Innovative Resource Recovery from Industrial Sites: A Critical Review

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Abstract: Global net-zero pledges are instigating a societal shift from a fossil-fuel-based economy to renewables. This change facilitates the use of batteries, solar photovoltaic (PV), wind turbines, etc., all of which are underpinned by critical metals. Raw metal extraction is not renewable and environmental pledges made by the 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 and 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; green solvents; renewable energy

1. Introduction

Critical metal demand has increased exponentially due to rapid industrialisation 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 the 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, and 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 aluminium [7]. In the last 30 years, the mining output for aluminium 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 a 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 wastes 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), is 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, such as lithium, are required immediately to meet the demand for 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 south waste of England [19]. Applying novel green technologies, e.g., green solvents, to a historic site to recover metals from 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 minimises 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 decarbonisation strategies, redevelop past metallurgical site deposits, and minimise the environmental impacts of recovery processes.
2. Contaminated Sites from Past Metallurgical Activity

2.1. 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 prioritised 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 and 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].

2.2. 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 5500 non-ferrous abandoned metal mines, and the 2008 Directory of Mines and Quarries identified 2455 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 organisation 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, and As [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.

2.3. 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 an important resource recovery site [15]. Traditional landfill mining is the process of extracting materials from d 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 valorisation 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]. In the EU, it has been estimated there are between 350,000 and 500,000 historic landfill sites representing a significant potential for metals, rare earth elements (REE) and secondary raw materials recovery [34]. Further to
this, there is a significant opportunity for waste-to-energy recovery [15]. However, implementation of ELFM on old and abandoned landfill sites remains relatively limited until now. 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 landfills, i.e., municipal solid waste, industrial waste, etc., climate, location, landfill type, age of waste and leachate pH [37]. Table 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, pelleting, 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.

When considering resource recovery from landfills, economic feasibility alone cannot demonstrate the economic value of landfill resource recovery [39]. Improved emerging extraction and separation processes, increased scarcity of resources and increased demand for land development increase landfill mining feasibility.

<table>
<thead>
<tr>
<th>Type of Landfill</th>
<th>Recovery Option</th>
<th>Limitations</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Soils</td>
<td>Soil Removal</td>
<td>Limited to small working areas</td>
<td>[40]</td>
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<tr>
<td></td>
<td></td>
<td>High initial costs</td>
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<td></td>
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<td>Extensive machinery required</td>
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<tr>
<td>Leachate</td>
<td>Coagulation/flocculation</td>
<td>High operating costs</td>
<td>[41,42]</td>
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<tr>
<td></td>
<td>Adsorption</td>
<td>Pollutant transfer between phases</td>
<td></td>
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<td></td>
<td>Membrane process</td>
<td>Low pollutant removal efficiency</td>
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<td></td>
<td></td>
<td>Low process performance</td>
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<tr>
<td>Waste Electrical and Electronic Equipment</td>
<td>Incineration</td>
<td>Secondary pollutants production</td>
<td>[43]</td>
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<tr>
<td></td>
<td>Acid leaching</td>
<td>Non-metal materials cannot be recycled</td>
<td></td>
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<tr>
<td></td>
<td>Hydraulic shaking bed separation</td>
<td>High operating costs</td>
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<td></td>
<td></td>
<td>Hard to recover metals except for copper</td>
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<tr>
<td></td>
<td></td>
<td>Toxic to the environment</td>
<td></td>
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<tr>
<td>Construction Waste</td>
<td>Landfill</td>
<td>High cost to recycle</td>
<td>[44]</td>
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<tr>
<td></td>
<td></td>
<td>Lack of enthusiasm to recover resources</td>
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<td></td>
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<td>Minimal communication between contractors</td>
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<tr>
<td>Wastewater</td>
<td>Membrane filtration</td>
<td>High operational costs</td>
<td>[45,46]</td>
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<td></td>
<td>Chemical precipitation</td>
<td>Not selective</td>
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<td></td>
<td>Biosorption</td>
<td>Toxic sludge generated</td>
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<td></td>
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<td>Disposal limits application (biosorption)</td>
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<tr>
<td>Hazardous Waste</td>
<td>Pyrolysis</td>
<td>Inefficient metal recovery</td>
<td>[47]</td>
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<td></td>
<td></td>
<td>Energy-intensive</td>
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<td></td>
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<td>High operation costs</td>
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<td></td>
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<td>Toxic dioxins and furans produced</td>
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3. Remediation of Contaminated Sites

