

Research



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Material efficiency: rare and critical metals

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In the last few decades, progress in electronics, especially, has resulted in important new uses for a number of geologically rare metals, some of which were mere curiosities in the past. Most of them are not mined for their own sake (gold, the platinum group metals and the rare Earth elements are exceptions) but are found mainly in the ores of the major industrial metals, such as aluminium, copper, zinc and nickel. We call these major metals 'attractors' and the rare accompanying metals 'hitch-hikers'. The key implication is that rising prices do not necessarily call forth greater output because that would normally require greater output of the attractor metal. We trace the geological relationships and the functional uses of these metals. Some of these metals appear to be irreplaceable in the sense that there are no known substitutes for them in their current functional uses. Recycling is going to be increasingly important, notwithstanding a number of barriers.

1. Introduction

The Romanian economist Georgescu-Roegen is best known for pointing out somewhat controversially—but correctly—that high-quality low-entropy resources such as oil and gas, and metals, are converted by the economy into high-entropy wastes. He went on to assert a 'fourth law' of thermodynamics, namely that mass, like energy, becomes increasingly unavailable and that, thanks to the second (and presumed fourth) laws of thermodynamics, those wastes cannot be returned to their original state without a great deal of free energy from an external source (i.e. the sun).¹ He went on to argue that solar energy is too diffuse to be used whence the global economy is living off (natural) capital.

¹Georgescu-Roegen's 'fourth law' was an unjustified extrapolation of the simpler statement that materials—such as rare metals—cannot be completely recycled [1,2].

He concluded that civilization will inevitably ‘run out of gas’, so to speak [3]. Is it true? Does it matter?

This irreversibility (owing to the second law) is obvious in the case of hydrocarbons. But we do not contemplate the recycling of hydrocarbons except perhaps in terms of bio-geological processes not relevant here. What about the ‘fourth law’? Given that transmutation of the elements is, and probably always will be, impractical, the ‘fourth law’ might be relevant in the case of industrially important but geologically scarce elements such as copper, nickel and zinc, not to mention the platinum group of metals (PGMs), indium, selenium, tantalum, tellurium and the ‘rare Earth elements’ (REEs), some of which are truly rare. It is clear that any given recycling process will be imperfect, again thanks to the second law. Does it mean that the end of civilization is inevitable?

Actually, it does not. Granted, the high-grade ores are being used up. Granted, the economist’s normal assumption that a higher price always calls forth new supplies (thanks to continuous technological progress) may not be universally true. Granted, there is such a thing as geological scarcity, especially as regards the ‘hitch-hiker’ metals such as gallium and tellurium that are obtained from the smelting or refinery wastes of major industrial metals but are never mined for themselves. Granted, recycling is currently very expensive and inefficient owing to a variety of legal, geo-political, environmental and institutional barriers that combine to ensure that recovery from electronic wastes is (currently) minimal. But, inefficient recycling also means that there will be a stockpile of low-grade materials, in slag heaps or landfills, including recycling process wastes that can eventually be treated as ‘ore’ [2]. The ore may be low in grade, but it is unlikely to be lower than the Earth’s crustal average. The only real limit in the long run is the availability of free energy (exergy) to drive the recovery process. Once that is understood, the notion of exergy efficiency is applicable.

In this paper, we summarize the current position with regard to the sources, uses and recycling potential of some key non-fuel materials.

2. What do we mean by materials efficiency?

Although energy and mass are inter-convertible, as Einstein showed, we take it that ‘material’ for present purposes refers to energy-as-mass. The first law of thermodynamics says that energy is conserved in every process, but, except for nuclear transmutation processes that rarely occur spontaneously on the Earth, mass is separately conserved. The notion of efficiency as applied to energy materials (fuels) refers to the conversion of useful energy (exergy) stored in chemical form to useful work. But, in reference to materials, that definition clearly does not apply because the services provided by materials other than fuels, especially metals, do not involve irreversible chemical transformation. They are essentially non-destructive. With a few exceptions (e.g. batteries), non-fuel materials do not change chemical form during use. What do we mean, then, in speaking of efficiency in regard to materials use? Roughly speaking, we mean doing more with less. We also mean conserving rare and irreplaceable resources for future use.

Hereafter, we focus primarily on the less common metals, as there is already a considerable literature on dematerialization, materials management and sustainability. That literature focuses on the major materials, such as iron and steel, aluminium, cement, plastics and paper [4–27].

How can we (society) do more with less and conserve scarce metal resources? As regards conservation of metals, the obvious answer is to reduce losses, at every stage of the life cycle. Over time, there are unavoidable losses at each stage but they can be reduced. An ideal (100% efficient) life cycle would keep the material in a single use, forever, without wear or loss. Of course the more valuable the material, the better it will be protected and kept in use. Gold and platinum jewellery come closest to this ideal. But some wear and some loss during recycling are inevitable. Unfortunately, the loss during a life cycle for most industrial metals is 20–50%—or more. In the case of the rare metals that we should be most careful not to waste, the loss per cycle is typically nearer 100 per cent, with a few exceptions. In fact, there is no meaningful ‘life cycle’ for many of these metals.

The second approach to conservation concerns the degree or quality of service provided by the material while in use. This applies to resources with destructive as well as non-destructive uses. For most destructive uses, such as combustion of hydrocarbons, the service is usually accomplished not by the material *per se*, but by the chemical potential, heat (or light) that is released during the process. In a few cases, the ‘destruction’ consists of an irreversible combination with another material such that the service is performed by the combination. (Portland cement being added to sand and gravel to make concrete would be an example.) In all of these cases, the conventional exergy efficiency measure is applicable.

However, in the case of non-destructive uses of metals, the service can usually be characterized by measurable performance characteristics of the material, such as thermal or electrical conductivity, or strength-to-weight. To make life more complicated, we do not care about these characteristics except insofar as they apply to a product or system. In products and systems, there are always trade-offs. In micro-electronics, the classic trade-off is between miniaturization (to reduce size and weight) and heat generation. The continuing progress of electronics technology (‘Moore’s Law’) is attributable mostly to continuing reduction in electric power requirements for semiconductors per functional use.

For most people, there is always a trade-off between cost, performance and reliability or quality. Since ultimate limits of service performance are hard or impossible to calculate for real materials, or real machines or devices, it is generally more practical to use relative rather than absolute measures. In practice, this means comparisons with the so-called ‘best available technologies’. Some examples will be discussed later.

3. Ordinary versus critical materials

Ordinary materials can best be defined by distinguishing them from ‘critical’ materials. We use the term ‘critical’ because it is common in the literature, although the criteria used vary from study to study. Metals are usually classed as critical if (because) they are geologically scarce, subject to potential supply constraints, costly, and needed for an economically important purpose where substitution is difficult because of their special or unique properties. Of these characteristics, the potential for supply constraints seems to be pre-eminent.

By contrast, ordinary materials are generally not scarce, and typically have many uses and many substitutes. Non-metallic materials often provide protection against the elements, and support for active agents, including people. To use a biological analogy, they often constitute the skin and bones of the ‘built’ economic system. In mass terms, by far the most important is concrete, followed by steel, wood and plastics. The other widely used non-metals include bricks and ceramic tiles, dimension stone, plaster and glass.

