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Elemental sustainability: Towards the total recovery of scarce metals

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ABSTRACT

Some modern so-called low carbon technologies are actually broadening concerns over future elemental sustainability for a wide range of elements. In order to address the rapid dispersion of metals, such as indium and silver, we need to be more innovative in recovery technologies that essentially turn a waste into a resource. A multi-disciplinary blend of chemistry, extractive metallurgy, engineering and biotechnology is required to realise this ambition.

1. Background

Climate change and peak oil crises have been making headlines with increasing intensity over the past decade and consequently solutions are being sought to lessen our dependence on oil. With new legislation and key buzz phrases like "low carbon technology" and "a low carbon future" driving technological change, can we be assured that everyone in the world will be able to enjoy a sustainable, high standard of living in the future?

Unfortunately, there is a serious problem. As new technologies are developed to tackle one challenge we are creating another through resource deficit. Many of the new low carbon technologies that are being touted as our saviours; wind turbines, electric cars, energy saving light bulbs, fuel cells and catalytic converters, require rare and precious metals for their production [1]. But traditional supplies of these elements are running out. Reserves of indium for example, vital for LCD screens, solar cells and semiconductors, may be used up in 13 years [2]. Unlike oil there are no bio-derived alternatives for palladium or platinum. These are unique and finite elements and we are quickly dispersing them throughout our environment, making it more costly and difficult to recover them. Additionally, it is not just the elements we consider exotic that are getting more difficult to access, many more elements that play a crucial role in our lives (Table 1), including phosphorous, aluminium and copper, are being depleted at a remarkable rate (Fig. 1).

A key concern regarding the availability of these elements into the future is their abundance and ease of accessibility. Currently, the majority are mined and extracted from primary ore in highly energy intensive processes that require a sufficient concentration of the element of interest. Fig. 2 shows the distribution of these elements across the globe. It is evident that concentrations of these elements are localised in limited areas, for example, South Africa possesses 89% of the worlds platinum group metals (PGM's) reserves. As oil is to the Middle East so elements will become to their locations as demand continues to increase. China has already realised this potential and now provides more than 95% of the world's supply of rare-earth metals [4]. This raises issues about security of supply. Countries whose manufacturing or technology base depends on imported metals are beginning to look for alternative sources. Other countries and companies, including Toyota, dependent on rare earths are racing to secure control of mines in Australia, South Africa and Greenland [4]. Current methods of mining also have a considerable impact on both the environment and our health. The discharge and dispersion of mining waste has led to elevated levels of metals in surrounding soil and water courses, resulting in destruction of vegetation and crops. This contamination can also enter the food chain due to initial uptake by edible plants [5]. In spite of the inherent disadvantages of current techniques, the concentrations of elements in the ores are so low that more expensive, milder methods would reduce profit margins and make recovery economically unviable.

We have only to study the recent trends in the price of many metals to realise that demand is catching up with the supply. The price of indium rose a staggering 800% in 6 years from approximately \$85/kg in 2002 [7] to \$685/kg in early 2008 [8]. As the

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Table 1
Elements with the lowest remaining reserves, their main uses and their percentage supply supported by recycling [3].

Element	Uses and reliant technologies	% Consumption met by recycling
Hafnium	Alloying agent, nuclear control rods, computer chips	0%
Rhodium/PGM's	Alloying agent, industrial catalyst, catalytic converters, fuel cells	0%
Silver	Catalyst, electronics, high-capacity batteries, antimicrobial in medicine	16%
Gold	Catalysts, electronics, coating space satellites, dental and medical implants, nanotechnology	43%
Zinc	Galvanising, dry batteries	26%
Gallium	Semiconductors, solar cells, MRI contrast agents	0%
Germanium	Semiconductors, solar cells, catalyst, optical equipment	35%
Arsenic	Semiconductors, solar cells	0%
Indium	Alloys, photocells, LCD and touch screens	0%
Antimony	Semiconductors, alloys, batteries, pharmaceuticals, catalyst, flame retardants	0%
Tin	Alloy, protecting coating	26%

recent economic crisis hit, manufacturing halted causing world commodity prices to plummet, indium alone dropped to $300/kg in 2009. However, this did not remain for long. Indium is back up to $650/kg (2010) as consumer demand has once again risen with several governments introducing incentives for electronic goods or cars to kickstart their economies. This has resulted in predictions that the demand for some elements will soon outstrip supply [2]. The key question is what will happen to the prices next and how will demand for all these metals that underpin our technologically advanced lifestyles be met sustainably in the future.

Reuse, recover, recycle must be the answer. The recovery and recycling of metals from waste streams is a cost effective and environmentally beneficial route to valuable materials. Current aluminium recycling supports 49% of aluminium consumption in the US [3]. It saves 95% of the energy and generates only 5% of the CO_2 compared to the mining and electrolysis of alumina from bauxite ore [9]. Research has indicated that significant energy saving can be made through recycling of metals [9,10]. Steel recycling saves 74% of the energy, 90% of virgin materials, reduces 86% of air pollution, 40% of water use, 76% of water pollution, 97% of mining waste and a considerable amount of consumer wastes generated, when compared with production from virgin materials [9]. Other elements that have been in use for decades are also already recycled to some extent (Table 1), although the techniques used tend to be limited in their ability to systematically recover all elements. On the other hand, there is little or no recycling of elements that are important for current and emerging uses, e.g. platinum, indium, gallium and hafnium. At the end of their life the products containing these elements; mobile phones, televisions and computers, are ending up in landfills or being incinerated and the elements are being lost. Japan has calculated that it has accumulated three times more gold, silver and indium in its waste, due to its high turnover of electronic goods, than the world uses in a year [11].

This emphasises the potential and necessity for a new approach to our waste. We must attempt to recover all elements and reuse them in close-looped systems either by recovering them through 'urban mining' from landfill sites, incineration ashes or waste waters, or designing the direct recycling of elements through intelligently designed disassembly of materials at their end of life. In addition, this should be using novel and benign methods that can reduce the environmental burden of mining and selectively target all elements for recovery. These measures should limit the demand for new supplies of elements, increasing the lifetime of our reserves infinitesimally.

