Recycling Rare Metals

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4.1 INTRODUCTION

The application of material flow analysis (MFA) to trace metals throughout their life cycle is an exercise for quantifying the magnitude of the uses and losses and identifying where they occur. Furthermore, by distinguishing between losses that are dissipative versus losses that are recoverable, the MFA can help us assess the potential for recycling of the material. This is a very practical analysis for geologically scarce metals used in new technology products such as smartphones, wind turbines, and solar panels. These metals e.g. gallium, germanium, indium, tellurium, tantalum, and platinum group metals (PGMs), are of special concern in terms of geological scarcity. They also pose a problem for recycling due to the trend toward miniaturization in their uses. Many of these metals are not found anywhere in high concentrations but are distributed as contaminants of other "attractor" metals to which they are chemically similar. For this reason, we call these metals "hitchhikers" when they accompany "attractors". For example, molybdenum, rhenium, selenium, silver, and tellurium are hitchhiker metals the production of which depends to a large extent on the mining and smelting of copper (Talens Peiró et al., 2013). Losses occur initially in the production process that, for the case of the hitchhiker metals, includes the mining of the "attractor" ore, mineral processing, and further extraction, separation, and refining processes. A very simple calculation can be performed to estimate the theoretical amount of the hitchhiker metal that could be extracted based on the quantity of the metal present in the ore. Even though the potential metal production estimated this way does not consider technological limitations and unavoidable losses, it serves to identify which metals offer opportunities for improved resource management and which ones are already being managed efficiently. We have performed these calculations for hitchhiker metals for which one might expect revolutionary demand due to their use in new technologies. We present the results in Table 4.1.

Metals for which potential mine production is comparable to current (2010) output do not have much margin for increasing recovery during the production phase. For example, cobalt from nickel ores is extracted efficiently (99%), whereas recovery from copper sulfide ores such as carrolite is less efficient (8%) resulting

TABLE 4.1 Potential and Actual Production of Hitchhiker Metals in 2010

"Attractor" Metals or Mineral Ores			"Hitchhiker" Metals				
Name	Reserves (10^6 t)	Production (10^6 t)	Name	Reserves (10^3 t)	Current Mine Production (t)	Potential Mine Production (t)	Recovery Efficiency (%)
Iron ore	87,000	2400	Rare earth oxides[a]	110,000	54,000	4,114,280	1
			Niobium[a]	2900	63,000	89,140	71
Bauxite	28,000	211.00	Gallium[b]	n.a.	106	10,550	1
Copper	630	16.20	Cobalt[c]	7300	31,000	408,800	8
			Rhenium[d]	2.5	46	9370	<1
			Molybdenum[d]	9800	133,000	281,050	47
			Tellurium[e]	22	475	1050	45
			Selenium[e]	88	3250	4210	77
Zinc	250	12.00	Germanium[e]	0.45	84	597	14
			Indium[f]	n.a.	574	1454	39
			Gallium[e]	n.a.	—	420	—
Nickel	76	1.55	Cobalt[g]	7300	44,000	44,600	99
			PGMs[d]	66	11	17	63
Tin	5.2	0.26	Niobium[d]	2900	2	373	1
			Tantalum[d]	110	102	746	14

Sources: (a) Drew et al. (1991), (b) Jaskula (2011), (c) Shedd (2011), (d) Habashi (1997), (e) USGS (1973), (f) Tolcin (2011), (g) Berger et al. (2011).

in losses of up to 378,000 t of cobalt. The table also serves to point out a potential source for gallium from zinc (420 t) that is presently not being exploited (Berger et al., 2011). On the other hand, the PGMs selenium and molybdenum are currently being produced near their mine potential from current sources. These metals are correspondingly important to recover and recycle to meet future demand. For the rest of the metals listed in Table 4.1, a significant fraction of the potential is ending up as waste.

Similarly, the subsequent life cycle stages have unnecessary losses and consequently opportunities for recovery. In the next few pages, we illustrate how material flow analysis is used to quantify the losses and recycling potential during the whole life cycle of several critical metals: indium, europium, gallium, and platinum group metals (PGMs).