Most of the non-metallic materials are quite cheap and rarely recycled (glass and paper are the two exceptions; ‘cheap’ is also a relative term). Most industrial materials are recycled only to the extent that they can be separated from other waste materials at a cost less than new primary materials. Sand and gravel, clay and dimension stone are usable almost as they come from the ground, except for washing, whereas concrete, ceramics and plaster would have to be sorted, crushed and/or ground up into powder before recycling is possible. Dimension stone, cobblestones, some bricks and some wood are re-usable, as such, within limits. But, as mentioned, only glass and paper can be collected and reprocessed at reasonable cost. Even so, the quality of the secondary version, in both cases, is significantly lower than the ‘virgin’ version.

The metals and semi-metals for which no short-term supply constraints have been identified, apart from iron and steel (including ‘stainless’ steel), include aluminium, arsenic, beryllium, boron, cadmium, chromium, copper, gold, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, niobium, rubidium, silicon, silver, tin, titanium, tungsten and zinc. Tin is on the verge of joining the ‘critical’ group because it is relatively scarce in geological terms, and its most important economic use now is in solder for electrical goods. In that application, which seems to be growing without limit, tin has almost no substitute except lead, which is toxic. However, its original use (as plating for ‘tin cans’) is declining, so there is no immediate supply

problem. Tungsten is another example of a metal that was formerly regarded as critical because of its uses in incandescent light bulbs and very hard alloys (tungsten carbide) for machine tools and armour plate. These uses have been displaced and the supply is adequate for now.

Mercury and lead are also both toxic and replaceable. Mercury is no longer an important industrial metal, despite an interesting past history [28]. Lead is no longer used as a gasoline ‘anti-knock’ additive in most countries, because of toxicity. Its primary use today is for automobiles. Lead-acid batteries are quite easily recycled, so the supply is not a problem.

Beryllium is toxic and has only minor uses, mainly as an alloying element for copper, but there are substitutes in that use and no immediate supply problem. Boron and lithium are fairly scarce, but are available from saline or dry lakes or (ultimately) the ocean. Boron has few uses and only its alloy with neodymium (in permanent magnets) might pose a future supply problem. Lithium is likely to become much more important in the future (for batteries) but existing resources seem adequate for some time to come.

In the case of metals, recycling is clearly worthwhile in the case of iron and steel, aluminium and copper because it requires much less energy than production from ore. Gold, silver, palladium and platinum are recycled because of their value. Lead from lead-acid batteries is recycled because the process is comparatively simple and collection is easy. For alloying and plating elements, such as chromium, cobalt, manganese, molybdenum, nickel, tungsten and zinc, the energy advantages of recycling are less clear. In some cases, as for copper and zinc in steel scrap, it is worthwhile mainly because those elements are undesirable contaminants. Chromium and titanium, which are largely used as oxides, are hardly recycled at all, as such. Chromium, cobalt, molybdenum and nickel are recycled as components of super-alloys or stainless steel, while manganese is recycled mainly in carbon steel.

Collection and sorting to facilitate recycling is always a problem for which no large-scale *generic* solution has emerged. There are two quite different cases. Iron and carbon steel and aluminium are in the ‘ordinary’ category, because they are not scarce, and are mostly used for structural purposes where ultra-purity is not crucial. For these, and the other metals noted above, the economics of recycling depends on the cost of energy and the logistics of collection and sorting. A significant fraction of each metal is lost simply because some metal-containing products have become so complex that separation of the metals is more difficult than starting from ore, unless the detailed design of the product is available.

Moreover, starting from mixed scrap, cross-contamination is a serious problem. It is ironic (pun!) that separating iron from copper is normal and feasible during the beneficiation stage, whereas separating copper contaminants from secondary iron is nearly impossible. As a consequence, secondary iron and steel in the economy are becoming increasingly contaminated by copper and are gradually declining in workability and quality. This ensures a continuing demand for virgin metal.

The criticality issue for rare metals has recently been recognized at government level. The first report on the subject in the USA was published in 2008 by the US National Research Council with the title *Minerals, Critical Minerals, and the US Economy* [29]. Another report on ‘materials security’ was published in the UK in that year [30]. Also in 2008, the United Nations Environment Program commissioned Öko-Institut in Germany to identify critical metals for future sustainable (‘green’) technologies and their recycling potential [31]. In the same year, the Shinko Research Co. in Tokyo, Japan, prepared a report on the development of substitutes for scarce metals for the New Energy and Industrial Technology Development Organization [32]. In June 2010, the European Commission published a report about critical raw materials [33]. Also in 2010, the US Department of Energy published a report on critical materials strategy [34] (see also [35–39]). (We are grateful to a reviewer for drawing our attention to several of these.)

4. On geological ‘hitch-hikers’

Another characteristic of the geologically rare and technologically critical metals is that most of them are not found in mineralized deposits, where they can be mined as such. The

historical response to threatened shortages of natural resources is to increase exploration and open new mines or wells, or to find a substitute. Economists traditionally assume that an increase in the market price will signal producers to increase output, and that the supply will automatically match the demand, more or less instantaneously. Indeed, empirical studies have demonstrated quite convincingly that resource prices, in real terms, have declined consistently since the industrial revolution [40,41]. Most economists consider ‘economic scarcity’ (signalled by rising prices) to be within their domain, but they reject ‘geological scarcity’ as a myth [42].

However, the economic theory depends upon an underlying assumption (never explicitly discussed) that the distribution of resources in the Earth’s crust is the result of a random process, and that the resulting distribution of deposits (quantity versus concentration) is smooth, with a single peak, something like a lognormal distribution. *In reality, the distribution of resources is not a smooth single peak function because the resources, both hydrocarbons and metals, were not distributed randomly in the first place.* They were created and distributed by complex geo-chemical processes resulting, in some cases, in multiple peaks.

Some elements that are geologically scarce in terms of parts per million in the Earth’s crust are, nevertheless, found in recoverable mineral deposits with far higher concentrations. Lead is one example. Yet, the majority of the atoms (of lead) are distributed randomly in ordinary rock with concentration even less than the crustal average. This situation seems to apply to copper, gold, lead, zinc and the PGMs in particular [43,44].

On the other hand, a number of other metals that are geologically less scarce, including—but not limited to—the so-called rare Earth elements (REEs), are not found anywhere in high individual concentrations. Instead, they are distributed essentially as contaminants, or trace elements, in the concentrations of minerals of certain ‘attractor’ metals, to which they are chemically similar. In the case of the REEs, the attractor metal is iron. A number of other rare metals are found in the ores of copper, lead, nickel or zinc. The situation resembles a star (the attractor) and its surrounding planets, or a human movie star and his or her entourage of fans and hangers-on. A simpler analogy is between the driver of a car and a hitch-hiker who goes along for the ride.

The key geological relationships are shown in figure 1. Data are mostly based on US Geological Survey commodity reports [45–50] and minerals yearbook [51]. Information is complemented from other sources: for iron ores [52], for rare Earth metals [53–55], for aluminium [56,57], for copper [58,59], for germanium [60,61], for nickel [62–66] and for PGMs [67].

