	2311431360	2.790394929	2607.928977
NTA	pH 8	3120137	1805788852	-	-

Average Commodity Price £/t		15,450.96			
		BOS-D		**Goethite**	
DES/CA	**Condition**	**Potential Mass Extracted (t)**	**Potential extraction value (£)**	**Potential Mass Extracted (t)**	**Potential extraction value (£)**
ChCl-EG	1:1	30960435.43	5400904847	1.274054893	3598.26602
ChCl-EG	1:2	28131003.43	5266029085	1.099460786	946.2763661
ChCl-EG	2:1	29166666.86	5981965394	-	-
ChCl-MA	1:1	28154911.43	3336506282	1.939969071	1950.691935
ChCl-MA	1:2	28913078.86	4443314276	-	-
ChCl-MA	2:1	26498914.86	3784186327	2.145455143	2214.850485
ChCl-U	1:1	26425136	5594836740	-	-
ChCl-U	1:2	26445504.57	6291353392	-	-
ChCl-U	2:1	26541097.14	4843191838	-	-
GLDA	pH 4	9353521.143	2284487805	-	-
GLDA	pH 6	24863460.57	4683914086	-	-
GLDA	pH 8	16739718.29	4016558082	1.344323786	2602.509328
EDDS	pH 4	6319413.714	2078875751	0.849053036	2492.624827
EDDS	pH 6	11507654.86	2247397099	-	-
EDDS	pH 8	8126356.571	2447786045	-	-
NTA	pH 4	8353404.571	2786447910	-	-
NTA	pH 6	12445926.86	3455893862	1.934499214	2887.311134
NTA	pH 8	6482182.857	4062309675	-	-

38. Contribution to knowledge

This study assessed the extraction efficiencies of DES and CA on real world metalliferous wastes; goethite, blast oxide furnace slags. CA were more effective than DES on Goethite. DES were more effective than CA from BOS-D.

Table 6.2 Contributions to knowledge achieved by this study

Study	Confirmation of Literature	Developments Of Knowledge	New Findings
Theoretical Knowledge	DES and CA can be used to extract metals (Chapter 3, 4 and 5). Metals can be extracted from BOS-D and goethite (Chapter 3 and 4). Mass transfer *e.g.*, viscosity, influences metal extraction (Chapter 3 and 4). Functional groups *e.g.*, carboxyl, influences metal extraction (Chapter 3 and 4). Increased proticity improves metal extraction (Chapter 3 and 4). The length of the DES and CA influences metal extraction *e.g.*, denticity (Chapter 3 and 4). NTA is the most effective for rare earth lanthanide extraction (Chapter 4). Alkaline earth metals are extracted more from goethite in basic conditions (Chapter 4).	DES and CA can effectively extract metals from metalliferous waste (Chapter 3 and 4). The structure and adsorptive nature of goethite influences leaching mechanisms (Chapter 3 and 4). The optimised mass transfer characteristics of ChCl-EG are more effective than the improved oxidation provided by ChCl-MA (Chapter 3 and 4). The preferred solvolysis mechanism of Si was found to be redoxlysis or acidolysis from goethite (Chapter 4).	The comparison of extraction efficiencies between DES and CA on the same metalliferous material (Chapter 3 and 4). The economic benefits of using CA and DES on past metallurgical site deposits (Chapter 3 and 4). The extraction efficiencies of CA and DES rivalled EDTA across a suite of critical metals; lithium, nickel, aluminum and cobalt (Chapter 4). CA are more effective than DES on goethite and DES are more effective than CA on BOS-D (Chapter 3 and 4). Redefine past metallurgical site deposits to resource extraction opportunities (Chapter 3, 4 and 5). A bioleaching to solvoleaching process can extract rare earth elements (Chapter 5).