4.2 INDIUM

In our economy, we use the life cycle of indium to illustrate how metal losses can be quantified from mining to end-of-life (EOL) based on consumption data for 2010. Based on knowledge of the processes and end-uses of indium, we differentiate between dissipative and recoverable fractions. The analysis is illustrated in Figure 4.1, which indicates the losses of indium during its life cycle in the present situation

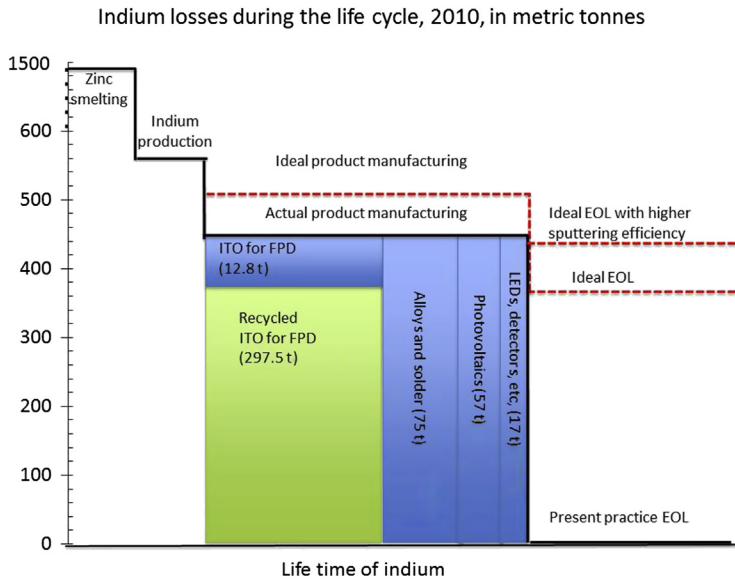Indium losses during the life cycle, 2010, in metric tonnes

FIGURE 4.1 Indium losses during its life cycle (2010) in metric tonnes.

(2010) and the potentially recoverable fraction marked by a more sustainable practice represented by the dotted line.

Indium is of special interest for several reasons. It is classified as a "critical metal" by numerous reports because it is a scarce metal that plays an important role in the solar energy industry, in flat screens, and in other new technology applications (US National Research Council and Committee on Critical Mineral Impacts of the US Economy, 2008; Buchert et al., 2009; European Commission, 2010a; Erdmann and Graedel, 2011). For many of these uses, there are no substitutes that offer the same performance. Furthermore, given the miniaturization trend required by new technologies, indium is used in very small quantities that impede its separation, recovery, and recycling. For example, a 2005 cell phone screen contained as little as 5.5 mg of indium per phone (the metals presently recovered from cell phones such as gold and silver represent 350 mg and 3.7 g, respectively) (Yoshioka et al., 1994; Hagelüken, 2007b). PC monitors contain between 79 and

82 mg of indium, whereas bigger liquid crystal display (LCD) television screens use 260 mg (Buchert et al., 2009). However, there are so many of these products that these small amounts of indium add up to a potentially important source for future supply. Without recycling or implementing substitutes, the sustainability of these technologies is questionable.

Indium is most commonly recovered as a by-product of the zinc smelting process from zinc-sulfide ores (sphalerite). Other minor sources are from tin and lead refining processes, which at the present time are not exploited. The content of indium in zinc concentrate varies depending on the geographic location of the mine. For example, Rodier gives 0.027% (by weight) of indium content in zinc concentrate for Kidd Creek, Ontario, Canada; 0.010% in Polaris, Northwest Territories, Canada; and 0.004% in Balmat, New York (Rodier, 1980). Based on the intermediate concentration of 0.010%, an average zinc content of 55% in zinc concentrate, and a global production of eight million tonnes of zinc in 2010, we estimate that

the amount of indium that could have potentially been recovered from zinc-bearing ores in 2010 is 1454 t. The USGS reports that 574 t of indium were produced globally for the same year (Tolcin, 2011). In other words, a third of the total indium currently available from zinc refineries is not recovered. This coincides with the amount Indium Corporation estimates is lost to tailings or non-indium-capable refineries (about two-thirds of all indium in zinc ores) (US Department of Energy, 2011). There is a margin for improving recovery at this initial stage, but it is still not economically attractive to do so.