Several of the non-critical elements listed in the previous section are actually ‘hitch-hikers’. Two major examples are arsenic (associated with copper) and cadmium (associated with zinc). Both have significant electronic uses, but both are toxic and neither appears to be irreplaceable. Both gold and silver (especially gold) are hitch-hikers, although still mined for themselves. An increasing fraction of the supply is from copper or zinc ores. Neither metal is regarded as critical. Gold is mainly used as an anti-inflation hedge, kept in bank vaults, and in jewellery (especially in India). Silver is also used primarily for jewellery and ‘silverware’. Both have electronic uses, which are the primary reason that electronic scrap is recycled at present, but the former use of silver for colour photography, once critical, is no longer significant [68].

The PGMs are mined for their own sake. The group consists of platinum, palladium, iridium, osmium, rhodium and ruthenium. Of these, the last four are hitch-hikers associated with the first two. The PGMs (gold and silver) are very scarce in geological terms. Apart from their major uses in catalytic convertors and industrial catalysts, platinum is used for jewellery in Japan, and rhodium is used for plating. All these metals have or may have unique catalytic properties, making them potentially critical in the future. Platinum and palladium are both recovered from electronic scrap today.

The case of tellurium, recently in the news, illustrates the problem. In brief, there are some tellurium minerals in the world, where tellurium takes the place of sulphur. One such is calaverite, which takes its name from Calaveras County in California, where it is found with gold in some quartz seams [69]. The Colorado ski resort at Telluride is another indication that telluride minerals

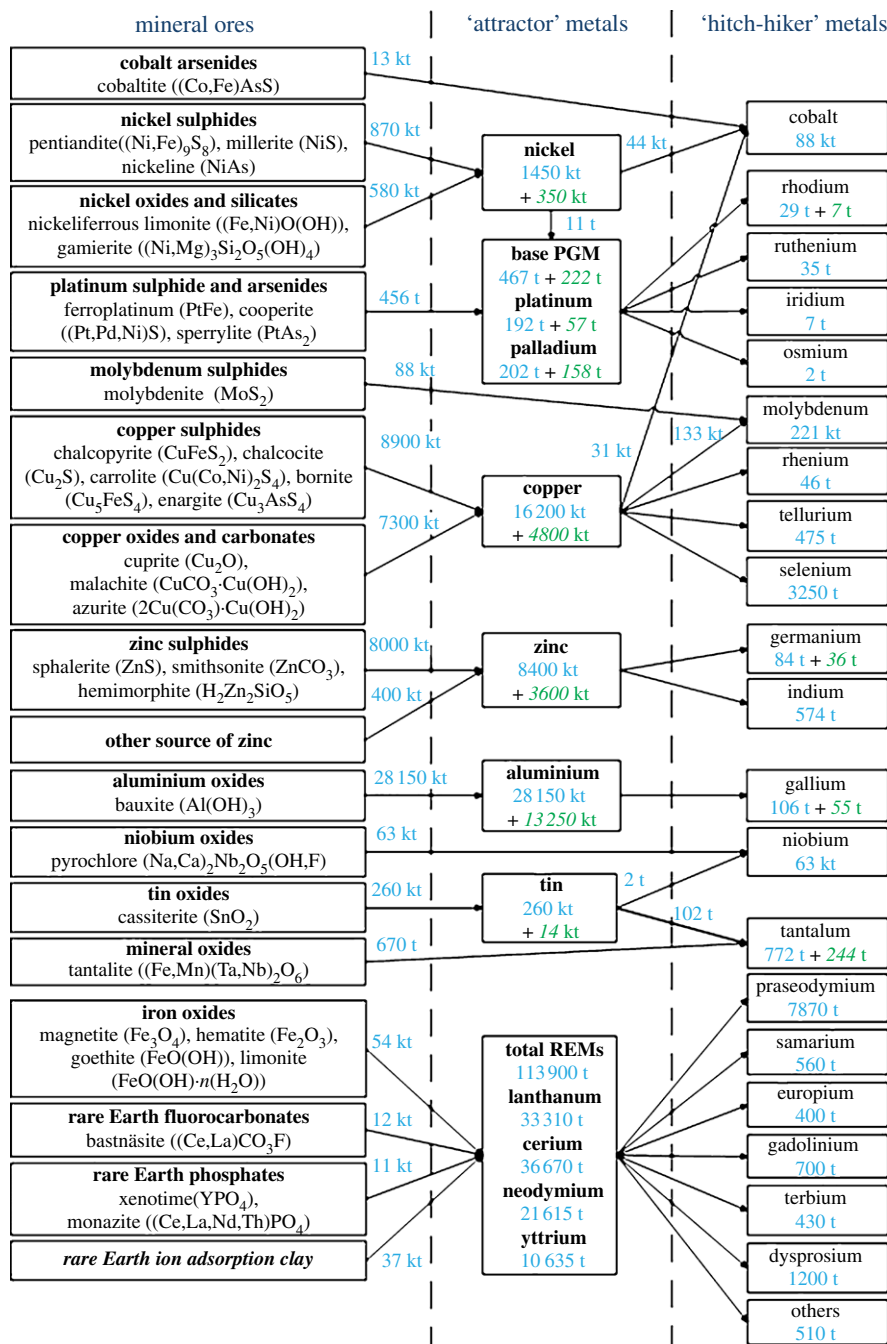


Figure 1. Worldwide production of mineral ores, base and hitch-hiker metals in 2010. Roman, amount of mine production; italic, recycling production; REMs, rare Earth minerals; t, tonnes; kt, 1000 tonnes. (Online version in colour.)

do exist (albeit not in that location). But the tellurium associated with gold is not recovered by the cyanide process, and the only economic source of tellurium today is in the residue (called 'slime') from the electrolytic step in copper refining.

To increase the output of one of the 'hitch-hiker' metals, short of a major and unlikely discovery, it is necessary either to increase the output of the 'attractor' metal or to increase the hitch-hiker's rate of recovery from the attractor's ore. The latter approach may, or may