The need to implement sustainable remediation technologies for the redevelopment of contaminated sites has been highlighted [48]. Several traditional remediation methods, including chemical, biological, and physical methods are well-established in the last two decades but still have shortcomings (Figure 1). When used independently of each other,
chemical and physical methods generate by-products that can be sourced from secondary sources of pollution, and they are not always cost-effective. Further to this, biological methods can be very time-consuming (can take several months to years) [49]. Recent research development has shown that using a combination of remediation methods or also called treatment train approaches allow one to overcome these drawbacks. However, the treatment train approaches are often focused on the removal or destruction of the contaminants rather than on the recovery opportunities. Recently, there has been a growing interest in recovering metals and other added value elements from various contaminated solid matrices (i.e., soil, slag, municipal solid waste, sludge, sediments), and the use of green chemistry is becoming a promising emerging approach for resource recovery from contaminated sites [34].

4. Management of Contaminated Soil

4.1. Physical Remediation Approaches

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 the 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 the 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].

Stabilisation of critical metals in soil can be achieved by applying high-temperature treatment (1400 °C–2000 °C) [44,50,52] with two main interactions: chemical bonding and encapsulation. Vitrification of industrial waste showed immobilisation 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) [57]. Temperature plays a vital role in metal recovery, showing low metal mobility at elevated temperatures [58]. Vitrification up to 1850 °C has been proven to efficiently stabilise 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 immobilised at 1350 °C whereas Zn, Ni, Mn, and Cu were immobilised 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 the 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].

4.2. Phytoremediation Approaches

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 for the removal of contaminants from the soil without destroying soil structure and fertility [61]. Festuca rubra L. is a commonly used grass, with recent research enhancing stabilisation 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 oxidised than contaminated soil. The main limitation is that most hyperaccumulators are specialised 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 minimise metal mobilisation in soil and contaminants by using plants to enable stabilisation [52,64]. Phytostabilisation does not remove the metal contaminants but accumulates them within the root and results in their 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 optimised stabilised 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].

Phytovolatilisation is a highly specialised mechanism. Subsequently, phytovolatilisation exploits genetically modified plants to assimilate metal into volatile forms which are then released into the atmosphere through plant transpiration as biomolecules [50,52]. Phytovolatilisation by Pteris vittata is the preferred biological remediation approach for As [67]. Phytovolatilisation 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 through 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].

4.3. Chemical Remediation Approaches

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 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 improvement is the most efficient strategy [62]. EDTA is known to be the most effective reagent for cationic metals (Cd, Pb, Co, Li, Hg, etc.,) [69]. While iron chloride (FeCl₃) 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-Na₂EDTA for soil washing heavy with removal efficiencies of 41.9% for As and 89.6% for Cd [71]. Metals are immobilised in the soil through three different reactions: complexation, precipitation, and adsorption [62]. This is achieved by the addition of immobilising 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 is efficient at absorbing metals with minimal environmental impact and 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 immobilisation 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 immobilisation 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].

5. 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 remedi-
ation 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 [73,77].

The absence of appropriate and sufficient recycling infrastructure has been highlighted as the main barrier to achieving a circular economy [78]. Using emerging green technologies for resource recovery will both improve sustainability and reduce the environmental impacts of processes involved in raw material extraction [79].

6. Emerging Extraction Techniques

Zeolites are naturally occurring, crystalline, hydrous silicates that can be modified depending on application [80]. The isomorphous substitution of silicon (Si$^{4+}$) by aluminium (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 [81]. 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 [80]. Clinoptilolite has been proven to be a good absorbent to remove metals from wastewater to below-drinking water standards [82]. 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 [82]. Yet, studies show that zeolites are unable to perform direct ion exchange as negatively charged ions limit permeability to anions [83]. Similar limitations in both natural and synthetic zeolites have been found in other studies [84,85].

Zeolites have been applied in the recovery of lithium; studies have successfully recovered critical metals from spent lithium iron phosphate (LiFePO$_4$) batteries using zeolites [86]. This demonstrates a novel approach for reutilising 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 [87]. Resulting in diminishing stocks of such materials, including lithium [88].

