

## Research article

## Assessing metal extraction from metalliferous waste: A study using deep eutectic solvents and chelating agents vs. ethylenediaminetetraacetic acid

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## 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) from heap piles at their respective sites and characterised via ICP-MS. 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 conditions e.g., temperature and agitation combined with a cascading leaching process could further enhance metal extraction potential.

## 1. 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 and 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

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(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 compares traditionally environmentally hazardous metal extraction processes e.g., EDTA, with 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 meet targets under circular economy and net zero strategies.

## 2. Materials and methods

### 2.1. Metalliferous waste collection and characterisation

The BOS-D samples were collected manually by randomly sampling 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 (Table 1), the samples were furnace for 550 °C for 2 h to remove biodegradable material (Cao et al., 2018).

Characterisation was carried out in duplicate with the values shown in Table 1 highlighting average concentrations.

### 2.2. 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

**Table 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     |
| Fe (mg/kg)                    | 589,000 | 305,000  |
| Cu (mg/kg)                    | 168     | 30,600   |
| Zn (mg/kg)                    | 25,700  | 113,000  |
| Pb (mg/kg)                    | 2670    | 35,300   |
| Li (mg/kg)                    | 6       | 4        |
| Al (mg/kg)                    | 3140    | 16,400   |
| Cr (mg/kg)                    | 205     | 330      |
| Mn (mg/kg)                    | 8520    | 2200     |
| Co (mg/kg)                    | 13      | 14       |
| Ni (mg/kg)                    | 77      | 51       |
| Cd (mg/kg)                    | 83      | 608      |

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. The justification of testing parameters is derived from the best results observed in the previous studies (Almubarak et al., 2022; Li et al., 2019). All CA and DES conditions were tested in duplicates (Table 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). Initial batch test results from BOS-D column studies informed the

**Table 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 CA3-C                   |
|                        | EDTA      | pH 4     | BOS-D Goethite Control-B or G |
|                        |           | 1:1      | BOS-D Goethite DES1-A-B or G  |
|                        |           | 1:2      | BOS-D DES1-B                  |
| Deep Eutectic Solvents |           | 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                  |

solvents used for the goethite samples.

### 2.3. Experimental design

Polycarbonate and PVC columns were used to ensure resistance to chemical interactions, with an internal diameter of 10 cm (Fig. 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 (Fig. 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 (Fig. 1).

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 h using a peristaltic pump to maintain sample saturation. Each solvent condition was tested in duplicate. After 2 h, 50 mL of leachate was 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 Fig. 2.

### 2.4. Metals analysis

The metal content of the 50 leachate samples was determined using inductively coupled plasma mass spectrometry (ICP-MS) (Elan 9000 PerkinElmer 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 µg ml<sup>-1</sup>, 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<sup>-1</sup>. For the trace element and rare earth elements concentrations ranges were 0.01, 0.1, 0.5, 1, 2 µg ml<sup>-1</sup>. 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.

### 2.5. 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. Extraction efficiency has been used to describe the percentage of metal extracted from the original metal concentration.