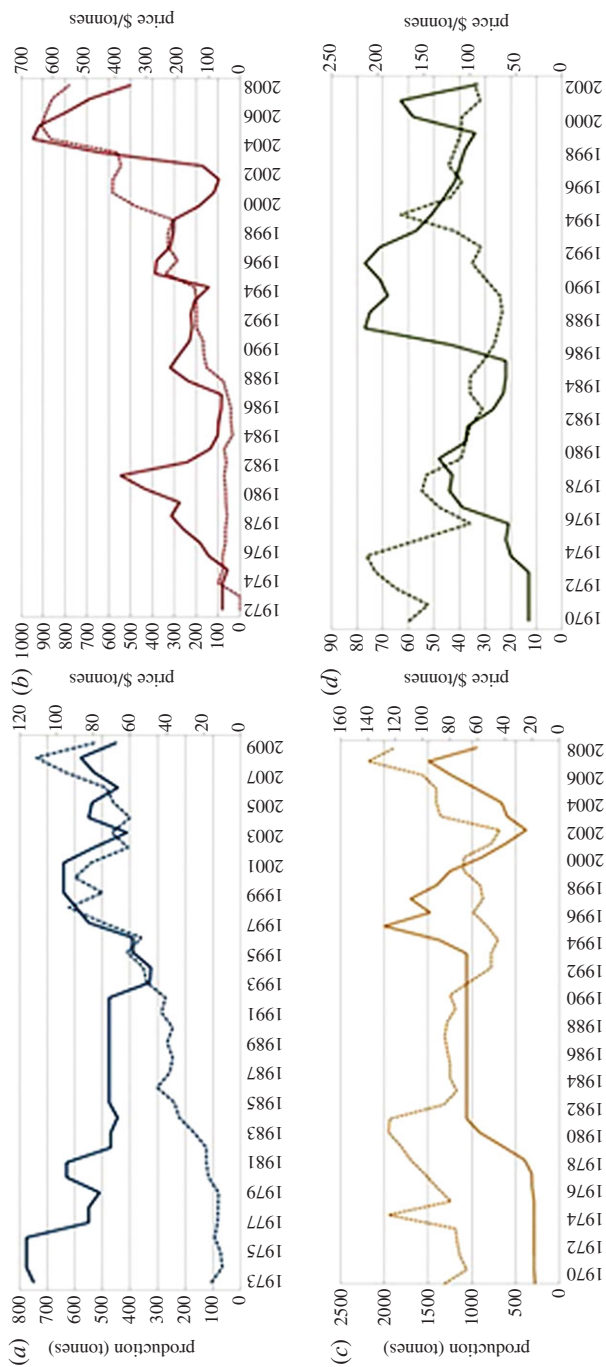


Figure 2. Prices (solid lines) and production (dotted lines) of the by-product metals: (a) gallium, (b) indium, (c) tellurium and (d) germanium. (Online version in colour.)

not, involve significant re-engineering of the whole beneficiation and refining process. In most cases, the recovery of a scarce 'hitch-hiker' was initially more or less accidental, and the original process design was never intended to save, still less to concentrate, elements that were viewed as contaminants.

This geological reality has an implication for economics. The immediate consequence is that higher prices do not automatically call forth greater output as conventional theory suggests, except where the hitch-hiker metal is not being fully recovered from existing refineries (of the attractor metal). This situation is shown in figure 2 for gallium, germanium, indium and tellurium. (These four cases were selected on the basis of availability of historical price information.) The correlation between price and output has clearly improved since the mid-1990s, suggesting that existing sources (ores of 'attractor' metals) are now being more systematically used than in the past. As will be noted later, it appears that there is considerable room for increasing the recovery rate still further for some of the scarce metals.

5. Substitution possibilities for critical metals

As noted above, economists (and many other people) tend to assume that, if a particular substance becomes geologically scarce, the answer will be to find a substitute. This point was especially emphasized in a famous 1976 paper by Harold Goeller and Alvin Weinberg which was published both in *Science* and in the *Review of Economic Literature*, probably a 'first' [28]. Their example was mercury, which has indeed had many past uses. A partial list includes medicinals, cosmetics, paint pigments, bactericides, fungicides, dental fillings, mercury vapour lamps, fluorescent lamps, as an amalgamating agent for gold mining and in the chlor-alkali manufacturing process. Virtually, all of these have already been replaced by better substitutes [28]. Today, there are only some minor uses of mercury in thermometers, batteries and switches for which no substitutes are available and the existing supply is adequate.

Yet, there are uses of some metals for which no substitute has ever been found or is likely to be found. The uses of mercury as an electrically or thermally conductive liquid at room temperature were noted above. Another example is worth noting: back in the early days of four-cycle internal combustion engine, when automotive engineers tried to increase the compression ratio to get better fuel economy, there was a problem of pre-ignition ('knocking'). Chemists were put to work to look for an anti-knock additive to gasoline.

The answer (found by analysis of the periodic table of elements, as it happens) was discovered rather quickly: it was tetra-ethyl lead [70]. This additive was patented and exploited by a company called Ethyl Corporation that sold the additive to the oil companies. To avoid paying the royalties, which were significant, all the oil and chemical companies—especially the huge German conglomerate IG Farbenindustrie—spent a lot of money trying to find a better substitute. There was none to be found.

Now lead additives have been banned, for excellent health and environmental reasons, but the substitutes (alcohols and aromatics) are not as effective, petroleum refining has become less efficient, the so-called octane numbers are lower and automobile engines now have significantly lower compression ratios than they did in the 1960s. This results in lower fuel economy (other factors remaining the same).

In some cases, there is no direct substitute but an alternative approach to the function uses a different physical principle. Tungsten has the highest melting point of any metal, hence its use in incandescent light bulbs. Incandescent light was ultimately replaced, of course, but not by a material with a higher melting point but by light from a different physical phenomenon, namely fluorescent lights and light-emitting diodes (LEDs). However, LEDs are probably as far as lighting technology can be taken. And it seems that indium and gallium (together) are needed for all the brightest LEDs. If there is a substitute to be found, it will almost certainly involve another of the rare metals. Cameras using LEDs and liquid crystal displays (LCDs) for colour photography have displaced cameras using chemical films. The substitution of optical fibres for copper wire as a telecommunications channel is yet another example.

Nevertheless, for some functions there are no substitutes. Fresh drinking water is the obvious example. But among metals, there are also cases in point. Mercury is the only metal that is liquid at room temperature and the only one that can ‘dissolve’ (by amalgamation) another metal. Tin is uniquely valuable for solder because of its low melting point. Tantalum is uniquely valuable for capacitors. Silver is the best known electrical conductor. PGMs have unique catalytic properties.

The geologically rare but critical metals (cobalt, gallium, germanium, indium, lithium, selenium, tantalum, tellurium, tin and some of the REEs) have uniquely valuable physical properties that make them critical especially for the electronics industry. All the phosphors used for lighting and displays use one or other of the REEs. Phosphors are used in cathode ray tubes, plasma video display screens, sensors and LEDs. The composition of phosphors—the selection of the host and activator—varies depending on the colour required for the end product. For red, the REE oxides used include yttrium, europium and gadolinium; for blue, europium oxide. For green, the hosts used are lanthanum, cerium and yttrium, while terbium and gadolinium are used as activators. The combination of red, green and blue produces white colour.

This situation is similar in regard to the future potential for thin film photovoltaic modules, e.g. copper–indium–diselenide, cadmium–telluride, gallium–arsenide or thin film silicon, virtually all of which require one or more of the critical metals [71].

There is another example, namely permanent magnets. The strongest known permanent magnet alloy is neodymium–iron–boron (hereafter referred to as NIB). NIB is both more economical and twice as strong for the same weight as the next best magnet alloy [72].

6. The materials life cycle

As one would expect for rare materials, many of their uses, for instance as activators and catalysts, involve very small quantities. Hence the sorting and separation from end-of-life products, such as e-waste, is extremely challenging. Moreover, the purity requirements for the rare and critical metals, in many applications, are much more extreme than is the case for most structural purposes. When a complex product such as an automobile reaches the end of its useful life in Europe, it is often loaded onto a ship and sent to Africa.

