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Challenges to achievement of metal sustainability in our high-tech society

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Achievement of sustainability in metal life cycles from mining of virgin ore to consumer and industrial devices to end-of-life products requires greatly increased recycling rates and improved processing of metals using conventional and green chemistry technologies. Electronic and other high-tech products containing precious, toxic, and specialty metals usually have short lifetimes and low recycling rates. Products containing these metals generally are incinerated, discarded as waste in landfills, or dismantled in informal recycling using crude and environmentally irresponsible procedures. Low recycling rates of metals coupled with increasing demand for high-tech products containing them necessitate increased mining with attendant environmental, health, energy, water, and carbon-footprint consequences. In this tutorial review, challenges to achieving metal sustainability, including projected use of urban mining, in present high-tech society are presented; health, environmental, and economic incentives for various government, industry, and public stakeholders to improve metal sustainability are discussed; a case for technical improvements, including use of molecular recognition, in selective metal separation technology, especially for metal recovery from dilute feed stocks is given; and global consequences of continuing on the present path are examined.

Key learning points

(1) Since Earth's metal supply is finite, burgeoning consumption of metals by consumers and industry is unsustainable without efficient recycling.
(2) Due to the unique chemical and physical properties of metals, scientific discoveries have enabled the creation of a myriad of high-tech products that have transformed 21st century society.
(3) Vastly improved value recovery from end-of-life metal products is needed both by increasing the rate of metal recycling and by improving the performance of collection and recycling technologies, some of which rely on informal methods that are disastrous from environmental and health standpoints but essential to the economies of many nations.
(4) Improved selective, environmentally friendly, and commercial processes for separation and recovery of metals (precious, specialty including rare earth, toxic, and radioactive) in pure form with minimum carbon footprint are essential to sustainability of metal life cycles from mining to end-of-life to recycling.
(5) Along with improvements in technology, increased awareness of the urgency of global metal sustainability and resolve-to-action on the part of public, government, press, scientific, and industry stakeholders is needed to ensure a workable solution to sustainability of metal life cycles for future generations.

1. Introduction

Complete metal sustainability cannot be achieved. Global metal supply is finite, and removing metals from Earth's natural stock results in a reduction of total metal supply, which cannot be replaced entirely since complete recovery of metals is not possible.[1] But to what extent can we approach metal sustainability? What do attainable metal life cycles look like, and how can we reach them? In this review, these questions are addressed, and possible answers presented. It is helpful in understanding issues associated with attainment of metal sustainability to know the status of Earth's metal supply including the origin and distribution of the supply, issues associated with metal mining and processing, the expanding number of uses to which many of these metals are put in our high-tech society, and the fate of metals present in end-of-life (EOL) high-tech products. A general schematic of this metal flow is given in Fig. 1.

The terrestrial metal supply has its origin in the stars, especially in supernovae explosions. Chemical elements formed in such stellar phenomena became part of planet Earth

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during formation of the solar system, ~4.5 billion years ago.[2] In our thin slice of time, these elements have been discovered one by one, their properties identified, and remarkably useful products created which contain many of them. These products have transformed our way of life, especially in recent decades. However, removing these elements from the Earth, processing them, incorporating them into useful commodities, and dispersing them as part of EOL products to the commons[3] (Section 4.1) have created significant and widespread environmental, health, social, and political challenges on a global scale.[4–7]

During the past half century, a huge upsurge in mining of metals from virgin ores to meet burgeoning market demands[8,9] has resulted from global consumption of new high-tech products containing base, precious, specialty including rare earth elements (REE), and other metals, even toxic ones, as essential components (Table 1 and Section 3.1). These high-tech products are essential in the functioning of modern society and are becoming indispensable worldwide as affluence and population increase. Specific metals ranging over the entire periodic table are required for optimal performance, if not the very existence, of modern high-tech products.[10] Each of these metals has distinct chemical and physical properties based on its nuclear and/or electronic structure that often cannot be duplicated by any other substance, natural or man-made. Substitution of a given metal in the product by other metals or by synthetic materials usually results in a marked decrease in performance and thus represents a trade-off to overcome price or supply limitations.[11] Mining of these elements in the variety and quantities required is a recent occurrence and has raised many issues.[1]

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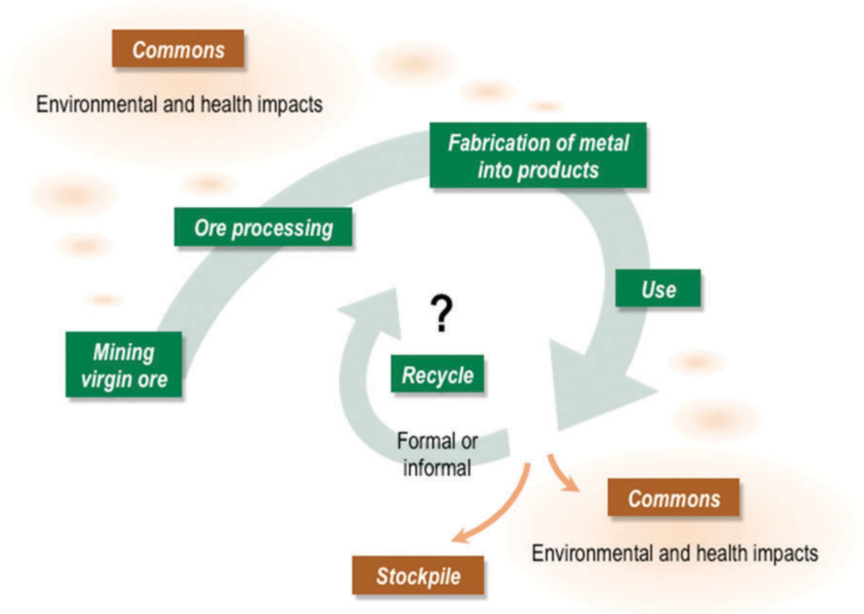

Fig. 1 Metal flow from virgin ore to ore processing and product fabrication to product use to product end-of-life with possible metal fates, including disposal (or leakage) to commons, temporary stockpiling, and formal or informal recycling. The commons (Section 4.1) includes landfill, incineration, mine drainage, ocean disposal, unregulated dumping, atmosphere, radioactive waste, and other repositories.

As metal use multiplies with the increase in both world population and the proportion of people in the middle class, future serious depletion of Earth's metal supply is inevitable. The global mining industry is larger than it has ever been and is producing minerals and metals at an increasing rate that dwarfs amounts produced in previous generations. Increased mining and ore processing has led to significant global environmental, carbon-footprint, health, energy, water, social, and political challenges,[1,4,6,7,12,13] including impending serious depletion of virgin metal resources, which is of concern for several elements such as Cu, Zn, and Pt.[1,13] Of course, depletion does not mean elimination of resources, but, rather, dissipation of amounts available to levels where extraction is not economical, at least at the present time.[1] All elements are found in the oceans, but, in most cases, at concentration levels far too low to permit their economic recovery. In a way, the situation with the oceans is synonymous with that occurring when EOL products are discarded into landfills, where metals contained in the products are present in very small concentrations making them essentially unavailable either to us or to future generations unless novel concentration and recovery technologies are developed.[1,4]

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It is imperative that a greater effort be made to significantly decrease introduction of metal emissions into the atmosphere, ground, and water surrounding mining sites, smelters, and metal-recovery operations involving EOL products. Regulations covering emissions into the commons are recent, and are found and enforced mostly in Organization for Economic Cooperation and Development (OECD) nations.[5,6] The United States is not a member of OECD (see Section 5.2 for an explanation), but is included with OECD nations in this paper. Environmental regulations, if they exist, are often lax in non-OECD nations and may be non-existent or non-enforceable in informal recycling operations in these nations where a large amount of precious metal recovery from EOL products takes place.[5,6] Processes involved in the production of metals from virgin sources, depending on the source, can release toxic metals (Table 1) into the commons in significant amounts.[5,12,14] Radioactive metals (Table 1) are found in nuclear wastes and in some metal ores, particularly those containing REE.[9,15,16] The release of radioactive elements into the environment has

Table 1 Classification of metals[a]

Category	Description	Metal
Base or major metals	Used in large amounts as a basis for societal infrastructure	Fe, Co, Ni, Cu, Zn, Pb
Precious metals	Used in small amounts; high economic value	PGM,[b] Au, Ag
Specialty metals	Usually used in small amounts to enable enhanced performance in modern high-tech products	REE,[c] In, Ga, Ge, Se, Te, Bi, Re, Nb
Hazardous or toxic metals	Toxic at low concentrations to living organisms	Cd, Hg, Pb, Tl, As
Radioactive metals	Disintegrate over time releasing hazardous radiation	U, Th, Ra, Cs

[a] Classification is somewhat arbitrary since a metal can often fit into more than one category depending on its use. The classification given generally follows that of Reck and Graedel,[10] and is intended to be helpful in identifying the roles of metals mentioned in the text. [b] Ru, Rh, Pd, Os, Ir, Pt. [c] Lanthanides, Y, and Sc.

increased as REE mining and processing has blossomed during the past few decades.[16] On the other end of metal life cycles, improper disposal of EOL products can result in significant environmental and health damage.[8,11,12] For example, ingestion of toxic metals such as mercury and arsenic has been suggested as a root cause of insidious human diseases that have become prevalent.[17]

The ability to recover target metals selectively and adequately from solutions or streams where they may be present at mg L^{-1} or lower concentration levels is of paramount importance in improving metal sustainability. Remaining virgin ore resources increasingly challenge separation methods, energy input, and water use as rich ores are depleted. At the other end of the metal life cycle, enormous quantities of metals, including those critical to the economy, are lost simply because they are sent to landfills instead of being recovered for reuse or environmentally safe disposal, largely because of inadequacies of traditional recovery methods and the added expense of such recovery. It is neither desirable nor economically feasible to recover all waste metals. However, arguments will be presented for increasing metal recovery rates for many of the metals listed in Table 1. Cleaning up environmental contamination represents a daunting challenge,[12] since toxic metals are released to the commons throughout metal life cycles as depicted in Fig. 1. These separation challenges present themselves as ''needle-in-the-haystack'' problems in which target metals are at trace levels in complex matrices. Conventional pyrometallurgical and hydrometallurgical technologies available for metal processing and recovery from such dilute sources include smelting, precipitation, solvent extraction (SX), ion exchange (IX), and an assortment of other techniques.[18–21] However, these technologies are challenged to selectively and adequately recover metals from dilute solutions in the mg L^{-1} concentration range, especially as matrices become more complex. As a result, effluent resulting from the use of these technologies (if they are used at all) is generally discarded to the commons through landfills and incineration and creates significant global environmental and health hazards especially in the case of toxic metals.[4,5,12]

The needle-in-the-haystack challenge, particularly, requires a new paradigm in separation technology. Fortunately, the critical concept of molecular recognition introduced several decades ago by Lehn[22] has opened a vista of new possibilities for addressing this challenge. Often associated with what is now called host–guest chemistry, molecular recognition entails the selective binding, usually with large $\log K$ values, of guest ions by inclusion, or at least partial inclusion, within host molecules, enabling the separation of metal ions to an interface or another phase. Precise complementarity of a host molecule for the size, shape, and charge of a given guest metal ion allows selective recognition of the metal even in the presence of high concentrations of competing ions in complex matrices. Application of molecular recognition to industrial and analytical problems has made possible highly selective separation of metals present in complex matrix solutions at mg L^{-1} concentration levels.[18,23] In the long run, these improved technologies will make possible effective recovery of formerly unrecoverable metals at low concentration levels, thereby reducing the need for toxic processing chemicals and the amount of waste generated.

Metal recycling rates from EOL high-tech products are, in most cases, very low (often <10–20%).[9,10] A consequence of low recycling rates is irrecoverable loss to the commons, and hence to society, of a large fraction of metals contained in EOL products, often after single and short use. Many of these metals are scarce. Their availability to us is a result of them being highly concentrated by Earth's geochemical processes.[1] Returning them to a widely dispersed state in landfills is wasteful and of major concern. In addition, replenishing them to produce new products requires mining of additional virgin ore with attendant environmental, health, energy and water concerns. Gordon *et al.*[13] have pointed out that ''As goods in use are increased and replenished, metal is transferred from the stock of ore in the lithosphere to a stock of metal-in-use providing services, and some of the metal in the original ore is transferred to wastes during mining, milling, and smelting. Over time, some of the metal-in-use recycles from old to new products, some is dissipated through corrosion and wear, and some enters waste repositories such as landfills in the case of EOL products that are not recycled. The relative sizes of the remaining stock in the lithosphere, the stock-in-use, and the stock transferred to wastes at any given time are measures of how far we have progressed toward the need for total reliance on recycling rather than on virgin ore to provide material for new products.'' Recycling requires an economical balance between benefits derived from recycling and input of primary resources required for recycling. An important means of increasing metal sustainability is to improve recycling efficiency.[7,10,24] Achievement of this goal involves increasing the effectiveness of collection of EOL products; improving the efficiency of technologies used for metal recovery, especially at low metal concentration levels, from EOL products; and promotion of increased awareness by concerned stakeholders in public, press, government, and industry sectors concerning the seriousness of the problem and the urgent need to find workable solutions.[4]

Metal flow from virgin ore to EOL products, and in some cases closing of the cycle to fabrication, is shown in Fig. 1. Collected EOL products can be treated in two general ways. They can undergo informal recycling, usually in non-OECD nations, where valuable metals are recovered often using primitive and environmentally irresponsible extraction and recovery techniques[6–8,10,25–27] or they can be treated by formal recycling using pyrometallurgical or hydrometallurgical procedures[1,10,24] for metal recovery and return to the fabrication step. Products not recycled are stockpiled or released to the commons. Metals contained in EOL products that are incinerated or deposited directly in landfills are presumed to be irrecoverably lost since the energy required to concentrate and recover them in their diluted state would be exorbitant. Stockpiling may take place at numerous points of metal life cycles, as in piles of low-grade ores or tailings at mines, in scrap-yards, in repositories such as drawers, or in EOL products. Stockpiled metals may or may not reenter the economy. To the extent metals are recovered and returned to the fabrication step, amounts of virgin ore that must be mined to meet the needs of society are reduced with attendant economic, water, and energy benefits.[1] Challenges associated with metal sustainability will be discussed with reference to possible means to decrease metal loss to the commons in the various steps in Fig. 1.

