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Abstract

A number of metals that are now important to the electronics industry (and others) will become much more important in the future if current trends in technology continue. It is generally accepted wisdom among economists that scarcity is not a problem for resources, because incipient scarcity sends a price signal that induces suppliers to increase output. Moreover, the history of resource use tends to confirm this hypothesis, in as much as resource prices have generally declined since the industrial revolution, despite enormous increases in demand. However for a certain group of by-product metals, the assumed relationship between prices and output does not hold. Options are limited. We discuss the implications.

Keywords: scarce metals, conductors and semiconductors, metabolism, material flow analysis

1. Introduction

Scientific progress has made possible to discover and make use of more and more elements in the periodic table. A number of metals that were formerly curiosities have now become essential for applications involving new functions. For example the use of integrated circuit technology to new areas, such as “smart” sensors and “smart” grids, the use of phosphors in competition with older types of light for illuminating systems in automobile headlights, streetlights and indoor lighting which is just starting. The list also includes applications of ultra-powerful permanent magnets to small electric motors (e.g. for disk drives and electric cars), small generators for wind turbines and magnetic resonance imaging (MRI) scanners, magnetic cooling, and so on.

The paper then focuses on those scarce metals that are not mined as such, but are now obtained exclusively, or mostly, as by-products of the major industrial metals listed above. This list includes gallium (from bauxite); arsenic, cobalt, molybdenum, rhenium, selenium, tellurium (from copper ore), cadmium, germanium and indium (from zinc); cobalt (from nickel) and rhodium and ruthenium (from platinum and palladium). The so-called ‘rare earths’ are included even though they are not geologically rare, because almost 50% of the world’s production is generated as by-product of iron ores in China. It can be argued that most of the rare earths are also by-products of the three most important ones, namely cerium, lanthanum and neodymium. We then allocate the amount of each critical metal in *new* technological functions. Estimating the amount of critical metals per function helps to characterize the form and composition of metals in waste streams, thus identifying which wastes are potentially more interesting to recover.

2. Criticality

Some of these metals are classed as “critical metals” due to their geological scarcity and supply risk. Concern about the future need for these metals in most developed economies has resulted in a number of reports discussing sources of supply and their criticality. In these reports the list of critical

metals is mostly agreed, although the criteria for defining criticality vary slightly. This is basically because the criticality of metals is judged in all cases from a resource-importing perspective.

The first report about critical metals was published in 2008 by the US National Research Council with the title *Minerals, Critical Minerals, and the U.S. Economy* [1]. It collected most of the discussions of the Committee on Earth Resources of the National Research Council (NRC) on the topic of non-fuel minerals, their availability and use in domestic applications, and their national importance in a global mineral market. The book includes the assessment of 11 potentially critical minerals (see table 1).

Also in 2008, the United Nations Environment Program (UNEP) commissioned Öko-Institut in Germany to identify critical metals for future sustainable (“green”) technologies and their recycling potential [2]. The technologies selected were electronic and electrical equipment (EEE), photovoltaic technologies, batteries and catalysts. The metals considered to be critical were tantalum, indium and ruthenium (one of the metals included in the platinum group) for EEE; gallium, tellurium and germanium for photovoltaic technologies; cobalt and lithium for batteries; platinum group metals (PGM) for catalysts and rare earth elements (REE) in general. The supply-side risks were assessed based on their global availability, geographical spread and prices. Overall risks were prioritized according to the demand growth, supply risks and recycling restrictions. The report established a list of critical metals in the short-term (within next 5 years), mid-term (until 2020) and long-term (until 2050). For short-term, the metals identified were tellurium, indium and gallium; for mid-term, rare earths, lithium, tantalum and platinum group. For the long-term, only germanium and cobalt might become critical. In contrast to NAS report, this study used a global perspective instead of a national point of view, thus the results were not specific to one country or region.

In June 2010, the European Commission (EEC) published its first report about critical raw materials. This was based on extensive background research provided by Fraunhofer Institute and Bio Intelligence [3]. The report includes an annex with detailed information about basic supply and demand statistics, economic importance, resource efficiency (recycling and substitution) and specific issues as trade and environmental issues for 41 raw materials. The types of risks considered included

the political-economic stability of the producing countries, the level of concentration of production, the potential for substitution, the recycling rate, and possible restrictions to protect the environment which could endanger the supply of raw materials to the EU. The report identifies 14 critical materials out of the 41 studied. The 14 critical raw materials identified have a high share of the worldwide production from China, Russia, the Democratic Republic of Congo and Brazil, together with low substitutability and low recycling rates.

In 2010, the OECD also announced the publication of a series of case studies and the critical metals used for them in order to assess future technologies. The first study on mobile phones provides a coherent methodological framework that can be used to perform other sustainable materials management studies [4]. The cell phone case study is organized in terms of the stages of its life cycle. Between the 14 metals identified only four were deemed to be critical: antimony, beryllium, palladium and platinum. Cobalt and tantalum were not included because batteries were not part in the assessment. Even though the report identifies critical metals it fails to deal explicitly with the potential for substitution.

Erdmann and Graedel have recently published a paper discussing extensively the different methodologies used for identifying critical metals [5]. Despite the different treatment of variables such as substitutability, time horizon and the aggregation level, the classification of the majority of materials as critical is consistent.

Table 1 below shows the list of critical metals published in each report. There are some metals included in all reports and some others in one or two reports. Three reports identify gallium, indium and tantalum, and two groups of metals, namely the platinum group metals (PGMs) and rare earth elements (REE). The NAS and UNEP reports also include lithium as critical. The Öko-Institute and EU reports include cobalt and germanium. The NAS and EU reports include neodymium as well as the REE group as a whole. In the more specific case study of the mobile phone, critical metals are identified as PGMs, antimony and beryllium. In general, we can say that there is a list of 7 to 9 metals and 2 groups of metals that are critical by some criteria.

NAS (2008)	Öko-Institut (UNEP) (2009)	EU (2010)	OECD (2010)
	Gallium (Ga) Indium (In) Platinum group (PGM) Rare earth (REE) Tantalum (Ta)		Platinum group (PGM)
	Lithium (Li)		
	Cobalt (Co) Germanium (Ge)		
		Antimony (Sb) Beryllium (Be)	
Niobium (Ni)		Niobium (Ni)	
Copper (Cu) Manganese (Mn) Titanium (Ti) Vanadium (Va)	Tellurium (Te)	Fluorspar (CaF ₂)* Graphite (C)* Magnesium (Mg*) Tungsten (W)	
9 metals 2 group of metals	7 metals 2 group of metals	9 metals 2 group of metals	2 metals 1 group of metals

* Not considered metals. PGM is used to refer to a group of six metals: platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os). REE consist of 15 elements which can be divided in heavy and light elements. Heavy rare earth elements (HREE) are Yttrium (Y), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). Light rare earth elements (LREE) include lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), and scandium (Sc).

Table 1. Critical metals identified in different reports.

REEs are of serious concern in all the published reports. As the interest in REEs keeps growing, the Öko-Institut published a second report for UNEP specifically focused on rare earths [6]. The report includes a concise review about reserves, mining data and processing with special attention to China. It suggests that shortages are likely for dysprosium, europium, lanthanum, neodymium, praseodymium, terbium and yttrium [7]. Such shortages will affect applications such as permanent magnets (Tb, Dy, Pr and Nd), for so-called nickel metal hydride batteries (Nd and La), efficient lighting devices (Eu and Tb), automotive catalysts (PGMs plus La) and future new technologies such as magnetic cooling and high temperature superconductors (Y). The situation can become especially critical for applications like energy efficient lighting and automotive catalysts.

As a way to overcome expected shortages, the report proposes a strategy for the development of a *green* rare earth economy. That strategy would be applicable to all the critical metals, of course. It would concentrate on enhanced recovery and recycling and develop green technologies that require less of the geologically scarce metals. Recycling of scarce metals is presently almost non-existent, except for gallium, germanium, platinum and palladium, mainly due to their dissipative applications

and low concentrations in electronic wastes (scarce metals generally end up in the slag of smelter plants or landfills). However there is one other option which we discuss in this paper, namely to increase the efficiency of by-product recovery of rare “hitch-hiker” metals from the ores in which they are found.

3. Prices and output

The historical approach to overcoming expected 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” (signaled by rising prices) to be within their domain, but they reject “geological scarcity” as a myth [8]. In fact, empirical studies have demonstrated quite convincingly that resource prices, in real terms, have declined consistently since the industrial revolution [9, 10].

Recent evidence pointing to “peak oil” suggests that the price of petroleum may be the exception to this rule [11, 12]. However the underlying reason why petroleum output now lags behind demand is that the economic theory depends upon the 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 vs concentration) is smooth, with a single peak, something like a log-normal function. 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, while the bulk of the atoms are distributed randomly in ordinary rock with concentration even less than the average. This situation seems to apply to copper, gold, lead and zinc, in particular [13, 14]. Although native copper is no longer found in significant quantities – having been used up long ago – copper was once mined in pure native form as recently as the early 19th century (in northern Michigan, among other

places). Gold was first found in nuggets of the pure metal, which is the only reason it found uses in prehistoric times.

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 concentrations. Instead, they are distributed essentially as contaminants, or trace elements, in the concentrations of minerals of other “attractor” metals, to which they are chemically similar, especially – as it happens – iron, though other rare metals are usually associated with 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. Graedel has called the attractor element and its entourage “parent” and “daughters”, which incorrectly implies that the attractor actually created the others in some abiotic process [15]. Hereafter, to avoid inappropriate analogies, we call the chemically similar but scarcer metals “hitch-hikers”.