High purity indium is used to make compounds with other metals for the manufacture of products. The most important is indium-tin-oxide (ITO) (78% indium, 17.5% oxygen, and 4.5% tin). Thanks to its electrical conductivity and optical transparency, ITO is used for transparent electrodes in products such as LCDs, TVs, and touch screens. Based on a previous study, we estimate that 425 t of indium were used for the production of ITO in 2011 (Talens Peiró et al., 2013). ITO comes as a powder and is deposited as a thin, film coating on a substrate via a process called "sputtering" that is reportedly only 3% efficient.

Sputtering deposition techniques vary, but the most common ones are electron-beam evaporation and physical vapor evaporation. Approximately 3% of the indium ends up successfully on the substrate, although 70% is target residual material (recycled by reducing to indium metal), 20% is deposited onto the surface of tools and chamber walls, 5% is etched from the substrate, and 2% ends up in faulty panels (Yoshioka et al., 1994). These percentages are based on a study from 2007, and it is possible that sputtering has become more efficient since then (Goonan, 2012). However, for lack of updated process data, based on these percentages we calculate that 12.8 t of indium are embodied in flat-panel display (FPD) products, 297.5 t are recycled to make more ITO, and 114.7 t are dissipated during the FPD production process. These quantities are shown in the product manufacture stage of Figure 4.1. The upper dotted line represents a greater amount of indium available if the sputtering process resulted in half the indium losses (58 t instead of 114.7 t). The figure also shows the fraction of the indium in ITO that is not successfully placed on the substrate and is recycled to make ITO.

Presently there is no indium recycling from post-consumer products that employ LCDs such as TVs, personal computers (PCs), mobile phones, and car navigation systems. The indium is diluted and dissipated in waste management schemes (recycling, landfill, etc.) at the EOL of the products. Sharp Corporation in Japan has invented a process for recovering ITO from LCDs, which involves crushing the screens into small chips and treating them in acid solution. A large-scale implementation in the future could result in an important source of indium (Kawaguchi, 2006). Given the growth in consumption of touch screens and flat-panel TVs, as well as the increase in average screen size, this recoverable indium is crucial for future supply. In Figure 4.1, the ideal EOL stage includes the indium embodied in LCDs, whereas the present situation shows no recovery.

Indium is also used to make alloys with base metals to lower their melting point. The indium-based alloys are used as fusible alloys (needed for devices such as fire sprinkler systems), holding agents, and solders. Indium solders are preferred in printed circuit board (PCB) assembly because indium is lead-free and has excellent wetting properties. Alloys of indium with precious metals such as gold and palladium are used in dental work due to their ductile nature. We estimate that 75 t of indium were destined for alloys and solders in 2010, of which 6 t were destined for PCBs (Talens Peiró et al., 2013). Some of these applications render the indium unrecoverable because it is used in such small quantities. PCBs are presently being recycled to recover copper, gold, silver, and palladium, but other critical metals such as

indium are not being recovered (Buchert et al., 2009). The use of indium in solders and alloys can be considered dissipative at the EOL. The "ideal" scenario represented in Figure 4.1 does not include the 75 t of indium destined for alloys and solders as recoverable.

The solar energy industry is also an important consumer of indium. According to industry figures, 57 t of indium were used in the form of copper-indium-gallium-diselenide (CIGS) employed as a semiconductor in photovoltaic cells in the form of thin-film photovoltaic material (Talens Peiró et al., 2013). ITO is used as an anode in the photovoltaic cells to increase the light conversion efficiency because of its light trapping properties and high transparency. Other indium compounds, such as indium antimonide (InSb), indium nitride (InN), and indium phosphide, are also used as semiconductors in photovoltaic cells and in other applications such as infrared detectors and thermal imaging cameras. Photovoltaic cells have a lifetime of 20−30 years, after which no recovery of indium is presently taking place. Potentially the indium present in the cells could be recovered in a similar fashion as the FPDs, and this is represented in the "ideal" scenario represented by the dotted line in Figure 4.1.