## 3. Results and discussion

### 3.1. Evaluating the effectiveness 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

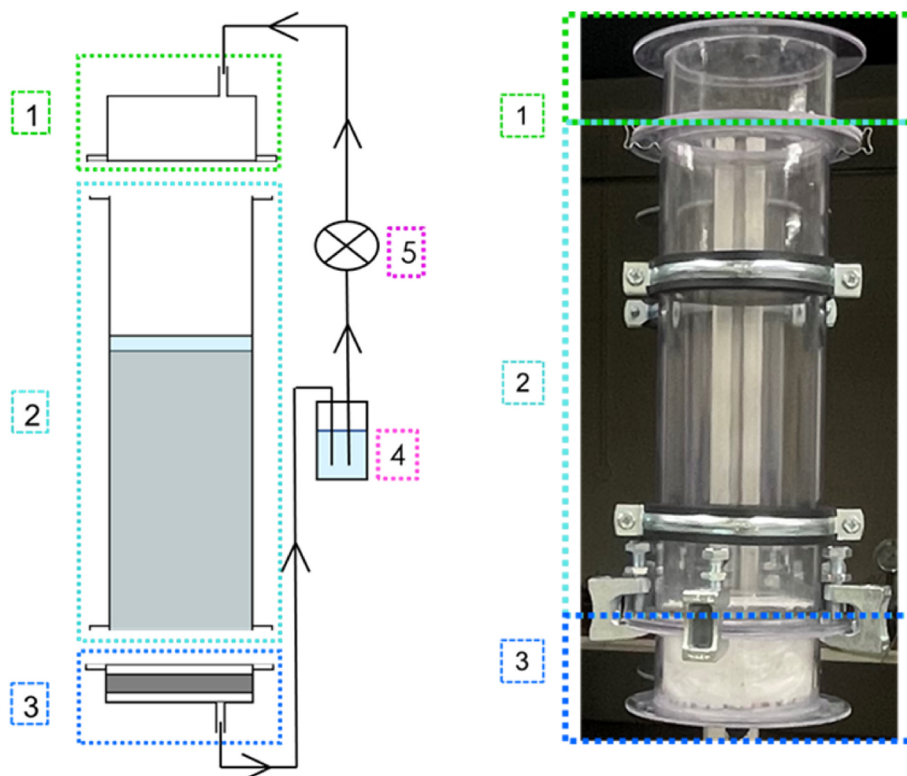


Fig. 1. Continuous column design. 1 - Top lid, 2 - working column, 3 - bottom lid, 4 - reservoir, 5 - peristaltic pump.

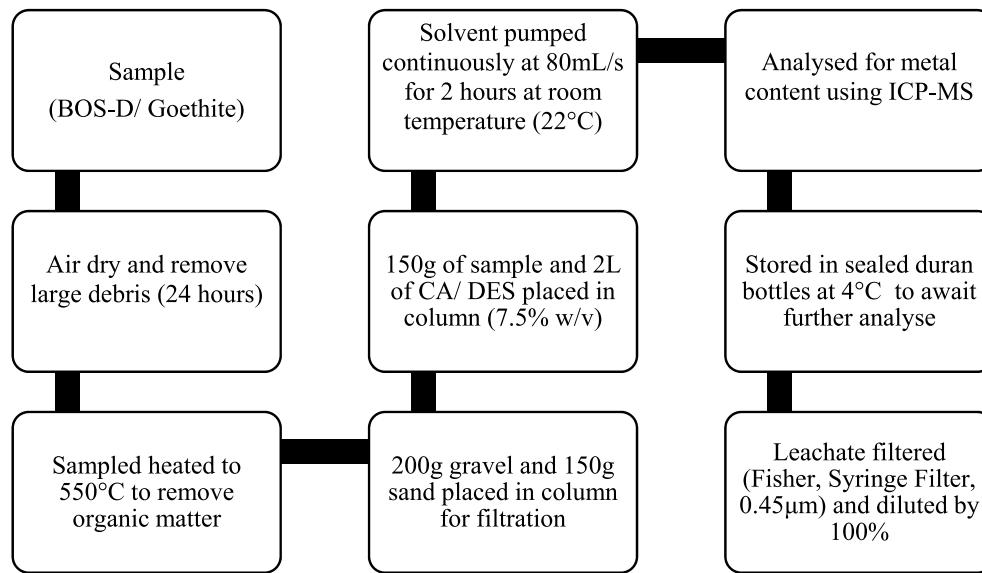


Fig. 2. Experimental design for the continuous column leaching study to extract metals using green solvents from past metallurgical site deposits.

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. (Fig. 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 (Fig. 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 (Nyamoto, 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% (Fig. 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 and Kołodyńska, 2016; Scheglova and 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 and 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 and Salzmann, 2018). CA2-6-B extracted 82% of Pb, CA3-4-B extracted 68% (Fig. 3). This supports the influence of proticity, specifically for Pb extraction (Scheglova and Popova, 2023).