The major objectives of this tutorial review are to understand element origins and how the present imbalance of metal supply and projected use came to be; critique methods used to process and recover metals in metallurgical and recycling procedures; present examples of commercial, environmental, and health effects related to metal use; discuss the importance and challenges of recycling, both formal and informal, as a means for improving metal sustainability; and outline global consequences, in both short and long terms, that could result if significant progress is not made in improving metal sustainability. Points presented will be illustrated using selected examples taken from a plethora of current literature describing issues and challenges associated with achieving metal sustainability.

2. Element origins and distribution in Earth's crust

Elements in the periodic table were created in the furnaces of stars and in powerful supernovae explosions that happened billions of years ago and continue to this day.[2] It is estimated that a supernova occurs in the Milky Way every 30 years. Remnants of one of these, observed in China in 1054 AD, persist today as the Crab Nebula. In each supernova explosion, matter is thrown out at incredible velocities and the surrounding space is seeded with enormous quantities of newly minted elements. As the gas cloud containing these elements cools, electrons fall into orbit about the nucleus of each element.

About 4.5 billion years ago, a new solar system formed in the Milky Way Galaxy approximately 35 000 light years from the galactic center.[2] This solar system consisted of a moderately sized star that we call the Sun and eight planets with assorted dwarf planets, planetary moons, and debris. The planet that

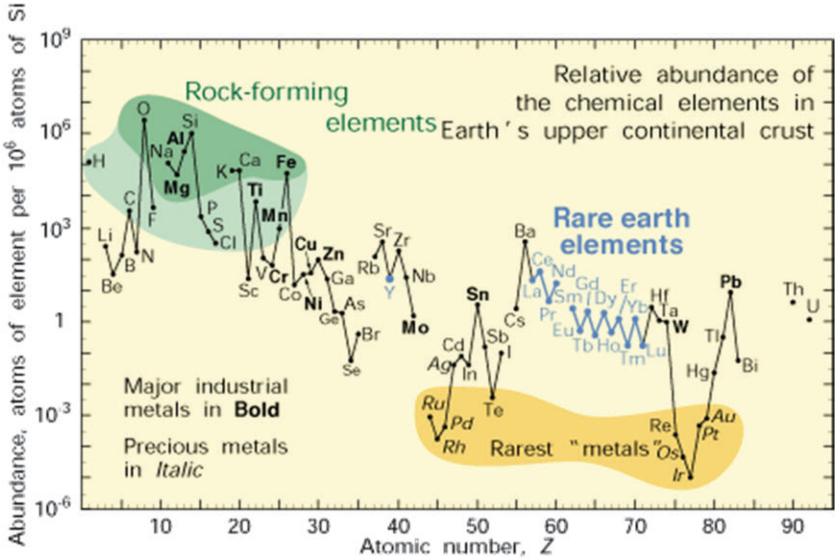

Fig. 2 Abundance (expressed as atoms of element per 10^6 atoms of Si) of the chemical elements in Earth's upper continental crust as a function of atomic number. Many of the elements are classified into the following (partially overlapping) categories: (1) rock-forming elements (major elements in green field and minor elements in light green field); (2) rare earth elements (lanthanides, La–Lu, and Y; labeled in blue); (3) major industrial metals (global production $> \sim 3 \times 10^7$ kg per year; labeled in bold); (4) precious metals (italic); and (5) the nine rarest "metals"—the six platinum group elements plus Au, Re, and Te (a metalloid). Reproduced with permission from U.S. Geological Survey, Department of the Interior. Accessed from website 8 October 2013. http://pubs.usgs.gov/fs/2002/fs087-02/

eventually would be called Earth was third from the Sun and 93 million miles distant. Earth has an abundant supply of various elements originally present in the gas cloud from which it formed. Element concentrations in Earth's crust vary over many orders of magnitude, as shown in Fig. 2. Earth's crust (only 0.2% of Earth's mass) is composed almost entirely of silicate minerals. Eight elements—O, Si, Al, Fe, Ca, Mg, Na, K—make up ~99% of the elements in the crust.[2] However, many of the remaining elements, although comprising only 1% of Earth's crust, have great metallurgical interest and are, in many cases, essential components of modern high-tech products.

Over Earth's history, geochemical processes have selectively concentrated metals into many minable deposits.[15] As pointed Q3 out by Kesler,[1] this selective concentration of metals has been very advantageous to society. Having metals in concentrated form negates the necessity of expending the energy required otherwise to recover them from their average concentration levels in Earth's crust. For example, Kesler[1] cites earlier work estimating that ''the total energy expended by Earth [processes] to form a Cu deposit is about 10 to 20 times the current market value of Cu.'' Base metals (Table 1) are the major constituents of ores worldwide.[2] Many less abundant specialty metals (Table 1) do not have their own minable ore deposits, but are found concentrated as by-products in ores containing one or more base metals (Section 3.1). The selective association between specialty and base metals results in concentration of the specialty metal far above its crustal abundance allowing it to be separated with much less expenditure of energy than might be required otherwise. Substitution of specialty metal for base metal in the crystal structure of ore minerals usually results from common affinity for the anion present, such as sulfide or oxide; same or similar ionic charge; and similar ionic radii.[2] Effects of these and other parameters, such as ligand-field strengths, on element distribution in Earth's crust have been discussed.[2] Recent market need for specialty metals required for new high-tech products has sparked increased economic interest in their recovery as by-products in base metal refining.[15]

3. Earth's metal supply

3.1 Production and use

Wilson[28] has argued that the search for metals for cosmetic, utilitarian, and military purposes has been an important driving force for societal advancement throughout recorded history. Until the mid-1950s, changes in society were associated with employment of relatively few metals,[11,28] most of which were recovered for reuse. During the past six decades, metal use has expanded to include a large portion of the periodic table. Q4 Hagelüken and Meskers[1] observed in 2010 that 80% or more of cumulative mine production of platinum group metals (PGM), Ga, In, REE, and Re has occurred over the last thirty years. In a special National Academy of Sciences report on critical minerals,[11] it is pointed out that since the early 1980s there has been a marked increase in the number of metals or their derivatives used in computer chips. This increase has resulted from technological advances requiring increasingly more specialized metal properties. In the 1980s, computer chips were made with a palette of twelve minerals or their elemental components. A decade later, sixteen minerals were used. By 2008, as many as sixty minerals or their elemental components were in use to construct the high-speed, high-capacity integrated circuits that are crucial to computer chip technology.[11] Along with the number of metals used, lack of recovery of them from EOL products is of great concern. Anastas and Eghbali[29] have discussed green chemistry as it relates to the life cycle of raw materials from product manufacture to efficiency and safety of the ultimate disposition of these products. The principles given by them have general applicability to achievement of metal sustainability.

Increased use of base metals has been fueled by the need to provide materials required for infrastructure needed by a population growing in number and affluence worldwide. Growth in the use of specialty and precious metals (Table 1) has its origin in unique chemical and physical properties possessed by these metals, which, generally, are much less abundant than base metals (Fig. 2). These properties in the hands of material scientists, chemists, physicists, and engineers have resulted in a myriad of new high-tech products now enjoyed by society.

As metal use increases and expands, concern grows about the future of this finite resource. Inevitable depletion of ore bodies requires that new ones be found or improved extraction procedures be developed in order to meet increasing demand for target metals.[1] Search for new ore bodies is ongoing and has increasingly led away from traditional mining areas in Europe and North America to mineral-rich locations elsewhere such as Asia, Africa, Australia, South America and even deep in the Earth's crust and on the ocean floor.[1,4] Kesler[1] has discussed the challenges that would be encountered with locating and mining Cu deposits deep in the Earth's crust. He and his co-workers have estimated that at a depth limit of 3.3 km there may be a resource of Cu amounting to 8.4×10^{10} tons of Cu or 5400 years of current production.

The grade of ore mined in a given location decreases with time and eventually becomes too low to be economical.[1,30] Improved extraction processes have made it possible to mine and process ores of increasingly lower metal content. However, Norgate[1] has observed that, as ore grades decline, there are Q5 large increases in gross energy and water requirements for metal production (Section 3.2). Water is used mostly in mineral processing and refining. The increased energy consumed derives primarily from the need in the mining and mineral processing stages to move and treat additional gangue material. Worrell[30] has estimated that annually (~2004) 6.4×10^9 metric tons of ore is extracted from the Earth, of which >90% is discarded as mine and mill wastes. He points out that with the increasing quantity of ores used the amount of energy needed to extract and process the ores has also increased dramatically. His conclusion is that this situation is unsustainable from environmental and long term economic perspectives. Ore mined for Cu in the United States has decreased in average grade (Fig. 3) from

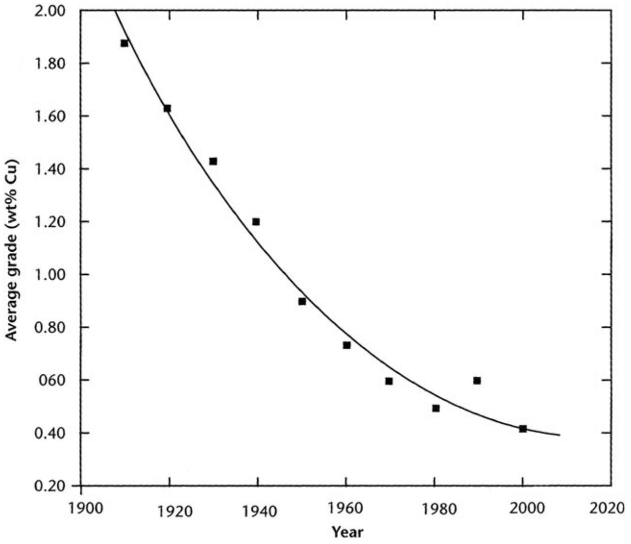

Fig. 3 Trend in the average grade of ore mined for copper in the United States during the 20th century. Reproduced from ref. 4 with permission.

$\sim$2% at the beginning to $\sim$0.4% at the end of the 20th century.[1,4,30] Concern has been expressed by Kesler[1] and Gordon *et al.*[13] that, in some cases, such as Cu, Zn, and PGM, minable deposits will approach exhaustion at some point in the future. On the other hand, some argue that Earth's stock of deposits will expand as increasing prices allow the exploitation of lower grade deposits. These contrasting views have been presented and discussed by Kesler.[1] Rare specialty elements such as In, Re, Nb, and Te are obtained solely as by-products of base-metal mining, being selectively concentrated by Earth processes in ores of these metals. Availability to commerce of these specialty elements depends on continued production of particular base metals.[1,15] These areas of concern provide valid reasons for improving metal sustainability by recycling to provide reliable alternative sources for these specialty metals, thereby reducing the need to mine virgin ore to replace discarded metals.[1]

The history of Cu illustrates the global challenges faced as a result of increased demand for metals and for by-product specialty metals found with them. Copper was discovered long ago, perhaps when some early observer noticed that a greenish stone heated in fire produced a material which possessed new and useful properties.[28] Valuable properties of Cu, which have sustained its use over the centuries and have made it an ideal material for creation of novel materials, include[28] ease of working by conventional industrial processes; suitability for alloying with many other metals; ease of joining by soldering and brazing; good combination of mechanical qualities; high resistance to corrosion; suitability for many artistic purposes; and, of great importance in the modern era, efficient and economic use as a conductor of electricity. Total amount of Cu produced prior to 1800[28] is estimated at about five million tons, less than is mined in a single year today. The history of Cu during the past 150 years illustrates marked increases in mining and ore processing operations necessary to meet the demand for this metal;[1] significant environmental, health, and carbon-footprint effects associated with Cu mining;[5,31] inevitable decreases of minable Cu ore sources over time resulting in worldwide searches for new Cu ore bodies;[1] increased interest in recovery of specialty metals as by-products in Cu processing as the need for these metals develops;[31] and challenges involved in recycling EOL products containing Cu and its by-product metals.[31]

Copper had limited use until the late 1800s when three events transpired that increased dramatically the need for this metal and forever changed our world. In 1876, at the Centennial event honoring the birth of the United States in Philadelphia, Alexander Graham Bell demonstrated his talking box using Cu as the electrical conductor.[28] In the last quarter of the 19th century, Edison and others developed many uses of electricity that required large quantities of Cu, which was ideal for electrical transmission.[28] In 1891, Marcus Daly discovered rich Cu-bearing ore at the Butte, Montana Anaconda mine.[32] Sudden need for Cu for electrical transmission led to the search for Cu ore bodies, such as the one in Butte. Rapidly expanding mining and processing of Cu followed at Butte and elsewhere.