Other semiconductor applications such as laser diodes, fiber optic telecommunications, detectors, and light-emitting diodes (LED) were responsible for 17 t of indium. Indium in the form of indium gallium nitride (InGaN) is used as a light-emitting layer in blue and green LEDs. Indium gallium arsenide (InGaAs) is a popular material in infrared detectors. We are not aware of any recovery of the indium used in these products, but potentially, this is a recoverable fraction because the indium is not dissipated during use.

As is illustrated by Figure 4.1, less than 1% of indium is presently recovered at EOL as has been shown by other authors (Graedel et al., 2011). However, what the figure also shows are the fractions of the indium produced that are not dissipative and that could potentially be recovered. Recovering indium from LCDs and photovoltaic cells could result in 384 t of indium at EOL (minus unavoidable losses). If we assume a 50% improvement in the efficiency of the sputtering process, the recoverable indium at EOL is further increased to 442 t. The use phase is not included in the diagram because we know of no losses of indium that occur during the use of the products described previously.

4.3 OTHER EXAMPLES OF RARE METALS

Other metal life cycles can be analyzed in a similar fashion. We next explain three examples of scarce metals: europium, gallium, and platinum group metals (PGMs), all used in low quantities, yet crucial for different technologies.

Europium is one of the 17 so-called rare earth metals (REMs). Its major mineral source is bastnäsite, a carbonate fluoride mineral found in association with (some) iron mineral ores (such as magnetite, hematite, goethite, and limonite). The content of bastnäsite in iron ores varies from 4−17%. Bastnäsite contains about 0.1−0.5% of europium, a very small concentration compared to lanthanum, cerium, and neodymium, which are found in 42−50%, 23−33%, and 12−20%, respectively (Gupta and Krishnamurthy, 1992). The commercial application of europium is based on its phosphorescence. It is added to semiconductors in trace amounts, either in the +2 or +3 oxidation state, to improve the emission of light in various wavelengths. Divalent europium (Eu^{+2}) tends to give blue phosphors, whereas trivalent europium (Eu^{+3}) gives red phosphors. Both of them combined with terbium-based phosphors yield white light (Gupta and Krishnamurthy, 2005).

In 2010, the entire global production of europium (404 t) was used in phosphors for cold cathode fluorescent lamps (CCFLs), in LEDs

fitted in LCDs for background illumination, and in LED for light bulbs. Although most of the market is now dominated by LCDs using LEDs, to estimate the amount of europium stock in EOL LCDs, we need to know the amounts contained by each type of background lighting. The amount of europium in LCDs using CCFLs varies from 8.10 mg for TV to 0.13 mg for notebook computers, whereas LCDs using LEDs contain an even lower amount: 0.09 mg for TVs compared to 0.03 mg for notebooks. Europium is also used to give a reddish color in warm white LEDs that have a correlated color temperature lower than 3000 K. The average weight of europium in warm white LEDs varies from 0.4 to 0.9 μg (Buchert et al., 2012). Considering that losses of europium from mining to the manufacturing of phosphors are estimated to be 25%, we estimate that the remaining 75% is all contained in LCDs and LEDs.

At present, europium is rarely recycled (Du and Graedel, 2011; Graedel et al., 2011). The most important obstacle is collection due to its use in very tiny amounts. As an example, recovering one ton of europium would require the collection of at least 1.3 trillion units of white light LEDs. From a technological perspective, the recovery of europium also requires detailed knowledge about the composition of the phosphors. For instance, phosphors generally contain other rare earth elements such as yttrium, cerium, and lanthanum in the support matrix, not to mention terbium and gadolinium as dopants. The combined use of rare earths in phosphors inhibits their recovery because they all have very similar properties. Hence, the separation of any one from the others requires many processing steps.

Although gallium is a relatively common element, it mainly occurs as a trace amount in bauxite and zinc ores such as sphalerite. At present, almost all gallium is obtained as a byproduct of alumina production from bauxite, which contains an average of 60 ppm (Gray and Kramer, 2005). In 2010, the world production of refined gallium was 161 t. Of that, 106 t were obtained as crude gallium and the remaining 55 t from preconsumer recycling (Jaskula, 2010). In 2010, 65% of gallium output was obtained as a "hitchhiker" of aluminum smelting. Table 4.1 estimates that the current production of gallium represents only 3% of the total amount contained in bauxite. It also identifies zinc ore as a potential source of gallium that is not being exploited at present.