Denticity refers to the number of groups donor 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 and 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

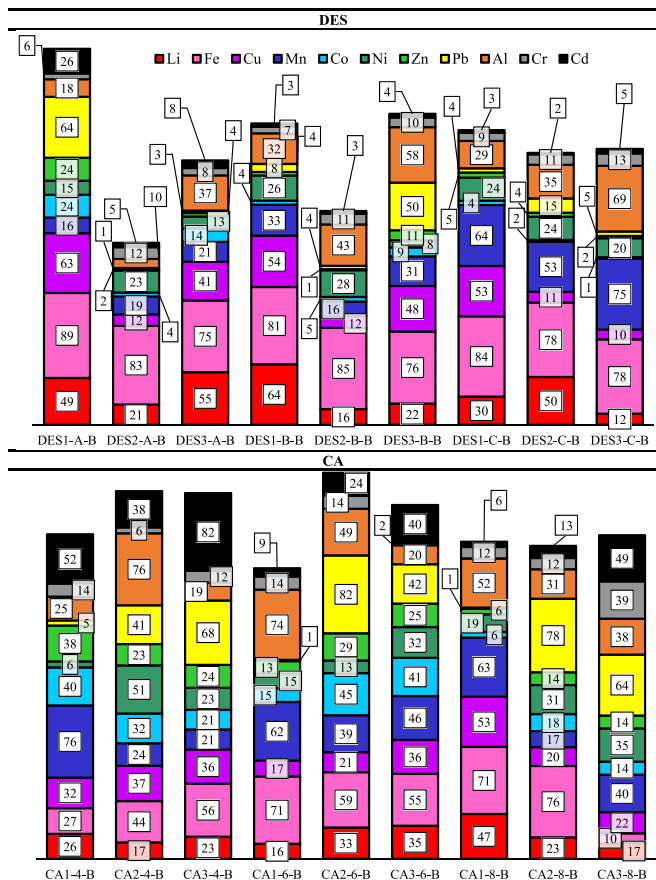


Fig. 3. Metal extraction efficiencies (%) as proportions using deep eutectic solvents in three ratios 1:1, 1:2 and 2:1 on blast oxide slag dust.

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 and 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 difference 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% (Fig. 3). Results are supported by (Qin et al., 2020). The HBD:HBA ratio can affect the strength of the DES hydrogen bond (Cui et al., 2017). 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 h and maintained at 7.5% (w/v) (Fig. 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 2 h 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 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 3**

Comparison of the most effective condition for critical metal extraction from BOS-D.

| Metal | DES1<br>(molar<br>ratio) | DES2<br>(molar<br>ratio) | DES3<br>(molar<br>ratio) | CA1<br>(pH) | CA2<br>(pH) | CA3<br>(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<br>& 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           |

### 3.2. 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% (Fig. 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 °C, continuous agitation for 30 min) 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

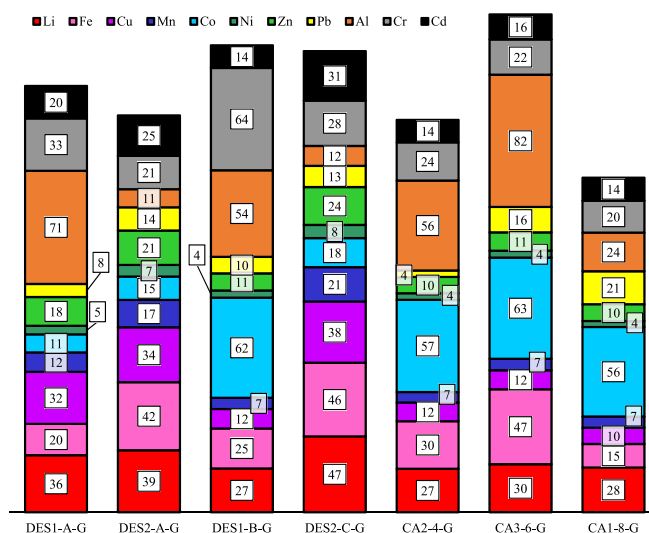


**Fig. 4.** Metal extraction efficiencies (%) by proportion, using deep eutectic solvents on goethite.

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 and Salzmann, 2018). The extraction of Fe was greatest with CA3-6-G (Fig. 4). 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 (Fig. 4). 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 (Fig. 4). 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% (Fig. 4). 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 and 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 due to 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).