Copper ore from Butte was sent, initially, to Wales for smelting and recovery of the Cu.[32] However, by 1900 at least seven mills and smelters were operating in the Butte region. Until 1955, Cu was mined underground at Butte. On 1 July 1955, Anaconda Mining Company began mining Berkeley porphyry Cu deposits as an open pit, which continued until 30 June 1982, when mining operations ceased.[4,32] At this time, pumps were shut off, and Berkeley Pit began to fill with water. Since 1982, incoming water became acidic by leaching metals from the surrounding rock and mine tunnels, eventually forming one of the largest Superfund sites in the United States (Section 4.2), and one of the largest accumulations of acid mine drainage in the world.[33]

Several specialty elements (Table 1) that have become essential in our 21st century technology are concentrated by geochemical processes in trace amounts in Cu ore. These elements were irretrievably discarded into tailings in early mining operations since there was no economic reason for recovering them. Copper processing is the main, and often the only, commercial source for certain of these elements. Molybdenite, MoS_2, is the predominant ore mineral of Mo mining.[15] Cu–Mo–Au porphyry ore deposits supply $\sim$75% of the world's Cu, 50% of the Mo, nearly all of the Re, and 20% of the Au.[15] Typical ore grades are 0.5–1.5% Cu, 0.01–0.04% Mo, and $<$1.5 g ton^{-1} Au.[15] Re and Te are among the rarest of metals (Fig. 2). Molybdenite is the primary source for Re, which is an essential component of super alloys used in, *e.g.*, turbine blades in the aerospace industry. Most Re is obtained as a by-product of molybdenite from Cu mines in Chile.[15] Tellurium is essential for current leading photovoltaic devices. The chief source of Te is as a by-product of electrolytic refining of Cu.[34] A change now under way in the Cu refining process to a less expensive SX-electrowinning procedure does not allow for recovery of Te, thus endangering its continued supply.[34] The cases of Re and Te raise an important issue. Continued availability of these rare specialty elements, selectively concentrated in Cu ores, depends on continued mining and processing of Cu and, in the case of Te, on the process chosen to refine Cu. Since the mining company's main interest is in Cu production, continued recovery of these and other specialty elements is at risk.[1,4] Dependence of supply of specialty metals on continued mining of major metals exists in several additional cases[1,15] including In, Ga, Se, Ge, and Bi. PGM, on the other hand, are typically mined for their own value,[15] which far exceeds that of the associated base metals.

Sphalerite (ZnS) is the most important source of In, which is obtained as a by-product of Zn mining.[15] Indium is about as abundant as Ag in Earth's crust (Fig. 2) but does not occur in sufficient concentration elsewhere than in ZnS to be mined profitably. In copper indium diselenide, In is used as a transparent absorbing semiconductor in solar cells. Indium's most important use (80%) is as indium tin oxide (ITO), which acts as a transparent conductor in liquid-crystal display (LCD) screens in flat-panel devices.[35] Forecast consumption growth rates for LCDs and solar cells project that supplies of In from primary mined Zn sources will be severely depleted by the early 2020s.[35] Estimated global reserves of In[35] range from 2800 (2006) to 11 000 (2007) tons with an annual consumption of 510 tons. Consumption is expected to grow to 1900 tons annually by 2030. Indium is a scarce commodity, yet its recycle rate is <1%.[10] Cadmium is also a by-product of Zn mining and processing.[15] Predictions indicate growing importance of solar panels with Cd–S/Cd–Te since Cd compounds provide a perfect match for the spectrum of the Sun. However, Cd compounds are extremely toxic[12] and considerable effort is being expended to find suitable substitutes.

REE are not as rare as is suggested by the name. Cerium is the most abundant REE, and its concentration in Earth's crust is similar to that of Cu and Pb (Fig. 2). All REE, except Pm, are more abundant than Au, Ag, Hg or PGM. However, despite being relatively abundant in Earth's crust, REE are rarely concentrated by geochemical processes into minable ore deposits.[16] REE are commonly found together in Earth's crust because they share a common trivalent oxidation state and have very similar chemical properties. Eu also has a stable divalent oxidation state, which allows it to substitute for Ca in plagiosite minerals.[15] Ionic radii of trivalent REE are large, precluding their incorporation into crystal lattices containing most trivalent ions. REE are divided into light (La–Eu) and heavy (Gd–Lu) metals.[15,16] Deposits usually have a preponderance of one type over the other, though ores rich in light REE, such as bastnaesite, are far more abundant. Trivalent Y, which has an ionic radius similar to that of the heavy REE, is found with these elements.[15]

Historically, world production of REE has come largely from deposits such as Bayan Obo in China (bastnaesite and monazite), Mountain Pass in California (bastnaesite), and heavy mineral placer deposits in India and South Africa (monazite).[16,36] Prior to ~1965, annual REE production was small and was largely from monazite sands (Fig. 4). REE-bearing minerals, once separated, contain as many as 17 individual REE (Table 1) which must be further separated and refined. REE are typically extracted and refined through multiple chemical processes to separate different REE and remove impurities. Thorium(IV) and, to a lesser extent, U(IV) are chemically similar to REE and, together with their radioactive daughters, especially Ra, constitute a ubiquitous and troublesome low-concentration radioactive impurity in REE minerals (Table 1), especially monazite sands.[15,16] Over Earth's lifetime, this radioactive decay chain has produced ~99% of terrestrial Pb[15] accounting for unusually high Pb concentrations in Earth's crust (Fig. 2).

China currently accounts for ~95% of global REE production (Fig. 4).[9,16] Of a total production in 2010 of 120 000 metric tons of REE, about 55 000 metric tons was produced as a by-product of the Bayan Obo Fe mine, which is the largest REE mine in the world.[16] Thus, ~44% of world REE production is a by-product. Of the remaining production, ~25 000 metric tons is produced as a primary product from ion-adsorption deposits.

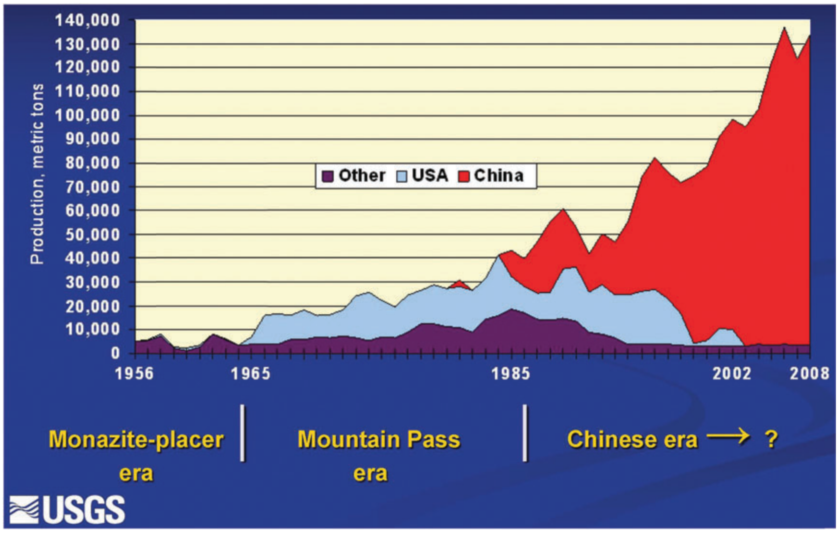

Fig. 4 Global rare-earth-oxide production trends, 1956–2008. The Mountain Pass deposit is in California, U.S.A. Reproduced with permission from U.S. Geological Survey, Department of the Interior. Accessed from website 30 October 2013. http://pubs.usgs.gov/of/2011/1042/of2011-1042.pdf

There is, presently, a worldwide scramble to bring other REE deposits into production. Notable among these is the Mountain Pass Mine in California with a rare earth oxide ore grade of 8.5%, the richest REE deposit in North America.[36] This mine produced the majority of REE prior to $\sim$1985[16] (Fig. 4). Upsurge of REE production beginning in $\sim$1965 coincides with the introduction of color television on a large scale and the use of Eu as the red phosphor. Mountain Pass mine closed in 2002 as a result of environmental restrictions and lower REE prices. Under new ownership, Mountain Pass Mine is back in operation and is projected to reach a future production level of 40 000 metric tons of rare earth oxide.[16,36]

REE are used widely in high-tech and clean-energy products because they impart special properties of magnetism, luminescence, and strength.[9,16] REE find use in weapon systems for the same reasons. These properties, derived from partially occupied 4f electron orbitals in most REE, make these elements superior, and often the only choices for specialized features in a variety of new products of importance to consumers worldwide. Amounts of REE used in each unit vary from $<$mg to several kg.[9] The number and variety of these products is truly amazing and includes solar panels; wind turbines; automotive catalysts; powerful permanent magnets; electric motors; high performance rechargeable batteries; numerous electronic commodities such as smart phones, flat screen devices, computer mother boards and hard drives; fluorescent bulbs; LEDs; and phosphors.[9,15,16] Concern about having reliable United States domestic sources of REE and other metals for national security reasons has been voiced.[11,16]

Future uses of REE might include magnetic refrigeration, taking advantage of high magnetic moments for Gd through Tm.[16] This new technology could be used in refrigerators; freezers; and residential, commercial, and automotive air conditioners. Magnetic refrigeration would be more efficient than gas-compression refrigeration and eliminate the use of refrigerants that are flammable or toxic, deplete the Earth's ozone layer, and contribute to global warming.

Production of U accelerated following World War II due to its use in military weapons and for nuclear power generation. Main producing countries of U are Kazakhstan, Canada, Australia, Namibia, Russia, and Niger.[15] Annual world production of U in 2009 was $\sim$50 600 tons.[15] The balance needed for annual consumption of 70 000 tons U required for the world's nuclear reactors is obtained from secondary sources, including former nuclear weapons, re-enrichment of depleted U, and stockpiles. Kim *et al.*[37] cite an OECD report that estimates conventional global U reserves at 6.3 million tons, approximately one century of supply at current consumption rates. Additional terrestrial U deposits will undoubtedly be discovered, but these facts have led to much interest in the recovery of U from seawater (Section 3.4) where the average U concentration is $\sim$3 μg L^{-1}.[15,37]

Thorium is a common trace impurity in U ores and in monazite placer deposits containing REE. India has particularly rich coastal placer deposits reportedly containing an estimated 400 000 tons of Th.[15] As greater amounts of REE are mined and processed to meet increased market demand (Fig. 4), concern for environmental and health effects of by-products U and Th together with their daughter products such as Ra and Rn becomes an important consideration. These radioactive species require special handling to prevent their entrance into the commons where they can have widespread environmental and health effects (Sections 4.2 and 4.3).

The major commercial deposits of PGM are located in only a few places—Russia, South Africa, Canada, United States, and Zimbabwe.[15] Platinum was used by native Americans in present day Columbia in pre-Spanish days.[28] The Spaniards named the metal ''platina'' or little Ag. They regarded Pt as an unwanted impurity in the Ag they were mining. Wollaston and Tennant, in 1800, succeeded in separating five of the six PGM,[28] *i.e.*, Pd (named after the newly discovered asteroid Pallas), Rh (after the Greek word for rose which is the color of aqueous solutions of Rh salts), Ir (after the Greek Goddess Iria), and Os (after the Greek word for odor, osme, because of strong and unpleasant fumes exuded by its volatile tetraoxide). In 1844, Ru was isolated and named after Ruthenia, the old Latin name for Russia.

The PGM supply in United States, Canada and Russia derives from Cu and Ni mining. Vast PGM deposits were discovered in the Transvaal in South Africa in 1935, leading to this region becoming producer of the majority of the world's PGM.[15,28] PGM are required in a variety of commercial, industrial, and military applications. Their use in electronic products, as well as catalysts in the automotive and petrochemical industries, has increased markedly in the past few decades.[15] Concern has been expressed that global minable supplies of Pt metals could be exhausted in the near future and that it is unlikely additional major deposits will be found.[13] Deposits are usually mined primarily for their Pt content. Thus, future availability of remaining Pt metals depends on continued mining of Pt ore. Labor unrest in South Africa in the PGM mining and processing industry has raised concern over possible constraints in PGM supply. Strikes could cause severe shortages of these metals. This illustrates the situation a nation, such as the United States, faces when it does not control sources of metals critical to products vital to that nation's security.

One of the earliest metals used by humans was Au.[15,28] Written references to Au date from the 12th Dynasty in Egypt, about 1900 BCE. Total Au recovered over human history is estimated to be 155 000 tons, which would fit into a cube $\sim$20 meters edge length.[15] Together with Pt and Re, Au is one of the rarest elements (Fig. 2). Despite this rarity, Au deposits are common, in large part because of lack of chemical reactivity of the metal. Gold is found in Cu porphyry deposits and fossil alluvial deposits, which account for 2/3 of world Au production.[15] Average Au concentration in ores is $\sim$3 g ton^{-1}. Gold is mined in many areas using primitive technologies including Hg amalgamation.[38] These activities account for extensive Hg pollution worldwide (Section 4.2). About 10% of the Au produced is consumed by industry for applications in electronics, dental applications, and architectural glass.[15] Gold is prized for its inertness, electrical and heat conductivity, and catalytic properties. Gold emerged in the late 20th century as an essential industrial metal because of its superior electrical conductivity, resistance to corrosion, and other desirable combinations of physical and chemical properties.

About 80% of total mine production of Ag is as a by-product, mainly from Cu, Pb, Zn, and Au ores. Economic viability of many base metal and Au deposits relies on by-product Ag.[15] Silver has many applications in jewelry, electronics, and various industrial processes.

Cadmium, Hg, and Pb are termed toxic metals because of their deleterious effect on human, animal, and plant health, even at very low concentrations.[12] These metals are present as impurities in sulfide ores of base elements. Lead and Hg are also found in minable ore deposits in which they are primary constituents.[15] There does not appear to be any danger of a shortage of these metals. However, there are health and environmental reasons to control their concentration levels in processing streams and to recover them in pure form before they enter the commons. Such recovery would allow them to be either reused or disposed of in an environmentally friendly way (Sections 4.2 and 4.3). Despite their toxicity, all three metals have important commercial uses. Cadmium is present in Ni–Cd rechargeable batteries (80% of total Cd consumption).[15] Primary uses of Pb are in lead-acid batteries for vehicles and other industrial applications (85% of total Pb consumption).[15] Toxicity of Hg has sharply curtailed its mining and use, especially in OECD nations.[14] However, this concern has not precluded its use in many non-OECD nations. China is the main supplier of mined Hg.[38] Mercury is widely used in fluorescent tubes that form the backlight to liquid-crystal displays of television sets and numerous other electronic devices.[15] In many parts of the world, Hg is employed on a small scale in Au amalgamation for recovery of Au. Sharp increases of Hg concentrations in the environment began in the late 1800s as shown in Fig. 5.[14] Of an estimated 5500 to 8900 tons of Hg emitted annually from all sources, ~10% is of natural origin and ~90% is of anthropogenic origin. The large increase in anthropogenic Hg emitted since ~1850, to ~20 ng L^{-1} in ~1990, is consistent with the rise of industrialization, primarily in Western Europe and the United States. These effects are examined further in Section 4.2. Spikes observed in Fig. 5 for eruption of three volcanoes (Tambora, Krakatoa, St. Helens) show Hg emissions from these sources, although large, to be short-lived and to not persist over centuries as do anthropogenic emissions.