Empirical Evidence	56% of Zn was extracted from electric furnace dust, comparable to Zn extraction from BOS-D using DES, 56% (Youcai & Stanforth, 2000) (Chapter 3). ChCl-EG 1:1 extracted 63% of Cu, this aligns with Qin et al., (2020) (Chapter 4). Rare earth lanthanides absorbed onto goethite precipitates rather than DES or CA (Chapter 3 and 4). EDDS, EDTA and ChCl-EG extracted <0.01% of Mn and <0.5% of Cu and Co. Results in Yue et al., (2023), where Cu and Co metal extraction is reduced when the concentration of Mn decreased (Chapter 5).	Li is extracted from BOS-D the most effectively with ChCl-EG 1:2, 54% and 64% Batch and column studies, respectively. This is supported by Chen et al., (2021) whom extracted 62% of Li from Li battery cathode (Chapter 3 and 4). NTA pH 4 extracted 82% of Cd from BOS-D which is similar to Saini et al., (2019) where 90% of Cd was extracted from charcoal powder (Chapter 4). Li extraction is not enhanced with high Co extraction as stated in Gupta et al., (2022) (Chapter 3).	DES had greater extraction efficiencies in 23 of the 25 metals analysed compared to CA on BOS-D (Chapter 3). In DES, 1:1 was the most effective condition for metal extraction from BOS-D, 58% (Chapter 3). In BOS-D, EDDS pH 4 was the most effective CA for metal extraction, 46% and ChCl-EG the most effective DES for metal extraction, 61% (Chapter 3). Metal extraction in batch BOS-D was greater using DES compared to EDTA, 51% and 48% respectively (Chapter 3). EDTA is more effective than DES and CA for metal extraction from goethite in batch studies, 48%, 18% and 27% respectively (Chapter 3). The extraction of metals from BOS-D was greater than goethite 51% and 22% respectively (Chapter 3). In all pH levels, NTA extracted 35% of metals from BOS-D, the most effective out of chosen CA and DES (Chapter 4). The chelation affinity hierarchy of EDTA was Fe > Cd > Cr > Zn in BOS-D (Chapter 4).

			ChCl-EG was the most effective DES on BOS-D, 32% across all conditions (Chapter 4). Rare earth lanthanides chelated in slightly acidic conditions, 37% in pH 6 from BOS-D (Chapter 4). The available BOS-D could provide enough Co for 26 cars while available goethite could provide enough for 84 cars using GLDA and NTA in pH 6 (Chapter 4).
Methodology	Batch and column studies methods can be used to effectively extract metals (Chapter 3 and 4). Particle size influences leaching kinetics (Chapter 3 and 4). Metals are extracted more from goethite in higher pH values (Chapter 3). NTA is more effective at neutral to basic conditions (Chapter 4).	Varying ratios of hydrogen bond acceptors and hydrogen bond donators in DES was assessed (Chapter 3 and 4). Varying pH levels in CA were assessed (Chapter 3 and 4). Metal extraction was greater using batch methods compared to column methods (Chapter 3 and 4).	pH had little influence in metal extraction from goethite (Chapter 3). Low pH was more effective than higher pH for metal extraction from BOS-D (Chapter 3).

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39. Future work

6.1.4 Optimise the solvoleaching process

The optimisation of the solvoleaching process will further enhance the extraction efficiencies of DES and CA. This includes varying the residence time, agitation, and temperature to optimise the operational conditions to maximise the extraction efficiency of green chelators and solvents.

Higher temperature can increase the activation energy of the chemical phase greater to that of the physical phase subsequently increasing reaction rate (Faraji et al., 2020). The desorption process in goethite is accelerated at higher temperatures, this could overcome potential hysteresis promoting potential metal extraction (Fischer et al., 2007).

Agitation improves the contact time, coupled with recirculation of green solvents and chelators the extraction efficiency could be improved.

6.1.5 A cascading leaching process

Though the metal extraction of DES and CA in chapter 5 were minimal, the reverse of the process e.g., solvoleaching to bioleaching, should be explored. The DES and CA may alter the chemical composition of the metalliferous material, possibly making metals more bioavailable. Alternate solvo-bioleaching steps could extract metals otherwise not extractable by the other process.

As previously stated, agitation can enhance metal extraction. A series of cascading reaction, with differing agitation levels, pH (CA), molar ratios (DES), and temperatures could facilitate the leaching environment favoured by metal or metal type advancing extraction.

6.1.6 A comprehensive techno-economic assessment

The ability of DES and CA to extract metals from BOS-D and goethite has been demonstrated. The potential commercial benefits have been acknowledged in Chapters 3 and 4. Development of a pilot study would inform a life cycle assessment to provide a comprehensive techno-economic assessment for green solvometallurgy.

6.1.7 Metal recovery

Sustainable metal recovery options from the leachate must be considered to maintain the environmental benefits of this process. Electrocoagulation is a promising option due to its low power consumption and minimal retention time. Reverse osmosis systems and UV water purifiers are used to decontaminate drinking water and could be developed for metal recovery from leachate.