To increase the output of one of the “hitch-hiker” metals it is necessary either to increase the output of the “attractor” metal or to increase the rate of recovery from the attractor’s ore. The latter approach is clearly more feasible than finding new sources (which may not exist), but 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. This situation is particularly critical 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 hitch-hikers [16]. However, the immediate consequence is that there is little or no correlation between prices and production output. More to the point, higher prices do not automatically call forth greater output as conventional theory suggests. This situation is shown in Figure 1 for gallium, germanium, indium and tellurium [17].

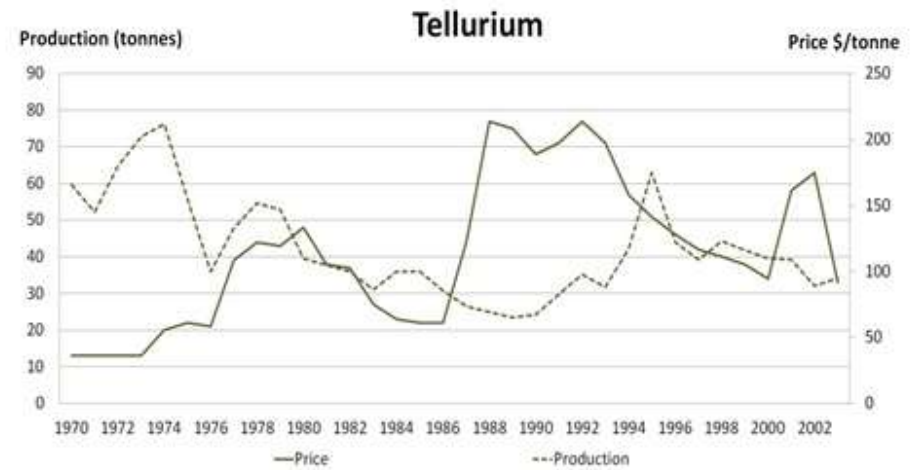
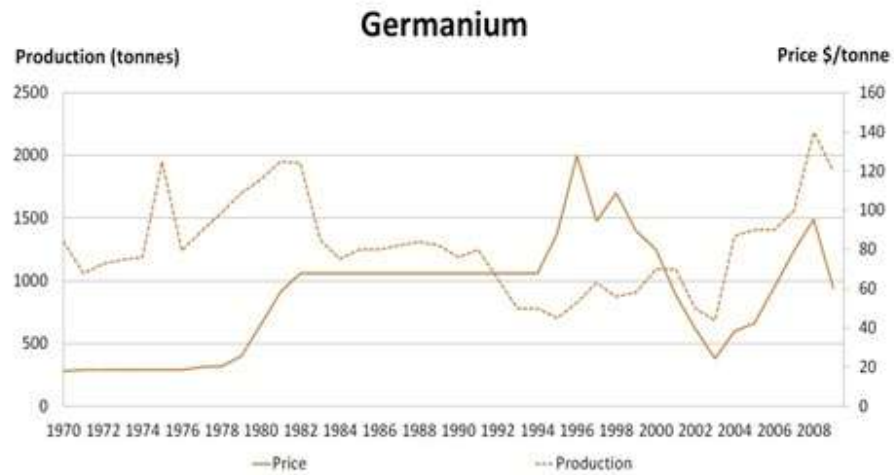
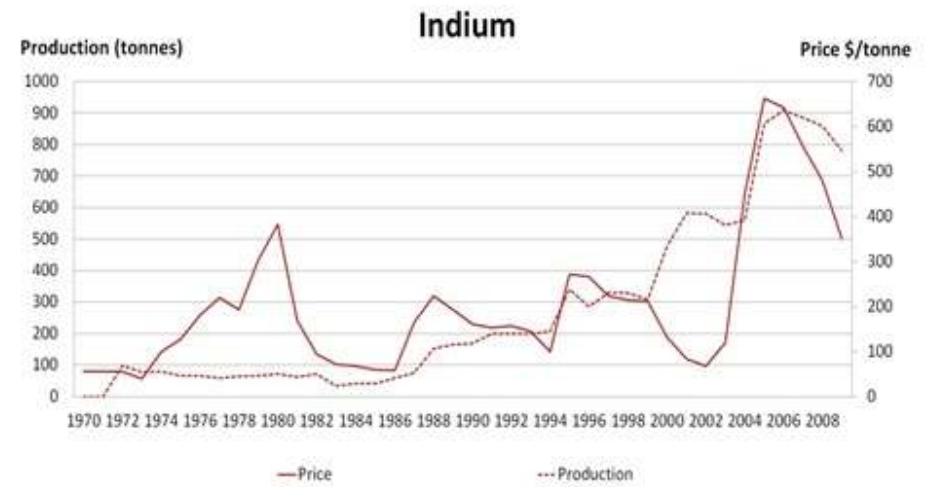
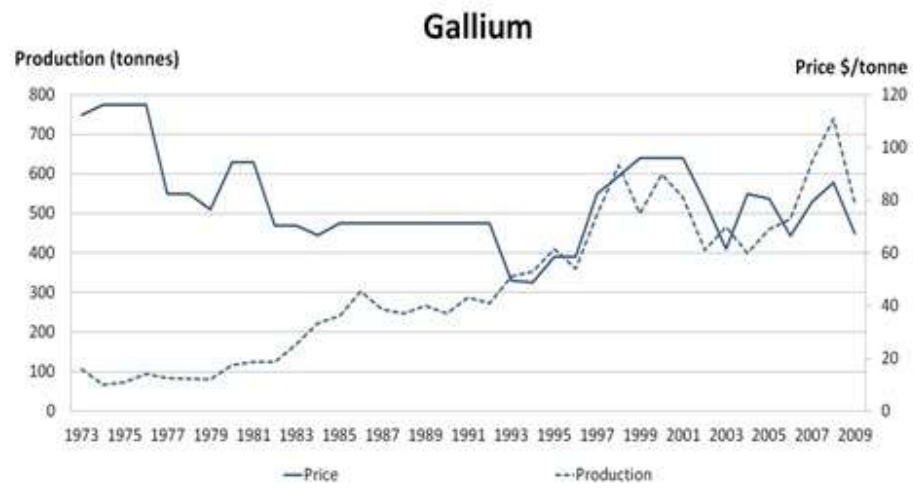


Figure 1. Prices and production of the by-product metals: indium, gallium, germanium and tellurium.

The strategy of increasing output by increasing the efficiency of recovery from existing mines is applicable to all metals, but especially to metals that are produced from ores mined for their content of the “attractor” metal. The major industrial metals in global commerce are classed as “rock-forming metals” by geologists. They are usually combined with oxygen, directly or indirectly (e.g. as carbonates or silicates). This group includes aluminum, iron, magnesium, manganese, phosphorus, silicon, tin and titanium. The alkali metals, sodium, potassium, calcium, lithium, boron and magnesium are mostly found as chlorides deposited in ancient sea-beds or dissolved in the existing oceans.

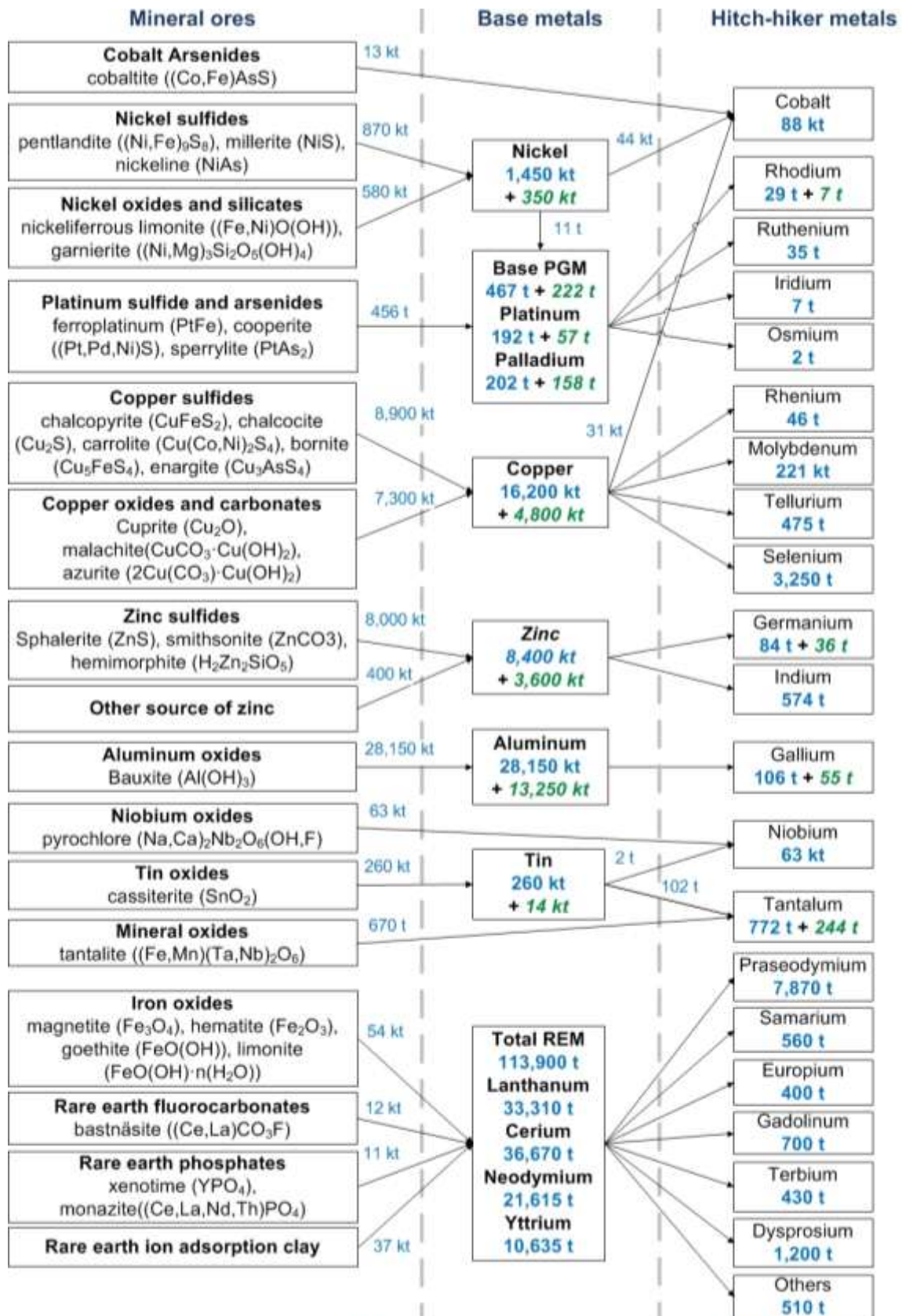
There is another group of important ore-forming metals, the chalcophiles, mostly found in combination with sulfur, viz. antimony, chromium, copper, lead, mercury, molybdenum, nickel, silver, tin, tungsten, vanadium and zinc. These are mostly mined from sulfide ores or from laterites that have been geologically metamorphosed (oxidized) by exposure to water. Some ores, including the best quality iron ore, and phosphate rock, are attributable to biological processes in the ancient oceans. Several important chalcophile metals are produced largely, if not entirely, as by-products of the mining of copper, lead, nickel or zinc. This is true of antimony, arsenic, bismuth, cadmium, cobalt, gallium, germanium, hafnium, indium, molybdenum, niobium, rhenium, selenium, silver, tellurium, thallium and uranium. Moreover, platinum group metals (platinum, palladium, iridium, osmium, rhodium, rubidium), known as PGMs are mainly found together in certain copper-nickel ores (the Merensky Reef in South Africa and Norilsk in Russia). There are a few other natural groupings. Niobium (formerly columbium) and tantalum are generally found together, or with zirconium and hafnium in a rare but mineable complex ore called pyrochlore or “coltan”, which is a combination of columbite and tantalite. Rubidium is associated with potassium-lithium ores. Uranium is often found with vanadium.