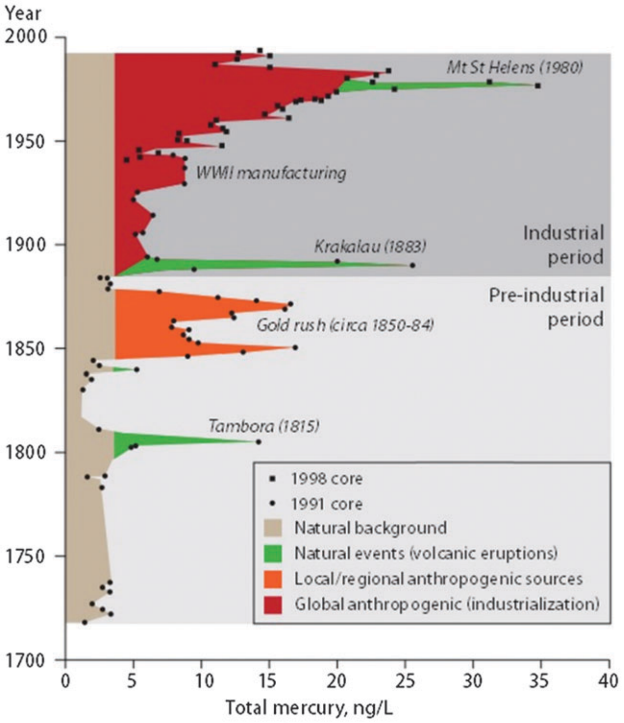

Fig. 5 Ice core record of deposition from Wyoming, USA. The elevated levels associated with the 1850–1884 gold rush probably reflect local/regional sources rather than a global signature. Increasing environmental levels of mercury associated with industrialization, however, are found in environmental archives like this ice core around the globe. Reproduced from ref. 14 with permission.

3.2 Energy and water impacts

The amount of energy and water consumed in producing metals from virgin ore is large. MacLean *et al.*[1] estimate that "mining and processing of metals utilize about 7% of total world energy and 0.03% of total world water." Norgate[1] points out that "it is almost inevitable that ore resources will deteriorate over time as higher grade resources are exploited and progressively depleted." The energy required to treat ores increases rapidly as ore grade decreases largely due to the additional energy that must be consumed in mining and mineral processing stages to move and treat additional gangue or waste material. The amount of energy involved is substantial. For example, Norgate[1] cites earlier work by him and Jahanshahi in which a change in Cu ore grade from 1% to ~0.25% was shown to result in a significant embodied energy increase that was highly dependent on grind size. For example, the embodied energy at 1% ore grade ranged from ~75 MJ kg^{-1} Cu (5 μm grind size) to ~125 MJ kg^{-1} Cu (75 μm grind size) while this energy at ~0.25% ore grade ranged from ~250 MJ kg^{-1} Cu (5 μm grind size) to ~475 MJ kg^{-1} Cu (75 μm grind size). The expected increase in energy as ore grade decreases is compounded by the increased energy required to achieve smaller grind sizes. Paralleling this increased energy is an increased requirement for water to treat the additional gangue material. Norgate[1] points out that a further consequence of the increased energy requirement as ore grade falls is increased greenhouse gas emissions. Recycling offers a viable means to partially offset the need to mine and process virgin ore and, thus, reduce the energy and water requirements of the mining and mineral processing stages.

3.3 Methods for metal retrieval

Despite the occasional discovery of rich sources of certain metals, such as manganese nodules on the sea floor, future challenges for mining of geochemically scarce metals lie in trends toward leaner concentrations and more complex mixtures in virgin sources and resulting process streams, as pointed out by Kesler.[1] Given finite crustal abundances, the probability of the discovery of significant new resources must decrease over the long-term. Perturbed by the occasional discoveries still to be expected,[4] the long-term trend progresses toward lower grade ores, especially for scarcer elements with increasing demand. This trend will stress currently used technologies, stimulating their improvement along with the development of alternative approaches that can deal better with low metal concentration levels and exploit the coincident metal values in a given source. In this section, the major methods for mineral processing in use, their advantages, and their limitations in the face of growing challenges will be described.

Methods for mineral processing may be categorized as either pyro- or hydrometallurgical.[18] Microbial methods might be considered as a third category; their major implementation is bioleaching, which provides feed for hydrometallurgical processing.[18,20,21] Although this discussion deals with mining of virgin sources, similar problems will be encountered in recovering metal values from EOL products as well as from various waste and environmental streams derived from processes used throughout material lifecycles (Fig. 1). All of the methods are fundamentally separations whose effectiveness in any given case is measured by selectivity, energy and water usage, and waste production. The total cost of material and energy consumption cannot exceed the cost of the metal values recovered, which places a premium on the robustness of separation agents and separation efficiency. Ideally, environmental costs should also be factored in, but usually they are not totally accounted for. Other factors being equal, selectivity largely determines how dilute the source is that can be treated, the recovery possible, the purity of the recovered metal, and waste production. Thus, selectivity becomes a critical parameter in examining recovery methods in light of metal sustainability.

Virgin sources of recoverable metal values are found in natural brines as well as ores. Natural brines include seawater, saline lake water, and geothermal brines. In total, brines contain vast amounts of metals with apparent opportunity for metal recovery in that the work and expense associated with mining, transporting, crushing, and grinding ores is avoided. Environmental costs associated with conventional mining are also avoided, adding incentive from the point of view of sustainability to utilize brines wherever possible. Seawater represents the largest resource in total for many geochemically scarce metals, greatly exceeding continental resources,[4] though high metal dilution (typically $<0.2\ \mathrm{mg\ L^{-1}}$) presents a daunting challenge for hydrometallurgical separations. Seawater is processed, however, to harvest salts of the abundant metals sodium, potassium, and magnesium.[4] These salts are recovered by crystallization techniques using solar evaporation, a simple technology requiring substantial acreage of evaporation ponds. Saline lakes and geothermal brines have higher contents of certain elements such as lithium, manganese, zinc, and boron, which may be economically recoverable.[15] Here, solar evaporation is again used, in which the abundant salts are first crystallized out, concentrating the desired scarce metals for subsequent precipitation by addition of suitable agents, such as carbonate or hydroxide.

Continental ore bodies constitute the primary source of the majority of metals.[15] Production of metals from ore encompasses many types of operations tailored to the ore and metals, but we may broadly consider the sequence to involve mining, beneficiation, separations, and metal production.[18,19,23] Mining entails extracting ore from an ore body, transportation, crushing, and grinding. Relying on physical separations such as froth flotation, beneficiation produces a concentrate that can be further processed using pyrometallurgical or hydrometallurgical separations. Although some ores such as bauxite may be sufficiently concentrated as mined for direct processing, ores of scarce metals typically require extensive beneficiation. This requirement is key for the economics of subsequent processing, which requires extensive use of separation agents, energy, and water as well as production of large amounts of waste. Concentrates from beneficiation are treated by various processes and separations to change the chemical form of the concentrate as needed, separate metals from gangue and from each other, and purify metal-containing product streams for final production of metals.[18]

Early processes for winning metals from their ores probably involved some form of pyrometallurgy.[28] Heat, perhaps from a campfire, could have caused the transformation of a rock into a new material with quite different, but useful, properties as mentioned earlier in connection with Cu (Section 3.1). This process, somewhat modified, has remained an important method of producing metals to the present day.[18,19] Pyrometallurgy, especially smelting, is the method of choice for winning metals from virgin ore and for recovery of metals in recycling. Smelting is economical at large scale, but is less effective in recovering metals present at low concentrations. In simpler forms, elevated temperature procedures are used to win metals in informal recycling of EOL products (Section 5.2) and to concentrate wastes by incineration (Section 5.1).

Modern state-of-the-art smelters are capable of recovering a variety of metals at high purity levels.[24,31] However, this purity comes with significant environmental costs.[4] Smelting processes result in emission of respirable particulate matter, which can contain a variety of pollutants including noxious gases (*e.g.*, SO_2, NO_x, PO_x); greenhouse gases; organics such as dioxins from combustion of plastic cases;[4] and toxic metals (Table 1).[12] Environmental regulations to limit emission and dispersion of toxic metals and organics into the commons are becoming more frequent worldwide as public awareness of environmental issues increases.[4,6] Low grades of most ores—PGM are a few grams per ton of mined material—result in >99% of the mined material becoming gangue, which may contain appreciable amounts of toxic metals and organics. Treatment of ore with various chemicals during processing results in additional potential environmental hazards. Smelters have large space requirements and operate at high temperatures, usually >1000 °C. Electricity used to attain this temperature is derived mainly from coal combustion producing a high carbon-footprint.[38] Replacement of coal as a source of electricity by green electricity sources such as wind power, solar, thermal, and photovoltaics has potential for reducing this carbon-footprint. A significant limit to pyrometallurgical processing of electronic wastes is the long inventory time for precious metals which are recovered at the end of the process.[19]

Hydrometallurgical techniques, either in ore treatment or in recycling, can offer important advantages over pyrometallurgical processes.[4,18,19,23] These advantages include diminished or eliminated air pollution, shortened treatment cycles, and higher metal recoveries. However, with traditional separation techniques such as precipitation, ion exchange, and solvent extraction, potential environmental pollution can be appreciable due to general use of solvents and other chemicals in refining processes. Also, water usage by hydrometallurgical techniques is significantly greater than for pyro processing.[4]

Selective precipitation of metal ions using various precipitants has been employed for centuries to remove metals from aqueous solutions and is a well known, inexpensive procedure widely used today.[18] Precipitation processes involve addition of chemicals (usually hydroxide ion or sulfide ion) to the system and result in the formation of particulate solids collected by filtration, centrifugation, or sedimentation. Depending on the application, these processes can be highly selective, as in precipitation of cesium with tetraphenylborate, or they can have low selectivity, as in precipitation with carbonate ion or hydroxide ion. In all cases, the matrix is altered by the precipitating agent, residues of which remain in solution, presenting possibilities of secondary-waste production or pollution. Co-precipitation of other components is a common problem. Precipitation becomes less effective for recovery of metals from dilute feeds, though it is used for water purification, *e.g.*, addition of iron hydroxide in excess to bring down various impurities.

Ion exchange is a highly effective separation technique mainly for dilute solutions and has been a mainstay of the water-purification industry. Ion exchange phenomena involving adsorption of metal ions by natural clays have been known for over 150 years.[18] Clay sorbents have the advantage of being inexpensive, but their selectivity is limited, they may be difficult to elute, their capacity is low, and they may be difficult to employ in columns. Development of synthetic resins in the 1940s marked a significant advance in development of commercial IX processes. Separation of REE into their individual components as part of the Manhattan Project in World War II was a notable achievement of IX. Later development of chelating resins was a significant advancement in applications of IX to metallurgical separations.[18] Ion exchange resins and chelation IX resins are routinely used in commercial systems to selectively separate metal ions. Ion exchange processes are simple in design, are applicable to dilute feeds, have high concentration factors, and have no loss of the separation agent (resin) to the environment. However, reaction kinetics are usually slow, the method is not applicable to concentrated feeds, and selectivity is usually limited, depending on the separation agent used. In ordinary IX, selectivity is based on ion charge (3+ > 2+ > 1+), and in chelation IX, on the use of ligands, which have selectivity for specific metals. Limited numbers of chelating agents have been used in chelation IX with the most common being iminodiacetic acid.

Solvent extraction involves transfer of a solute from one liquid phase to another immiscible or partially immiscible liquid that is in contact with the first phase.[18] The first phase (aqueous) contains the metal to be concentrated into the second phase, an organic solvent comprised of a diluent such as kerosene and an extractant, usually an organic chelating agent. Solvent extraction has been used in commercial operations for over a century, and due to its flexible chemistry and wide variety of potential extractants has been adopted for major uses in the nuclear and metal industries. Because of its good selectivity and adaptability for remote processing, SX has become the workhorse separation method for nuclear separations. In the metal industry, the largest use of SX is in recovery of Cu from ore leach solutions, amounting to approximately a quarter of global Cu production. Limitations of SX include the use of volatile, combustible, and toxic solvents and traces of solvent components carried into effluent streams.[29] Considerable chemical knowledge is required of operators. Kinetics may be an issue with certain chelating agents and metals. However, clean and selective SX systems can be developed as shown in ^{137}Cs recovery from nuclear wastes (Section 3.4).

Bioleaching of minerals[21] and bio-processing of solid wastes and secondary resources such as electronic wastes for metal extraction[20] have become important commercial enterprises during the past half-century. A variety of microorganisms have been employed. Bio-extraction of metals from various metal-containing wastes and by-products with a variety of microbes such as bacteria, fungi, and archaea is being increasingly explored as a means of resource recycling and pollution mitigation.[20,21] Mechanisms of metal extraction processes have been studied including the action of excreted complexing agents such as carboxylic acids and CN^-. Shortcomings of bioleaching include long time periods, very low pulp densities in tank reactor systems, and low efficiency levels of extractions. However, bioleaching also has advantages including low cost which may be one-half to one-third that of conventional processes, low amounts of hazardous emissions, and low tech systems with the use of naturally occurring biocatalysts.[20,21] It has been suggested that bacterial cyanide generation has the potential of replacing cyanide chemicals to leach gold under alkaline conditions making Au recovery much simpler and less pollutive.[20]

3.4 Future issues for sustainable metal processing

As ores, natural brines, and recycling streams become increasingly dilute or complex, processing costs to recover and purify metals contained therein increase. Challenges to economics include increasing complexity of the processing needed and increased consumption of resources, energy, water, and labor.[1] Eventually, traditional techniques such as pyrometallurgy, precipitation, and solvent extraction become less practical. With extreme dilution, some fundamental limitations are reached. A few examples of metal recovery from dilute feed stocks are now presented.