This paper suggests directions for turning this vision into reality, highlighting new sources of scarce elements, introducing developing techniques that could be used for their recovery, emphasising gaps in our knowledge and drawing these together to offer innovative solutions for the future.

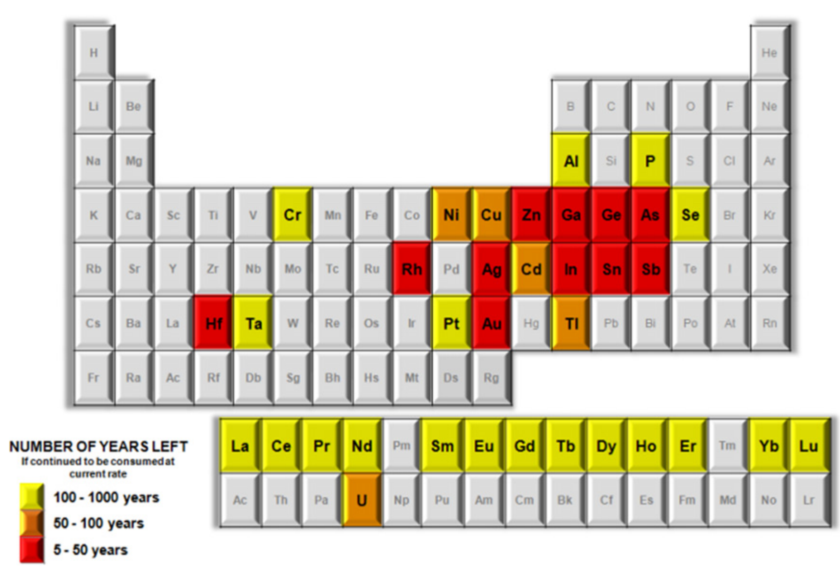
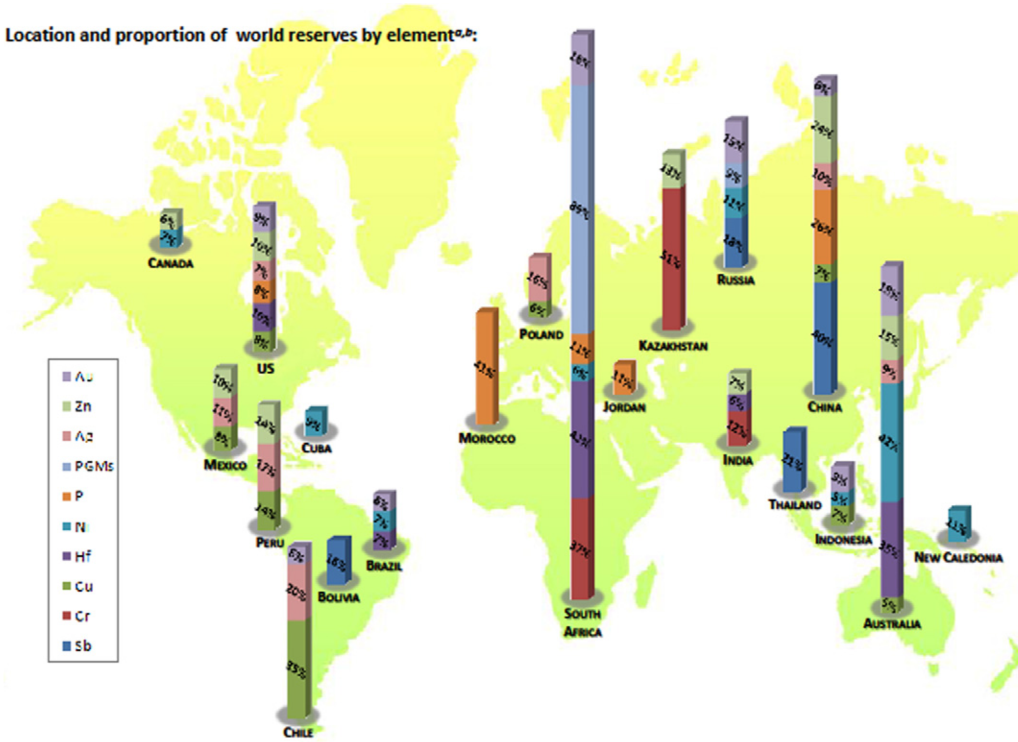


Fig. 1. Number of years remaining of rare and precious metal reserves if consumption and disposal continues at present rate. Data from Ref. [2].



World total reserves by mass a:

Sb	2.1 (million tonnes)	Cr	350 (million tonnes)	Cu	540 (million tonnes)	Ni	71 (million tonnes)	P	16 (billion tonnes)
PGMs	71 (million kg)	Ag	400 (thousand tonnes)	Au	47 (thousand tonnes)	Hf	660 (thousand tonnes)	Zn	200 (million tonnes)

[a] Reserves: defined as known economically recoverable amount at time of survey, 2010. [b] Reserves below 5% not shown.

Fig. 2. Distribution of rare and precious metal reserves around the world. Data from Ref. [6].

2. New sources of elements

With the prospect of increasing demand, combined with the rising cost and scarcity of a wide range of precious elements necessary to new and existing technologies, novel methods must be identified for the recovery of these metals. Due to the general dispersion of elements throughout the environment there are several potential sources for the recovery of rare and valuable materials: enriched municipal and industrial solid waste; end-of-life consumer electrical and electronic products (e-waste); landfill sites; metalliferous soils; low grade ores; tailings and aqueous wastewaters. This can be considered to be ‘double green’ as it reduces hazardous waste whilst simultaneously supplying an alternative to virgin resources.

2.1. Municipal solid waste

Municipal solid waste (MSW) offers one of the largest potential resources for recycling and recovery of a multitude of different elements, with an estimated 1636 million tonnes generated globally every year [12] and with levels continuing to rise [13]. MSW is a combination of a variety of wastes including organic, plastic, glass and electronics and has a varying composition in different localities around the world, particularly dependent on the degree of industrialisation (Fig. 3) [14]. It is obvious that the precious and scarce elements that we have already used and disposed of must be distributed in the environment around us. MSW from either domestic or industrial sources is a prime target due to its concentrating of materials in specific, known locations.