### 3.3. Comparison of metal groups

#### 3.3.1. Blast oxide slag dust

Alkaline metals (Li) were the least extracted metal group using CA but the second most when DES were applied (Fig. 5). The most effective CA for Li extraction was CA1-C-B with 47%. Results align with (Zing and 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 and 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 (Fig. 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

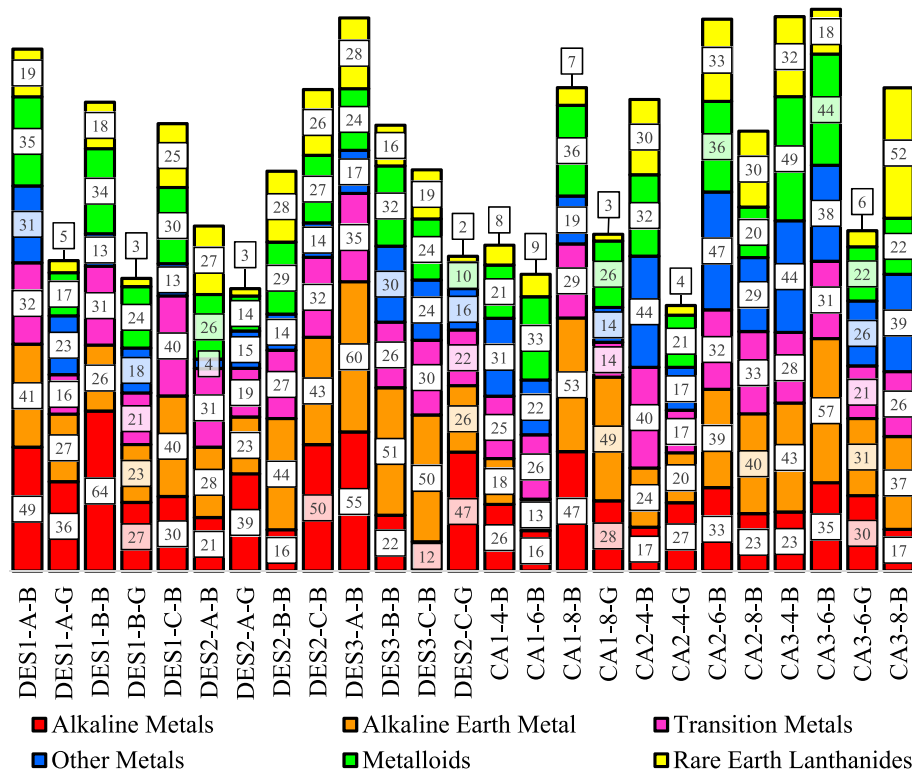


Fig. 5. Comparison of extraction efficiencies (%) for deep eutectic solvents (DES) and chelating agents (CA) grouped by metal type on blast oxide slag dust and Goethite. Data labels indicate the metal extraction yield (%). Calculated based on proportion of individual metal extraction within metal groups.

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  $\text{DES2} > \text{DES3} > \text{DES1}$ , 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  $\text{DES1 } 47\% > \text{DES3 } 30\% > \text{DES2 } 29\%$  (averaged across molar ratios) (Fig. 5). Results are supported by Chen et al. (2021) whom 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 (Fig. 5). The extraction of Pb was greater using CA than 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 AlOmar 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 (AlOmar 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 and Salzmänn, 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% (Fig. 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 (Fig. 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 and Salzmänn, 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 (Alcilar 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 donors 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 and 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 (Fig. 5). Lanthanides are known to be preferentially chelated in basic conditions and are known to be difficult to separate due to lanthanide contraction (Bart, 2023; Moldoveanu and 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 and 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).

### 3.3.2. 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 and 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 and 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 (Fig. 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 and Salzmänn, 2018; Salami and Adekola, 2002).