All of the 17 rare earths elements (REE) are usually found together, mostly in bastnäsite ores ($[\text{La,Nd}](\text{CO}_3)\text{F}$) with iron, in Bayan Obo (Inner Mongolia) or monazite ore ($[\text{Ce,La,Nd}](\text{PO}_4)$) with radioactive thorium (Mountain View, California, Kerala, India) [18]. Most of the present REE production comes from bastnäsite because monazite ores contain traces of thorium and consequently

refining generates radio-active waste. But any given one of the minor rare earths can only be obtained by separating it from the others, which is difficult due to their chemical similarity [19].

4. Major industrial metals and their co-products

In this section, we show the “attractor” metals that are sources of the scarce “hitch-hikers” noted above, many of them categorized as critical. We quantify the flows of hitch-hiker metals from mineral ores and base metals. Material Flow Analyses (MFA) has been focused to date on a few base metals that dominate the metallurgical market in mass terms: iron and steel, aluminum, copper, zinc, lead and nickel [20, 21 “Statistical Summary”]. In this section, we include the amount of hitch hikers produced from base metals and other mineral sources, most of the time missing in MFA studies. There are some metals which are partially obtained from mineral ores as for example cobalt, niobium and tantalum. Cobalt is presently obtained 85% as by-product of nickel and copper, and only 15% mined for itself from cobalt arsenides [20]. Niobium is mainly produced from niobium oxides (pyrochlore) plus a marginal amount (less than 1%) as by-product of tin. Tantalum is 87% produced from mineral oxides (tantalite) and 13% as by-product of tin. The rest of mineral included as hitch-hickers are all currently produced as by-product from base metals. Rhodium, ruthenium, iridium and osmium are by-products of platinum and palladium obtained from platinum sulfides and arsenides. Rhenium, molybdenum, tellurium and selenium are all by-products of copper. Germanium and indium are by-products of zinc, and gallium of aluminum. Praseodymium, samarium, europium, gadolinium, terbium and dysprosium are by-produced of lanthanum, cerium, neodymium and yttrium, which are partially obtained from iron ores. Overall, almost all major industrial base metals have “hitch-hiker” metals associated with them. Apart from rare earth elements, copper minerals have the most diversity of by-product metals. Copper ores, worldwide, are associated with 8 by-product metals (plus some PGMs) of which 4 are considered critical. At present only 3 critical metals of them are being actively co-produced. For additional description on base metals and their by-products go to appendix 1. Figure 2 shows the mineral ores, base metals and hitch-hiker metals produced in 2010.



Mine production amounts are represented in blue whereas recycling production is in italics and green.
Units: t are tonnes and kt are 1,000 tonnes.

Figure 2. Worldwide production of mineral ores, base and hitch-hiker metals in 2010.

5. Output of hitch-hikers

To increase the production of by-product metals, which are physically scarce, there are two options: (1) to recover greater amounts from other (“attractor”) mineral ores by increasing the yield and efficiency of extraction and production processes, or (2) by increased recycling. A first estimate on the potential output of by-products can be based on their theoretical content in the mineral ore. For a more accurate estimate, the extraction and production processes for each by-product metal should be further assessed and evaluated. A detailed study to identify the end-products where by-product metals are embodied is needed in order to evaluate their potential recovery (this is discussed in sections 6 and 7). In this section, we focus on the potential output of by-product metals as compared them with current production. This comparison provides a measure of how efficiently (in mass terms) by-product metals are now being recovered.

Iron by-product metals: rare earths. In 2010, about 48% of rare earth oxides were produced as by-product 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 [22]. In 2010, 54,000 tonnes of 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 3.5 million tonnes of rare earth oxides and 89,100 tonnes of niobium [23].

Aluminum by-product metals: gallium. Bauxite contains an average of 42.5% of aluminum and 0.0065% of gallium [24]. In 2010, world mine production of aluminum was 28.15 million tones, yielding 106 tonnes of gallium. Based on the average content of gallium in bauxite however, theoretically about 4,000 tonnes of gallium could have been recovered already. Since there is a lot of bauxite in the world, future gallium production may be quite significant.

Copper by-product metals: cobalt, rhenium, molybdenum, tellurium and selenium. Cobalt is a by-product of copper and nickel ores. In 2010, the total global production of cobalt was 88,000 tonnes, of which 35% was produced from copper and 50% from nickel [25 “cobalt”]. As by-product of copper, cobalt is contained in sedimentary copper deposits which are mainly composed by copper

oxides and carbonates. In 2010, the production of 7.3 million tonnes of copper from these deposits supplied 31,000 tonnes of cobalt. Theoretically, for each tonne of copper mined 56 kg of cobalt are available which implies a potential production of 409,000 tonnes [26].

Rhenium and molybdenum are also recovered as by-products of the roasting of copper-porphyry ores (copper sulfides). These ores contain an average of 0.3% to 1.6% of copper, depending on the mine, plus 0.01% to 0.05% of molybdenum and a minimum of 0.001% of rhenium [27]. Since porphyry ores account for 55% of world copper production, we can estimate an average potential output of 281,000 tonnes of molybdenum and 9,370 tonnes of rhenium. Actual production for that year was 221,000 tonnes of molybdenum and 46 tonnes of rhenium [25], so it appears molybdenum is being extracted rather efficiently, but rhenium is not.

Tellurium and selenium are also co-products of copper refining from various copper ores. For each tonne of copper refined there are 65 grams of tellurium [28]. In 2010, with total world copper production of 16.2 million tonnes, it appears that 1,050 tonnes of tellurium were potentially available for recovery but not recovered. Selenium is produced entirely as a by-product of copper refining although coal is by far the most abundant source. For each tonne of copper produced, there is 180-340 grams of selenium content [28]. From this we estimate that 2,920 to 5,510 tonnes of selenium could have been recovered in 2010. Production data shows that world actual production of selenium was 3,250 tonnes. This implies that recovery efficiency is quite good.

Zinc by-products: germanium and indium. Currently germanium and indium are co-produced with zinc from sphalerite (ZnS), a zinc sulfide that contains up to 0.05% germanium and indium along with 67% zinc [28]. If we assume that almost all zinc comes from sphalerite, 615 tonnes of indium and 5,970 tonnes of germanium could have been recovered in theory, as compared to actual output of 574 and 120 tonnes respectively. In 2010, there were 8.4 million tonnes of zinc produced along with 84 tonnes of germanium and 574 tonnes of indium. Although not exploited at present, sphalerite is also an important resource of gallium. Sphalerites contain about 65% of zinc and 0.04% of gallium [28]. In 2010, the zinc production was 8.4 million tonnes, thus almost 490 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.

Nickel by-products: cobalt and PGMs. The vast majority of cobalt resources are in nickel-bearing laterite deposits (nickel oxides and silicates) and sedimentary copper deposits of Congo and Zambia. Laterite deposits contain an average of 1.3% of nickel and 0.1% of cobalt and supply about 40% of nickel production [29]. In 2010, the production of 580,000 tonnes of nickel from laterite could have yielded 58,000 tonnes of cobalt. Overall, the potential production of cobalt as by-product of nickel and cobalt is estimated in 467,000 tonnes at current rates of copper and zinc output.