But under increasingly strict rules, the end-of-life vehicle will go to a specialized dismantler. The ideal dismantler removes storage batteries containing lead, electronic items and wiring, window glass, plastic, copper or aluminium body parts and trim, stainless steel items, catalytic mufflers, tyres and other rubber items as hoses. Ideally, it also recovers potentially re-usable components, such as electric motors, pumps, transformers, engines or axles that can be re-used as such, or remanufactured easily.

The non-reusable items (and many re-usable ones) enter a scrap stream. Scrap is sold to a variety of recyclers, ranging from glass producers, lead, copper and aluminium recyclers, steel companies and electronic recyclers. We will have more to say about the latter, later. The plastics are usually burned off by the dismantler, or (ideally) in a specialized incinerator where pollutants are captured and removed, and useful heat may be recovered. What is left is the frame and parts of the body, consisting of steel (the frame) and cast iron (the engine block), plus a variety of other metals such as zinc (from anti-corrosion coating), chromium (decorative plating), and copper or aluminium wiring that is too difficult to remove by hand. This agglomeration is then crushed and broken up by very crude machines. It is then packaged for shipping to either an integrated steel mill or a secondary steel mill where it is melted in an electric arc furnace.

As mentioned earlier, there is no practical technology for separating metals not normally found together in ore, from a remelt furnace where the composition of the inputs is not very precisely known in advance. Putting it another way, to close the material life cycle more effectively, the composition of the scrap must be very precisely known so as to optimize the recovery process [73]. For instance, it is impossible, at present, to separate copper or aluminium contaminants from remelted scrap iron or steel. Similarly, it is difficult to remove contaminants (such as REEs) from remelted electronic scrap that consists mostly of aluminium. This imposes limits on the

quality of the recycled material and, at the same time, constitutes a significant and permanent loss mechanism for the contaminant metals [74].

Consider, now, the electronics sector. When a TV set or a PC or a printer or cell phone reaches the end of its useful life, it may go directly to a landfill but—in a closed cycle—it will be collected and sent to a specialized dismantler who separates e-components from the rest of the product, either mechanically or (if costs allow) by hand. The electronic components of more complex products (such as a car) are scattered around the vehicle. There are as many as 25 small electric motors in the car, all containing neodymium-based magnets. There is a motor-generator, also containing neodymium, dysprosium, praseodymium and terbium. There are a variety of sensors, containing yttrium. There is an LCD screen on the dashboard, containing cerium, yttrium and europium phosphors (possibly also indium) and a number of LEDs, possibly including the headlights.

If the car is a hybrid, the nickel-metal hydride (NiMH) battery contains a rare Earth mischmetal (with composition 50% lanthanum, 33% cerium, 10% praseodymium and 3% of neodymium and samarium) and cobalt. The lithium battery contains about twice the amount of cobalt as a NiMH battery. Internal combustion vehicles contain in their catalytic convertor approximately 9 g of PGMs (mainly palladium, with platinum and rhodium) plus up to 285 g of the rare Earth oxides (mainly cerium plus lanthanum, neodymium and praseodymium) and zirconium. In fact that is not all, because there are fuel additives, glass polishers and so on, also containing REEs.

The ideal dismantler will pick out the components containing valuable materials, but many (especially outside Europe) would not bother. If the electronic items are segregated, they will be sorted and sent on to a specialized mechanical e-waste pre-processor. The current situation is that most unsorted e-wastes will be collected and shipped to a country with low-cost labour and little or no environmental protection. There, perhaps in China, the mixed scrap will be leached, probably by cyanidation (the standard process for gold recovery), to recover the copper, gold, silver and palladium, for all of which there is a steady market.

The leachate is dangerously toxic, not only because of cyanide, but also because of contamination by lead and cadmium, and possibly arsenic, antimony and bismuth. This sludge, or gunk, is supposedly sealed in plastic containers and stored somewhere out of sight or disposed of somehow. It disappears from our radar screen at any event. (The situation is much the same with nuclear waste, which is still being stored in drums because no permanent disposal site has yet been decided upon.) The current situation is simply that, apart from copper, gold, silver, platinum and palladium, despite very high prices for rare metals, they are not being recycled.

Yet much more must be done. We mentioned neodymium, the rare Earth metal that is a component (with boron and iron) of the best known permanent magnet material. This alloy is now essential to a variety of products requiring small, powerful electric motors or generators from hard disks to hybrid or electric cars and wind power generators. Global reserves are limited and almost all of the existing mines are in China, which currently controls virtually 100 per cent of the supply of this metal. While other mines may come online in the next decade, it is evident that recycling of this unique magnetic material is necessary, at almost any cost. Yet this will be extraordinarily difficult, because today only 26 per cent of the current supply is used for motors or generators. The rest is used mostly for hard disks in PCs and laptops or audio equipment (such as microphones or speakers), where efficient recovery would depend on precision dismantling or some new generic (biological?) recovery process nobody has yet imagined.

(a) Options to increase future supply

The historical approach to increase supply and avoid shortages of natural resources is to increase exploration and open new mines. Economists traditionally assume that this mechanism is always operational, i.e. that an increase in the market price will signal producers to increase output, and

that it will happen. Most economists consider ‘economic scarcity’ (signalled by rising prices) to be within their domain, but they tend to reject ‘geological scarcity’ as a myth [42]. In fact, empirical studies have demonstrated quite convincingly that resource prices, in real terms, have declined consistently since the industrial revolution [40,41]. However for hitch-hiker metals, the assumed relationship between prices and output does not automatically hold [75]. Thus, the future supply and production of hitch-hikers will depend partly on technology and partly on geological scarcity *per se*.

Geological scarcity can be overcome, in principle, by increasing the recovery rate of hitch-hikers from ‘attractor’ metals, by improving extraction efficiency, enhanced recycling of end products that contain these metals and by developing alternative technologies that avoid their use [76]. Improving extractive efficiency—up to a point—is probably more feasible for many rare metals than finding new sources (which may not exist). However, it may involve significant re-engineering of the recovery process. In most cases, the recovery of a scarce ‘hitch-hiker’ was initially more or less accidental, and the original process design was never intended to save, still less to concentrate, elements that were viewed as contaminants. Increasing output by improving the recovery from existing mines is applicable to all metals, but especially to hitch-hiker metals that are obtained from the ores of an ‘attractor’ metal.

The second option, to increase the production of hitch-hikers by recycling end products, needs detailed study of process options, as well as estimates of future demand for the functional capabilities provided by those products. The third option, to develop technologies not using critical metals, involves ‘thinking out of the box’, where critical metals seem to have unique advantages over other materials. For instance, neodymium magnets are 10 times stronger than the strongest ceramic magnets. This makes it possible to use smaller magnets to get the same holding capability, and it has enabled many new uses. But there may be alternatives: in early 2012, the Japanese company Nidec exhibited a prototype of its switched reluctance (SR) motor for electric vehicles (EVs) and hybrid electric vehicles. SR motors use a magnetic reluctance torque to generate a turning force and do not use magnets at all [77].

The following paragraphs discuss the potential for increasing the extractive output of specific metals. A first estimate of the maximum potential output from existing ‘attractor’ metal ores can be based on the average content of each hitch-hiker in the ore and current mine production.