40. References

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7. Conclusions

41. Contribution to knowledge

As discussed in Chapter 7, this work has contributed to further the understanding of metal extraction opportunities using DES and CA from metalliferous waste and has compared the metal extraction possibilities from two types of past metallurgical site deposits; BOS-D and goethite. The extraction efficiencies of DES and CA were compared on the same material; DES more efficient than CA for metal extraction from BOS-D and CA was more efficient in goethite. An initial economic assessment demonstrates the feasibility of the application of DES and CA on past metallurgical sites, this is reflective of the results. The principal outcome of this study demonstrates that is it possible to extraction metals from contaminating past metallurgical site deposits reducing the legacy of pollution whilst generating a potential revenue.

Table 6.2 has summarised the contribution the knowledge from Chapters 3, 4 and 5.

42. Conclusions

The conclusions detailed are correspond to the project objectives stated in Chapter 1, with the exception of the critical review in Chapter 2 (Objective 1).

Objective 2: To investigate the potential for metal extraction from blast oxide furnace slags and goethite cake using "green solvents" through batch and column chemical leaching.

- Metal extraction was 29% greater from BOS-D than goethite in batch and 6% in column studies.
- DES had greater extraction efficiencies in 23 of the 25 metals analysed compared to CA on BOS-D in batch studies.
- Metal extraction in BOS-D using DES was 51% compared to 48% when using EDTA.

- ChCl-EG 1:1 was the most effective condition in BOS-D across batch and column studies, 61% and 24%.
- GLDA pH 8 was the most effective condition for metal extraction in the batch goethite study, 30%.
- NTA pH 6 was the most effective condition for metal extraction in the batch goethite study, 28%.
- EDTA is more effective than DES and CA for metal extraction from goethite in batch studies, 48%, 18% and 27% respectively

Objective 3: To evaluate the efficiency of sequential bioleaching to chemical leaching methods for metal removal and provide recommendations for scaling up the process.

- Across 25 metals, EDDS pH 4 extracted 4% of metals from BOS-D bioleaching residue.
- *A. ferrooxidans* extracted 57% of rare earth elements from initial BOS-D.
- EDDS pH 4 extracted 13% of rare earth elements post-bioleaching with *A. ferrooxidans.*
- EDTA pH 4 and ChCl-EG 1:1 both extracted 1% of metals from BOS-D bioleaching residue.
- Recommendation to change the sequence of leaching to solvoleaching using ChCl-EG 1:1 to bioleaching using *A. ferrooxidans.*

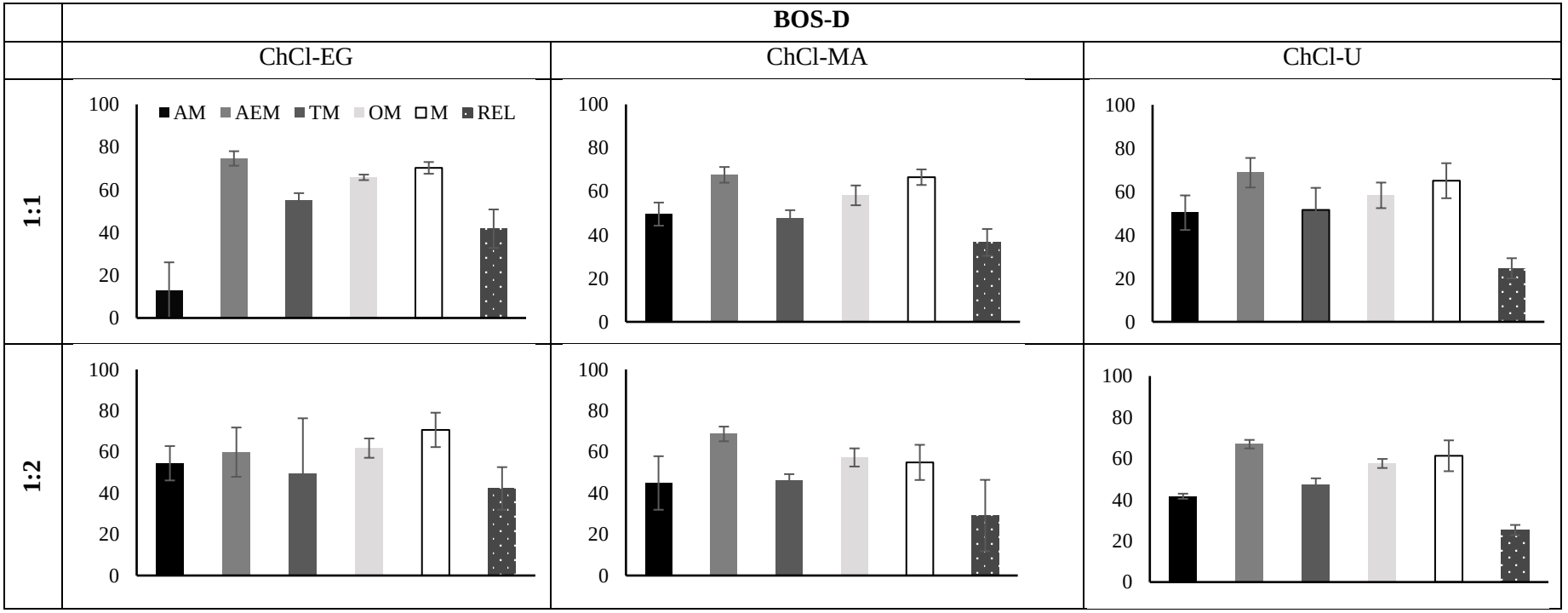
Objective 4: To provide a techno-economic assessment of the solvometallurgical process.