In 2010, the total production of PGMs was almost 690 tonnes out of which 456 tonnes were mined as such, 11 tonnes were a by-product of nickel and 222 tonnes were recycled [30]. The mine production of platinum and palladium was 192 and 202 tonnes respectively. The total production of the PGM by-products metals was 73 tonnes: 29 tonnes of rhodium, 35 tonnes of ruthenium, 7 tonnes of iridium and 2 tonnes of osmium [31]. PGM produced as by-products of nickel were mainly in Botswana, Canada and Australia [25]. Russia might also produce some amount of PGM as a by-product; however national figures do not specify it. The content of PGM in nickel deposits varies depending on the type of the mineral deposit. In South Africa, the average platinum grade is around 27g/tonne whereas in Russia, the average PGM content is 15 g/tonne in nickel sulfide ore deposits [32]. Taking as an average 20 g/tonne and the total world nickel production from sulfide ore for 2010 of 870,000 tonnes, it seems that 17 tonnes of PGM were potentially available for recovery [33]. PGM can be additionally recovered from pyrrhotite, an iron sulfide mineral associated with nickel sulfide ores. The ore mineral contains up to 30 and over 5 g/t of rhodium and ruthenium and iridium, respectively [34].

Recycling is a significant source of PGMs, unlike the other metals, as it provides 222 tonnes mainly from auto-catalyst (37%), electronics (51%) and jewelry (12%) [25 “Platinum group metals”]. The highest amount of PGM recycled is palladium (158 tonnes) followed by platinum (57 tonnes) and rhodium (7 tonnes). The major amount of palladium, 114 tonnes, is recovered from electronic products. Platinum and rhodium are mostly recycled from three way catalyst in internal combustion

vehicles. There is no published information about the recycling of ruthenium, iridium and osmium. These metals could especially recycle from electronic devices where they are used in small quantities for electric contact, printed resistors and in alloys for spark plug contacts in airplane and automobile engines [35].

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 (tin) ore contains about 0.03% of niobium and 0.01% of tantalum, which leads to a potential production of 780 and 260 tonnes respectively [36]. In 2010, their production from tin was 2 tonnes and 106 tonnes, respectively.

Table 2 shows the resources for both base and hitch-hikers metals, and their production in 2010. The last column of the table gives the theoretical potential production of these metals based on their content in mineral ores. As illustrated, only for few by-product metals as molybdenum, selenium, indium and cobalt, the current mine production is near its potential production. For the rest of metals listed in the table, current production amounts are far from those theoretical amounts which mean that there is a large quantity of valuable metals in wastes and emissions.

Base metal	Reserves (10 ⁶ tonnes)	Production (10 ⁶ tonnes)	Hitch-hiker metal	Reserves (10 ³ tonnes)	Current mine production (tonnes)	Potential mine production (tonnes)	Material efficiency (%)
Iron ore	87,000	24.00	Rare earth oxides	110,000	54,000	3,500,000	0
			Niobium	2.9	63,000	89,100	0
Aluminum	28,000	28.15	Gallium	n.a.	106	3,970	3
Copper	630	16.20	Cobalt	7,300	31,000	409,000	8
			Rhenium	2.5	46	9,370	0
			Molybdenum	9,800	221,000	281,000	79
			Tellurium	22	475	1,050	45
			Selenium	88	3,250	2,950- 5,000	65
Zinc	250	8.40	Germanium	0.45	84	5,970	1
			Indium	n.a.	574	615	93
			Gallium	n.a.	-	492	-
Nickel	76	1.45	Cobalt	7,300	44,000	58,000	76
			PGMs	66	11	17	65
Tin	5.2	0.26	Niobium	2.9	2	780	0
			Tantalum	110	102	260	39

Table 2. Resources, current mine and potential production of base and hitch-hiker metals.

Comparing the potential production values with the current production can serve as a rough estimate of the efficiency of hitch-hikers production. For a more accurate estimation, we need to additionally consider that all metals have to be mined, beneficiated, smelted, refined, alloyed in some cases, shaped and formed. Each step along this chain of processes involves waste and waste streams, consisting partly of process losses due to incomplete recovery or separation, and partly due to cleaning or surface preparation involving acids or alkalis, e.g. to prevent corrosion or prepare a surface for plating. These reactants combine with the metal and the compounds become part of a waste stream. Plating processes (especially chrome plating) also generate wastes that can be harmful or toxic. The assessment of waste flows along all the stages from extraction to end-products helps in estimating potential recovery and recycling, as well as environmental impacts. To do so, a more detail assessment of the extraction and refining processes is in order.

6. Functions of hitch-hiker metals.

There are a number of functions that are especially relevant to future demand for critical metals. For the present study we have identified six major functions: dopants for semiconductors, catalysts, electrical storage batteries, alloying elements, additives to glass and abrasives.

6.1. Dopants for semiconductors.

Dopants are trace element that added in very low concentration in compounds to modify their electrical or optical properties. Dopants are used in semiconductors for various reasons, to improve properties such as electrical conductivity, absorption or emissions in various wavelengths, etc. They are used in printed circuit boards, phosphors, photovoltaic cells, detectors and optical fibers.

6.1.1. Printed circuit board. A printed circuit board (PCB) is an electronic module where electronic elements (such as microprocessors (chips), resistors, capacitors, sensors and magnets) are assembled to perform a specific function in electronic devices (e.g. detector, amplifier, receiver, oscillator, etc.).

There are several by-product metals used in printed circuit boards: indium, gallium and germanium.

Indium is used in electronics for fixing semiconductors chips to a base, for assembling semiconductors devices and hybrid integrated circuits. In 2010, there were 6 tonnes used in minor alloys. Gallium is another critical metal used in PCBs. In 2010, about 74% of gallium was used in integrated circuits [25 “Gallium”]. The most important gallium compound is gallium arsenide (GaAs), which can convert electrical into optical signals at high speed with low power consumption, and better resistance to radiation compared to other compounds [27]. GaAs is also used in PCBs for high performance computers, smart phones and telecommunication via high speed wireless. In 2010, 106 tonnes were used in PCBs. Germanium is used in the form of silicon-germanium (SiGe) in transistors of PCBs to amplify and switch electronic signals and power. In 2010, about 9 tonnes of Germanium was used in electrical and electronic applications.

6.1.2. Phosphors. Phosphors are materials that are phosphorescent (emission of light) or fluorescent (emission of a light previously absorbed). Phosphorescent materials are known for their use in radar screens and glow-in-the-dark toys, whereas fluorescent materials are used in cathode ray tubes (CRT)

and plasma video display screens, sensors, and light-emitting diodes (LEDs). Phosphors consist of a host material with an added activator or dopant. The most common phosphors are copper-activated or silver-activated zinc sulfide, which are not by-product materials. Strontium and calcium sulfides are also used in some applications, but they are also not critical. However, strontium aluminate activated by europium and dysprosium is a newer phosphor that is 10X brighter, 10X longer lasting (and more expensive) than zinc sulfide. The composition of phosphors - the selection of the host and activator - varies depending on the color required for the end product. For red, the RE oxides used includes yttrium, europium and gadolinium. For green, the hosts used are lanthanum, cerium and yttrium while terbium and gadolinium are used as activators. For blue, it is mainly used europium oxide. The combination of red, green and blue gives white color. Phosphors are largely used for lighting (84%), followed by LCDs (12%) and plasma displays (4%) [7]. In 2010, 930 tonnes of rare earth hitch-hikers were used to produce phosphors [6].

Indium and gallium are used in virtually all light-emitting diodes (LEDs) and laser diodes. The indium-gallium pair is combined with a variety of other elements (aluminum, antimony, arsenic, nitrogen or phosphorus to create different color LEDs). Indium is also a substrate coating for some applications. Indium-based LEDs are used predominantly to optically transmit data and, to a lesser extent, in LED displays and computer monitors where image stability is of great importance. Thin films of Indium-tin oxide (InSnO) is the primary material for touch panels, liquid crystal displays (LCDs) and electroluminescent lamps [27]. In 2010, about 436 tonnes of indium was used in phosphors: 425 tonnes for flat plasma display (FPD) and 11 tonnes for LEDs.

Gallium nitride (GaN) and gallium arsenide (GaAs) are used in optoelectronic devices as laser diodes, LEDs and photo-detectors [25 “Gallium”]. In 2010, about 29 tonnes of gallium was used in phosphors. Germanium combined with magnesium as fluoro-germanates ($Mg_{28}Ge_{10}O_{48}$ and $Mg_{56}Ge_{15}O_{66}F_{20}$) are used in lamps as a constituent of fluorescence coating [27]. In 2010, about 9 tonnes of germanium were used in EE applications.

6.1.3. Photovoltaic cells. Photovoltaic cells are solid state device that convert sunlight directly into electricity. The materials used in photovoltaic (PV) cells are carefully selected based on their

absorption capacity of the solar spectrum, thus to generate as much electricity as possible. There are two major types of cells: crystalline and thin film. The world solar energy market today is 90% dominated by crystalline silicon cells. However, thin film cells are gaining market share and may eventually dominate, because they have more potential for future cost reduction [37]. There are three thin-film technologies, all using critical metals. They are cadmium-telluride (CdTe), copper indium gallium selenide (CIGS) and triple-junction cells made of gallium arsenide (GaAs), germanium and indium gallium phosphide (GaInP₂). Triple-junction cells are the most efficient solar cells to date [38]. In 2010, there were 3 tonnes of gallium, 57 tonnes of indium, 325 tonnes of selenium and 124 tonnes of tellurium used in thin film solar cells.

6.1.4. Detectors. Detectors are devices that can detect a change in temperature, radiation, etc. There are two critical metals used in detectors: indium and tellurium. Indium is mainly employed for temperature detection. It is used as alloys with bismuth in combination with lead, cadmium and tin, to hold alarms, water valves and door opening mechanisms where other methods of measurement are impracticable [27]. Its melting indicates that the temperature settled is attained and thus a system/action comes into operation. In 2010, 6 tonnes of indium were used.

Tellurium is an additive to selenium in photoreceptors. It increases the sensitivity and broadens the spectral response of photoreceptors. However the amount of tellurium used for detectors is unknown.