Japan has shown interest in the potential of its MSW as an ‘urban mine’ with national concerns over securing future natural resources, particularly due to its current utilisation of 30% of the world’s annual consumption of rare metals [15]. Researchers have estimated the amount of rare and precious metals accumulated in Japan since WWII in goods and waste and have calculated that the country has accrued a larger amount of gold and silver than that in the reserves of the richest resource possessing country for each element respectively. Significant quantities of indium, tin, tantalum, platinum and lithium have also been amassed [11]. Similar levels of these elements are likely to be found in other industrialised nations and therefore MSW, both past and present, offers a significant opportunity for the recovery of scarce elements.

The majority of the MSW generated has, in the past, ended in landfill as a contained and controlled management system. However, as a result of environmental concerns related to greenhouse gas emissions and leaching of toxic compounds, land use pressures and the economic costs of waste disposal, alternative waste disposal methods including incineration, composting and recycling are rapidly being adopted (Fig. 4) [16,17]. Incineration or waste combustion is quickly expanding in countries which can afford the infrastructure costs, both for reasons of waste reduction and energy recovery.

Little information is currently available about the content of precious and scarce elements in MSW. However, Japan’s concern about future resource supply, combined with its high use of incineration, has sparked the interest of researchers to study the elemental potential of incineration residues [11]. Around 10% of Japan’s fly ash and bottom ash residues from incineration are treated by ash melting plants to form fly ash (10%), molten slag (70%) and molten metal (3%). Currently the majority of all of the thermally treated residues are either sent to landfill or used for construction, whilst some of the molten metal is recycled. Analyses of the fly ash fraction from ash melting shows the majority of the composition to be chlorine, potassium, calcium and sodium, due to the volatility of these elements at the temperatures used (Fig. 5).

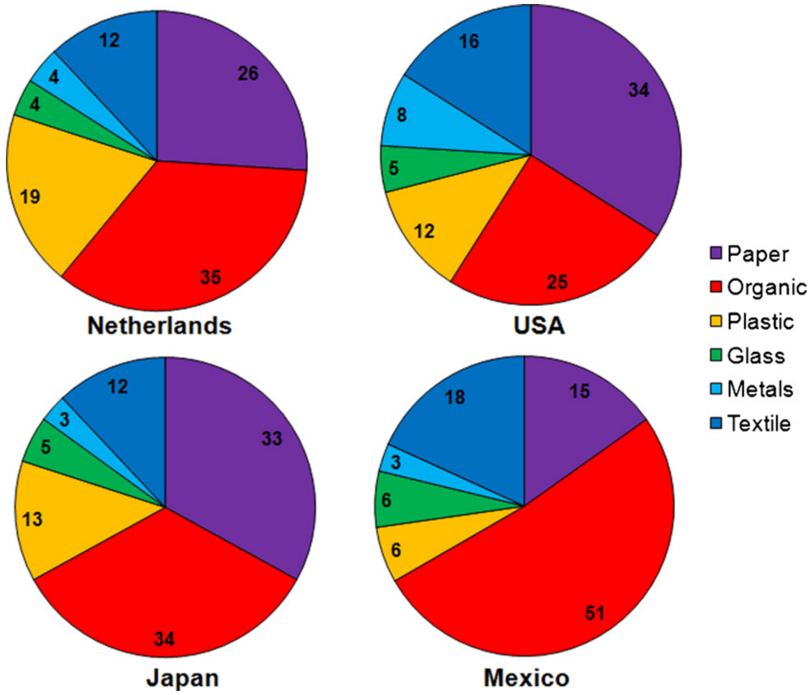


Fig. 3. Composition of solid waste in different countries. Data from Ref. [14].

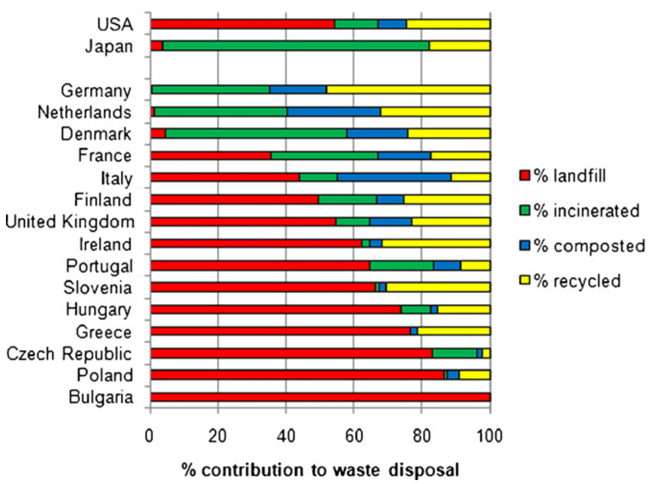


Fig. 4. Contribution of different methods to municipal solid waste disposal in different countries around the world. Data from Refs. [17,18].

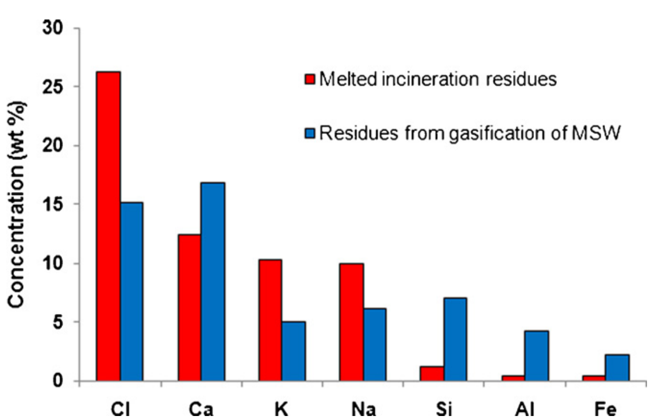


Fig. 5. Major elemental composition of municipal solid waste incineration residues. Data from Ref. [15].