About 66% of the gallium consumed in 2010 was used in integrated circuits (ICs). Phosphors accounted for 18%, thin films 2%, and the remaining 14% of gallium consumption was for research and development, specialty alloys, and other applications (European Commission, 2010b; Talens Peiró et al., 2013). The most important gallium compounds are arsenides, nitrides, and phosphides. Gallium arsenide (GaAs) and aluminum gallium arsenide (AsGaAl) can convert electrical signals into optical signals at high speed with low power consumption, and better resistance to radiation compared to other compounds (Habashi, 1997). They are widely used as substrates in the manufacture of semiconductor components as transistors and ICs for the electronics and telecommunications industry. For example, a mobile phone contains from 0.3 to 1.5 mg of gallium, and fourth generation smartphones use up to 10 times that amount (Talens Peiro and Villalba Méndez, 2011; Jaskula, 2013). Gallium nitrides (GaN) are primarily applied in light-emitting diodes (LEDs) for the backlighting of LCDs for TVs and notebooks. Buchert et al. estimates that an LCD TV contains 4.90 mg and a notebook 1.60 mg of gallium (Buchert et al., 2012). Gallium phosphides and phosphides complex of gallium, aluminum and indium are also used for the production of optoelectronic components and ICs. Gallium is also used in thin-film solar cells as CIGS and in the triple-junction cells: indium gallium phosphide (GaInP$_2$) (Green and Emery, 2011).

More than 85% of gallium ends up in theoretically nondissipative uses: electronics,

phosphors, and thin film photovoltaic panels. The numerous steps during manufacturing and the high quality requirements for most of the electronic products using gallium lead to substantial processing losses. Typically only 20−30% of the gallium is finally embodied in the end-products (Koslov et al., 2003). For instance, in the production of GaAs substrates, 30% of the initial gallium is embodied in the final product; the remaining 70% is lost during such processes as etching and polishing. Eichler estimates that nearly 35% of the losses can still be recovered in the different steps (Eichler, 2012).

In CIGS manufacturing, gallium can be deposited in the absorber cell layer by various technologies: electron-beam (EB), electrochemical deposition, and co-evaporation. The amount of gallium deposited for electron-beam and co-evaporation is only 20% of the total gallium input. For electrochemical deposition, the amount deposited is 30% of the total input (Kamada et al., 2010). Based on the fact that a 1 MW CIGS panel contains about 3.5−4 kg of gallium, we estimate that 7.5−16.5 t of gallium are wasted during the manufacturing stage (Kalejs, 2009; Christmann et al., 2011). New developments to minimize the loss of gallium during CIGS manufacturing are based on using inkjet printing for deposition. This technology could reduce the amount of gallium wasted by 90% and thus reduce the cost of thin-film solar cells (Quick, 2011).

At present, gallium is only recovered from new scrap (preconsumer scrap) generated during the manufacturing of semiconductors, mainly from GaAs wafer waste, and from liquid phase deposition. There are several options for the recovery of gallium from semiconductor waste: thermal dissociation, oxidation with oxygen, nitriding in ammonia, and chlorination with chlorine gas (Koslov et al., 2003). Most of the difficulty in recycling gallium is due to the problem of separation from the other components of contact alloys such as indium, tin,

germanium, lead, silver, copper, and gold. In 2010, about 55 t of gallium were produced from preconsumer scrap (Jaskula, 2013).

Many efforts to recycle gallium focus on increasing the collection of EOL products. In Europe, the PV Cycle association, which represents more than 90% of the EU photovoltaic market, recently set up a voluntary collection and recycling scheme. In 2010, PV Cycle collected about 80 t of modules. In 2011, this grew to 1400 t and, in the first two quarters of 2012, 2250 t (Neidlein, 2012). In the EU, photovoltaic module take back and recycling became mandatory in February 2014. Even though thin films represent only 5% of the current photovoltaic panels market, they may eventually dominate the future market because they have more potential for cost reduction. Moss et al. estimates that thin films will have a market share of 18% by 2020; thus, gallium demand would increase to 14 t (Moss et al., 2011).