Microbial technology shows promise to recover critical metals whilst producing electricity as microbial fuel cells [89]. Microbial fuel cells are bio-electrochemical systems that convert chemical energy within organic matter into electrical energy using the metabolic activity of microorganisms and have relatively low costs and are sustainable [90,91]. Metal removal using microbial fuel cells was through; bio-reduction, bioaccumulation, biosorption and biomineralisation [92].

Although promising, microbial fuel cells cannot treat all metal ions [93]. Reduction is only performed when thermodynamically favourable, i.e., the target metal has a high standard potential [94]. If metals have comparable or lower redox potentials such as Ni, Pb, Cd and Zn [95], an external power supply is required for reduction. To overcome this, Cr reduction was successfully used to power another reactor to reduce Cd simultaneously [96]. Other studies used either a Cr or Cu microbial fuel cell to successfully drive Cd reduction
using no external energy supply [93,97]. 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 [93]. It has been found, with no exception, that all metals were proven to be toxic to S. oneidensis and at certain concentrations show inhibition of voltage [98]. Critical metals reduce anodic performance by inhibiting microbes due to metal toxicity [99]. Although <100 µg/L for Cu and <1 mg/L for Cd, voltage output was improved [98]. 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 [93]. The scaling up of microbial fuel cells is limited due to wastewater capacity and the fuel cell architecture [93].

7. Green Solvent Leaching

Established commercial processes for chemical leaching for metal resource recovery, such as from coal fly ash [100], electronic wastes [101], and sewage sludge [102] amongst other avenues. There are varying degrees of success dependent upon metal type (89% of rare earth metals (e.g., neodymium, cerium) [100], 90% of Au [101], and 46% of heavy metals [102]. 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” [103]. Neither sulphuric (H₂SO₄) nor nitric acid (HNO₃) are green solvents yet are extensively used to recover metals from industrial waste with varying efficiency. Table 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 H₂SO₄ through combination batch leaching strategies are very selective for Al but proved to be inefficient [104]. 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 [104]. More than 85% of Zn, Mg, Cu, and Al was recovered from municipal waste, e.g., bottom and fly ash (Table 2) [105]. Bottom and fly ash represent the most hazardous residue from municipal waste thus providing the largest concentration for secondary resource recovery [105]. It has been shown that H₂SO₄ changes the pH function leading to leaching performance in certain elements; Ca and Al respond well to the change, but Zn and Cr react with amphoteric behaviour [105]. When NaOH is used as a reagent for the simultaneous extraction of Zn and Mg from Zn-C alkaline. The Zn had a recovery yield of 82% and Mg 96% [106]. Sodium hydroxide works in acidic conditions which are appropriate for the metals concerned, however, Mn recovery could be further improved using H₂SO₄ to reduce insoluble Mn⁴⁺ to soluble Mn²⁺ [106]. The use of NaOH and H₂SO₄ can leave a legacy of pollution when used in situ, which can manifest in acid rain and high toxicity to the aquatic ecosystem [106].

Table 2. Critical metals and the recovery yield dependent upon extraction process.