In addition, many of the scarce and valuable metals highlighted earlier are present in both the fly ash and molten metal in significant quantities. In several cases, for zinc, lead, copper, silver, indium and palladium they are found at levels higher than found in primary ores (Fig. 6). Of the other elements present, nickel, chromium, tantalum, vanadium and zirconium, tended to mostly remain in the molten slag [18]. Copper, tin, antimony, silver and palladium were found to be more concentrated in the molten metal than the fly ash, whilst the incineration residues generally show a higher concentration of metal than the gasified MSW. This suggests a degree of controllability in the fractionation of elements during the thermal processing of wastes. Incineration processes can have unwanted environmental impacts from the release of toxic volatiles and therefore may not be the best process for recovery of metals, however, this demonstrates that these elements are present in significant quantities in MSW and that environmentally benign methods need to be designed for their recovery.

The source of many of these scarce elements in incineration residues and therefore municipal solid wastes is expected to be electric and electronic equipment [19] or flame retardant materials in the case of antimony [11]. A personal computer with a CRT

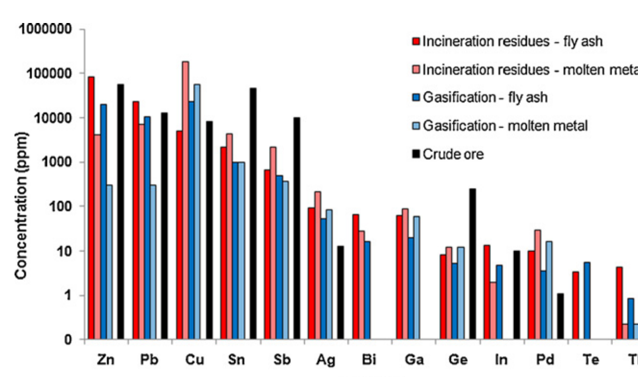


Fig. 6. Precious and rare metal composition of municipal solid waste residues and comparison to concentration in primary ore. Data from Ref. [15].

screen typically weighs 25 kg and contains 43.7% metal and 17.3% electronic components [20]. Analyses show a wide variation in the elemental composition of electronic wastes, nevertheless, the concentrations of various precious metals and other valuable elements are high. Around 5–20% of circuitboard scrap is copper, whilst there is typically 200–1000 ppm Ag, 50–300 ppm Au and 10–100 ppm Pd, with the concentrations gradually decreasing in modern appliances as technologies improve [21]. The precious metal content of these wastes creates an incentive for the direct recycling of these materials, yet, electronic waste may still contribute as much as 8% by volume of MSW in rich countries [22] with much of it still and certainly in the past, going to landfill or incineration.

This indicates that both past and present MSW is a potential, vital resource for the recovery of precious and scarce elements. Consequently, much more knowledge is needed about the composition and flow of different waste streams and the composition of elements in landfills to enable directed research towards the recovery of all elements.

2.2. Waste electrical and electronic products (e-waste)

The amount of waste electrical and electronic equipment (WEEE or e-waste) produced globally is increasing rapidly. According to StEP [23], more than 24 million PCs were manufactured in the US in 2006, whilst approximately 14 million PCs were sold in China in 2005. In 2006, mobile phone sales alone reached 896 million units worldwide. In the 27 countries of the European Union (EU) it was estimated that 10.3 million tonnes of electrical and electronic equipment (EEE) was delivered to the market in 2005 [24]. At the same time, huge volumes of e-waste have been generated globally. A recent WEEE report [24] indicated that in the EU roughly 8.3 million to 9.1 million tonnes of e-waste were generated in 2005, and by 2020 this figure will rise to 12.3 million tonnes. A rough estimate by the authors of this paper of global e-waste generation is between 40 and 50 million tonnes per year.

This waste is a significant potential resource for the supply of scarce and valuable metals. According to Meskers [25] in 2008 the 1300 million new mobile phones produced worldwide, consumed approximately 12,000 ton copper, 4900 ton cobalt, 325 ton silver, 31 ton gold and 12 ton palladium. For personal computers and laptops, in 2008 the 300 million new units produced consumed roughly 150,000 ton copper, 9100 ton cobalt (Li-ion batteries for laptops), 300 ton silver, 66 ton gold and 24 ton palladium [25]. However, e-waste also frequently contains toxic and hazardous materials, and so therefore requires careful and special treatment.

The increasing volume, potential high value and content of toxic and hazardous materials has led to more e-waste being separately collected and legal limitations being placed on its disposal, although large amounts are still landfilled or occasionally mixed in MSW streams. Globally, only a small portion of well separated e-waste is treated; two good examples of industrial practice are at Umicore in Belgium and New Boliden in Sweden. Landfill and illegal trading are still challenging issues. Illegal trading of e-waste from the western world to developing countries causes serious environmental problems and high risk to the human health.

However, the current recycling and refining technology can only recover a small part of the metals, and most of the valuable “strategic metals” are getting lost. The United Nations recently called for urgent actions to recycle these valuable metals. The effective recycling and refining of scarce metals from end-of-life (EOL) electronic equipment have become a global issue for economical, technological, social and environmental concerns.

2.3. Mine waste and soils

Traditional pyro- and hydrometallurgical metal recovery processes are performed on ores containing a large concentration of the desired element. However, as described earlier these ore bodies are found only in specific small locations and for many elements they are rapidly being depleted. This is encouraging researchers and companies to find new ways to recover elements from the low-grade ores, mine tailings and dumps that have been left behind from previous mining operations particularly for ores containing copper, iron, zinc and gold [26]. The quantities of these mining wastes available for extraction is expected to be considerable with approximately 2.2 billion tonnes of rock and 1.1 billion tonnes of tailings from ferrous metal, non-ferrous metal and industrial mineral mining predicted to be stored in the EU alone [27].

Another source of metals from a more dispersed environment are soils, either from weathered mineral landscapes such as ultramafic soils which are relatively high in nickel, chromium, manganese, cobalt, titanium, iron and other metals [28] or from industrially contaminated soils. There is also growing interest in road side dust as a source of platinum due to its loss through engine exhausts from catalytic converters. 1.5 ppm of platinum has been found in the dust, with potential further enrichment in the waste collected by road sweeping machines [3].