PGM is the term used for a group of six metals: platinum, palladium, rhodium, ruthenium, iridium, and osmium. They tend to occur together in primary and secondary mineral deposits. In primary deposits, they are found in platiniferrous ores in association with iron sulfides and sulfides of nickel, cobalt, and copper. Economical deposits mainly contain sperrylite ($PtAs_2$), cooperite (PtS), stibiopalladinite (Pd_3Sb), laurite (RuS_2), ferroplatinum (Fe−Pt), polyxene (Fe−Pt−other platinum metals), osmiridium (Os−Ir), and iridium platinum (Ir−Pt). PGMs can also be found in secondary deposits formed by weathering and washing of primary deposits. The content of PGM varies depending on the type of mineral deposit. In South Africa, the average platinum grade is about 8 g/t of ore, but it can reach 27 g/t in deposits associated with nickel ore. In Russia, where platinum is obtained as a by-product of nickel and copper, the average grade is about 5 g/t. The average grade can reach 15 g/t in sulfide deposits (Renner, 1997). In 2010, the world production of PGM was 689 t; 456 t were obtained from platinum

sulfides and arsenides, 222 t from recycling, and 11 t were obtained as hitchhikers of nickel (Talens Peiró et al., 2013). According to Table 4.1, the current production of PGM as a hitchhiker of nickel is near its potential level.

Among the PGM group, we can differentiate subgroups based on production quantities. Platinum and palladium are a first group of metals produced in multiples of 100 t/year. Rhodium and ruthenium are a second group produced in multiples of 10 t/year; iridium and osmium can be regarded as a third group, produced in very small quantities. In brief, rhodium, ruthenium, iridium, and osmium can be regarded as by-products (or "hitchhikers") of platinum and palladium. In 2010, the global production of PGMs was: 249 t of platinum, 360 t of palladium, 36 t of rhodium, 35 t of ruthenium, 7 t of iridium, and 2 t of osmium.

PGMs are exceptional oxidation catalysts. They are electrically and thermally conductive and offer a high oxidation resistance combined with extraordinary catalytic activity, chemical inertness, high melting point, temperature stability, and corrosion resistance (Lofersky, 2010). Almost 50% of the demand for PGMs is for use in automobile catalytic converters, 14% is used for jewelry, 9% for investment,

4% for other electrical uses, 1% for catalysts in the chemical industry, 1% for alloys with electrochemical applications, less than 1% for the glass industry, and the remaining 22% to other unspecified uses (Lofersky, 2011). See Figure 4.2. Some PGMs are lost from their extraction in the manufacturing of end-products. Dissipative uses of PGM include dental restorative materials and in the glass industry for the development of flat-panel displays as LCDs, plasma (PDP), and as LEDs (Buchert et al., 2009). The PGMs used as catalysts in the chemical and petrochemical sectors are mostly close-loop recycled, and the amount dissipated during use is negligible. Platinum used in jewelry accumulates over time, but some is recycled. Recoverable fractions of PGM include automobile catalytic converters and from electrical uses. Figure 4.2 shows platinum's dissipative (regarded as lost), stock, and recycling fractions.

As illustrated in Figure 4.2, almost 40% of platinum is lost in nonrecoverable uses, 18% is added to the stock of end-products, and 23% is recycled. Platinum is lost when it is used in medical applications, in the glass industry, and for other uses such as automotive sensors, the coating of aircraft turbine blades, and spark
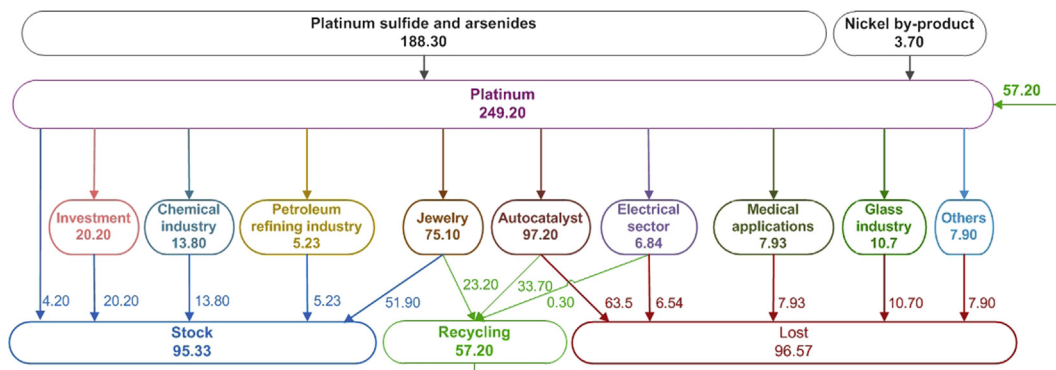