Unlike transition metals, alkali earth metal extraction decreased with increased acidity e.g., DES2-A-G which is pH 1 extracted 23% of alkaline earth metals (Fig. 5). Baldermann et al. (2020) found that Ba extraction is governed by surface complexation 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 presence 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% (Fig. 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 penetrate 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 likelihood 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 & Salzmänn (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% (Fig. 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 and Larachi, 2018). Studies have found that rare earth lanthanides can substitute for  $\text{Fe}^{3+}$  within the goethite structure (Dutrizac and 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 (Fig. 5). CA1-8-G was the most efficient across all metalloids extracting 26%. The extraction of Sb was negligible due to high affinity to goethite (Burton et al., 2020). CA1 is known to have an affinity to B (Pańczuk-Figura and 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 redoxolysis or acidolysis. DES2, has previously stated had the most efficient mass transport properties out of the DES owing to improved extraction efficiencies (Abbott et al., 2009).

Hysteresis can occur in the desorption of metals from goethite (Fischer et al., 2007). This study was conducted over 2 h. If the study was completed over a longer course of time, metal extractions could have improved to account for the hysteresis.

### 3.4. Economic assessment

The results from this study 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. Using the total available sample material present at the respective sites, the maximum extraction efficiency achieved in this study, the potential gross revenue of key metals necessary in renewable technologies and energy storage have been summarised in Table 4. The commodity price at the time of writing has been used to calculate the potential gross revenue of metal extraction from available BOS-D and goethite at their respective sites (Trading Focus Economics, 2023). The initial economic assessment does not account for relevant life cycle assessments or post-treatment and purification processes. It is a brief feasibility assessment and demonstrates the potential metals that could be recovered to offset treatment costs and provide a source of revenue. DES have the potential to be more profitable when applied to BOS-D and CA to goethite. In align with critical metal demand and green targets and initiative, the potential revenue demonstrated in Table 4 could improve socio-economic standards, alleviating pressure on existing raw extraction processes whilst generating more immediate stores (Huntington et al., 2022).

In general, the results in this study align with similar literature for metal extraction from metalliferous waste. However, there has been no previous study analysing the potential of applying DES or CA on material like BOS-D and goethite. This study has demonstrated that it is possible to extract metals using green functional chemistries and should be used to expand this area of research further. A study comparing a wider array of green CA and DES is needed to find a solvent/chelator that is more selective and efficient. Optimisation of the process to include increased temperature and time to overcome hysteresis in goethite, agitation and varying w/v ratio could improve extraction efficiencies with DES and CA.

## 4. 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

**Table 4**

A techno-economic assessment of potential commercial revenue generated from this study using DES or CA (commodity prices accurate at time of writing ([Focus Economics, 2023](#))).

| Available material (t) |                            |                                                         |       | BOS-D       | Goethite   |
|------------------------|----------------------------|---------------------------------------------------------|-------|-------------|------------|
|                        |                            |                                                         |       | 400,000,000 | 75,000,000 |
| Metal                  | Use                        |                                                         | Units |             |            |
| Li                     | Energy storage (batteries) | Most effective deep eutectic solvent or chelating agent | –     | DES1-B-B    |            |
|                        |                            | Extraction efficiency                                   | %     | 64          |            |
|                        |                            | Potential mass extracted                                | mt    | 0.05        |            |
|                        |                            | Potential Revenue                                       | £     | 11,869.19   |            |
| Co                     | Energy storage (batteries) | Most effective deep eutectic solvent or chelating agent | –     | CA2-6-B     | CA3-6-G    |
|                        |                            | Extraction efficiency                                   | %     | 45          | 65         |
|                        |                            | Potential mass extracted                                | mt    | 0.21        | 0.67       |
|                        |                            | Potential Revenue                                       | £     | 7018.20     | 22,391.40  |
| Cu                     | Wind power                 | Most effective deep eutectic solvent or chelating agent | –     | DES1-A-B    | DES2-A-B   |
|                        |                            | Extraction efficiency                                   | %     | 63          | 31         |
|                        |                            | Potential mass extracted                                | mt    | 4.3         | 3.7        |
|                        |                            | Potential Revenue                                       | £     | 29,057.93   | 25,003.32  |
| Zn                     | Wind Power                 | Most effective deep eutectic solvent or chelating agent | –     | CA1-4-B     |            |
|                        |                            | Extraction efficiency                                   | %     | 38          |            |
|                        |                            | Potential mass extracted                                | mt    | 130.5       |            |
|                        |                            | Potential Revenue                                       | £     | 313,222.19  |            |
| Al                     | Solar power                | Most effective deep eutectic solvent or chelating agent | –     |             | CA3-6-G    |
|                        |                            | Extraction efficiency                                   | %     |             | 82         |
|                        |                            | Potential mass extracted                                | mt    |             | 153.0      |
|                        |                            | Potential Revenue                                       | £     |             | 346,392.00 |

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.