6.1.5. Optical fibers. Optical fibers are flexible, thin and transparent fibers made of pure silica that allows the transmission of high volume data over long distances. They have the advantage of low loss and immunity to electromagnetic interference as compared to metal wires. Optical fibers consist of a transparent core enclosed by one or several layers of materials with a low index of refraction, usually called preform. The preform is commonly made by chemical vapor deposition (CVP). The chloride gases most widely used are silicon and germanium tetrachlorides are injected together with oxygen. The CVP process involves heating with hydrogen together with different metal chlorides to 1,600°C produce oxide particles. After the deposition, the molten preforms are drawn (like wire) to form the long and thin fibers. Apart communication uses, they are also used for special purpose illumination (in

places where ordinary light cannot penetrate), sensors and fiber lasers. In 2010, about 36 tonnes of germanium was used in infrared optics, and 30 tonnes was used for high quality lenses and window material for infrared applications [3]. In 2010, 66 tonnes of germanium was used. Glass fibers for long-distance transmission are doped with erbium, which acts as a laser amplifier (dopant amounts are unpublished).

6.2. Catalysts.

Catalysts are substances that slow (negative catalyst) or speed up (positive catalyst) the rate of chemical reactions. They are not consumed and can be reused over and over subsequent reactions. Negative catalysts, also regarded as inhibitors, act by slowing the reaction rates. They are important in medicine in treating mental illnesses, high blood pressure, cancer and a myriad of other health problems. Positive catalysts help lower the activation energy making the reaction to happen in shorter time. Positive catalysts are widely used in manufacturing and industry. There are three major manufacturing sectors using critical metals as catalyst: automobile, petroleum and industrial chemicals.

6.2.1. Automobile. Catalysts are used in catalytic converters of automobiles as part of the exhaust system to accelerate the oxidation of carbon monoxide, nitrogen oxides and un-burnt hydrocarbons. An automobile catalytic converter is composed of a ceramic or metal honeycomb structure of channels coated with so-called “wash-coating” catalysts (a combination of PGMs) and rare earth oxides [39, 40]. 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 reduces nitrogen oxides to pure nitrogen and oxygen. Rare earth oxides are added to the wash-coating to improve the thermostability of the alumina substrate and ensure the activation of catalyst at high temperatures [18, 41]. Since 1981, catalytic converters have been included as standard equipment in most cars, and today, over 95% of new cars sold worldwide are fitted with them.

A catalytic converter contains an average amount of about 2g of Pt-Rh or Pt-Pd [42]. In 2003, each auto catalytic converter contained about 285 g of REO [43]. However, the amounts needed per car

have decreased dramatically. In 2010, the production of 70.5 million cars required a total of 6,810 tonnes of RE metals, including 135 tonnes of praseodymium. Based on these numbers, a new vehicle only requires about 98g of RE metals [44]. In 2010, auto catalysts used 30 tonnes of rhodium in automotive convertors.

6.2.2. Petroleum refining. In petroleum refining, catalysts are used during fluid catalytic cracking (FCC) to improve the yield of light hydrocarbons. They are also used in catalytic reforming of the heavy, high boiling fraction that is left over from the distillation of crude oil at atmospheric pressure. FCC is the process by which long complex organic molecules and heavy hydrocarbons are broken down into simpler and lighter molecules usable as gasoline and liquefied petroleum gas (LPG). The most widely used catalysts in FCC are the so-called zeolites, which are synthetic aluminum silicate (silica-alumina) structures with a tremendous surface to volume ratio [45]. In addition to PGMs, these zeolites contain rare earth elements, lanthanum and cerium, to improve catalytic stability at high temperature and to increase catalyst activity and gasoline selectivity [27, 46]. Each liter of hydrocarbons feedstock into the FCC process requires about 4.66 kg of catalyst. Commercial catalysts are composed of 85% amorphous silica-alumina cracking catalyst and 15% zeolites [47] [48].

The content of rare earths in the catalysts can vary from less than 1% to as much as 3% [49] [50, 51]. In 2008, the feedstock treated by the FCC process was 1,668 million liters [52]. Assuming that the input of RE metals for FCC was 16,110 tonnes, each liter of feedstock processed requires an average of 9.7 g of RE (much more than the 0.2% REO content estimated by another author) [53]. The only two rare earth metals used for FCC are cerium (1,610 tonnes) and lanthanum (14,500 tonnes).

Platinum and palladium supported on aluminum silicates (zeolites) are also used in hydrotreating processes. The most important reactions using PGMs are dehydrogenation, isomerization and dealkylation. Rhenium in a rhenium-platinum alloy is used for catalytic reforming. Rhenium acts as a promoter for the platinum catalyst [27]. About 30% of the catalysts used in FCC contain rhenium [54]. In 2010, just 9.24 tonnes of rhenium were used.

6.2.3. Industrial chemicals. Catalysts consisting of critical metals are mainly used in the production of plastics, especially polyethylene terephthalate, fibers and nitrogen-based compounds. Cobalt and

germanium are used in the production of polyethylene terephthalate and synthetic textile fibers. Cobalt is also used in steam reforming for hydrogen production, and in the Fisher-Tropsch process for the hydrogenation of carbon monoxide into liquid fuels [55]. Cobalt and molybdenum are also used for the hydrodesulfurization of petroleum [56]. Germanium catalysts are specifically used when the final product must be a colorless fiber or plastic as in photographic films [27]. In 2010, 8,000 tonnes of cobalt and 30 tonnes of germanium were used for these processes.

Tellurium employed for acrylonitrile ammoxidation by the Nitto process and the production of tetramethylene glycol synthesis by the Mitsubishi process. It is also used as a catalyst in rubber processing and for the synthetic fiber production [3]. In 2010, 100 tonnes of tellurium was used in these processes.

Platinum group metals are used in the production of some ammonia-based compounds, notably nitric acid and hydrogen cyanide [57, 58]. The production of nitric acid uses platinum-rhodium gauzes for the oxidation of ammonia to nitric acid. The production of hydrogen cyanide uses platinum-rhodium or platinum-iridium as a catalyst for the oxidation of ammonia and methane. Platinum oxide ($\text{PtO}\cdot 2\text{H}_2\text{O}$) is used for the hydrogenation of alkenes and carbonyl groups in the pharmaceutical industry. Palladium chloride is important for large scale oxidation of ethylene to acetaldehyde. Rhodium is used for oxo synthesis of aldehydes from alkenes. Rhodium iodide is used as catalyst precursor in the carbonylation of methanol to produce acetic acid. Ruthenium and osmium oxide are used for hydroxylation, oxidation and epoxidation. In 2010, 3 tonnes of rhodium, 3 tonnes of ruthenium and 0.4 tonnes of iridium were used for these purposes. The amount of osmium oxide used has not been disclosed (but it must have been extremely small).

Molybdenum-based catalysts have a number of important applications in plastics industries. It is used in the selective oxidation of propene, ammonia to acrylonitrile, acetonitrile and other chemicals which are raw materials for the plastics and fiber industries [27]. In 2010, 11,050 tonnes of molybdenum was used.

REEs are also used for the production of other industrial chemicals, although there are no quantities published. For instance, cerium is used as catalyst for ammonia synthesis, hydrogenation,

dehydrogenation, polymerization, isomerization and oxidation. It is also added in the production of styrene from methylbenzene [27]. Rare earth salts have higher polymerization temperatures, compared to transition elements, reducing the cooling stage of the polymer, and replacing toxic aromatic solvents by aliphatics.

6.3. Electrical storage

Electricity, unlike other energy carriers, can only be used as it is being generated or converted immediately into another form of energy such as thermal, kinetic or chemical. On the macro-scale, storage of electrical energy makes it possible to balance intermittent supply and demand. This represents a possible approach to compensating for the intermittency of solar and wind energy output. The major methods to store electrical energy are batteries (electrochemical) and capacitors (electric charge). In the distant future electrical energy may be stored in superconducting magnets.

6.3.1. Storage batteries. Batteries can be divided into two types: primary batteries, which are meant to be used once, and then discarded, and secondary batteries which can be recharged and used many times. Critical metals are used in the manufacturing of two types of secondary batteries, namely nickel metal hydride (NiMH) and lithium ion (Li-ion) batteries. NiMH batteries contain nickel and cobalt, but also lanthanum which is generally supplied in the form of mischmetal (a mix of lanthanum, cerium, neodymium and praseodymium) in the anode. Li-ion batteries contain both cobalt and lithium. In 2010, the world cobalt production was about 75,900 tonnes. Rechargeable batteries consumed about 20,000 tonnes of cobalt, the highest single use [3, 25 “Cobalt”]. The amount of cobalt for NiMH and Li-ion batteries is estimated in 1,200 and 18,800 tonnes respectively.

One expert estimates that 12,660 tonnes of RE metals were used in NiMH battery alloys [7]. Mischmetal composition varies widely; it can be lanthanum rich or cerium rich and may contain several other rare earths. Morgan estimates the average composition as follows: 50% lanthanum, 33% cerium, 3% neodymium, 10% praseodymium and 3% samarium (ibid). Thus the amount of each RE metals in NiMH is probably about 6,330 tonnes of lanthanum, 4,230 tonnes of cerium, 1,265 tonnes of neodymium, 420 tonnes of praseodymium and 420 tonnes of samarium. Maurel reported that addition

of 1 % of yttrium oxide improves the cycle lifetime of the cell by a factor of 2 compared with that of a cell without yttrium. However none of the source we have seen reported yttrium in batteries [59].

Ruthenium and iridium, two PGM hitch-hikers, have also been used in membrane cells for chlor-alkali production, replacing so-called mercury cells [31]. Unfortunately we have no quantitative data, although the industry is very large.