FIGURE 4.2   Substance flow analysis of platinum in 2010 (in metric tonnes).

plugs. It is also lost from the fraction of automobile exhaust converters and electrical equipment not collected and adequately recycled.

In 2010, automobile catalytic converters used 99 t of platinum, 204 t of palladium, and 30 t of rhodium (Butler, 2011). Catalytic converters are part of the exhaust system designed to accelerate the oxidation of carbon monoxide (CO), nitrogen oxides (NO$_x$), and unburnt hydrocarbons. They are composed by a ceramic or metal honeycomb structure of channels coated with so-called "wash-coating" catalysts that are composed of a combination of PGMs and rare earth oxides (Borgwardt, 2001; Lifton, 2007). The best known combinations of PGMs are platinum–rhodium (Pt–Rh), platinum–palladium (Pt–Pd), and a three-way combination of all three metals (Pt–Pd–Rh). The first two combinations accelerate the complete oxidation of carbon monoxide and hydrocarbons. The three-way catalyst also reduces nitrogen oxides to pure nitrogen and oxygen. PGMs are fixed in the wash-coat surface usually by impregnation or by coating with a solution of hexachloroplatinic (IV) acid ($H_2PtCl_6 \cdot 6H_2O$), palladium chloride ($PdCl_2$), and rhodium chloride ($RhCl_3$) salts. As the solvent evaporates, a dry layer of the PGM salts results in the surface of the honeycomb structure (Ravindra et al., 2004).

PGM losses during the wash-coat formation range from about 2–6% as maximum (Patchett and Hunnekes, 2012). Taking into account that current catalytic converters contain an average amount of about 2 g of PGM, about 4–12 mg of PGM are lost during manufacturing (Yentekakis et al., 2007). Based on the data shown in Figure 4.2, we estimate that between 2 and 6 t of platinum were lost during wash-coat formation in 2010. PGMs are also lost during automobile engine operation due to the rapid change of oxidative/reductive conditions, high temperature, and due to mechanical abrasion. The average quantity of PGMs released into the environment is in the range of 65–180 ng/km (Ravindra et al., 2004).

A possible way to estimate the amount of PGM lost during vehicle operations is to consider the current stock of vehicles in service and the average distance traveled by them.

A more accurate estimate of the amount of PGMs potentially recoverable can be compiled by counting deregistered vehicles. A case study in Germany estimated that only 41% of catalytic converters from deregistered vehicles reach dismantler facilities, and about 70% of the PGMs contained in those converters are recovered. The remaining 59% of catalytic converters are not separated from the vehicle and are not recycled. Many (perhaps most) are exported to areas without adequate recycling infrastructure. In some cases, convertors are not removed from car bodies before being shredded, or they are mistakenly sorted into the wrong fractions, from which separation is not feasible (Hagelüken, 2007a). In 2010, there were 33.7 t of platinum, 41.2 t of palladium, and 7.3 t of rhodium recycled from automobile catalytic converters (Lofersky, 2011).

In the electrical sector, PGMs are used for active components such as transistors, ICs, thick-film hybrid circuits and semiconductor memories, and also in passive components, which include multilayer capacitors, thick-film resistors, and conductors. The most important PGM used in electronics is ruthenium in combination with platinum, palladium, and iridium in alloys. Ruthenium is used in small quantities to increase wear resistance for electric contacts, and in microelectronics in computer hard disks, multilayer ceramic capacitors, and in hybridized ICs. At present, neither ruthenium nor iridium is recycled (Lofersky, 2011).