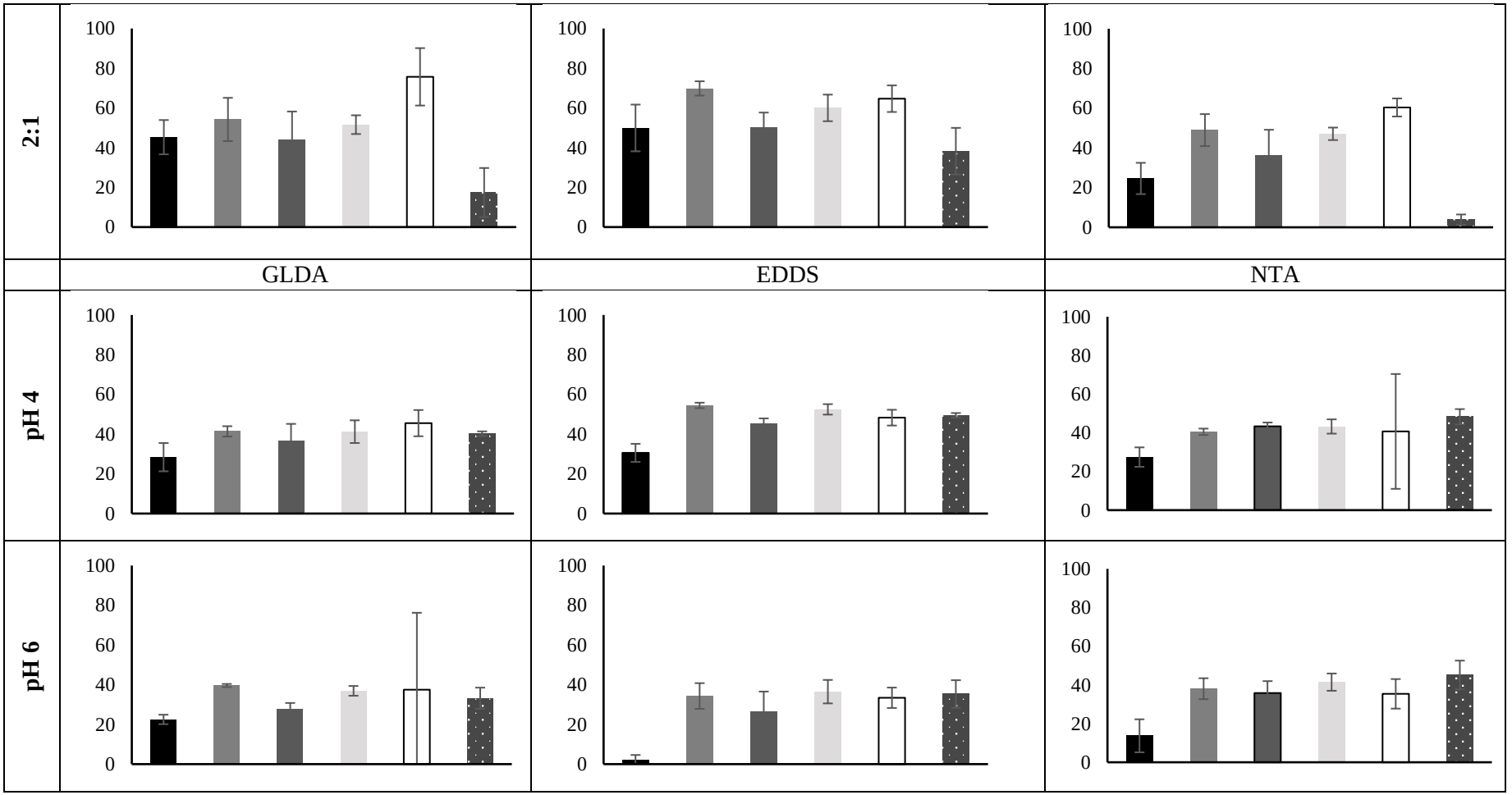
- There is economic benefits from applying DES and CA to BOS-D and goethite
- The extracted metals could general enough potential revenue to offset treatment costs.
- DES have the potential to be more profitable when applied to BOS-D and CA to goethite.