2.4. Aqueous wastewaters

Aqueous wastewaters offer a further route to the recovery of metals. Mining processes often use aqueous/organic-based metal extraction which produces large volumes of wastewater with low concentrations of dissolved metal [29]. At source recovery of valuable and potentially environmentally hazardous elements is an obvious method to prevent them entering the complex natural ecosystem. The development of such technology is also a necessity for the tens of millions of tonnes of dry sewage sludge generated from the treatment of municipal wastewater every year worldwide [30]. Sludge or biosolids are frequently applied as a fertiliser due to their rich content of nutrients, however, they also contain 0.5–6% by dry weight of trace and heavy metals which reduces the use of this treatment but also provides an opportunity for metal recovery [30]. The nuclear industry, electroplating and metal processing operations also produce wastewaters containing Cr, Ni, Cd, Zn, Cu, U and precious metals [31].

3. State-of-the-art technology for metal recovery from waste

3.1. Recycling and recovery of steel and base metals

As highlighted at the beginning of this article, the recovery and recycling of metals from wastes and end-of-life products is not new. Over 35% of steel [32], more than 30% of aluminium [33], 30% of zinc [34], 35% of copper [35] and over 50% of lead [36] supplied to the market have been produced from secondary resources in recent years. Steel recycling is exclusively carried out alongside primary steelmaking using Basic Oxygen Furnace (BOF) or Electric Arc Furnace (EAF) steelmaking processes whilst non-ferrous metals are mostly recovered separately in secondary smelters processing only non-ferrous scrap metals or industrial wastes. However, these metals are still not recovered to their maximal extent. For instance, municipal solid waste and landfill sites contain significant quantities of steel and base metals such as copper and aluminium that are still not effectively recovered using state-of-the-art technology. Physical recovery using magnetic separation and eddy current separation can regain approximately 55–60% of the metals from waste combustion/incineration bottom ashes [37], but the rest of the metal in the bottom ash and fly ash are lost. New and more efficient physical and metallurgical recovery technologies are vitally necessary in the future to ensure 100% recovery.

3.2. Recovery of precious and platinum group metals (PGMs)

In contrast to steel and bulk base metals, recovery of scarce and precious metals are much more difficult due to their very low concentrations and dispersion in a wide range of waste streams. Collection and concentration are the first and most important steps. The current industrial practice is to capture these precious metals with bulk production of heavy metals such as copper and lead. Smelting of copper and lead concentrates together with gold/silver concentrates, or mixing with pre-sorted e-wastes, can bring precious and PGMs into the copper and lead stream. At the end of the refining step of copper or lead through electrorefining, the precious and PGMs are transported to the anode slime. The anode slime becomes a much richer raw material for precious metals recovery through leaching and electrowinning processes, sometimes in combination with roasting – a high temperature pyrometallurgical conversion process. For the concentration of precious metals in solutions, ion exchange and adsorption are broadly used in the precious metals recovery [21].

3.3. Recovery of rare-earth metals

Rare-earth metals consist of 17 elements, from the lanthanide group (15 metals) plus scandium and yttrium. The term ‘rare’ can be misleading since rare-earth elements (REE) have a greater abundance in the earth’s crust than silver, and are more or less equal to that of copper (50 ppm) and lead. Nevertheless, REE are much less concentrated in exploitable ore deposits, particularly the heavy rare-earth elements (HREE) – lanthanum to europium. In comparison to precious metals and PGMs, rare-earth metals are even more scarcely dispersed in EOL products and wastes. Rare-earth metals are not currently recycled, but as highlighted earlier they are gaining attention worldwide due to their localised occurrence and production and their critical importance in high-tech products. Efficient collection, separation and recovery technologies are not yet available, although some initial efforts are being made [38]. Examples include the recycling of rare-earth magnet powder from hard disc drives (HHD) through selective crushing, hydrometallurgical separation, and recovery of neodymium and dysprosium. However, this is in a very preliminary research stage.

3.4. Techno-economical challenges

Not only technology but also economic factors play an important role for the recycling and recovery of scarce metals, Recently, Hagelüken and Meskers [39] described the techno-economical challenges involved in the metallurgical recovery of rare and rare-earth elements, the so called ‘technology metals’, at the end of the recycling chain. These ‘technology metals’ are crucial ingredients in many high tech and clean tech products and their use in such applications has increased significantly in recent years. However, their absolute mass in a single product is usually very low and they are mostly embedded in complex assemblies combined with other elements, which complicates recycling. Two main groups of products need to be distinguished. Firstly, products in which technology metals are combined with precious metals, creating inherent economic recycling incentives which can lead to additional recovery of special metals as by-products if appropriate processes are used (e.g. mobile phones). More challenging are products where such ‘paying metals’ are missing and the special metals content does not offer sufficient economic attraction (e.g. thin film photovoltaics). To address both product groups metallurgical recovery processes need to be further developed and measures need to be taken to ensure that end-of-life products enter the most advanced recycling channels.

4. Novel methods for the recovery of scarce metals

Several sources for the recovery of scarce and precious metals have been described above as well as traditional methods for their recovery. Further knowledge is required about many of these wastes in order to ascertain the elemental content and speciation of the trace metals within them. Moreover, new efficient, clean and cheap methods are needed for the recovery of these metals to ensure that complete closed-loop recycling is possible. Some novel methods of recovery, including the use of hyperaccumulating plants, biosorption using biomass and bacterial leaching, are in their infancy but have great potential.

4.1. Metal hyperaccumulation

Hyperaccumulation of metals by plants has been studied in recent years due to interest in the bioremediation of soils and the potential for phytomining of valuable metals. Hyperaccumulation refers to the accumulation of elements that are usually toxic to plants at concentrations 100 times greater than in ‘normal’ plants growing in the same location [40]. Metals are extracted from soil or water and translocated to the above ground tissue in the plant. Harvesting, combustion and smelting of the ash should enable production of pure metal [28]. Nearly 450 plant species have been reported to hyperaccumulate metals [41], of which most are nickel hyperaccumulators that have adapted to the ultramafic soils around the world. Other, either natural or induced hyperaccumulators, are additionally known for most precious or scarce elements (Table 2).