6.3.2. Capacitors. Tantalum capacitors can store and regulate the release of an electrical charge. They are essential components of all kinds of electrical and electronic circuits, partly for safety reasons and partly for other reasons. The charge in a capacitor gradually leaks out, but some materials are much better than others. The best capacitor material is tantalum. Capacitors account for about 60% of global tantalum output. Major end uses for tantalum capacitors include automotive electronics, pagers, personal computers, and portable telephones. They have also medical uses as components of hearing aids and pacemakers. In automobiles, tantalum capacitors are part of GPS and ABS systems, airbag protection systems, and ignition and motor control modules. Other electronics with tantalum capacitors include digital and video cameras, video game consoles, laptops and cell phones [3]. In 2008, the amount of tantalum used in capacitors was 605 tonnes.

6.4. Alloying elements

An alloy is a mixture of two or more metals to get better characteristics than either metal alone.

The characteristics of alloys vary depending on their composition.

6.4.1. Permanent magnets. The world market for permanent magnets, by type, is estimated to break down as follows: 34% hard ferrites, 65% rare earth magnets, and 1% aluminum-nickel-cobalt (Alnico, which used to be the only option) [60]. Ferrite magnets contain some lanthanides, although the amounts contained are not published [6]. There are two types of permanent magnets containing rare earth elements, namely samarium-cobalt and neodymium-iron-boron (hereafter referred as NIB). Samarium cobalt ($\text{Sm}_2\text{Co}_{17}$) magnets were the first magnets containing rare earth elements. They are still used in small electronic equipment as watches, aerospace equipment, microwave technology, but lately they are being replaced by NIB, which is both more economical and twice as strong for the same weight [19]. It is estimated that 500 tonnes of SmCo magnets were produced in China in 2008

[61]. The Cobalt development institute estimates that 5,600 tonnes of cobalt used in SmCo magnets. From this the quantity of samarium can be estimated.

There are three iron-boron formulations: neodymium-iron-boron or NIB ($\text{Nd}_2\text{Fe}_{14}\text{B}$), praseodymium-iron-boron ($\text{Pr}_2\text{Fe}_{14}\text{B}$) and neodymium-dysprosium-iron-boron ($\text{Nd}_{10}\text{Dy}_4\text{Fe}_{80}\text{B}_6$). The last two are usually combined with the first in NIBs. On average, neodymium-iron-boron magnets contain 30% rare earths, 69% iron and 1% boron. The 30% RE component is made up of 70% neodymium, 24% praseodymium, 5% dysprosium and 1% terbium [7]. NIBs are used in small but powerful; motors for electric vehicles (EVs), wind turbo-generators, magnetic resonance imaging (MRI) and some other electronic components. In future they might be used for magnetic levitation (“mag-lev”) trains.

In 2010, there were 24,060 tonnes of RE metals used in permanent magnets including 16,700 tonnes of neodymium, 5,630 tonnes of praseodymium, 1,200 tonnes of dysprosium, 480 tonnes of gadolinium and 50 tonnes of terbium. About 98% of these amounts were used in NIB magnets. The NIB market at present is divided as follows: 61% in electrical and electronic devices, such as hard drives, microphones and loudspeakers, 15% in wind turbines, 14% in electric vehicles, and 10% in MRI scanners. The wind and EV shares are likely to increase in the future.

In 2010, 26 tonnes of ruthenium, a PGM ‘hitch-hiker’, were used along with platinum in perpendicular magnetic recording hard disk drives, which are now ubiquitous in computer equipment.

6.4.2. Other metal alloys. The critical metals used in alloys are cobalt, indium, niobium, tellurium, tantalum, tungsten and REEs (scandium, yttrium and cerium). Cobalt is extensively used as an alloying metal to produce high temperature, magnetic and electro-deposited alloys. In 2010, 16,600 tonnes of cobalt were used in so-called “superalloys”, which are used for jet engines’. The addition of indium to ball (or roller) bearings confers high resistance to fatigue and seizure. These bearing are used in aircraft, automobile and turbo-diesel truck engines, and also in other minor alloys applications [27]. In 2010, 69 tonnes of indium were used in bearings.

Niobium (formerly columbium) is mainly used in alloys to provide high strength at high temperatures. About 90% of the global niobium output was used in steelmaking to produce iron-

niobium alloys (containing between 40% and 70% niobium) and stainless steel [25 “Niobium & tantalum”]. Low niobium steel alloys are also used for car bodies, construction, off-shore platforms and pipelines. The stainless steel is used in car bodies, kitchen appliances, and equipment for the chemical industry. In 2008, 63,000 tonnes of niobium were used, of which 42,840 tonnes were used in steel, 13,860 tonnes in specialized ferro-niobium alloys for construction and 6,300 tonnes were used in other alloys.

Tellurium is used in alloys together with steel, copper, lead and cast iron. In steel and copper alloys, tellurium improves machinability without reducing conductivity. In lead alloys, it improves resistance to vibration and fatigue. In cast iron, it is used to control the depth of chill and in iron as a stabilizer [3]. In 2010, usage was 200 tonnes.

Tantalum is used for the construction of chemical equipment, aircraft engines and stationary gas and steam turbines [3]. In 2010, 40 tonnes of tantalum were used for process equipment. Another hitch-hiker used in minor alloys was iridium. In 2010, 4 tonnes were used for iridium-tipped spark plugs.

Rhenium has a high melting point and crystalline structure which makes it an excellent refractory metal. It is mainly used in high temperature thermocouples, electric and electronic control devices, metallic coating and corrosion resistance alloys [27]. In 2010, 32,340 tonnes of rhenium were used for these purposes.

Molybdenum is also an excellent refractory metal used mainly as an alloying agent in cast iron, steel, and super-alloys to enhance hardness, strength, toughness, and wear- and corrosion-resistance. It is principally used in the form of molybdic oxide (MoO_3) or ferro-molybdenum (FeMo), and frequently in combination with or added to chromium, manganese, nickel, niobium (columbium), tungsten, or other alloy metals [21 “Molybdenum”]. In 2010, 145,860 tonnes of molybdenum were used for alloying.

In 2010, 7,965 tonnes of REO were used in non-battery alloys with iron and aluminum [7]. The rare earths (RE) are used mostly in the form of mischmetal. The average composition is 50% lanthanum, 33% cerium, 3% neodymium and 10% praseodymium [7]. The amount of mischmetal in

alloys is estimated to be in the range of less than 1% to 2-4% depending on alloy. Mischmetal are used as minor alloys for controlling inclusions and improving the performance for steel and iron. For instance, cerium combined with sulfide form particles more rounded that are less likely to generate cracking. They are also used in zinc galvanizing applications as for zinc-aluminum alloy named galfan (Zn-5Al-MM). Galfan is composed by 95% zinc, 5% aluminum and less than 1% of mischmetal. It is often used to be as the coatings for steel, to enhance the product life for certain applications [62].

Some reports suggest that also scandium, yttrium and samarium are also used in some alloys. Scandium-aluminum alloys are suitable for light weight construction, as in military aviation. Scandium is used for hardening other metals, especially in aluminum-scandium (Al-Sc), titanium-scandium (Ti-Sc) and beryllium-scandium (Be-Sc) alloys for the aerospace industry. Yttrium added to steel in small amounts improves the granular structure; added to cast iron in fractions of a hundredth of a percent it doubles the hardness and increases wear-resistance by a factor of four. Neodymium-doped yttrium-aluminum garnets ($Y_3Al_5O_{12}$ or YAG) are widely used in lasers. Cerium is used as minor alloys for casting of steel and iron. Yttrium, lanthanum and cerium are also added to heat-resistant superalloys. Despite the description of all these uses, none of the reports about REE provides quantity data for these metals.

6.4.3. Cemented carbides. Cemented carbides are hard materials used in machining tough materials such as carbon steel or stainless steel, as well as in situations where other tools would wear away. Carbide tools withstand higher temperatures than standard high speed tungsten-steel tools. There are two critical metals used in cemented carbides: cobalt and tungsten. Cobalt is used in as a bonding agent in cemented carbides and diamond tools. Those carbides are used anywhere between as cutting tools for metals, rocks and other materials with high strength. The most commonly used is a tungsten carbide containing 2% and 30% cobalt. The properties of cemented carbides are controlled by the amount of cobalt present and the particle size of the carbide used. The hardness of the cemented carbides increases with decreasing the particle size and with increasing cobalt content [27]. It has the ability to produce hard superalloys with nickel and iron to provide superior thermal, corrosion and

wear resistance in applications like turbines, motors and chemical equipment [3, 27]. In 2010, 14,400 tonnes of cobalt were used for hard metals and hard facing tools respectively

Tantalum-tungsten alloys and tantalum containing superalloys have high temperature resistance and strength. In 2010, 161 tonnes of tantalum were used for cemented carbides.

6.5. Additives

Additives are substances added to preserve the quality and appearance of coatings, and for coloring. They are widely used in the glass and ceramic industry for quality and as colorants. Rhodium is used during the melting of liquid crystal display glass to reduce the defects. In 2010, 2 tonnes of rhodium were used. There are several critical metals used as coloring additives: cobalt, indium, lithium, and REE: In 2010, 7,200 tonnes of cobalt, 5 tonnes of indium and 325 t of selenium were used as ceramic and glass additives. The total amount of REE used as additives is 17,420 tonnes [63]. Of this 63% was used in glass and 37% in ceramics [7].

6.5.1. Glass pigments. Hitch-hiker metals used as pigments in glass include selenium and RE metals. Selenium can be added as pigments for different reasons: to neutralized the green color that iron compounds usually add to glass and to add red color which reduces the amount of sunlight that gets through the glass. In 2010, 975 tonnes of selenium were used.