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<thead>
<tr>
<th>Metal</th>
<th>Extraction Process</th>
<th>Source of Waste</th>
<th>Recovery Yield (%)</th>
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<tbody>
<tr>
<td>Al</td>
<td>Chemical Leaching (NaOH, HCl, H₂SO₄) Welding Slags</td>
<td>80.00</td>
<td>[104]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chemical Leaching (H₂SO₄)</td>
<td>Spent hydrodesulphurisation catalyst</td>
<td>11.03</td>
<td>[107]</td>
</tr>
<tr>
<td></td>
<td>Chemical Leaching (NaOH)</td>
<td>Calcined spent catalyst</td>
<td>89.00</td>
<td>[106]</td>
</tr>
<tr>
<td></td>
<td>Chemical Leaching (H₂SO₄)</td>
<td>Municipal solid waste</td>
<td>&gt;85.00</td>
<td>[105]</td>
</tr>
<tr>
<td>Cu</td>
<td>Chemical Leaching (H₂SO₄)</td>
<td>Municipal solid waste</td>
<td>&gt;85.00</td>
<td>[105]</td>
</tr>
<tr>
<td></td>
<td>Bioleaching</td>
<td>Steel slag</td>
<td>27.00</td>
<td>[106]</td>
</tr>
<tr>
<td></td>
<td>Chelating Agent (EDTA)</td>
<td>Artificially contaminated soil</td>
<td>93.90</td>
<td>[108]</td>
</tr>
<tr>
<td></td>
<td>Chemical Leaching (HNO₃)</td>
<td>Sulphide tailing</td>
<td>85.00</td>
<td>[109]</td>
</tr>
</tbody>
</table>
Table 2. Cont.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Extraction Process</th>
<th>Source of Waste</th>
<th>Recovery Yield (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Chemical Leaching (H₂SO₄)</td>
<td>Spent hydrodesulphurisation catalyst</td>
<td>96.25</td>
<td>[107]</td>
</tr>
<tr>
<td></td>
<td>Chemical Leaching (HNO₃)</td>
<td>Sulphide tailing</td>
<td>54.60</td>
<td>[109]</td>
</tr>
<tr>
<td>Mn</td>
<td>Chemical Leaching (NaOH)</td>
<td>Spent batteries</td>
<td>96.00</td>
<td>[110]</td>
</tr>
<tr>
<td></td>
<td>Chemical Leaching (H₂SO₄)</td>
<td>Municipal solid waste</td>
<td>&gt;85.00</td>
<td>[109]</td>
</tr>
<tr>
<td>Zn</td>
<td>Chemical Leaching (NaOH)</td>
<td>Spent batteries</td>
<td>82.00</td>
<td>[110]</td>
</tr>
<tr>
<td></td>
<td>Bioleaching</td>
<td>Steel slag</td>
<td>60.00</td>
<td>[111]</td>
</tr>
</tbody>
</table>

Deep eutectic solvents (DESs) are novel ionic liquids that obey the green chemistry principles and have been described as the most promising discoveries in green chemistry as an alternative solvent [108]. 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 [108]. As a result, DESs are 100% atom economy and due to hydrogen bonds, reactivity is limited reducing environmental impacts [109]. DESs can be infinitely reused, renewed, biodegradable and are non-toxic. The solvents have very low vapor pressure, low flammability, and high thermal stability [110]. Currently, the applicability of DESs is limited to liquid-liquid extraction (LLE) as DESs are predominantly hydrophilic and LLE is highly basic with low water content [112]. Studies are biased toward hydrophilic DESs rather than hydrophobic DESs. Hydrophobic DESs are an emerging novel concept, developed in 2015 [113]. When water is added to hydrophobic DESs, electrical conductivity and viscosity are improved as a result [114]. When the water content is above 2% w/w in hydrophobic DESs enhances mass transfer allowing the free flow of ions in the medium [115]. Like their hydrophilic counterparts, hydrophobic DESs are considered ‘green solvents’ but there has been little research to monitor their toxicity, vapor pressure, or bioavailability [116]. Of the DESs, the so-called natural DES e.g., ChCl:citric acid impose a high environmental impact as a result of water consumption and carbon dioxide emission from the fermentation phase to synthesise citric acid [114]. When comparing global warming potential, natural DES such as ChCl:citric acid, produced 4.3 kg CO₂-equ per kg which is 58% higher than ChCl:ethylene glycol [106]. However, methane oxidation has been used as a green alternative option for metal recovery [115] yet has a 25 global warming potential (per 100 years) which is significantly higher than DESs [117]. DESs are categorised under the umbrella term of ionic liquids which are considered a strong alternative to conventional solvents [111]. The difference between ionic liquids and DESs is the chemical formation and the source of their starting materials [118]. 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) [108]. Additionally, ionic liquids are usually 5–10 times more expensive than conventional solvents so have not met expectations as an alternative option [119]. 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 [115,120]. 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 [121]. The ideal, universal “green” solvent, applicable to all situations does not exist due to limitations regarding instability, applicability, and sustainability [122].

Batch tests have been advantageous as redox conditions can be controlled, the simple laboratory set-up required, and fast yielding results [123]. When compared to continuous column leaching, batch tests have a higher standard deviation, this is attributed to artefacts resulting from secondary compound mobilisation or cross-contamination [123]. Initially,
the batch approach underpredicts effluent concentrations during percolation, yet long-term over-estimate concentrations [123].