Although seawater is a vast potential source of many metals, their extreme dilution tests the limits of practical recovery. An excellent example is recovery of U from seawater,[37] where concerns for energy security drive research efforts in several countries. The total inventory of U in the oceans is estimated at

4.5×10^9 tons, which may be compared with the estimated 5×10^4 tons of U produced worldwide in 2009.[15] However, because the concentration of U in seawater averages a scant 3 $\mu g\ L^{-1}$, energy consumed in even pumping water for processing can exceed the value of recoverable U. Thus, passive techniques are required if there is any hope for economical recovery.[4] The prototype technology being developed currently involves a synthetic fibrous polymer adsorbent mimicking passive filtering actions of fan-like seafloor plants. Among a host of sorbent materials tested in decades of effort, fibrous polyacrylamidoxime materials are emerging as most promising. The benchmark capacity of 3.2 mg g^{-1} sorbent is likely to be exceeded in the near future in the United States. An economic analysis indicates that production costs for U stem from mooring and sorbent aspects. Sorbent capacity and recyclability are critical properties of the sorbent, where capacity reflects the selectivity of U uptake in a huge excess of competing ions. If capacity can be boosted to 6 mg g^{-1} sorbent sustained for 10 uses of sorbent, the cost of U recovery can drop to about $350 per kg, which compares well with the peak price of U in 2007–2008.[37]

Similar limits are reached in treating ores, where diminishing ore grade ultimately leads to unaffordable energy costs for moving, crushing, and grinding rocks. Thus, any recovery of metals in this limit requires techniques that can treat the ore in place. Because of poor economics, little has been done in this area for metal recovery in contrast to the expanding magnitude of *in situ* oil and natural gas extraction. *In situ* leaching has been practiced on a limited scale, for U as an example, but it is applicable only where groundwater contamination can be avoided.[4] More experimental techniques such as electro osmosis have been explored for the purpose of environmental remediation of metal contaminants.[39] Long-term developments can be expected from this quarter driven by regulatory compliance and liability.

Treatment of low-grade secondary ores gives a picture of which technologies apply when standard pyrometallurgical and hydrometallurgical practices are not applicable. Most noteworthy in this regard are heap bioleaching processes for metal sulfides, which have been steadily, albeit slowly, improving since the 1950s with advances in engineering of heaps, aeration techniques, and use of thermophilic microbes.[20,21] The advantage of heap bioleaching lies in avoidance of milling costs associated with grinding, beneficiation, and tank leaching. Copper recovery by bioleaching of heaped sub-economic ores has seen the largest application, but Au is also recovered from refractory ores in this manner, and technologies for other metal sulfides have reached or exceeded pilot scale. Mechanisms vary according to metal and mineralogy, but in all cases, the process occurring is the net oxidation of the sulfide mineral by air, facilitated by microbes. Target metals are released into solution where they can be treated by downstream hydrometallurgical processes.

The importance of beneficiation of mined ores will increase as ore grades decline. Following crushing and grinding of ores to liberate the mineral particles of interest, physical separations are undertaken to produce a concentrate for further processing either at the mining site or at external facilities. The effectiveness of beneficiation processes has a direct bearing on the economics of downstream processes, which otherwise will be burdened with excessive amounts of gangue material that will wastefully consume energy, water, and chemicals. One of the most effective beneficiation techniques is froth flotation, which employs selective adsorbent molecules called collectors to bind to surfaces of target minerals, rendering the particles hydrophobic. Passage of air bubbles through the slurry results in a froth to which are attached the hydrophobic particles. The role of the collector molecules, which must act in concert with other agents used in flotation such as depressants and frothers, entails selective adsorption onto the mineral of interest. Current approaches aim to match surface structure with chelating functionalities on the collector to maximize selectivity.[40] An excellent example is beneficiation of bastnaesite ore at the Molycorp Mountain Pass mine, where ore initially at 7% rare earth oxide can be beneficiated to 65% rare earth oxide.[36]

In the face of increasing challenges, successful separation technologies will be those that can recover metals with high energy efficiency[29] with good yield and purity, adding additional value by simultaneously recovering multiple metal values from the same stream. Separation agents featuring high selectivity with desired selectivity patterns will be the key to achieving this goal. During the past two decades, a breakthrough in achieving extremely high selectivity in separations has been obtained through introduction of molecular recognition principles in designing powerful new separation agents. Some examples of separation agents selective for metal ions by metal–ligand coordination are given in Fig. 6. In general, molecular recognition can be applied in many types of separation techniques that employ metal-selective ligands, wherein the ligands may best be described as ion receptors or hosts. In SX, the receptors must be lipophilic and usually bear bulky alkyl groups.[18] This is also true in liquid-membrane transport and extraction chromatography. Ion exchange, chelation IX, and sorbent materials can involve receptors bound to porous solid supports. Receptors used in crystallization result in precipitation of the bound metal in an insoluble phase, or in reverse, the binding action of the receptor results in the dissolution of the target metal. In all cases, the receptor serves to selectively bind the target metal ion through multiple donor–acceptor interactions up to and including encapsulation. The binding results in the target ion being moved to or across an interface where it is concentrated for a subsequent recovery step in which the bound metal is released and the receptor material recycled.[18]

Although it may seem counterintuitive to employ more sophisticated and costly reagents when the return per unit volume of feed decreases, the high selectivity and reusability of molecular recognition products are actually what can make the process economical. This goal is achieved by increasing the capacity of the separation agent, the concentration factor obtainable, the effectiveness of product recovery and release, and the purity of the product obtained while decreasing the consumption of reagents and waste production. Molecular

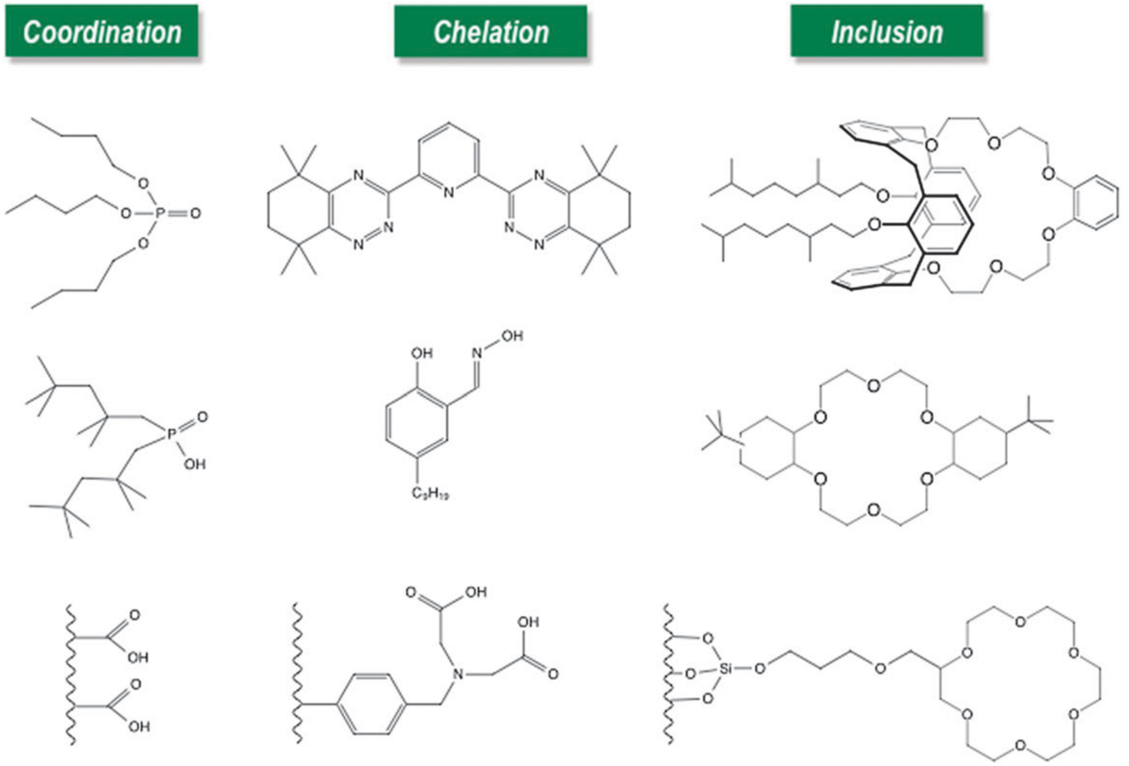

Fig. 6 Some basic receptors selective for metal ions. Ligands used in solvent extraction and ion exchange exhibit varying degrees of molecular recognition. As shown in the left column, simple monofunctional ligands possess useful selectivity according to the coordination preferences of the donor groups. Selectivity may be controlled in a limited manner by changing substituent groups and the chemical matrix. Obtained by joining multiple functionalities into one ligand, chelation provides enhanced binding strength for metal ions that are both attracted to the donor atoms of the ligand and fit within its "bite." Strongest molecular recognition results from inclusion within a cavity formed by the ligand donor atoms, favoring only ions that fit within the cavity and that have complementary geometrical and electronic bonding requirements.

recognition simplifies and therefore economizes what would otherwise be great complexity in treating dilute feeds, where multiple steps get reduced ideally to a single step. If the separation material used can be recycled many times with negligible losses, costs then reduce to energy and chemical inputs and operating expenses. In this way, molecular recognition can extend the lower limit of dilution that can be economically treated. Because some solvent is always lost to aqueous effluents in each SX cycle, liquid–liquid extraction loses its effectiveness in the 100 to1000 mg L^{-1} range depending on the metal and application; without a downstream solvent-recovery process, such losses have potential environmental consequences. Robust molecular recognition materials in which the receptor is covalently bound to a solid support, thereby preventing its loss, can provide the needed recyclability to treat metal-containing streams at $<$100 mg L^{-1}. Historically, unsolved problems in treating wastes in the nuclear industry have driven much of the early progress in molecular recognition for separations, where the limits of selectivity are tested by the complexity of aqueous mixtures and where other costs of handling highly radioactive streams dwarf costs for separation materials. Hydrometallurgical applications of molecular recognition are now well established. Examples of successful industrial implementation are presented below.

Use of molecular recognition for nuclear-waste cleanup has been reported by Moyer.[41] In this application, known as the caustic-side solvent extraction (CSSX) process, radioactive fission product ^{137}Cs is removed from Cold War defense nuclear waste using the calixarene-crown ether depicted in Fig. 7 as the extractant. Cesium is present at 10–100 mg L^{-1} concentration levels in this alkaline matrix, which contains $\sim$5.6 M Na. Cesium must be removed to >99.9975% and concentrated 15-fold, which can be achieved owing to the high selectivity of the extractant, with a single-stage Cs/Na separation factor exceeding 10 000. Thus, the CSSX process sends a stream of nearly pure $CsNO_3$ in nitric acid at pH 3 to the vitrification plant and a highly decontaminated waste stream for economical disposal. Pilot-plant data show that residues of organic solvent in the aqueous

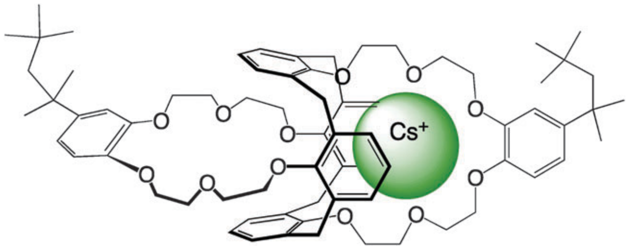

Fig. 7 Calix[4]arene-bis(*t*-octylbenzo-crown-6) (BobCalix), shown with a Cs^{+} ion bound in one of two identical cavities formed by the facing aromatic rings and polyether chains.[41]

effluent streams can be reduced to <10 mg L^{-1} with a downstream coalescer, demonstrating that the issue of solvent residues in SX can be minimized. CSSX was selected over competing IX and precipitation technologies owing to its adjudged lower technical risk, while costs were comparable.

While applications of molecular recognition gain advantage from the peculiar economics of radioactive material processing, important inroads in hydrometallurgical metal recovery point to a growing role in metal sustainability. Not surprisingly, its first such uses lie in recovery of high-value metals, where it is ideally suited for the highly dilute, complex mixtures encountered. No examples of molecular recognition for SX or crystallization can be cited as being in plant-scale use, but selective ligands tethered to solid supports have made applications possible using convenient column techniques.[18,23,42] The advantage of this approach lies in the ability to treat large volumes of solution while the sorbent material in the column steadily loads the target metal ions. Small amounts of an appropriate eluent solution then bring the loaded metal off of the column in a highly concentrated and pure stream. In one application, spent catalysts are digested, yielding an acidic solution containing mg L^{-1} levels of Pd. This solution is passed directly through the column, which selectively binds the Pd, subsequently releasing it to the eluent at high concentrations (g L^{-1}) that can be sold directly or reduced to Pd metal.[23] Selective sorbent technology is also used for commercial recovery of Pd from native ore.[23] Advantages over conventional technologies include quantitative and selective removal of Pd, dramatically increasing Pd yield with reduced amounts of Pd going to recycle, elution from the resin in pure form, and simplified downstream recovery of other Pt metals. Thus, high selectivity results in more rapid and economical Pd recovery by elimination of several process steps and of additional added reagents. Another example is the recovery of Rh from spent automotive catalysts and other feeds.[23] Benefits include significant reduction in process time, reduction in floor space, and use of small volumes of wash and eluent, both of which can be recycled, resulting in essentially a zero-discharge process.