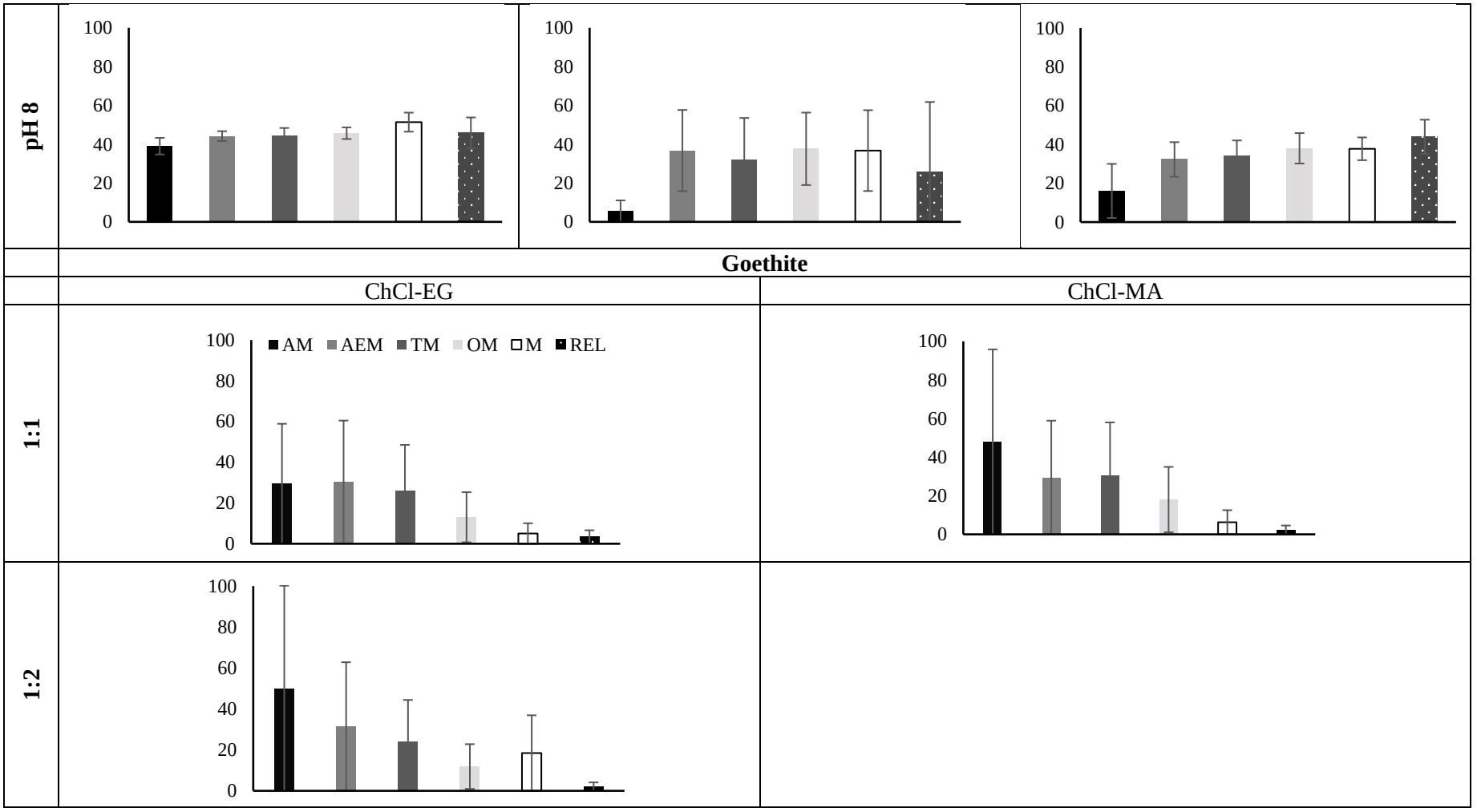
Appendices

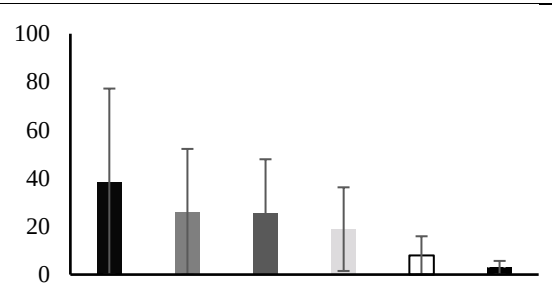
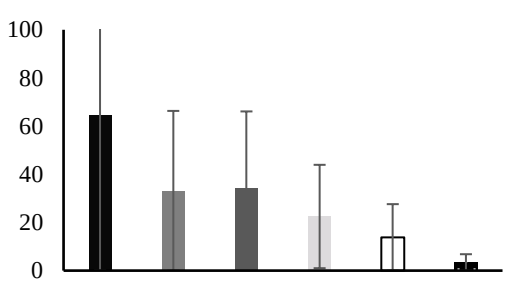
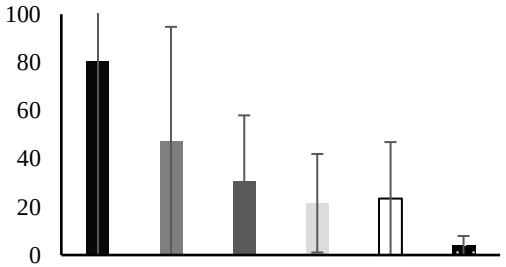
43. Appendix 1 Comparison of metal extraction by group from BOS-D and goethite in batch studies

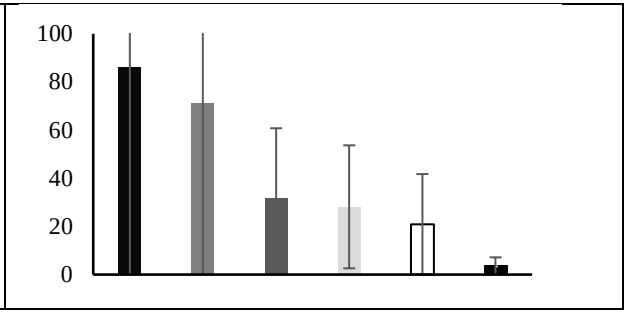
Table A1 Metal group extraction by solvent and condition from BOS and goethite in batch. AM = Alkaline Metals, AEM = Alkaline Earth Metals, TM = Transition Metals, OM = Other Metals, M = Metalloids, REL = Rare Earth Lanthanides (bars represent standard deviation).




2:1
pH 4
pH 6
GLDA
EDDS
NTA
100
80
60
40
20
0


pH 8
100
80
60
40
20
0
Goethite
ChCl-EG
ChCl-MA
1:1
1:2
AM
AEM
TM
OM
M
REL

2:1			
	EDDS	NTA	GLDA
PH 4			
PH 6			

PH 8			

44. Appendix 2 Metal group extraction from BOS-D and goethite in batch studies

Table A2 Metal group extraction using deep eutectic solvents and chelating agents on BOS-D and goethite in batch.