Packed column studies are relatively simple to operate—low initial and operational costs, no moving parts, and a limited facility footprint [122]. Column leaching has been found to be suitable for both organic and inorganic compounds [124]. Though, pulsed columns apply mechanical energy, enhanced mass transfer from the generation of dispersed droplets [122]. This is supported by the German Institute for Standardisation. 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 [125]. 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 [123]. Limited studies explore the potential for using DESs to recover high yields (>85%) of critical metals from industrial slags, particularly blast oxide furnace slags.

Of the limited metal extraction using solvents in extraction column models, there is a focus on hydrodynamics and the prediction of mass transfer coefficients [122]. When modelling pack column extraction, there are two key models: the axial dispersion model and the population balance model (PBM) [122]. The axial dispersion model can be used to predict the overall mass transfer coefficient for samarium and gadolinium in an extraction column [126]. However, the axial dispersion model does not consider the change in the interfacial area due to droplet breakage and coalescence [122]. The PBM considers droplet dynamics due to coalescence and breakage [122]. Previous literature has highlighted extraction column modelling, but more consideration is necessary regarding droplet breakage, coalescence, and metal ion mass transfer.

8. Development Challenges and Growing Demand
8.1. Recovery of Metals to Meet Sustainable Development Goals

Sustainable development is at the core of resource resilience and management [127]. A CE business model falls into two groups: one that fosters reuse, and extended service life through repair, remanufacture, and upgrades, and the other as turning old resources into new resources by recycling [128]. Both models close the loop on resources and minimise waste (Figure 2). The current CE model extends conventional waste and by-product service life and recycles materials in applications where most of the economic value of the product has been lost [129]. The longer products remain in the inner circles of Figure 2 the more sustainable they become due to the demand for energy and fewer resources being lower in these stages. The inner circles demand fewer resources and energy. The time resources kept in the inner circles should be maximised.

Figure 2. Current concept for the circular economy model, adapted from [129]. Arrows represent flow of materials.
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 [130]. The main aim of the ‘Green Deal’ is the complete reduction in net emissions of greenhouse gases by 2050 in the whole Union [127]. 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 [127]. The emphasis is on mineral resource management and decoupling economic growth from resource usage [131]. Ensuring the security of raw materials depends on the country, due to the lack of native deposits, imports of materials are necessary [127]. Imports are not always secure due to both political and economic instability [132]. The European Institute of Innovation and Technology on Raw Materials was established in 2014 with three strategic goals: securing the supply of raw materials, designing innovative solutions, and closing material cycles [128]. A global shift towards a CE is crucial in the implementation of a resource-efficient and environmentally friendly approach to future material management [122]. 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” [133].

8.2. Political Perceptions

Access to critical metals is restricted by political, environmental, economic, legal, and social factors [134]. The high risk of supply disruption is not always implied from actual physical resources [44]. Additionally, there is an imbalance of exploitation and production on increased supply risk [135]. 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 [136]. In 2017, only three critical metals (tin, tungsten, and lead) were mined in the UK [130]. As there is a limited number of producers, this means that suppliers can intentionally limit supply and drive-up prices [44]. The supply risk is also a direct consequence of illegal mining and exploitation of raw materials [135]. 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 [137].

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 [138]. Implementing extended producer responsibility schemes to ensure manufacturers are responsible for the product’s entire life cycle, including disposal [134]. 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 regarding critical metal recovery [139,140].

9. 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 minimising 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.

**Author Contributions:** Conceptualisation, V.E.H., F.C. and S.T.W.; writing—original draft preparation, V.E.H.; writing—review and editing, S.T.W. and F.C.; visualisation, V.E.H.; supervision, S.T.W. and F.C.; project administration, S.T.W.; funding acquisition, S.T.W. and F.C. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the European Regional Development Fund as part of the Interreg Northwest Europe project “Regeneration of past metallurgical sites and deposits through innovative circularity for raw materials” (REGENERATIS) (NWE918).

**Acknowledgments:** The authors would like to thank Interreg Northwest Europe, European Regional Development Fund for supporting this research through the REGENERATIS project.

**Conflicts of Interest:** The authors declare no conflict of interest.

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