#### CRedit authorship contribution statement

**Victoria E. Huntington:** Writing – original draft, Validation, Methodology, Investigation. **Frederic Coulon:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Stuart T. Wagland:** Writing – review & editing, Supervision, Resources, Project

administration, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Stuart Wagland reports financial support was provided by European Commission. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix 1

Summary of metal extraction (mg/kg) for deep eutectic solvents and chelating agents used on blast oxide slags dust and goethite.

**Table A1**  
Metal group extraction using DES and CA on BOS-D and goethite.

| 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) |
| <b>BOS-D</b>       |                         |                                      |                                |                                            |                                                              |                                        |                                   |                                   |                            |                                 |                                     |                                             |
| DES1-A             | 167.10                  | 116.72                               | 310,328.25                     | 20,224.75                                  | 696,611.04                                                   | 588,955.19                             | 485,415.11                        | 91,924.10                         | 7886.07                    | 7066.83                         | 261.87                              | 18.65                                       |
| DES1-B             | 63.57                   | 24.37                                | 299,724.25                     | 19,325.25                                  | 1,162,915.17                                                 | 69,146.83                              | 619,813.81                        | 11,857.60                         | 9128.77                    | 1225.63                         | 266.50                              | 6.98                                        |
| DES1-C             | 29.59                   | 11.27                                | 275,865.25                     | 31,069.75                                  | 956,143.26                                                   | 115,652.91                             | 615,989.42                        | 23,980.61                         | 12,376.85                  | 3226.44                         | 243.82                              | 3.27                                        |
| DES2-A             | 21.25                   | 6.78                                 | 220,012.00                     | 102,605.00                                 | 1,089,970.12                                                 | 104,257.14                             | 649,386.46                        | 8217.19                           | 18,001.98                  | 469.66                          | 237.99                              | 3.51                                        |
| DES2-B             | 16.40                   | 4.31                                 | 201,497.25                     | 96,989.75                                  | 933,021.90                                                   | 14,930.53                              | 631,079.91                        | 8764.30                           | 16,999.79                  | 640.35                          | 236.67                              | 0.54                                        |
| DES2-C             | 50.20                   | 34.99                                | 144,973.25                     | 67,834.75                                  | 1,321,477.16                                                 | 349,336.98                             | 611,355.61                        | 23,761.40                         | 16,927.94                  | 1605.70                         | 242.71                              | 3.18                                        |
| DES3-A             | 55.24                   | 3.21                                 | 272,674.25                     | 85,165.25                                  | 1,517,993.50                                                 | 787,341.82                             | 620,357.91                        | 30,346.70                         | 18,297.63                  | 783.04                          | 235.17                              | 5.36                                        |
| DES3-B             | 22.17                   | 11.54                                | 268,417.75                     | 94,857.25                                  | 1,484,358.22                                                 | 552,886.84                             | 544,046.71                        | 34,939.30                         | 13,123.45                  | 1926.24                         | 271.97                              | 30.97                                       |
| DES3-C             | 11.64                   | 8.51                                 | 261,723.75                     | 46,937.25                                  | 1,312,840.04                                                 | 498,842.57                             | 606,916.11                        | 6616.30                           | 17,082.95                  | 1313.14                         | 262.77                              | 33.98                                       |
| CA1-4              | 26.47                   | 4.49                                 | 279,870.25                     | 5315.25                                    | 4,314,636.79                                                 | 1,069,370.56                           | 437,754.21                        | 33,334.60                         | 15,636.72                  | 1287.83                         | 300.33                              | 1.43                                        |
| CA1-6              | 16.03                   | 0.27                                 | 321,938.75                     | 5402.75                                    | 1,733,510.73                                                 | 9412.94                                | 546,323.71                        | 13,129.30                         | 8479.50                    | 6529.66                         | 297.07                              | 1.82                                        |
| CA1-8              | 47.45                   | 35.54                                | 137,242.25                     | 739.75                                     | 1,742,500.12                                                 | 64,730.00                              | 600,474.91                        | 19,802.10                         | 5696.18                    | 698.01                          | 304.68                              | 8.43                                        |