Solvent mixture condition		**Element group mass (mg)**											
		Alkaline Metals (Li)	**Alkaline Metals** (Standard deviation)	**Alkaline Earth Metals** (Mg, Ba)	**Alkaline Earth Metals** (Standard deviation)	**Transition Metals** (Fe, Cu, Sc, V, Cr, Mn, Co, Ni, Y, Mo, Ir)	**Transition Metals** (Standard deviation)	**Other Metals** (Zn, Pb, Al, Ga, Cd)	**Other Metals** (Standard deviation)	**Metalloids** (Si, B, As, Sb)	**Metalloids** (Standard deviation)	**Rare Earth Lanthanides** (La, Ce, Nd)	**Rare Earth Lanthanides** (Standard deviation)
BOS-D													
ChCl-EG	1:1	450.717	99.189	646.658	74.310	611.945	30.488	611.680	25.152	674.660	26.852	449.162	38.693
ChCl-EG	1:2	522.941	7.654	574.675	150.955	529.977	88.777	603.404	45.070	678.261	80.127	405.330	99.432
ChCl-EG	2:1	434.619	77.183	520.266	107.420	462.737	141.824	515.495	45.377	726.366	138.880	210.309	118.728
ChCl-MA	1:1	475.593	43.375	648.984	38.421	525.107	37.419	533.377	43.675	638.543	34.402	350.524	59.397
ChCl-MA	1:2	430.977	19.774	659.479	86.637	506.094	31.937	524.395	42.268	555.487	53.271	339.537	106.021
ChCl-MA	2:1	479.235	52.944	670.240	64.617	526.155	72.749	560.238	64.341	620.657	64.230	368.464	111.130
ChCl-U	1:1	482.877	80.372	659.614	63.414	496.747	97.673	531.093	56.641	624.319	77.474	272.753	15.362
ChCl-U	1:2	400.018	3.827	642.508	23.833	467.899	21.014	529.270	21.059	588.371	71.801	246.305	19.889
ChCl-U	2:1	236.121	5.741	469.795	112.168	361.866	23.368	427.164	30.244	579.248	43.609	170.194	21.172
GLDA	4	272.543	20.412	397.281	48.885	322.166	81.378	367.841	54.863	436.988	63.436	385.850	11.459
GLDA	6	216.089	14.033	380.130	11.835	257.951	28.462	312.870	23.627	402.020	41.884	318.739	51.043
GLDA	8	374.523	7.654	424.223	40.897	379.738	39.029	412.527	28.775	493.388	47.098	440.673	75.811
EDDS	4	293.485	4.465	522.746	32.738	425.340	26.847	470.133	25.370	463.672	38.119	475.039	10.857
EDDS	6	92.875	95.043	329.353	25.812	236.889	95.750	311.664	49.990	320.761	49.319	338.968	66.769
EDDS	8	427.954	211.774	367.118	107.282	304.929	193.810	403.126	113.395	396.922	115.798	441.527	151.575
NTA	4	263.437	17.860	389.014	30.932	356.918	18.917	374.713	35.390	442.605	16.739	463.627	38.011
NTA	6	131.409	71.442	365.175	57.302	309.806	59.149	353.023	42.785	361.826	46.958	433.263	71.281
NTA	8	154.173	121.834	309.760	91.643	289.191	73.787	315.509	75.340	378.476	47.040	422.095	84.518
Goethite													

ChCl-EG	1:1	1.017	0.368	0.875	0.378	0.389	0.325	0.342	0.162	0.256	0.063	0.045	0.041
ChCl-EG	1:2	0.806	0.626	0.414	0.393	0.428	0.301	0.281	0.148	0.173	0.231	0.043	0.026
ChCl-MA	1:1	0.687	0.599	0.485	0.368	0.353	0.382	0.216	0.225	0.178	0.078	0.045	0.029
ChCl-MA	2:1	0.613	0.483	0.380	0.326	0.341	0.322	0.187	0.236	0.154	0.099	0.027	0.035
EDDS	4	0.512	0.806	0.342	0.414	0.341	0.428	0.230	0.281	0.095	0.173	0.030	0.043
NTA	6	0.788	1.006	0.601	0.592	0.361	0.381	0.274	0.269	0.164	0.293	0.045	0.050
GLDA	8	0.780	1.077	0.609	0.893	0.360	0.398	0.294	0.352	0.180	0.261	0.040	0.045

45. Appendix 3 Metal group extraction from BOS-D and goethite in column studies

Table A3 Metal group extraction using DES and CA on BOS-D and goethite in column studies.