In 2010, only platinum and palladium were recycled from electrical and electronic waste. The amount of platinum recovered represented 5% of the amount consumed, as shown in Figure 4.2. In 2010, there were 113.7 t of palladium recycled from electronic waste, whereas the global sales of palladium for electronics were 43.9 t (Lofersky, 2011). These

figures show that the recycling system and the technology for recovering palladium are functioning. In fact, in 2010, recycled palladium supplied 44% of the world's production. Platinum and palladium were also recycled from jewelry: 23.2 t of platinum and 2.5 t of palladium.

4.4 THE DISTANT FUTURE: GEORGESCU'S LAST LAUGH?

Georgescu-Roegen proclaimed that "matter matters" and asserted that the "entropy law" is the "taproot" of economics (Georgescu-Roegen, 1971). His point was that dissipation of matter (i.e. chemical elements) due to the impossibility of perfect recycling constitutes a "fourth law" of thermodynamics and an unavoidable limit to economic growth. He was wrong about the fourth law and wrong about the technical impossibility of recycling, given an unlimited supply of useful energy (exergy) (Ayres, 1999). This technical error has somewhat discredited his entire thesis. However, the long-term prospects for technologies that utilize geologically scarce "hitchhiker" metals are very poor from an economic perspective.

As noted earlier, the short- to medium-term situation is that most rare metals are currently underexploited in the sense that the potential supply from mining of the important primary ("carrier") metals (iron, aluminum, copper, zinc, nickel, etc.) is larger than the actual output. In some cases, the potential supply is hundreds of times larger than the current consumption; therefore, there is no immediate need for recycling. But in other cases (e.g. cobalt and molybdenum), current output is reasonably close to maximum potential output, given the current demand for the associated carrier metal (e.g. copper). Of course, the potential supply of copper is also limited, although not (it seems) for many decades to come.

With regard to standard industrial metals such as iron and aluminum, the ores or possible ores are plentiful, and most of the uses are not inherently dissipative. There are dissipative uses of iron such as nails and small hardware items, as well as rust from structural beams and iron oxide pigments. There are dissipative uses of aluminum, especially aluminum foil and aluminum bottle caps. Hence iron and aluminum will be mined to some extent even in the very distant future unless those "wasteful" uses are also eliminated. Nickel, cobalt, and molybdenum will be recycled to a high degree because their metallurgical uses, such as in stainless steel or refractory (heat resistant) alloys, are such that collection and separation are not too difficult. Copper, zinc, and lead are very easily recycled. In the case of copper, it is easy to recycle copper roofing, copper tubing for water, and copper from household wiring, motor and generator windings, and so forth. But copper for computer chips, brass cartridges for bullets, and copper chemicals are very difficult or impossible to recycle. In the case of lead, old water pipes, radiation shielding, and lead-acid batteries are easily recycled, but lead-based solder is not, and lead bullets and lead shot for shotguns are quite dissipative. Zinc has few metallic uses except for some kinds of hardware. Zinc coating for iron ("galvanizing") is one of that metal's biggest uses. Recovery of zinc from galvanized scrap iron is possible but not very profitable. Similarly, PGMs are easily recycled from industrial catalysts, or fuel cells, but it is getting very hard to recover PGMs from automobile exhaust systems unless the EOL vehicles are carefully dismantled prior to scrapping operations. However, in the very long run, automotive vehicles with internal combustion engines that burn gasoline or diesel may be largely replaced by electric vehicles.

For the major metals, we may never eliminate the need for some mining activity, but the resource base is large enough that no supply crisis is likely for centuries to come. Recycling will

never be 100% effective, thanks to the Second Law, but fairly high recovery rates from demolition scrap and scrap cars can be foreseen. Also, the value of secondary metals (especially gold and silver) is already keeping some mines open. Similarly, the increasing value of some very scarce metals, such as indium or tellurium, may eventually justify the investment in large-scale recovery and in the recycling of certain electronic items such as touch screens or PV panels.

Unfortunately, new IT products, such as iPhones and iPads, use more and more of the scarce metals in trace amounts. It is important to ensure that this trend toward micro-miniaturization does not prevent us from recovering these metals. In the future, this will require much higher prices—such as those that we now see for gold and platinum. From a systems perspective, this may have to be accomplished by innovative means such as "renting" the scarce materials. The implications of such schemes will require extensive study and analysis.

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