| CA2-4              | 17.40                   | 1.28                                 | 231,260.75                     | 3322.75                                    | 3,380,127.77                                                 | 536,453.49                             | 472,263.91                        | 11,658.90                         | 4123.33                    | 329.66                          | 225.34                              | 4.94                                        |
| CA2-6              | 33.16                   | 4.58                                 | 180,604.25                     | 55,609.75                                  | 2,497,795.13                                                 | 1,185,069.75                           | 431,705.31                        | 82,566.90                         | 12,742.30                  | 7199.31                         | 192.00                              | 53.73                                       |
| CA2-8              | 22.81                   | 2.84                                 | 286,262.75                     | 4507.75                                    | 1,516,517.38                                                 | 1,325,546.00                           | 528,765.21                        | 19,926.00                         | 14,291.99                  | 2158.80                         | 225.96                              | 8.37                                        |
| CA3-4              | 23.45                   | 7.33                                 | 166,118.75                     | 48,832.25                                  | 2,662,640.58                                                 | 1,071,899.30                           | 481,744.61                        | 44,672.20                         | 12,263.73                  | 4717.69                         | 179.35                              | 34.51                                       |
| CA3-6              | 35.08                   | 6.32                                 | 151,844.75                     | 117,812.25                                 | 2,711,877.44                                                 | 2,602,346.46                           | 492,901.41                        | 83,129.00                         | 9195.03                    | 8513.01                         | 191.91                              | 41.51                                       |
| CA3-8              | 16.58                   | 3.57                                 | 263,815.75                     | 10,727.25                                  | 5,336,030.98                                                 | 50,961.80                              | 531,064.81                        | 30,976.60                         | 17,489.09                  | 2679.25                         | 156.84                              | 23.84                                       |
| <b>Goethite</b>    |                         |                                      |                                |                                            |                                                              |                                        |                                   |                                   |                            |                                 |                                     |                                             |
| DES1-A             | 2.50                    | 0.00                                 | 332.11                         | 0.00                                       | 26,881.91                                                    | 11.86                                  | 26,137.92                         | 34.20                             | 2309.74                    | 1.45                            | 4.89                                | 0.00                                        |
| DES1-B             | 2.82                    | 0.07                                 | 337.92                         | 8.26                                       | 25,857.52                                                    | 703.35                                 | 28,177.40                         | 341.24                            | 2216.15                    | 7.15                            | 4.94                                | 0.01                                        |
| DES2-A             | 2.38                    | 0.18                                 | 304.61                         | 21.01                                      | 19,821.63                                                    | 3738.30                                | 26,850.10                         | 1608.83                           | 1838.23                    | 420.27                          | 4.96                                | 0.05                                        |
| DES2-C             | 2.04                    | 0.24                                 | 276.88                         | 19.78                                      | 18,632.44                                                    | 5599.89                                | 26,398.76                         | 1617.48                           | 1973.30                    | 168.95                          | 4.98                                | 0.03                                        |
| CA2-4              | 2.82                    | 0.04                                 | 337.05                         | 6.75                                       | 24,457.95                                                    | 297.93                                 | 28,670.91                         | 110.99                            | 2128.47                    | 13.26                           | 4.91                                | 0.01                                        |
| CA3-6              | 2.71                    | 0.04                                 | 318.95                         | 0.79                                       | 19,235.65                                                    | 1830.10                                | 26,676.35                         | 803.82                            | 1956.42                    | 54.38                           | 4.78                                | 0.01                                        |
| CA1-8              | 2.79                    | 0.05                                 | 332.53                         | 11.40                                      | 29,070.44                                                    | 393.62                                 | 28,497.18                         | 858.01                            | 2291.71                    | 7.94                            | 4.96                                | 0.02                                        |

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## **Assessing metal extraction from metalliferous waste: A study using deep eutectic solvents and chelating agents vs. ethylenediaminetetraacetic acid**

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