Pilot trials have shown that nickel can be economically extracted from ultramafic soils [42] and that the metal can be recovered in a relatively pure form [43]. Thallium, a valuable metal with a relatively low abundance in nature, is readily accumulated by some species. *Iberis intermedia* (candyduft) is able to produce 40 kg/ha of Tl from lead/zinc mine tailings containing locally an average of 10 ppm Tl [44]. Cobalt and gold are also considered good potential candidates for phytomining due to their high value. Plants do not normally accumulate gold as it needs to be solubilised, which can be achieved by adding chelators such as ammounium thiocyanate. This approach has enabled accumulation of up to 57 mg/kg Au from a synthetic ore [45] which can form as gold nanoparticles within plant cells, adding additional interest [28].

Phytomining or phytoremediation opens up the opportunity to recover elements from low-grade ores, mineralised or contaminated soils, mine tailings and waste waters (via hydroponics) that would be uneconomical by conventional methods. It also provides an added environmental benefit of restoring degraded land and producing energy by burning the biomass. However, in order to harness the full potential of this ideal green technology, plants must be developed with multiple beneficial traits: toleration and single-metal accumulation of a range of metals in the harvestable parts of the plant deep roots; rapid growth and high biomass yield. At present, no plant is known with all of the above attributes [41]. Genetic modification could hold the key to opening up this technology in the future, but this must be done in way that would not introduce negative ecological impacts. In addition, this technique needs to be proven in field conditions, on a larger scale and for a variety of different elements, particularly the rare and precious metals.

Table 2
Number of known hyperaccumulators with their species and lower limit for hyperaccumulation of various metals [28].

Element	Lower limit for hyperaccumulation (g/kg)	No. known hyperaccumulators	Name of species	Accumulation (g/kg dry)
As	1	5	*Pteris vittata*	22.6
Ag	0.001	–	*Brassica juncea*	–
Au	0.001	–	*Brassica juncea*	0.01
Cd	0.1	2	*Thlaspi caerulescens*	3
Co	1	30	*Haumaniastrum robertii*	10.2
Cu	1	34	*Ipomea alpine*	8.4
Pb	1	14	*Thlaspi rotundifolium*	8.2
Mn	10	11	*Macadamia neurophylla*	55
Ni	1	320	*Alyssum betolonni*	13.4
Tl	0.1	1	*Iberis intermedia*	4.1
U	1	–	*Atriplex confertifolia*	0.1
Zn	10	16	*Thlaspi calaminare*	10

4.2. Biosorption

A potential method for metal removal in wastewaters is the use of biosorbents. Current studies have focused on biomass components, typically polysaccharides, with carboxyl, hydroxyl, amine or phosphoryl functional groups that can interact with metal ions either through electrostatic interactions, ion exchange or complexation of metal ions. There is only a small amount of available data on the recovery of precious metals from wastewater streams (Table 3) although this area of research is more developed for the removal of base metals. Chitosan has been of especial interest due to its ease of modification and the straightforwardness of protonation of the amino sites in acid medium, increasing the electrostatic interactions.

Precious metal uptake has been found to be highly pH dependent with gold, platinum and palladium all showing maximum sorption under acidic conditions, except when using sulfur-grafted chitosan, where the influence of pH on gold uptake was decreased by altering the sorption mechanism. A major difficulty with this technique is the competition for uptake between different ions of similar classification as hard, soft or borderline acids or bases as defined by Pearson. Difficulties with separation of freely suspended adsorbent can be reduced by immobilising the particles in packed or fluidised bed reactors [31].

Macro algae's, commonly known as seaweed, are also renowned for their excellent metal-sorbing properties. They are unique from other biosorbent materials as they have a rigid macro-structure that enables them to withstand the conditions of the adsorption process [31]. Brown algae are particularly suited due to their polysaccharide content; initial adsorption via anion exchange is facilitated by participation of the carboxyl groups in uronic acid, with a second phase of adsorption taking place as these anions diffuse into the cell structures of the algae. Brown, marine and freshwater macro algae's have been shown to successfully capture various elements including Au, Cd, Co, Cu, Ni, Pb, Pd, Pt, U, Th and Zn [46]. For the uptake of cadmium, seaweed samples outperformed commercial ion-exchange resins by 500%, with commercial resins adsorbing 30 mg/g and *Ascophyllum nodosum* (a breed of brown algae) adsorbing 170 mg/g [46].

To make biosorption a truly useful process, elements must be easily desorbed and concentrated for recovery. Complete desorption of metal cations from seaweed biosorbents has been achieved using a suitable eluant, in most cases a mineral acid, although the need for this step could potentially be eliminated by simply pretreating the seaweed with potassium hydroxide [47]. The elution of adsorbed copper from *Sargassum filipendula* has been shown to be more than 95% for three different eluents: $CaCl_2$, $Ca(NO_3)_2$ and HCl [48]. These results indicate the potential for a low cost continuous metal adsorption–desorption system therefore making the recovery of metals from the liquid phase an economically viable solution.

Table 3
Precious metal biosorbents [29].

Biosorbent	Metal	Maximum uptake (g/kg)
Chitosan (sulfur-grafted)	Au (III)	0.624
Condensed tannin gel particles	Au(III)	8
Cladosporium cladosporides strain	Au (III)	0.036
Calcium alginate beads	Au (III)	0.29
Egg shell membrane	Au (I)	0.147
Chitosan (sulfur derivative)	Pd (II)	0.352
Bayberry tannin	Pd (II)	0.033
	Pt (IV)	0.046
Chitosan flakes (glutaraldehyde crosslinked)	Pt (II)	0.346

4.3. Bioleaching

The solubilisation of metals for uptake by both plants and biosorbents is fundamental to this success. The use of microbes for the solubilisation of elements is poised at the brink of a breakthrough as a major new technology due to industrial interest focused on copper, nickel, cobalt, zinc, gold and silver [22]. Metal species are vital to microbes for structural or catalytic functions. The harnessing of these processes could provide selective solubilisation and recovery of elements in a non-traditional way. Bioleaching has been successfully used on sulfidic ores, the main metal containing minerals, with over 160,000 tonnes of copper ore treated by bioleaching daily [49]. For gold, this method is used to oxidise the refractory host minerals before recovery of the gold by cyanidation treatment [50], which has been found to improve the recovery of the gold contained within the ores from 50% to 95% [51]. The main technologies used are either heap or stirred-tank leaching [21].