(i) Iron by-product metals: rare Earth elements

In 2010, almost 50 per cent of REEs were produced as by-products of iron ores, mainly in Bayan Obo mines (China). Iron mineral ores in that mine contain 350 kg of iron, 60 kg of rare Earth oxides and 1.3 kg of niobium [78]. In 2010, 54 000 tonnes of the rare Earth metals were produced from Bayan Obo. Baosteel, the company operating the mine, aims to produce 24 million tonnes of iron, which means a potential future production of 4.1 million tonnes of the rare Earth oxides and 89 000 tonnes of niobium (actually the world production of niobium could be completely supplied from iron ores) [79].

(ii) Aluminium by-product metals: gallium

Bauxite contains an average of 0.005 per cent (50 ppm) of gallium [80]. The world mine production of bauxite in 2010 was 211 million tonnes, which implies that 10 550 tonnes of gallium is potentially recoverable, per year. In 2010, gallium production was only 106 tonnes, only 1 per cent of the estimated recoverable amount. Gallium is also obtainable, in principle, from coal ash. US coal ash contains, on average, about the same, or even slightly more, gallium ([81,82], ch. 14).

(iii) Copper by-product metals: cobalt, rhenium, molybdenum, tellurium and selenium

Cobalt is mostly a by-product of copper and nickel ores. In 2010, the total global production of cobalt was 88 000 tonnes, of which 35 per cent was produced from copper and 50 per cent from nickel and the remaining 15 per cent from cobalt arsenides [51]. As a by-product of copper,

cobalt is contained in sedimentary copper deposits which are mainly composed of copper oxides and carbonates. The sedimentary copper ore deposits in Zambia and Zaire reach 0.4 per cent cobalt concentration, making it the dominant global source [69, p. 188]. In 2010, the production of 7.3 million tonnes of copper from oxides and carbonates supplied 31 000 tonnes of cobalt. Theoretically, for each tonne of copper recovered 56 kg of cobalt is available. This implies a potential production of 408 800 tonnes [83].

Rhenium and molybdenum are also recovered as by-products of the roasting of copper-porphyrus ores (copper sulphides). These ores contain an average of 0.95 per cent of copper, 0.03 per cent of molybdenum and a minimum of 0.001 per cent of rhenium [65]. Since porphyry ores account for 55 per cent of world copper production, we can estimate an average potential output of 281 050 tonnes of molybdenum and 9370 tonnes of rhenium. Actual production for 2010 was 133 000 tonnes of molybdenum and 46 tonnes of rhenium, so it appears that molybdenum is being extracted rather efficiently, but rhenium is not [51].

Tellurium and selenium are also co-products of copper refining from various copper ores. For each tonne of copper refined, there is 65 g of tellurium [84]. In 2010, the total world copper production was 16.2 million tonnes, and thus the production of tellurium could be 1050 tonnes (twice the production documented). Selenium substitutes for sulphur in a wide variety of minerals although none are mined for their selenium content. It is now produced entirely as a by-product of copper refining, although coal ash is by far the most abundant source. (Average US coal ash contains about 60 ppm of selenium ([81,82], ch. 14).) For each tonne of copper produced in the USA, there is 0.26 kg of selenium, but from Canadian refineries, selenium recovery is about 0.64 kg per tonne of copper [85, p. 706]. We found no data for other countries. However, if the US selenium recovery rate is applied to world copper production, about 4200 tonnes of selenium could have been recovered, although if the Canadian rate were applicable, potential selenium recovery would be closer to 13 000 tonnes. The actual world production of selenium was 3250 tonnes. Thus, selenium recovery efficiency seems to be somewhere between 25 and 75 per cent.

(iv) Zinc by-products: germanium and indium

Currently, germanium and indium are co-produced with zinc from sphalerite (ZnS), a zinc sulphide that contains an average of 0.005 per cent germanium, 0.005 per cent indium along with 67 per cent zinc [65]. If we assume that 95 per cent of zinc was primarily produced from sphalerite, about 600 tonnes of germanium and indium could have been recovered, when compared with reported production of 574 and 84 tonnes, respectively. Sphalerite also contains an average of 0.005 per cent of gallium, although it is not recovered at present [84]. In 2010, almost 420 tonnes of gallium could have been recovered. Besides sphalerite, there are other mineral ores that contain germanium and indium, but in such low quantities, and so dispersed, that they will probably remain uneconomical for many years.

(v) Nickel by-products: cobalt and platinum group of metals

The vast majority of cobalt resources are in nickel-bearing laterite deposits (nickel oxides and silicates) and sedimentary copper deposits in the Congo and Zambia. Laterite deposits contain an average of 1.3 per cent of nickel and 0.01 per cent of cobalt and supply about 40 per cent of world nickel production [66]. In 2010, the production of 580 000 tonnes of nickel from laterite could have yielded 44 600 tonnes of cobalt. Overall, the potential production of cobalt as a by-product of nickel is estimated to be 453 000 tonnes at current rates of copper and zinc output.

In 2010, the total production of PGMs was 690 tonnes, out of which 456 tonnes were mined from primary sources, 11 tonnes were co-produced from nickel ores, and 222 tonnes were obtained from secondary production [46]. PGMs from nickel ores were mainly obtained in Botswana, Canada and Australia [51]. The content of PGMs in nickel deposits varies depending on the type of the mineral deposit. In South Africa, the average platinum grade is around 27 g per tonne, whereas in Russia the average PGM content is 15 g per tonne in nickel sulphide ore

Table 1. Resources, current mine and potential production of base and hitch-hiker metals.

'attractor' metals		'hitch-hiker' metals			
name	production (10 ⁶ tonnes)	name	current mine production (tonnes)	potential mine production (tonnes)	recovery efficiency (%)
iron ore	24.00	rare Earth oxides	54 000	4 114 000	1
		niobium	63 000	89 140	71
aluminium	28.15	gallium	106	10 550	1
copper	16.20	cobalt	31 000	408 800	8
		rhenium	46	9370	<1
		molybdenum	133 000	281 050	47
		tellurium	475	1050	45
		selenium	3250	4210	77
zinc	8.40	germanium	84	600	14
		indium	574	600	96
		gallium	—	420	—
nickel	1.45	cobalt	44 000	44 600	99
		PGMs	11	17	63
tin	0.26	niobium	2	370	1
		tantalum	102	750	14

deposits [86]. Taking as an average 20 g per tonne and the total world nickel production from sulphide ore for 2010 of 870 000 tonnes, it seems that 17 tonnes of PGMs were potentially available for recovery [87]. PGMs can be additionally recovered from pyrrhotite, an iron sulphide mineral associated with nickel sulphide ores [88]. The ore mineral contains between 5 and 30 g per tonne of rhodium, ruthenium and iridium collectively.

Secondary production from recycling electronic equipment and other scrap is a significant source of PGMs [51,67]. The highest amount of PGMs is recovered from electronic products, especially printed circuit boards (PCBs) and three-way catalysts of internal combustion vehicles. PGM metals could also be recycled from electronic devices where they are used in small quantities for electric contact, printed resistors and in alloys for spark plug contacts in aeroplane and automobile engines [89].