Besides direct recovery of metals, selective sorbents employing molecular recognition can be valuable in metal purification processes. High purity Co is required for many applications and Cd, if present, must be removed to concentration levels as low as 10 mg Cd per kg Co. van Deventer[42] reports one example in which Cd at trace levels ($\sim$6 mg L^{-1}) was removed from a Co electrolyte solution containing 60 g L^{-1} Co as well as other metal impurities using molecular recognition sorbents.[42] An upgrading ratio of 480 was achieved, *i.e.*, 2.9 g L^{-1} Cd loading onto the resin from a solution containing 6 mg L^{-1} Cd in a background of 55–60 g L^{-1} Co. Cadmium can then be eluted from the resin and recovered as pure metal.

In smelting and refining Cu, removal of impurities such as Bi to specified concentrations is difficult, but necessary.[43] Bismuth is particularly harmful when it is present in Cu cathodes because it causes brittleness in the Cu metal structure, and can hinder the cathode's subsequent use in wire-drawn products. Control of the Bi content of the Cu electrolyte in these cases is necessary to produce the high purity Cu required in high-tech applications. Solid sorbents using molecular recognition are employed commercially worldwide to maintain Bi impurity levels at target mg L^{-1} concentration levels in Cu tank-house solutions. Bismuth is eluted from the column, resulting in a highly concentrated several g L^{-1} bismuth sulfate solution that can be marketed to offset the cost of its removal.

Chelating resins have found important applications in recovering metals from dilute aqueous solutions,[42] though their selectivity is limited in comparison with molecular recognition. Purification of cobalt sulfate is a noteworthy application in that normally Ni separation from Co is a challenging chemical problem.[42] A chelating resin bearing bispicolylamine functionalities has found application in accomplishing this separation, achieving a Ni loading of 16 g L^{-1} from a 25 g L^{-1} Co solution containing 0.7 g L^{-1} Ni.[42] Aminomethylphosphonic acid resins have found application in removing Cu and Zn to <2 mg L^{-1} from Co electrolytes containing 15–50 g L^{-1} Co. Other important chelating resins contain iminodiacetic acid and methyldiphosphonic acid as active components.

4. Environmental aspects of metal use

4.1 General

Hardin[3] discussed the dilemma of depletion of a resource shared in common by individuals, acting independently and rationally according to the self-interest of each, despite their understanding that depleting the common resource is contrary to long-term best interests of the group. This assessment may be applied to many human activities including environmental consequences of actions related to the metal cycle in Fig. 1. Appropriate use of the commons is compatible with metal sustainability.[4] However, improper use is antithetical to sustainability, because as a resource is depleted without replacing it, access to it by present or future generations becomes more limited. Once taken from the Earth, metals continue to exist in some form in the environment. The choice is whether their fate should be controlled as much as possible or they should be discarded and allowed to move essentially unhindered through the commons. Once EOL metals or EOL products containing them enter the commons, it is usually beyond the reach of present technology to recover metals effectively, since their concentration is markedly reduced (Section 3.4). However, their environmental and health effects persist and can result in damage to the immediate surroundings, and, in some cases, to the extended global community. Thus, recovery of metals before they enter the commons is desirable. However, this is a formidable task that is being tackled with mixed results by the global community. These ideas are explored in the following sections.

4.2 Ground, air, and water contamination

Insidious buildup in the commons of waste metals has far-reaching environmental and health consequences.[12] Metals are essential to the functioning of our society; yet if care is not exercised in their production, use, and disposal, they enter the commons where they can be severe hazards. Deleterious effects of mining, metal processing, and informal recycling on the environment are extensive. In 1998, Lichti and Mulcahy[44] reported that in the United States alone there were more than 250 000 abandoned sites, over 20 000 kilometers of rivers and streams contaminated by acid mine drainage, and 180 000 contaminated lakes and reservoirs. Strict environmental laws passed in OECD nations in the latter part of the 20th century have markedly reduced the amount of waste material in these regions that enters the commons.[6] However, unregulated dumping still occurs, particularly in non-OECD nations where environmental laws either do not exist or enforcement is lax.[6] Too often, little or no effort is made to restore the environment if it has been damaged. Landfill and incineration are primary methods worldwide for dispersal of EOL products into the commons[5] and there are environmental and health concerns with both of these practices, as will be discussed. Several examples of metals entering the environment are now given to illustrate these and related concerns, one involving Cu from several decades ago illustrating the continuing environmental effect of acid mine drainage sites, and two involving REE and Hg mining which present significant current global environmental and health concerns.

Berkeley Pit (Section 3.1) is the remnant of approximately one century of Cu mining in one of the most important mining complexes in the world.[32,33,44] During excavation of Berkeley Pit, over 3×10^8 cubic meters of rock were removed, producing nearly the same amount of gangue, since the Cu content was relatively small. Since 1982, ground and surface water have entered the Pit, raising the level by April 2012 to 5301 feet above sea level. The critical level is 5410 feet at which Berkeley Pit solution will enter the local aquifer. This could happen by 2022, but current pumping of mine solution from the Pit makes it unlikely. Main metals present are Al, As, Cd, Ca, Cu, Fe, K, Mg, Mn, Ni, Na, Pb, Zn, and Si. Chloride ion and sulfate ion are the major anions present. The pH is 2.5–3.0. Metal concentration levels exceed discharge regulations as defined by the United States EPA Gold Book (environmental standards for pristine water supplies) by large amounts, often orders of magnitude. In the mid-1990s, the water level was rising at a rate of ~8 m per year. In 2006, Berkeley Pit was estimated to contain >130 billion liters of acid mine drainage.[33] Recovery of metals from the site is accomplished in one case by pumping deep Pit solution to the surface where it is passed over scrap Fe to reduce and precipitate the Cu.[33] The resultant Fe(III)-enriched solution is returned to the lake. In effect, this procedure replaces one contaminant by another. Minimal efforts have been made to restore this acid mine drainage site. Extensive studies have been made of new microbiological organisms that grow under acidic conditions present in Berkeley Pit and which may be of pharmaceutical interest.[33]

Schüler *et al.*[16] have authored a comprehensive study on REE and their recycling as a final report to the Greens/European Free Alliance Group in the European Parliament. In this report, environmental aspects of mining and processing REE in China and the rest of the world (Fig. 4) are described in detail. It is pointed out that refining of REE concentrate is an energy-intensive process causing extensive air and water emissions. In the largest Chinese REE mine in Bayan Obo, located in northern China, surface mining extracts a bastnaesite–monazite-mix containing light REE and Th. Severe environmental problems and health hazards in mining, concentrating, and processing the mined ore are documented in the report.[16] A large number of chemical materials are used in these processes, leading to a huge amount of gas, water, and solid waste. The tailings produced are transported to large nearby areas and piled up. The tailings contain extensive waste material including radioactive Th and U with their daughter products. The tailings impoundment/reservoir of the whole mining operations (iron ore and rare earth concentration plants) is twelve kilometers in length and covers eleven square kilometers. This area is about 100 times the size of the alumina factory waste pond that collapsed in Hungary on August 4, 2010 releasing 600 000 to 700 000 cubic meters of toxic red sludge into its surroundings.[16] The amount of tailings at the Bayan Obo site was estimated (~2010) to have reached 150 million tons. The average Th content in the tailings and residues is reported to be 0.0135%.[16]

Heavy REE are mined from ion adsorption deposits in southern China. These are among the few REE deposits without accompanying radioactive elements. However, other environmental and health problems associated with processing these ores are similar to those found with the Bayan Obo ores.[16] There are also numerous small illegal REE mines in China. It is estimated that large amounts of REE material are illegally mined and smuggled out of China. It is probable that most of these smaller mines do not have adequate treatment systems or any system for environmental protection.[16]

Outside of China, two mining and processing projects are either operational or nearly so. These are Mountain Pass in California, and Mt. Weld in Western Australia with further processing in Malaysia.[16,36] These projects have passed national approval procedures and are assumed to have installed technologies for advanced environmental standards. Of course, significant reduction of environmental damage compared to old outdated techniques requires responsible management of monitoring by appropriate authorities and project operators.

The greatest proportion of anthropogenic emissions of Hg to the atmosphere comes from Asia which contributes ~50% of the global total, which was estimated at 1960 tons in 2010.[14] China alone accounts for about one-third of total global Hg emissions. Qiu *et al.*[38] have reviewed widespread contamination in China of air, water, and soil by Hg and the relationship of this contamination to the metal industry there. Over the past few decades, China has become the major global producer and user of Hg, and the largest Hg-emitting nation with rapidly increasing atmospheric emissions.[14,38] Emission inventories as well as modeling work confirm that smelting of nonferrous metals is a major anthropogenic Hg source in China.[38] The second largest source of Hg emissions in China is from Zn smelters where Hg is present as an impurity in Zn/Pb production.[38] China is one of the largest producers and consumers of lead and zinc in the world.[15] Qiu *et al.*[38] cite earlier work that estimates that Hg emission to the atmosphere from Zn production in China during the period 2002–2006 was 80.7–104.2 tons per year while that for Europe, North America, and Australia where Hg emission controls are used was 7.5–8.2 tons per year. Two additional major Hg pollution sources in China are roasting of cinnabar (HgS) and use of Hg in artisanal and small-scale Au mining (ASGM).[14] On a global scale, ASGM is prevalent in South America and sub-Saharan Africa as well as China.[14] ASGM is largely unregulated and often illegal. Qiu *et al.*[38] estimate that Hg released into the atmosphere has an average residence time of 0.5–2 years, making it probable that atmospheric Hg contamination (Fig. 5) has worldwide implications, especially for human health, in the global commons.

4.3 Human and animal health

Pan *et al.*[12] have reviewed the effects of toxic elements As, Cd, Hg, Tl, and Pb (Table 1) on human health. Some anthropogenic sources of these metals include animal feed additives and sulfide ore roasting (As); rechargeable batteries, electronics, phosphate fertilizers, metallurgical works, and municipal waste (Cd); fluorescent lighting, catalysts, batteries, metallurgical works, pesticides, dental preparation, solid waste combustion, ASGM, and coal combustion (Hg); lead-acid batteries, solder, ammunition, metallurgical works, vehicle emissions from leaded gasoline, water pipes, cisterns, and solder (Pb); and metallurgical operations, pesticides, electrical uses, and electronic industries (Tl). Toxic metals enter the commons by many pathways (Fig. 1) with resulting deleterious effects on human health.[12] The scale and impact of anthropogenic sources have increased dramatically with industrialization and globalization. Global exposure to these toxic elements has become especially important in recent decades as the amount of mining, smelting, and refining of base metals has increased and mining activities have spread worldwide. Knowledge of speciation of these metals is of great importance in identifying their potential to cause environmental and health damage.[12] For example, Hg especially in aquatic systems can be methylated by bacteria to form extremely toxic fat soluble species, *i.e.*, CH_3Hg^+ and $(CH_3)_2Hg$, which easily cross the blood–brain barrier in humans and are responsible for neurotoxic disease.[12] Accumulation of methylated Hg in rice and fish has been the cause of much human suffering and death,[12,38] one notable incidence being that which occurred in Minimata Bay, Japan, in the mid-twentieth century.

Tsydenova and Bengtsson[5] discuss the hazard to human health associated with treatment of waste electronic and electrical equipment (WEEE) as well as environmental and occupational impacts of methods used to treat WEEE. Size reduction of waste items is commonly done by shredding, which results in the formation of dust containing many hazardous substances including plastics, metals, ceramics, and silica. Pyrometallurgical treatment of WEEE generates metal fumes containing Hg, Pb, and Cd as well as toxic organics such as dioxins and furans. Incineration and land filling have significant risks including formation of toxic metal particles and formation of furans and dioxins during incineration and leaching and evaporation of various metal and organic substances in landfills. In OECD countries, these recycling hazards are minimized by regulatory requirements. In non-OECD countries, these activities are usually unregulated, leading to significant documented health hazards for untrained workers and significant environmental damage. Of particular concern are health effects from treatment of WEEE during informal recycling (Section 5.2).

Concern has increased that rapid spread of toxic metals in small concentrations throughout the commons will have serious and long-lasting effects on the health of the world's population, especially children. Gailer[17] has reviewed geochemical and anthropogenic activities that adversely affect human health using examples taken worldwide. An important side effect of coal combustion is emission of toxic metals in particulate form into the commons. This is an important public health hazard especially in non-OECD nations where enforcement of environmental laws, if they exist, is often lax. Gailer[17] observes that, ''Based on the established adverse health effects of the big four elements of environmental concern—As, Cd, Pb, and Hg—on human health, the search for functional connections between exposure to certain inorganic environmental pollutants and specific human diseases will become increasingly important in the near future.'' Gailer[17] concludes: ''The projected increase in the emission of toxic metals and metalloids into the environment from the combustion of fossil fuels, the deposition of electronic waste in landfills (global production was estimated at 20–25 million tons/year in 2009) and ongoing mining activities combined with the recently observed increased incidence rate of particular human diseases (*e.g.*, type 1 diabetes, autism, and oropharyngeal cancer) necessitate increased efforts to be directed towards elucidating the complex biomolecular mechanisms which link the exposure of humans to a certain environmental pollutant with specific diseases.'' Refer to ref. 17 for references supporting the statements contained in the quotation. Gailer[17] states that discovery of these biomolecular mechanisms will require a long-term research effort to obtain information necessary to support legislative measures to restrict the emission of specific inorganic pollutants into the environment. Considerable success in this regard has been made, deleterious human health effects of toxic metals, especially among children, have been recognized, and laws defining allowable metal concentration levels are in place in many nations.

Rajaganapathy *et al.*[45] examined heavy-metal (Cd, Hg, Pb) pollution in India as it affects people and domestic animals. They found that heavy-metal toxicity is a major current environmental health problem and is particularly dangerous because of bio-accumulation through the food chain for both domestic animals and humans. Anthropogenic activities such as burning of fossil fuels, mining and metallurgy industries, and transport sectors redistribute heavy metals into the commons. Accumulation of heavy metals in the animal population was much greater in the vicinity of these activities. Subsequently, paths of heavy metals from their source through domestic animals to humans are evident. These authors point out that this problem exists in many areas of the world. They recommend that international agencies become more actively concerned about heavy metal pollution and its consequences on the health of domestic animals and humans.