The major RE glass additives are cerium and lanthanum oxides. Adding cerium to glass helps overcome the decolorizing to yellow green caused by iron oxide, always present as an impurity glass. Cerium is also a good UV and IR absorbent and thus used in protective glasses, as for example in quantities of 2-4% for glass blowing and welding goggles [64]. Lanthanum is used in silica glasses to give a high index of refraction and low dispersion in lenses for autofocus single-lens reflex (SLR) cameras and video cameras. The purity of rare earth additives must be of 99.9-99.995%. Lanthanum is used in laser crystals yttrium-lanthanum-fluoride (YLF) composition [19]. Other REE used in lower amounts are neodymium, yttrium and praseodymium. Neodymium and praseodymium are used for coloring. Neodymium colors glass bright red, praseodymium colors glass green, and their combination blue [64]. Yttrium is used in the form of yttrium-aluminum garnets ($Y_3Al_5O_{12}$) to form synthetic crystals that are widely used as an active laser medium in solid-state lasers [18]. YAG lasers may use

neodymium for its optimal absorption and emitting wavelength to be used in various medical applications, drilling, welding and material processing. Other REE used as additives are erbium, ytterbium and holmium are used in luminescent solar concentrators and light sources for fiber optics and in laser materials [64]. There is no published data disclosing the amounts of these individual metals in the glass industry. However, in 2010, 11,000 tonnes of RE metals were used, among them 110 tonnes of praseodymium and 440 tonnes of other minor RE metals hitch-hickers.

6.5.2. Ceramic pigment. The total amount of REEs for ceramics pigments in 2010 was 6,420 tonnes [63]. The main REEs used are yttrium (3,400 tonnes), lanthanum (1,090 tonnes), cerium (770 tonnes), neodymium (770 tonnes) and the hitch-hicker: praseodymium (385 tonnes). Rare earths are becoming important for new engineering ceramics. Yttrium is used combined with silica for turbine blade applications. Yttrium and cerium are used in partially stabilized zirconia (PSZ) and tetragonal zirconia polycrystals (TZP), both high performance ceramics with excellent toughness and strength properties at low and intermediate temperatures. End products of these ceramics containing yttrium are components for so-called adiabatic diesel engines, cutting tools, wire drawing dies and furnace elements for use up to 2,000°C in oxidizing atmospheres. Lanthanum is used in lead zirconate-titanate (PLZT), a transparent ferroelectric ceramic material.

Cerium is used as a phase stabilizer in zirconia based products and in various ceramics including dental compositions [64]. Neodymium is used in ceramic glazes to produce blue to lavender colors [65]. Praseodymium incorporated in a zirconium silicate lattice is used for the production of high temperature resistance lemon yellow pigments for the ceramic industry [64].

6.6. Abrasives

Rare earth elements are excellent abrasives for glass polishing in the manufacture of LCD, optical glass, mirrors, photo-masks, plate glass, lenses and cut glass. Rare earth powders apart from providing a high mechanical abrasion react with the surface of glasses providing a high quality finishing [61, 64]. There are various grades of rare earth oxide polishing powder. They can be composed of cerium oxide alone, or with a content of 45%-75% cerium with the remainder of other rare earth oxides [66]. Tao estimated the composition of waste polishing powder as: 0-35% lanthanum, 50-99% of cerium, 0-

15% neodymium and 0-5% of praseodymium [61]. Morgan estimates the average composition of polishing powder to be: 32% lanthanum, 65% cerium and 4% of praseodymium [7]. In 2010, usage was 4,330 tonnes of lanthanum, 8,940 tonnes of cerium and 480 tonnes of praseodymium. About 40% of rare earth polishing powder was consumed in the LCD industry in 2008 [67].

Figure 3 below summarizes the uses of hitch-hiker metals as best we can determine them from published data.

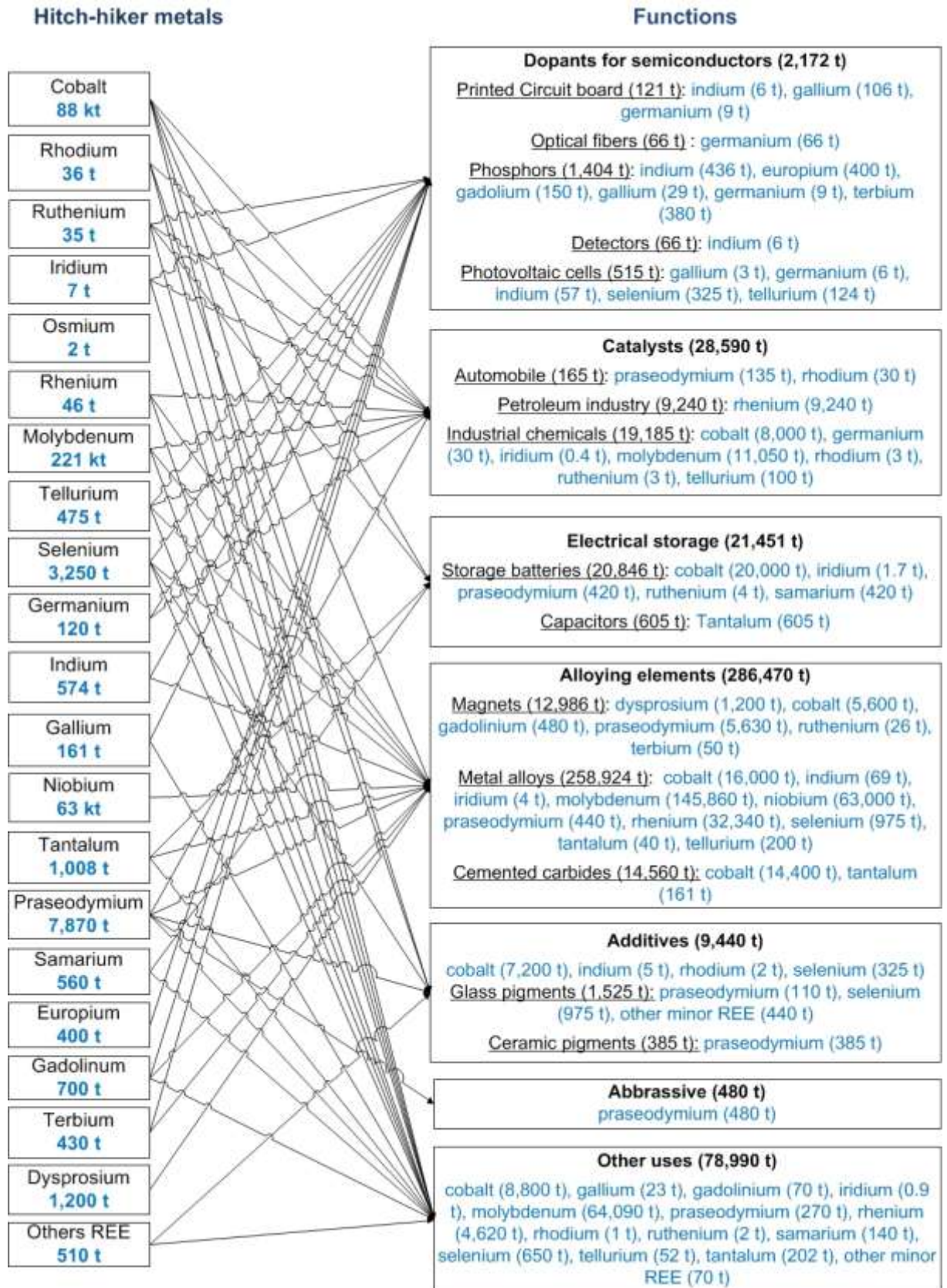


Figure 3. Functions and end-products of hitch-hiker metals for 2010.

7. Recovery potential of critical and by-product metals

Now that the hitch hiker metals have been identified and quantified in intermediate products, we can also estimate their content in end products. This quantification helps do some estimation about their recovery. Not all hitch hiker metals can be recovered in practice. However, if we know what the intermediate and end-products are used for, a theoretical potential recovery can be calculated for non-dissipative uses. Figure 4 show the intermediate and end products of rare earth metals. Appendix 2 describes the procedure for their estimations.

For example, let us trace the 24,060 tonnes of REM used in magnets in 2010, which lie under the function “alloying metals” in figure 2. Magnets are used in wind turbines, electric vehicle batteries, magnetic resonance imaging (MRI), electronic products and magnetic cooling applications. If we know the amount of each metal present in each of these end-products, we could calculate what could, in theory, be recovered at the end of life. Following our example, based on several references and estimations, we calculated that 1,300 tonnes of REM were embodied in magnets of wind turbines, of which 910 tonnes were of neodymium. Using the same approach, we found that 3,358 tonnes of neodymium were used in magnets in electric vehicles, and 450 tonnes in MRI and 11,980 tonnes in electrical and electronic devices, totaling 16,700 tonnes of neodymium that could in theory be recovered at some point in the future. This is a substantial amount if we compare with neodymium production for that year which was 21,615 tonnes. According to Graedel, the actual end-of-life recycling rate for neodymium is less than 1% [68].

If we look at phosphors applications, in 2010 a total of 8,250 tonnes of REM were consumed. These ended up in lighting applications, liquid crystal display screens (LCD), and plasma panels. If we trace europium which is the only metal known that can emit blue light, 24.5 tonnes were used in lighting, 19.5 in LCD and 6 in plasma panels, adding to a total of 50 tonnes of europium used for blue phosphors. Graedel estimates that less than 1% of europium is recycled at the end of life of these products. Please see appendix 2 information for a full explanation of potential recovery of REEs as well as data sources.

As the demand of hitch hiker metals increases in the future, it will become necessary to increase the recovery of these metals at the end of life of the products that contain them, and improve present production from base metals. What is clear is that future supply and production of these hitch hiker metals will depend on these factors as well as geological scarcity, rather than price.