(vi) Tin by-products: niobium and tantalum

Niobium and tantalum are mainly mined from pyrochlore and tantalite, respectively. They are also obtained from tin slag. Cassiterite ore contains about 70 per cent tin and 0.2 per cent of tantalum, which leads to a potential production of 750 tonnes [65]. In 2010, production of tantalum from tin ore was 102 tonnes (13% of its total world production).

Table 1 shows the production of attractor and hitch-hiker metals, and the potential production of hitch-hiker based on their content discussed above. The relation between the current production and potential production of hitch-hikers can be defined as 'recovery efficiency'. The maximum recovery efficiency might be in most cases less than 100 per cent, first because of the composition in which the 'hitch-hiker' is in the mineral ore, and second because of the limitations of actual technology. Despite all these constraints, estimating recovery efficiency is still useful to provide a first estimate of the potentiality for extracting minerals more efficiently.

As table 1 shows, for cobalt from nickel ore and indium from zinc ore the recovery efficiency approaches 100 per cent as their potential and current production are very similar. For other hitch-hikers, such as selenium, niobium from iron ore and PGMS, the recovery efficiency is quite high (up to 77%). For the rest of the metals, especially the REEs gallium, rhenium and niobium from tin ore, the current production amounts are far below theoretical potential, which seems to mean (assuming the data are correct) that there is a large quantity of valuable metals being lost in wastes and emissions. For a more accurate estimate, the extraction and production processes for each hitch-hiker metal should be further assessed and evaluated.

7. Recycling of rare metals

A current example is the Umicore integrated smelter–refinery facility in Hoboken, near Antwerp, Belgium. It can treat up to 350 000 tonnes per annum of secondary materials bearing precious metals used in electronics (or elsewhere, for that matter). In 2007, the plant recovered 30 tonnes of gold, worth \$2.6 billion, plus 10 other metals, including 37 tonnes of PGMs, 1000 tonnes of silver and 68 500 tonnes of other metals (mostly copper, nickel and lead) worth \$0.4 billion. About 13 million tonnes of CO₂ would have been emitted by the primary production processes for those metals, whereas only 3 million tonnes of CO₂ was actually emitted by the Hoboken plant. This means a saving of about 80 per cent in terms of greenhouse gases.

This facility was once a conventional smelter of imported copper, lead and zinc ore concentrates from Africa. In 1997, it was converted to its present use as a dedicated smelter–refinery of precious metal-bearing materials, by an investment of over \$500 million. (A new ‘green-field’ plant would have cost more than twice as much [90].)

The first step in the recovery process is a conventional copper smelter, where the sulphur dioxide is captured and converted to sulphuric acid in a separate location. There is a parallel operation for recycling scrap containing lead, which also accepts lead-containing slag from the copper smelter, while copper matte goes back to the copper smelter and indium–tellurium residue goes to another refinery. Nickel speiss is separated and sent to a separate nickel smelter that also takes scrap and sends PGM residues back to the copper complex. The copper from the smelter is then leached and selenium residues from the copper leachate go back to the lead refinery. The residues from that refinery contain useful amounts of selenium, tellurium and indium.

The precious metals associated with copper, together with silver residue from the lead refinery and PGM residue from the nickel refinery, then move on to further refining operations to recover the precious metals (PGMs, Ag and Au). The Hoboken complex produces six products, in addition to sulphuric acid and slags, namely copper, lead, nickel and three residue streams, one containing precious metals, one for indium, selenium and tellurium and one for heavy metal residues (Pb, Bi, Sb, Sn and As). All in all 17 metals are now being recovered by Umicore at the present time, but a number of important ones are not included in that list. Even so, there are only five such rare-metal recovery complexes in the world at the present time, of which three are in Europe. Recovery efficiency of more than 95 per cent for gold is claimed and close to 100 per cent for copper and PGMs.

The recovery and recycling of rare hitch-hikers from end products is presently almost non-existent, except for gallium, germanium, platinum and palladium. This is mainly due to their dissipative applications and low concentrations in end products. Most critical elements still end up in the slag of smelters or in landfills. Evidently, the technology exists for part of the recycling task, though there is a long way to go. There is no technology (in the Western world at least) for the recovery of the REEs gallium, germanium or tantalum. Batteries containing lithium, cobalt and manganese could be, but are not (yet), recycled. Prices are too low. There are many other barriers standing in the way of widespread application of these technologies. These include laws restricting international shipments of wastes (including e-waste), but most of the inefficiencies are in the area of collection and pre-processing. Price incentives such as returnable deposits, as well as regulations, are needed to prevent illegal shipments of waste (mislabelled as ‘for re-use’), to stop backyard recycling (for inefficient gold recovery), etc.

Identifying and quantifying hitch-hikers by functional use helps identify which specific intermediates and end products use them. This helps us to focus on the potential for recycling. Talens Peiro *et al.* [91] have considered that, in 2010, 24 060 tonnes of REEs were used in magnets, under the function ‘alloying metals’. Magnets are used in wind turbines, EVs, MRI, electronic products and magnetic cooling applications. If we know the amount of each REE in each of these end products, we can calculate what could, in theory, be recovered at the end of life. Based on several sources, they estimated that 1300 tonnes of REEs were embodied in the magnets of wind turbines, of which 910 tonnes were neodymium. Using the same approach, we found that 3358 tonnes of neodymium were used in magnets in EVs, 450 tonnes in MRI units and 11 980 tonnes in electrical and electronic devices, totalling 16 700 tonnes of neodymium that could in theory be recovered at some point in the future. This is substantial compared with neodymium production for 2010 (21 615 tonnes). According to Graedel *et al.* [38], the actual end-of-life recycling rate for neodymium is less than 1 per cent.

In the case of phosphors, a total of 8250 tonnes of REE were consumed in 2010 [91]. These ended up in lighting applications, LCDs and plasma panels. If we trace europium, which is the only metal used as a dopant for blue light, 24.5 tonnes were used in lighting, 19.5 tonnes in LCDs and 6 tonnes in plasma panels, adding up to a total of 50 tonnes. Graedel *et al.* [38] estimated that less than 1 per cent of europium is recycled at the end of life.

Recycling intermediates and end products is challenging for several reasons. Hitch-hikers are highly disaggregated in end products whose disassembly is unpractical if not impossible; PCBs are a good example. Despite the amount of critical metals being very low, the concentration is still high if compared with the ore grade in mineral ores. For instance, a PCB and a mobile phone contain 80–100 g per tonne of palladium, 40 times more concentrated than the original mineral ore [92].

Another significant way to enhance recycling is to improve current collection rates. All effort for developing high-technology recycling solutions for the efficient recovery of hitch-hikers will be wasted if collection rates remain low. For example, the current collection rate of multi-functional mobile phones is about 3 per cent, whereas by smelting and refining about 95 per cent of hitch-hikers can be recovered [92,93].

There is also a need to improve the tracing of end-of-life equipment containing hitch-hikers. For instance, although the European Union has banned the export of waste electronics and electrical equipment, there is still a considerable fraction of electronic devices (especially laptops, notebooks, tablets, etc.) that never reach legal collection points. Action is required in order to avoid the improper disposal of such equipment. Thus, it is important to quantify the amount and types, and especially make consumers more conscious about the importance of recycling those complex products by using proper procedures.