Williams *et al.*[8] have reviewed the environmental, health, social, and economic implications of global reuse and recycling of personal computers. They examined global informal recycling (Section 5.2) of electronic waste and significant deleterious health effects that result from this activity. Environmental and health impacts of informal recycling are severe. For example, circuit boards are treated to extract Cu and precious metals using acid, cyanide, and/or Hg amalgamation, sometimes next to rivers in many non-OECD nations. In Guiyu, a large city in China, daily exposures of workers to dioxins and furan is 15 to 56 times higher than the World Health Organization's recommended limits. Eighty percent of 165 children in Guiyu had blood Pb levels exceeding 10 μg dL^{-1}, the level considered allowable by the United States Center for Disease Control and Prevention. Williams *et al.*[8] conclude: "While further work is needed, these initial studies suggest that the environmental impact of informal recycling are [is] the most significant of human health impacts associated with the lifecycle of information and communication technology [ICT] equipment."

Schüler *et al.*[16] cite studies of the health effects of REE mining and related activities in China. A twenty-year study has shown that long term exposure to radioactive Th dusts has significantly increased the mortality rate of workers in the Baotou Obo mine area. Groundwater pollution from the tailings pond has entered the wells of nearby villages affecting livestock, agriculture, and health of villagers. Seepage into water systems has the potential for much more widespread environmental and health effects.

The REE situation is of interest because of the recent upsurge in mining of these metals (Fig. 4) and the high probability that their widespread use will increase in the future as demand for high-tech products increases. In addition, the recovery rate of REE from EOL high-tech products is ∼1%,[9,10] necessitating expanded mining of virgin ore into the foreseeable future to meet market demand for these metals. Mining and processing of REE ores has been localized in China for over a decade, but is set to expand to other nations.[9,16,36] Without strict adherence to environmental regulations and use of advanced mining and processing techniques, the potential threat to the environment and human health is appreciable. Expansion of REE mining activities affords the opportunity to develop global REE resources in a sustainable, environmentally friendly way building on experiences in China and elsewhere during the past few decades. Accomplishment of this goal will require use of latest technology in the mining and processing of REE ores. A major challenge is the disposal of large amounts of waste which include used process chemicals and, in nearly every REE deposit, significant amounts of Th, U, and their daughter products, which are not now recovered as by-products. These challenges are being addressed by the Mount Weld (Australia) and Mountain Pass (California) mining operations.[16,36]

5 Recycling

5.1 Metal recycling rates

Improvement of metal sustainability requires effective recycling programs. Reck and Graedel[10] have reviewed the status and challenges involved in metal recycling. They summarize findings from an earlier 2011 United Nations study that defined and quantified global EOL recycling rates (EOLRR) for 60 elements. A number of significant findings from the United Nations study are pertinent to this review. (1) EOLRR values for common base metals (Fe, Ni, Co, Cu, Zn) are a little above 50%. (2) The EOLRR value for Pb is ∼80%. (3) A large number of elements, especially specialty metals, including REE, are seldom, if ever, recycled. (4) EOLRR values for precious, toxic, and radioactive metals depend on the use to which the metals are put. For example, recycling rates for Pt, Pd, and Rh are ∼50% from automotive catalysts but only ∼5–10% from e-waste.[10]

Reasons for variations in recycling rates are complex. High recycling rates for Pb (∼80%), base metals (∼50%), and PGM from automotive catalysts (∼50%) result from closed loops in recycling these elements (Fig. 1).[10] A key link in these loops is an effective collection system for the EOL product. In the case of Pb, this collection system is particularly efficient, since the main use of Pb is in a single product, lead-acid storage batteries. Effective stringent regulations are in place worldwide for collection of these batteries and recycling the Pb they contain[10] providing a nearly closed loop for Pb use. A similar situation exists for waste automotive catalysts, which are easily removed from vehicles, collected together, and transported to locations where PGM are recovered, usually by pyrometallurgical means.[24] Even with this closed loop, recycling of PGM from these products is only ∼50%. Specialty metals in long-lived products such as Nd in hybrid car batteries and in wind turbines have a much better chance of being recycled than the same element in small short-lived items such as smart phones.

The recycling situation becomes direr when recovery of metals from EOL e-wastes is considered. EOLRR values for electronic products are low (∼20%), but those for many of the metals they contain are even lower, 0–15%.[10,46] For example, the EOLRR value for Au, an important constituent of cell and smart phones, is 10–15%, that for Ru, an essential component of computer hard disks is 0–5%, and that for Pd, another important component of cell and smart phones, is 0–5%.[10] Low EOLRR values mean that significant amounts of valuable metals enter the commons (Fig. 1), being lost in landfills and waste dumps, in incinerator wastes, or in stockpiled items in closets or drawers. E-wastes provide a good illustration of a situation where the need to recover the metal for reuse is often critical, but market value of the metal is not sufficient to make recovery feasible. Precious metals and Cu are sufficiently valuable to merit economic recovery. However, recovery of other

Table 2 Barriers to effective recycling, especially of e-waste

(1) Each recyclable unit contains small amounts of metals (g to $<$mg)
(2) Economic incentive to recycle due to low metal value per unit is lacking
(3) Traditional commercial recycling technologies are not adequate for recovering small amounts of metals present in modern products
(4) Products contain a complex mixture of metals, and the composition changes over time
(5) Collection procedures are scarce or do not exist
(6) Costs of collection and transportation of units to smelters are large
(7) Recycling is not part of a collection chain that includes smelters
(8) Product design makes disassembly and material separation difficult
(9) Public awareness of impending loss of crucial resources is low
(10) Public is not attuned to local recycling procedures, if any

metals may not be economically feasible even though several of them are deemed critical to the economies of the United States and other nations.

Recovery rates for PGM contained in e-waste products are low ($<10\%$).[10] Possible reasons for these low rates are given in Table 2. Products containing the metals are small, relatively inexpensive, generally have a short life span, are not easily collected or dismantled in their EOL state, are not part of a collection chain, and are distributed in large numbers all over the planet. Each device contains small amounts of a wide range of elements which may total as many as 40.[47] The quantity of metals in a single mobile phone is small but the cumulative amount in the several billion such phones extant is huge and increasing with time as the production of these items increases rapidly. Beigl *et al.*[47] summarize reported amounts of several precious metals and Cu in these devices. Amounts given in g metal per kg of mobile phones are (range in parentheses) Cu (113–142), Ag (1.22–3.13), Au (0.22–0.33), and Pd (0.06–0.13). Since the lifetime of a mobile phone is estimated to be 1.5 to 2 years[47] and the metal recovery rate is low, there is a constant need to replenish the metals needed for new products by mining and processing additional virgin ore.[6]

REE are considered the most critical materials group, with the highest supply risk.[9] The five most critical REE are Nd, Eu, Tb, Dy, and Y. Binnemans *et al.*[9] present a critical review of the challenges associated with recycling REE and of the state of the art in preprocessing EOL materials containing REE and final recovery of REE. These authors conclude that, in addition to mitigating supply risk to many nations, recycling of REE from EOL products can significantly reduce environmental challenges associated with REE mining and processing. A drastic improvement in EOL recycling of REE (presently $<1\%$) is stated by them to be a strategic necessity. Effective recovery of the five most critical REE from their EOL products means that less REE ores need to be mined to meet the global demand for these five critical metals avoiding buildup of an undesirable surplus of other less critical REE that are unavoidably mined with them.[9]

The choice of recycling the elements mentioned or of irrecoverably discarding them into the commons should be a thoughtful one in which consequences of the choice are weighed by interested stakeholders, which would include industry, government, and the public. Currently, the choice is largely economics and convenience. As an even wider variety of elements are expected to be used in future high-tech products which inevitably will be produced in coming years, irrecoverable depletion of metal resources by discarding these products into the commons, often after short-use periods, is not sustainable. Alternatives to this action should be carefully considered and evaluated.

Collection systems for formal recycling of e-wastes in OECD nations are inadequate. For example, Oswald and Reller[7] cite a study by the United Nations University that reports that $\sim 30\%$ of total e-waste is collected by the collection schemes implemented by member states of the European Union (EU). These collection rates are lower for items <1 kg in weight. Beigl *et al.*[47] describe the collection of mobile phones in the EU in detail. These authors find that making collection easily accessible with numerous collection points is important in successful collection systems. It is of interest that collection systems in OECD nations for transport of e-waste to non-OECD nations for informal recycling appear to be functioning well (Section 5.2). The flourishing informal and recycling trade in non-OECD nations would not be possible without effective collection and shipment of huge amounts of e-waste from OECD nations. In the United States, e-waste not formally recycled is stockpiled, shipped overseas, or enters the commons by being discarded in landfills, deposited in waste dumps, or incinerated.[6] A significant amount of EOL e-waste is shipped from OECD to non-OECD nations for reuse or dismantling for precious metal content.[47] Nearly 400 million electronic products were discarded in the United States in 2010, according to the EPA, amounting to 2.4 million tons of e-waste.[46] Only 27% of this e-waste was collected for recycling and $\sim 80\%$ of this amount was shipped to non-OECD nations.

5.2 Informal recycling

Informal recycling refers to the practice used worldwide, but especially in non-OECD nations, to dismantle, using untrained workers, electronic and other waste products and retrieve value, mainly precious metals and Cu, using primitive extraction and recovery techniques.[6,25] In 1994, 65 parties of the Basel Convention representing most developed countries at that time voted by consensus for a full ban on the export of hazardous waste materials from OECD to non-OECD nations.[4,7] The United States was not a signatory to the Basel Convention but supports the ban. The Basel Convention agreement has been only partially successful in halting the informal recycling trade and appears to be losing the battle.[8] World leaders in producing WEEE in 2007 were United States (2 250 000 tons) and

Table 3 Reasons underlying present low-end management of e-waste and the prevalence of informal recycling sectors in non-OECD countries[25]

(1) Unwillingness of consumers to return and pay for disposal of their old EEE[a]
(2) Uncoordinated high level of importation of e-waste as second-hand devices
(3) Lack of awareness among consumers, collectors, and recyclers of potential e-waste
(4) Lack of funds and investment to finance improvements in e-waste recycling
(5) Absence of recycling infrastructure or appropriate management of e-waste
(6) Absence of effective take-back programs for EOL EEE[a]
(7) Lack of interest/incentive in e-waste management by multinational IT[b] companies
(8) Absence and/or lax implementation of e-waste specific legislation

[a] Electronic and electrical equipment. [b] Information technology.

China (2 212 000 tons).[6] The United States does not have a consistent, working policy to prevent the export of this material to non-OECD nations.[6]

Despite the Basel Convention ban, significant amounts of e-waste are transported illegally from OECD to non-OECD nations where part is repaired and reused, but much undergoes informal recycling that leads to severe health and environmental problems.[7,8,25] Informal recycling is widespread[5,6,8,10,25–27,46] and has become vital to the economies of many nations, both those which provide e-waste and those which process it. Disrupting the trade would, in many cases, have severe economic repercussions, especially to non-OECD nations.[8,25,26] On the other hand, serious health and environmental issues result from informal recycling procedures. Waste material discarded has little economic value, but contains unrecovered metals, some of which are critical for the global economy. Usually, these critical metals have one short use before being discarded. Depending on how the product cases were processed, discarded material may also contain organics such as dioxins that are injurious to human health and agricultural well-being.[25]

Chi *et al.*[25] and Streicher-Porte *et al.*[27] discuss the status of informal e-waste recycling with special emphasis on China and India, respectively. Informal recycling is not limited to these countries. It is widespread in many other non-OECD nations[5,6] since the value of metals in e-waste products invites this activity. In China, e-waste is mainly recycled by the informal sector.[25] Numerous waste recycle workers are hired at extremely low wages and work under conditions where crude and pollutive recycling methods are used for manual dismantling of the item, separation of reusable components, and quick recovery of contained metals. Unused material is discarded into landfill or incinerated creating extensive and serious environmental problems and irrecoverable loss of valuable metals to the commons. Working conditions are usually primitive, exposing workers and others to extensive health dangers. Similar situations exist in India[27] and in many other non-OECD nations.[6,8] Williams *et al.*[8] state that addressing problems associated with informal recycling should be a major worldwide priority of environmental management efforts.

The major reasons for the thriving state of China's informal recycling sector[25] are sufficient and continuing supplies available from illegal imports from OECD nations and domestic individual collections, low treatment costs due to simple and pollutive methods used, development of simple dismantling processes which maximize recovery of functional value by efficient manual separation of reusable components and parts, and steady downstream demand for precious metals recovered in the operation. In Table 3, reasons underlying the present low-end management of e-waste and the existence of informal recycling sectors in non-OECD nations as given by Chi *et al.*[25] are summarized. Examination of statements in Table 3 provides an understanding of the underlying reasons for the flourishing informal sector trade. These statements set forth the challenges that must be met in order to improve recovery of metals from EOL products. Especially important challenges involve achievement of recognition of the problem by stakeholders and enlisting their active cooperation in finding acceptable and workable solutions. Informal recycling is an established fact in a large number of non-OECD nations and practitioners of this activity must be included in discussions of recycling policy. However, since the practice of informal recycling is essentially unstructured, this inclusion will be difficult to achieve.