4.4. Integration with metallurgical recovery process

Integration with existing metallurgical recovery processes with novel methods may be beneficial and necessary particularly for the purification, concentration and separation of the valued/targeted metals from impurities. The use of existing technologies for final metal extraction following bioleaching, biosorption or hyperaccumulation could include:

(a) Separation and concentration: solvent extraction, ion-exchange, membrane technology (see for instance the paper in the same issue on 'Efficient technologies for worldwide clean water supply'), supercritical fluid treatment, precipitation and crystallisation.
(b) Metal extraction and precipitation: electrowinning and/or electrorefining, cementation, gas reduction.

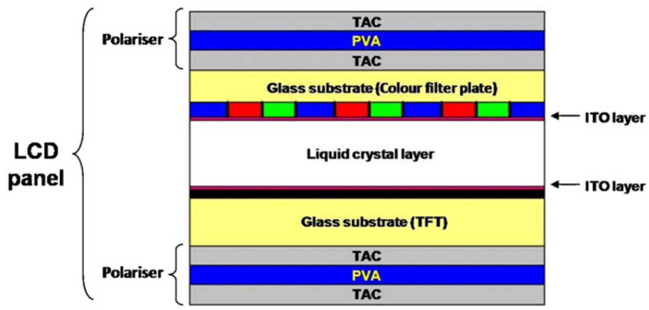


Fig. 7. Basic construction of an electro-optic LCD device (side view).

Innovation in initial metal extraction from new sources of scarce metals, combined with existing metallurgical operations, will lead to a new processing flowsheet and technology, tailored to each individual waste stream for different targeted metals. Reduction in waste production must be at the core of this new methodology. Socio-techno-economic challenges in reaching total recycling processes will drive future R&D efforts for the recovery of scarce metals from new resources.

5. Elemental recovery for 2030

By combining these different alternative sources of rare and precious metals: municipal waste, aqueous wastewaters, electronic goods, low grade ore and soils; with novel and benign technologies as well as the current state-of-the-art we could reach our vision of complete closed-loop cycling of all elements by 2030. We can revolutionise our interaction with the fundamental elements of nature, switching from dispersing elements throughout our environment to concentrating them in synthetic ores for useful applications.

5.1. Example: recovery from waste electronics

As mentioned previously the growing production of electrical and electronic equipment (EEE) has resulted in an increase of these devices as a waste. Liquid Crystal Display (LCD) screens are of particular interest due to their high content of the scarce element indium, ubiquitous use in electronic goods and their growing waste stream. An estimated 2.5 billion LCDs are approaching their end of life, with LCD waste the fastest growing waste stream in the European Union. The WEEE Directive of the European Parliament and the Council on Waste Electrical and Electronic Equipment requires the disassembly of all LCDs with an area greater than 100 cm^2 and those containing mercury backlights [52]. Once the backlight has been removed an LCD is rendered 'safe' and may be sent for incineration or landfill [53]. Both options are wasteful and potentially hazardous to the environment. In the UK alone it is predicted that over 10,000 metric tonnes of LCD will be available for recycling in 2010, containing 9 tonnes of liquid crystals; 900 kg of indium and 8,000 tonnes of optical quality glass [54]. The development of an innovative holistic strategy for the recovery and reuse of valuable materials from LCD panels is key to the successful utilisation and reduction of this waste stream [53].

An electro-optical LCD device (Fig. 7) comprises a thin film of nematic liquid crystal sandwiched between two glass substrates (TFT and colour filter plate) whose inner surfaces have been coated with a transparent electrical conductor, indium tin oxide (ITO) [53,55]. The ITO is a mixture of indium(III)oxide (80–90%) and tin(IV)oxide (10–20%) [49]. Polarisers are attached to the outer surface of the glass substrates and are comprised of a layer of iodine doped polyvinyl-alcohol (PVA) sandwiched between two protective sheets of triacetylcellulose (TAC).

Indium is a silvery-white rare metal with an estimated abundance of 0.24 ppm in the Earth's crust [53,56]. The extraction of indium takes place as a by-product of zinc mining of sphalerite mineral ore typically containing 1–100 ppm indium, as it is uneconomic to mine alone. Greater than 65% of the total globally extracted indium is used in the manufacture of indium tin oxide (ITO) for LCDs. The rapid growth in LCD production, together with a decline in zinc mining, has resulted in significant increases in indium prices, as discussed previously. It has been estimated, based on zinc reserves, that world reserves of indium are 2600 tonnes [56,57]. This will inevitably be depleted with increases in the production of LCDs. It is therefore vital for the future of this technology and others that full recovery of indium and other valuable elements is achieved.

The current processes used for the recovery of elements from WEEE are pyrometallurgy and hydrometallurgy [20]. Of these, pyrometallurgy is the most utilized industrial method for metal recovery. It involves the thermal treatment of crushed WEEE by incineration, smelting or high temperature gas phase reactions [21]. These processes generally form a large unwanted slag phase containing impurities such as zinc, iron, aluminium and lead and ceramic or glass components. Only partial separation of metals can be achieved using pyrometallurgy, further refining using hydrometallurgical or electrochemical processes is necessary to recover precious metals such as platinum and palladium.

In comparison, hydrometallurgical processes are more precise and easily controlled [21]. They typically use strong acids or bases to leach metals out of WEEE. The resulting metal solution undergoes multiple separation, purification and recovery steps in order to isolate and concentrate the elements [58]. Unfortunately, this method could have damaging toxicological impacts due to the large amounts of reagents used and the content of the waste waters formed.