Leaching Condition	Element group mass (mg)											
	Alkaline Metals (Li)	**Alkaline Metals** (Standard deviation)	**Alkaline Earth Metals** (Mg, Ba)	**Alkaline Earth Metals** (Standard deviation)	**Transition Metals** (Fe, Cu, Sc, V, Cr, Mn, Co, Ni, Y, Mo, Ir)	**Transition Metals** (Standard deviation)	**Other Metals** (Zn, Pb, Al, Ga, Cd)	**Other Metals** (Standard deviation)	**Metalloids** (Si, B, As, Sb)	**Metalloids** (Standard deviation)	**Rare Earth Lanthanides** (La, Ce, Nd)	**Rare Earth Lanthanides** (Standard deviation)
BOS-D												
DES1-A	167.10	116.72	310328.25	20224.75	696611.04	588955.19	485415.11	91924.10	7886.07	7066.83	261.87	18.65
DES1-B	63.57	24.37	299724.25	19325.25	1162915.17	69146.83	619813.81	11857.60	9128.77	1225.63	266.50	6.98
DES1-C	29.59	11.27	275865.25	31069.75	956143.26	115652.91	615989.42	23980.61	12376.85	3226.44	243.82	3.27
DES2-A	21.25	6.78	220012.00	102605.00	1089970.12	104257.14	649386.46	8217.19	18001.98	469.66	237.99	3.51
DES2-B	16.40	4.31	201497.25	96989.75	933021.90	14930.53	631079.91	8764.30	16999.79	640.35	236.67	0.54
DES2-C	50.20	34.99	144973.25	67834.75	1321477.16	349336.98	611355.61	23761.40	16927.94	1605.70	242.71	3.18
DES3-A	55.24	3.21	272674.25	85165.25	1517993.50	787341.82	620357.91	30346.70	18297.63	783.04	235.17	5.36
DES3-B	22.17	11.54	268417.75	94857.25	1484358.22	552886.84	544046.71	34939.30	13123.45	1926.24	271.97	30.97
DES3-C	11.64	8.51	261723.75	46937.25	1312840.04	498842.57	606916.11	6616.30	17082.95	1313.14	262.77	33.98
CA1-4	26.47	4.49	279870.25	5315.25	4314636.79	1069370.56	437754.21	33334.60	15636.72	1287.83	300.33	1.43
CA1-6	16.03	0.27	321938.75	5402.75	1733510.73	9412.94	546323.71	13129.30	8479.50	6529.66	297.07	1.82
CA1-8	47.45	35.54	137242.25	739.75	1742500.12	64730.00	600474.91	19802.10	5696.18	698.01	304.68	8.43
CA2-4	17.40	1.28	231260.75	3322.75	3380127.77	536453.49	472263.91	11658.90	4123.33	329.66	225.34	4.94
CA2-6	33.16	4.58	180604.25	55609.75	2497795.13	1185069.75	431705.31	82566.90	12742.30	7199.31	192.00	53.73
CA2-8	22.81	2.84	286262.75	4507.75	1516517.38	1325546.00	528765.21	19926.00	14291.99	2158.80	225.96	8.37
CA3-4	23.45	7.33	166118.75	48832.25	2662640.58	1071899.30	481744.61	44672.20	12263.73	4717.69	179.35	34.51
CA3-6	35.08	6.32	151844.75	117812.25	2711877.44	2602346.46	492901.41	83129.00	9195.03	8513.01	191.91	41.51
CA3-8	16.58	3.57	263815.75	10727.25	5336030.98	50961.80	531064.81	30976.60	17489.09	2679.25	156.84	23.84
Goethite												

DES1-A	2.50	0.00	332.11	0.00	26881.91	11.86	26137.92	34.20	2309.74	1.45	4.89	0.00
DES1-B	2.82	0.07	337.92	8.26	25857.52	703.35	28177.40	341.24	2216.15	7.15	4.94	0.01
DES2-A	2.38	0.18	304.61	21.01	19821.63	3738.30	26850.10	1608.83	1838.23	420.27	4.96	0.05
DES2-C	2.04	0.24	276.88	19.78	18632.44	5599.89	26398.76	1617.48	1973.30	168.95	4.98	0.03
CA2-4	2.82	0.04	337.05	6.75	24457.95	297.93	28670.91	110.99	2128.47	13.26	4.91	0.01
CA3-6	2.71	0.04	318.95	0.79	19235.65	1830.10	26676.35	803.82	1956.42	54.38	4.78	0.01
CA1-8	2.79	0.05	332.53	11.40	29070.44	393.62	28497.18	858.01	2291.71	7.94	4.96	0.02