8. Conclusions and implications for closed cycle manufacturing

In the very long run, there is a clear case and a potential for closed cycle manufacturing. The market for post-consumer recycled materials from electronics will undoubtedly be stronger in the future because of the scarcity of some critical metals. But market forces alone will not go far enough. As already noted, it is currently profitable to recover gold, silver and the noble metals from e-waste, but the waste remaining after the high value elements are removed becomes even more difficult to recycle. An integrated facility to recover the other valuable materials is very capital intensive, and such a facility (at present) would almost certainly have to rely on fees from other industrial waste generators that are, in turn, subject to strictly enforced environmental regulations.

Unfortunately, the fee-based model does not work for consumer products in Europe, and still less in the developing countries, unless they are first collected by an intermediary, such as a retail outlet. At least one US electronics chain is ‘offering’ a large item collection service to its customers, who have to bring the item to the store and to pay a fee. Other retail stores take back old TVs or PCs if the customer buys a new one. However, despite the Waste Electrical and Electronic Equipment Directive (in Europe) the ‘take back’ option has not yet adequately been supported by

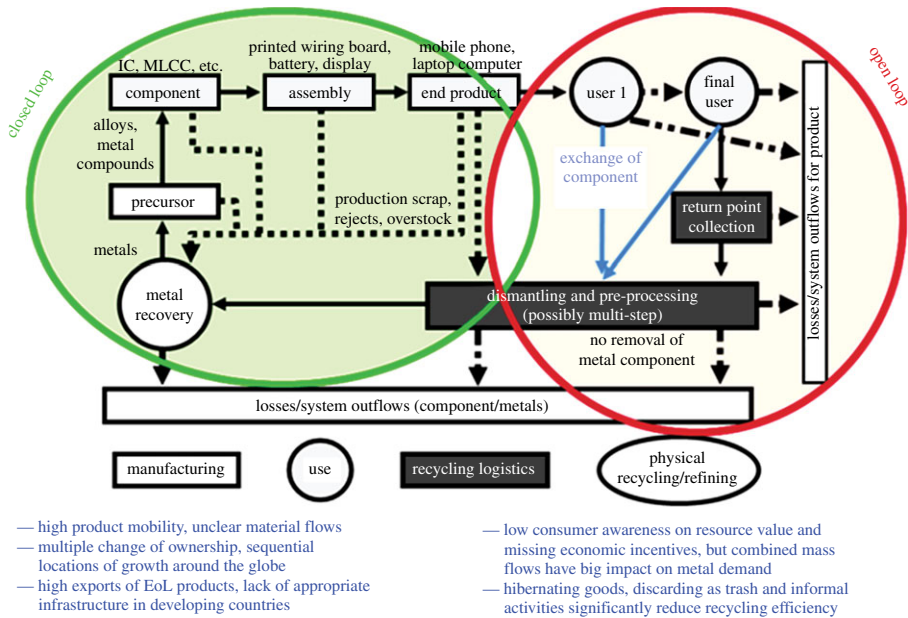


Figure 3. Open loop character of consumer goods as the most significant driver for losses. IC, integrated circuit; MLCC, multi-layer ceramic chip (capacitor). (Online version in colour.)

legislation in the USA or Europe. A much more effective option would be for each purchased item to carry a legally mandated returnable deposit, from 2 to 10 per cent of the sales price (smaller for higher priced items). The money would have to be kept in a separate account and returned when the item is brought back.

Extended producer responsibility (EPR) is a strategy designed and implemented in the European Union to promote the integration of environmental costs associated with goods throughout their life cycles into the market price of the products (for definitions and description, see http://www.oecd.org/document/19/0,3343,en_2649_34281_35158227_1_1_1_1,00.html). EPR uses regulatory means to hold producers liable for the costs of managing their products at end of life. This tactic attempts to force a transition from traditional end-of-pipe waste ‘diversion’ programmes (no matter who funds the programmes) to ‘cradle-to-cradle’ recycling systems designed, financed and managed by the product manufacturers themselves.

EPR is predicated on the fact that producers have control over product design and marketing, and therefore have the greatest ability (hence responsibility) to reduce toxicity and environmental harm [94]. Some producers’ strategies can be regarded as responses to EPR: (i) green design, (ii) green manufacturing, (iii) green procurement, (iv) green recovery agencies, (v) use of eco-labelling, and (vi) the establishment of corporate alliances. Leading industrial companies have acquired ISO 14000 certification—an internationally developed voluntary standard for environmental management, partly in response to EPR but also partly to meet consumer demand. However, it is not clear whether EPR does, or can, provide incentives strong enough to close the materials cycle. The missing piece of the puzzle seems to be incentives for metallurgical firms to invest in e-waste recycling.

For both environmental and resource scarcity reasons, there is a need for regulations or incentives to induce original equipment (brand name) manufacturers (OEMs) to monitor and manage both scarce and hazardous materials throughout the life cycle, ‘from cradle-to-grave’ (open loop) and—wherever feasible—‘from cradle-to-cradle’ (closed loop). See the schematic of figure 3.

A new technology that may facilitate closing the loop is radio-frequency identification (RFID), a very small chip—potentially microscopic—that can be implanted in a product to identify its

source and track it from owner to owner [95]. This technology is already operational and it could be used in the near future to keep track of manufactured products as large as cars and as small as cell phones. It would be fairly straightforward to use the RFID technology for the purpose of sorting end-of-life items by manufacturer, and even by age. The next step would be for the manufacturer, or his agent, to collect and ship the items back to a specialized recycling operation.

The two major barriers to closed loop manufacturing are (i) lack of strong incentives, such as returnable deposits, not only to enforce EPR in the developed countries, but also to facilitate the implementation of new ideas, such as life cycle ownership of scarce metals, and (ii) corruption, weak contract enforcement and weak 'rule of law' in too many developing countries.

Even in developed countries, especially with the current economic crisis, scavengers are partially displacing formal waste collectors. Such informal recycling constrains the profitability of the legal system. It also can result in environmental damage owing to the scavenger's lack of knowledge about the toxicity of some of the materials involved, especially those from electrical and electronic equipment.

The life cycle ownership concept would allow an OEM to own and rent the scarce materials in its products, rather than selling them with the product itself. This would enable the original manufacturer to demand the return of the specified materials at the end of product life or pay for their market value. It would also provide a strong financial incentive to recyclers to adopt better processes. Of course, this would be impossible to enforce in the present world. But if the returnable deposit or other regulations enabled OEMs to keep track of their products and if the e-recycling industry were better organized, closed cycle manufacturing would be more feasible.

Other barriers are also very important [96]. Perhaps the most important is a general fear of, and resistance to, change. This resistance is encouraged by all groups or sectors that foresee adverse consequences for themselves. For instance, one of the major arguments in favour of closed loop manufacturing is that it would create incentives to increase product life and reduce the consumption of primary resources. But such a change would clearly have a negative impact on the suppliers of those resources. Similarly, it would have a negative impact on those who encourage and profit from rapid obsolescence.

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