Instead, an ideal future scenario could combine bioleaching and biosorption of WEEE to selectively recover all elements without the need for toxic reagents or energy intensive processes. Bioleaching is being investigated particularly in the mining industry for extraction of copper and gold from sulfidic ores, however, their utilisation for electronic waste is in its infancy. A few studies do show it has potential with 14.9% of the gold in printed circuit board solubilised using *Chromobacterium violaceum* [58] and 90% of the available Al, Cu, Ni, and Zn leached from electronic scrap dust using *Thiobacill* [59]. This involved a two-step process with initial incubating of the bacteria to prevent the alkalinity of the metal waste killing the micro-organisms. The use of chelators also improves the concentration of scrap that can be solubilised and prevents metal precipitation [60]. Very little work has looked at the biosorption of precious metals from WEEE leachate. One study suggested a three step process could selectively recover and separate Au(III), Pd(II) and Cu(II) by biosorption [61]. Recent research has also suggested that a polysaccharide extracted from Japanese algae could recover indium from waste LCD screens by gelling in the presence of the trivalent anion [62]. Further research is vital to fully realise the potential of bioleaching and biosorption for metal recovery from WEEE both individually and in combination and to integrate traditional and novel methods for final metal recovery.

Even more important for the future is the design of new EEE prior to manufacture, to integrate methods for the easy separation and recovery of valuable components at their end of life [63,64]. The use of smart materials and designed active disassembly would greatly facilitate either the direct reuse of high value components or the recycling of scarce elements into new materials. Directed research into developing so called 'smart materials' and technologies should lead to greater recovery of elements and reductions to incineration and landfill in the future.

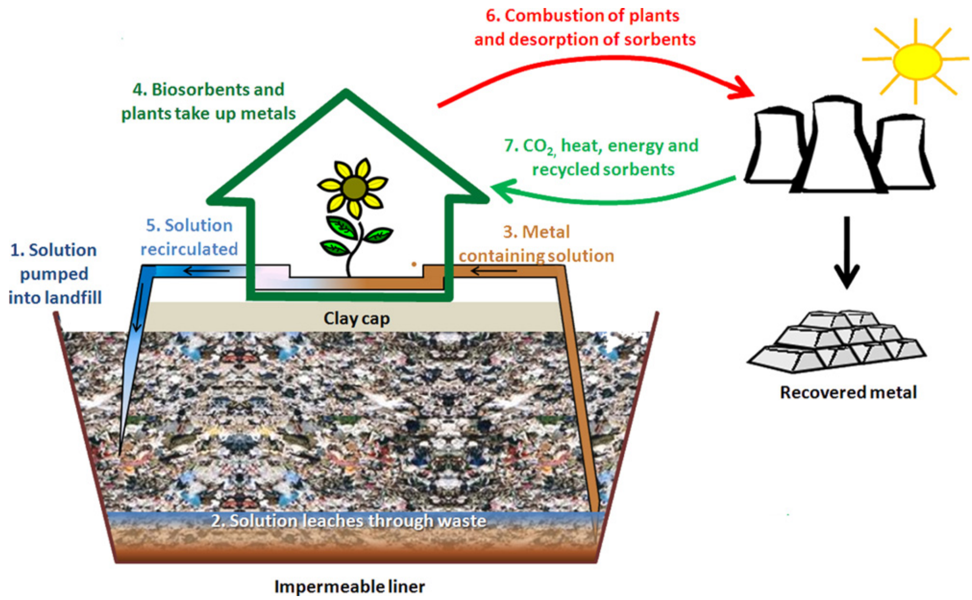


Fig. 8. Potential method for recovery of valuable resources from landfill sites.

5.2. Example: urban mining from a landfill

Another example of how benign techniques could be combined in the future to create a complete and sustainable recovery of elements is in an urban mine or landfill. As described earlier a large volume of municipal solid waste is disposed of annually, much of it still heading to landfill sites. A typical landfill site has an impermeable liner and clay cap. Precipitation on landfill sites seeps through the waste material and is recovered through leachate collection systems for processing to remove pollutants and prevent contamination of the local environment. Only around 0.02% of the metals that enter into the landfill sites are removed via the leachate over 30 years [65]. Most of this is during the initial stages, when the fermentation and hydrolysis of cellulose and hemicelluloses to acids and alcohols by bacteria under anaerobic conditions creates an acidic environment that can solubilise the metals [65]. A process could be imagined that combines bioleaching, biosorption and phytoextraction in a typical urban landfill in order to recover the valuable elements still contained within it (Fig. 8).

Process:

1. Water containing bacteria or fungi is pumped into the landfill.
2. The bacteria or fungi dissolve metals into the water as they seep through the landfill.
3. Leachate is pumped to the surface via leachate collection systems.
4. Water containing solubilised metals is passed through a series of biosorbents and plants grown using hydroponic methods within an enclosed greenhouse.
5. Extracted leachate is returned to the landfill site to repeat the process.
6. Plants are harvested and combusted. Biosorbents are desorbed. Metal is recovered by smelting.
7. The energy, CO_2 and heat produced from the combustion of the plants are recycled to run the system and improve plant growth. Biosorbents are returned to the system for reuse.

In order for this process to be successful much more research is required about: the elemental content of landfill sites; how effective bacteria or fungi would be at solubilising elements within them; creating selective biosorbents and hyperaccumulators that are tolerant to high concentrations of other elements and understanding any potential negative environmental impacts of the process. However, the benefits could be enormous by turning an environmental blemish and resource drain into an urban mine, recovering scarce elements and providing financial benefits to the local population.

This by no means covers all possible solutions to the challenge of elemental sustainability, other lateral and innovative methods and technologies are needed that provide ground breaking solutions to our scarce element dilemma. In addition, the socio-environmental-techno-economic balance of possible solutions needs to be examined to determine which of the alternatives are the most rapidly deployable and the most sustainable.

6. Concluding remarks

The 20th century is likely to be viewed by future generations as a period of uncontrolled and badly thought out economic growth which was fuelled by consumption of scarce and non-renewable resources. To make matters worse, we turned those precious resources into environmental problems through the creation of enormous amounts of difficult waste. This unsustainable and selfish behaviour cannot be changed overnight, especially as emerging nations bring ever-larger populations to the table of consumption where greed not need is the mantra. This century must see a fundamental change in our attitude towards resources (a socio-economic challenge) and must physically address the waste and resource issues (a techno-scientific challenge). Sustainable technologies are available to revolutionise resource utilisation; we must hope that they can be applied in time to maintain our highly populated planet before other revolutionary forces prevail.

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