The high monetary value of Au ($1210 U.S. per ounce on 29 December 2013, London Metal Exchange) and the concentration of Au of up to 4 g per personal computer mother board provide strong incentives to recover this metal.[27] The value of precious metals together with the reasons outlined in Table 3 accounts, in large part, for recent development of thriving and widespread use of informal recycling in non-OECD nations. Estimations are that as many as 2% of the population in Asian and Latin American cities depend on waste picking to earn their living.[25] This percentage includes more than e-waste, but the number suggests how prevalent the practice is and the degree to which its economic value is important to a sizeable part of the population in many nations.[8] These data suggest how difficult it would be to implement safer and more effective recovery processes in these nations. For example, there is no incentive for those engaged in informal recycling to recover elements that are critical, but have little economic value; consequently, these elements are irrecoverably lost to the commons as the waste is discarded. Enforcement of any regulations on informal recycling is difficult, since the operation can easily and quickly be transferred elsewhere.[25]

Ongondo *et al.*[6] have critically analyzed WEEE management, including recycling practices in nations worldwide. The review and references contained therein provide detailed information concerning management of a variety of electronic wastes by OECD and non-OECD nations. Quantities of WEEE are given for each country with estimates of amounts generated, amounts exported legally and illegally, and existing legislation. An example is India, where significant amounts of domestic WEEE are produced in addition to illegal imports of 50 000 tons annually. The majority of the imported WEEE is destined for informal recycling, which is illegal in India. However, the law is circumvented by renaming imported waste. The Indian government is drafting new legislation designed to prevent illegal importation of WEEE. Conclusions of the authors[6] are instructive and describe the situation in most non-OECD nations. "This lack of control and regulation of the WEEE recycling industry has led the poorest members of the population to find an economic benefit in recovering valuable parts from WEEE while discarding the unwanted bits and pieces. These activities are carried out in an unprofessional manner with very high risks to health and the environment. There are only three licensed waste sites in the entire country [India] and much solid waste containing heavy metals and hazardous substances is landfilled."

Chi *et al.*[25] point out that potential economic and environmental benefits of e-waste recycling have attracted interest from the formal sector in China. By government action and producers' take-back programs, an effort is being made, especially in electrical and electronic manufacturer-dense regions such as Beijing and Shanghai, to institute formal recycling programs.[25] However, Chi *et al.*[25] cite studies showing that these "programs have not, as yet seen any success, being unable to compete with the informal sector, most notably in collecting e-waste and in covering the costs of environmentally sound processing."

No single answer exists for implementation of effective recycling. A combination of approaches is needed from stakeholders in industry, government, the research community, the press, and society. Given that the livelihood of so many people, especially in non-OECD countries, depends on informal recycling the path to environmentally safe metal recovery will likely require involving these people in some way in formal recycling. The suggestion has been made that potential economic and social benefits could be gained by involving the informal sector in formal waste management.[25] Causing this to happen entails in part a technical challenge since economical separation technology for environmentally safe recycling in the formal sector largely does not exist.

5.3 Financial benefits of recycling

There are significant economic incentives to recover precious metals and Cu from EOL e-waste in the so-called above-ground or urban mining.[7,19,24,48] Hagelüken and Meskers[1] report that 80% of the monetary value in mobile phones and computer circuit boards is due to precious metals and ~15% to Cu. Q8 According to Hagelüken,[24] computer motherboards contain ~200–250 g ton^{-1} of Au, mobile phones contain up to 359 g ton^{-1} of Au and 130 g ton^{-1} of Pd, and automotive catalysts may contain up to 2000 g ton^{-1} of PGM. These metal amounts are significantly higher than those found in virgin ores, where the Au or PGM content on average is ~10 g ton^{-1}.[24] There are other advantages to urban mining. EOL products contain much lower levels of harmful elements, common to ores, such as As, Hg, and S. Metals can usually be extracted from used electronics with far less environmental impact than extraction of the same metals during the mining process.[24] Elemental content and concentrations in EOL material are usually known, making design of separation processes easier. Large amounts of gangue produced in mining virgin ore are not produced in above-ground mining providing large energy and water savings. With these advantages of urban mining, why is it not done on a large scale? Possible reasons are found in Table 2 (items 2, 3, 5, 8, 9) and in Table 3 (items 4, 5, 6, 7). Also, collection of EOL items, mainly in OECD nations, for informal recycling in non-OECD nations is simply easier than alternatives and provides an immediate profit.

A business opportunity exists to establish a link between collection of WEEE and appropriate clean green chemistry[29] separation technology to compete with the present movement of these spent products to the commons or to non-OECD nations for informal recycling. However, the negative experience of China[25] in setting up formal recycling procedures to compete with established informal recycling systems (Section 5.2) suggests that significant challenges exist in achieving this goal.

Precious metals are currently recovered from EOL products by pyrometallurgy in copper smelters.[5,31,48] The International Precious Metal Institute (IPMI)[31] has pointed out that "the most environmentally sound final disposal of mobile phones is through metal recovery by a copper smelter, followed by metal-specific refining." IPMI also states that "only a few Cu smelters in the world [at that time, 2003] have the specialized material handling equipment and pollution control systems that are appropriate for metal recovery from mobile telephones." Nakajima *et al.*[48] give a thermodynamic evaluation of precious metal recovery from mobile phones using a pyrometallurgical process involving copper smelting. They found that the precious metals distribute to the Cu phase from which their recyclability is >90%. Unfortunately, too few Cu smelters exist globally to process the large amount of EOL electronic and other waste. In addition, these smelters are not near the point of origin of the majority of the waste, making this option unattainable in the foreseeable future.

6. Challenges in achieving metal sustainability

In the Brundtland Report[49] it is stated that "Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs." This is another way of expressing the golden rule, "Do unto others as you would have them do unto you." Sustainability is further clarified in this Report by indicating that "In general the rate of depletion should take into account the criticality of that resource, the availability of technologies for minimizing depletion, and the likelihood of substitutes being available." It is also stated that "With minerals and fossil fuels, the rate of depletion and the emphasis on recycling and economy of use should be calibrated to ensure that the resource does not run out before acceptable substitutes are available.'' In the twenty-five years since the document was issued, the use of mineral resources in greater amount and variety has sharply increased,[1,10] and the need for sustainable development of these important resources has become ever more critical.

Achievement of improved metal sustainability is challenging considering the many areas in Fig. 1 where irrecoverable metal losses may occur and the low recycling rates for high-tech products[10] (Section 5.1). Though total sustainability may not be achievable, there are multiple areas in the mining, processing, use, and recovery of metals (Fig. 1) where greatly improved metal sustainability can be obtained. Obstacles to the attainment of increased global metal sustainability are summarized in Table 4. Consequences of failure to surmount these obstacles are also indicated. Several features emerge from the listings in Table 4. An important consequence of metal loss in many of the cases is the requirement to mine and process additional virgin ore to replace the metal, with attendant energy and environmental costs, in order to produce new products. The result is negative metal sustainability. The lack of effective collection systems which could lead to formal recycling of EOL high-tech products results in large and irrecoverable metal losses to the commons. Urban mining (Section 5.3) offers a promising, but presently largely unused, means of recovering metals at low energy cost and of improving metal sustainability. Achievement of this goal would be consistent with the principles of green chemistry set forth by Anastas and Eghbali.[29]

Metal sustainability could be significantly improved if more effort were expended in using available and developing new technologies for passive metal extraction and concentration from stocks containing metals at several mg L^{-1} and lower concentration levels (Section 3.4). Introduction of responsible recycling procedures into the informal recycling system could be beneficial in recovering critical metals that otherwise enter the commons. The degree to which these goals can be implemented will determine our global success in improving metal sustainability.

A significant challenge, as indicated in Tables 3 and 4, is how to involve concerned stakeholders in the discussion and to convince them that it is in their best interest to recycle EOL products, especially small items such as cell phones and computer motherboards.[7] Kaushal and Nema[50] have suggested an approach based on game theory to increase recycling rates of computer waste. Stakeholders, in their approach, include manufacturers, producers, regulators, consumers, recyclers, and waste-disposal agencies. The common regulatory approach to recycling relies on making producers alone responsible for

Table 4 Obstacles to attainment of increased global metal sustainability

(1) Minimal efforts to factor cost of EOL care into original cost of high-tech products
Consequence: less incentive for users and producers to recycle products.

(2) Lack of effective EOL product collection systems for formal recycling
Consequence: without formal recycling, the continuing supply of EOL products is consigned to landfill, incineration, storage, or collection for eventual informal recycling. Replacement of metal lost requires mining and processing of additional virgin ore.

(3) Easy entry of imported EOL waste into non-OECD nations from OECD nations
Consequence: a flourishing global informal recycling trade exists, often disregarding existing law in either OCED or non-OECD nations (Section 5.2). This waste material is not available for formal recycling.

(4) Widespread and growing use of wasteful informal recycling processes for metal recovery from EOL high-tech products
Consequence: loss to the economy of considerable precious metal value and all specialty metal value. Significant health dangers exist for workers and others. Unregulated disposition of waste products into the commons can cause severe environmental damage. Replacement of metal lost requires mining and processing of additional virgin ore.

(5) Minimal use of available technologies and little effort to develop new technologies for recovery of desired metals at low concentration levels
Consequence: without recovery, metals enter the commons through settling ponds, landfill, incineration, or other means. Replacement of metal lost requires mining and processing of additional virgin ore.

(6) Lack of efforts to promote urban mining for its economic and conservation advantages
Consequence: loss to society of potential metal value. Replacement of metal lost requires mining and processing of additional virgin ore at greater environmental and economic cost than would have been required for urban mining.

(7) Inadequate effort to access metal value from oceans, natural brine solutions, and effluents from natural leaching processes using passive energy-conserving separation and concentration systems
Consequence: such resources contain large quantities of needed metals and their successful retrieval would negate the necessity of energy-intensive mining and processing of virgin ore.

(8) General ignorance of the public sector about issues related to metal sustainability
Consequence: sporadic, largely unorganized, and ineffective efforts by public, especially in non-OECD nations, to obtain legislation regulating metal emissions into the commons.

(9) Minimal effort to involve appropriate stakeholders in seeking solutions to growing environmental and health hazards from EOL products and mining wastes entering the commons
Consequence: lack of cooperation, especially in non-OECD nations, among industry, government, and public stakeholders to control metal emissions and to enforce metal emission laws, if in place.

recycling their product.[47] Kaushi and Nema[50] suggest that applying take-back schemes with financial incentives to consumers and economic penalties to those who do not follow prescribed procedures for discarding e-waste would be useful to discourage land disposal of computer waste. Studies of this type could prove helpful to government agencies that are seeking novel means to encourage recycling. At the present time, the cost of recovery of EOL products is not factored into item costs (Tables 3 and 4). The situation with electronic products and resulting e-wastes is a good example of negative externality, a commercial activity that adversely affects other parties without this effect being reflected in the cost of the item.

Significant improvement of metal sustainability requires a change in mindset among stakeholders.[4,8] For example, present recycling action is to discard EOL high-tech products to the commons, either before or after precious metals have been recovered.[5,6] Metal sustainability would be enhanced significantly if, wherever possible, metals were recovered in pure form for reuse (Table 4). Of course, it is neither possible nor desirable to recover all discarded metals;[6] however, for reasons given in this review, recovery of precious metals, many specialty metals, and certain hazardous metals is highly desirable for economic, national security, health, and/or environmental reasons. In addition to improved recovery of metals and more efficient processing of ores, attainment of metal sustainability requires active, intelligent participation of all stakeholders in the effort as has been elucidated by Ongondo *et al.*[6] Rankin[4] observes that mining and metal industries are driven by shareholder value and wealth creation. He considers tensions between industry's global commercial aspirations and political and social interests of national and local stakeholders to be among the most pressing risks facing the industry. Thus, accomplishment of improved metal sustainability requires an active education process to inform and convince all stakeholders that this achievement is in their best interest.

Improvement in sustainability of our finite metal resources represents a significant global challenge. Recycling rates for many metals critical to our economy are near zero (Section 5.1) and large amounts of unrecovered critical and toxic metals end up in the commons from which they are not recoverable using present technologies. Education and cooperation among involved stakeholders on a global scale are needed to arrive at a consensus and plan of action about preservation of these critical metal resources for future generations.[6] It is certain that, if they had the opportunity, our descendants would opt for preservation of these resources so they could enjoy the kind of life we do. This, after all, is the meaning of sustainability.[49]

7. Conclusions

Metals are an integral, albeit little understood or appreciated, part of our lives. During the past half century, new high-performance materials and products of all types have changed life on Earth in remarkable ways. Many of these new products and materials derive their uniqueness from distinctive electronic and physical properties of the metals involved. Future scientific discoveries and technological advances will continue to provide new devices and products that will create demand for metals in ways that cannot be anticipated. Population growth, as well as an increasing proportion of the global population entering the middle class, will also fuel demand. These growth factors will continue to put pressure on the source part of the material life cycle, namely mining and processing of virgin ores (Fig. 1). However, these same growth factors will make it more incumbent on industry and society to increase the proportion of metals that are conserved in ore processing and that are recycled. In principle, depletion of ore bodies and ore grade with increases in attendant energy, water, and land usage coupled with increasing demand ultimately will increase the economic incentive for recycling through increased metal prices. Add to this environmental and health costs borne by metal losses to the commons through EOL and other routes (Fig. 1), and we can expect, on economic grounds alone, that recognition of the overall importance of recycling in metal life cycles will increase. Government regulation and education of society will provide additional driving forces for recycling. However, developments in any part of the metal life cycle cannot take place without technological advances and the scientific research that underlies them. In particular, progress in separation science and technology will play an integral role in improving metal sustainability. As economic incentives drive industry and environmental perils drive government regulation to improve separations at all stages of a metal life cycle, research can be expected to increase separation efficiency, reduce losses, decrease pollution, and ultimately reduce costs to the point where industry can afford to implement new processes. For reasons outlined in this review, molecular recognition will open doors to new processes that can provide the unprecedented selectivity needed to concentrate and recover metals from dilute sources and complex matrices. Thus, in the end, the solution to improved metal sustainability will arise from both technological and societal action. We started this review by pointing out the impossible challenge of achieving the ideal of metal sustainability. We have presented examples of the stark economic and environmental consequences of continuing on the path of unsustainable depletion of natural metal resources and uncontrolled losses of metals to the commons. Understanding the precariousness of our supply of scarce yet essential metals should provide ample incentive for the application of creativity and dedication to achieving the highest possible level of metal sustainability.

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