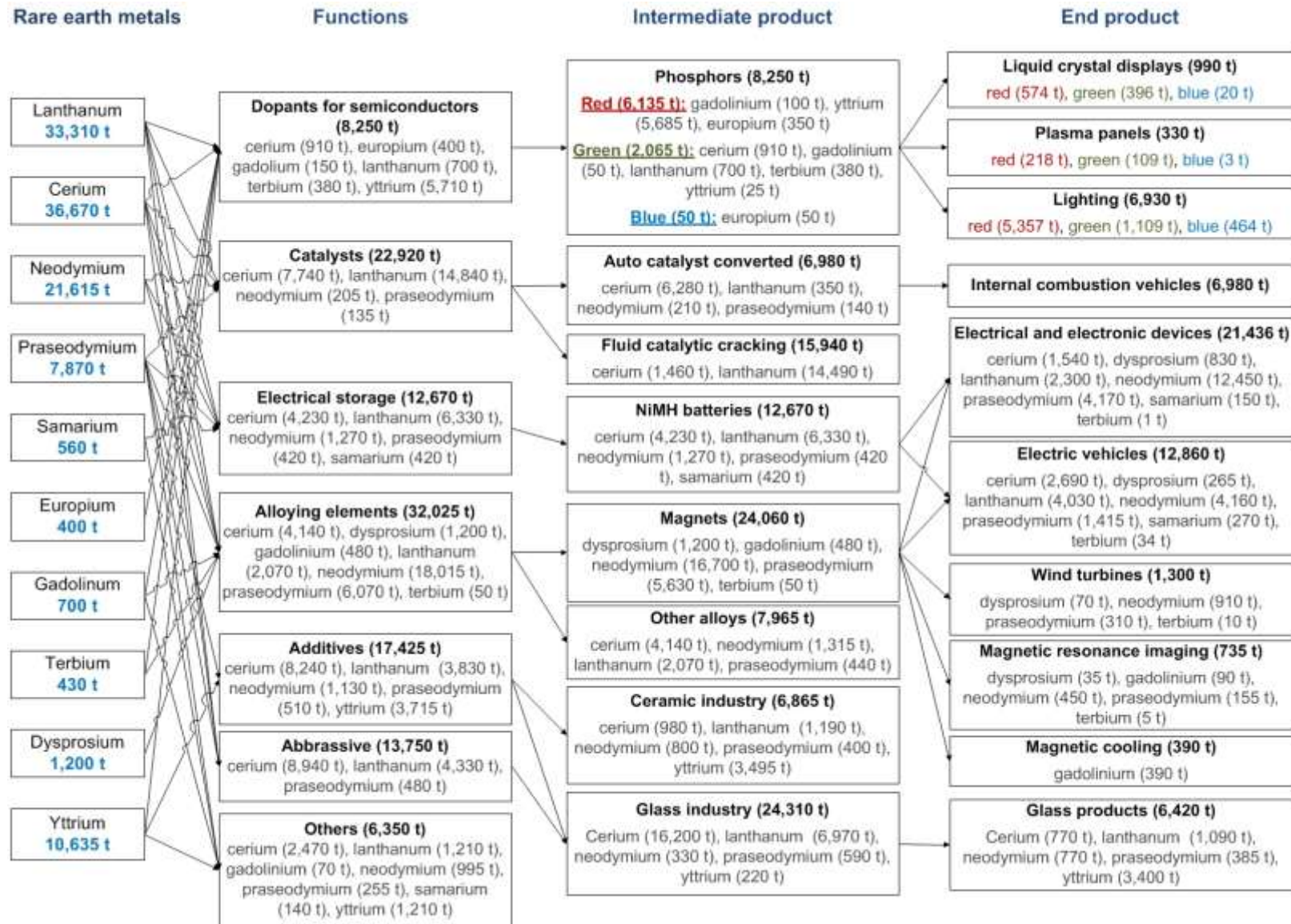


Figure 4. Rare earth metals contained in intermediate and end products.

8. Acknowledgments

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9. Appendices

Appendix 1. Major industrial metals and their co-products.

In this section, we discuss the “attractor” metals that are sources of the scarce “hitch-hikers” noted above, many of them categorized as critical. We quantify the major flows of base and by-product metals. The base metals studied are iron ore, aluminum, copper, zinc, lead and nickel.

Iron, steel and aluminum are used primarily for structural purposes, to provide strength to buildings (as in ferro-concrete), protection against the elements (roofs, siding), channels or containers for fluids (pipes, tanks, pots and pans) and as external “skin” for mechanical or electrical devices performing many functions, including kitchen appliances, vehicles and even PCs. Most machines are made from steel. Pig iron and steel are by far the major products among all the basic metals produced annually. Steel is important because of its price and the possibility of being alloyed and heat-treated to obtain a wide variety of characteristics for special applications. In 2010, the world production of iron ore was 24 million tonnes [21 “Statistical Summary”, 69]. Pig iron is mostly produced from iron ore or scrap by the basic carbo-thermic reduction process (blast furnace using coke as the reductant) and in smaller amounts by direct reduction using hydrogen [70]. Carbon steel is the most common form, but steel is often alloyed with other metals, especially manganese, chromium (in stainless steel), cobalt, molybdenum, nickel, tungsten and vanadium, depending on the application. In China, as mentioned, some iron ores are associated with bastnäsite ((Ce,La)CO₃F) and monazite (Ce,La,Nd,Th)PO₄, all an important resource for rare earth elements (REE) [21 “Rare earths”]. In 2010, the world production of RE was 113,900 tonnes, almost 50% of which were by-produced from iron ore originated in the Bayan Obo mine located in Inner Mongolia (China) [18, 21 “Rare earths”, 71].

Aluminum is lighter than steel, more malleable and virtually immune to corrosion due to the thin but impermeable oxide payer that forms on the surface. Because of its light weight it is used for aircraft and truck bodies (and perhaps auto bodies in the future), while its corrosion resistance accounts for its uses as roofing, facing, window frames and similar purposes, in buildings, as well as for foil and cans. It is by far the most widely used non-ferrous metal [21, 72]. Although it is the second

most abundant element in the earth crust, its only mineral resource at present is bauxite, which contains from 40-60% aluminum oxide (Al_2O_3) [73]. Aluminum is produced by the two stage process starting with separation of aluminum oxide (alumina) from bauxite by the Bayer process (which generates a caustic waste called “red mud”) followed by electrolytic smelting by the Hall-Heroult process. Presently, aluminum production is also the main source of gallium. In 2010, the world production of gallium was 161 metric tonnes, 55 tonnes of which were recycled from scrap [21 “Gallium”]. A minor source of gallium is from zinc ores such as sphalerite.

Copper is an all-purpose metal. Apart from its attractive color, it is extremely malleable and ductile, a good heat (and electrical) conductor, as well as being nearly as corrosion resistant as aluminum. Copper has several chemical uses. It is mainly used for water pipes and tubes in buildings, but also for roofing, for heat exchangers, as brass (an alloy with zinc used for castings) and in bronze, but especially for electrical wiring. It is the second non-ferrous metal used worldwide. There are about 160 copper-bearing minerals, but most important deposits are the so-called porphyry ores (about 70% of global reserves especially located in Chile, Peru, Zambia and Southwest of US), sedimentary (oxide) ores (25% of global reserves located in Zaire, Zambia, USSR) and 5% are “other” ores as native copper [74].

Regarding copper production, between 50-60% comes from porphyry ores (sulfide ores), mainly chalcopyrite (CuFeS_2) followed at a distance by chalcocite (Cu_2S), bornite (Cu_5FeS_4) and enargite (Cu_3AsS_4) [72]. Copper ores contain some nickel, lead, zinc and tin, as well as by-product metals cobalt, germanium, molybdenum, gold, platinum group metals, rhenium, selenium, silver, tellurium and tin. Of these, only cobalt, germanium, platinum group metals and tellurium are classed as critical and only cobalt and tellurium are presently co-produced with copper [21 “Selenium & Tellurium”, 25 “Cobalt”]. In 2010, about 35% of the world’s cobalt output (31,000 tonnes) was co-produced from copper ores. The global output of tellurium was estimated in 475 tonnes, almost all supplied as anode slimes of electrolytic copper refining. Molybdenum, rhenium and selenium are non-critical metals that are by-products of copper ore. In 2010, the output of molybdenum was (221,000 tonnes), rhenium (46 tonnes) and selenium (3,250 tonnes) [21, 25 “Molybdenum”]. Porphyry ores also supply some gold,

silver, tin and arsenic as by-products. Sedimentary copper oxide ores provide 20% of world copper production, as well as some lead, zinc and silver [75].

The single greatest use for zinc (as well as chromium and tin) is as coatings (galvanizing, chrome plate, tin plate) to protect iron or steel surfaces from rust. Some zinc is used for small castings. Brass is probably the second most important use. Zinc is also used in primary batteries and in chemicals. The major source of zinc is sphalerite (ZnS), followed at distance by smithsonite (ZnCO₃) and hemimorphite (H₂Zn₂SiO₅) [25 “zinc”]. Sphalerite is associated with lead, cadmium, and iron sulfides, and to lesser extent to copper sulfides, gold and silver minerals. In 2010, the world production of zinc was estimated in 8.4 million tonnes, over 65% from sulfide ores. The most important by-product of zinc mining is cadmium. In 2010, the world production of cadmium was 22,000 tonnes. A few years ago cadmium has a few uses as a red-orange pigment, but was otherwise mainly a toxic waste. Today cadmium has a significant use in rechargeable batteries for small appliances, although this use is already being challenged by lithium.

There are three other, more critical “hitch-hiker” metals contained in zinc ore: namely gallium, germanium and indium. Of all these three, only germanium and indium are now recovered, but gallium is not.¹ In 2010, the worldwide production of germanium was 120 tonnes, mostly obtained by leaching of zinc residues. About 36 tonnes was from recycling new scrap especially from electronic devices and coal fly ash [25 “Germanium”]. There is a considerable potential to produce germanium from coal fly ash in the future as coal combustion under certain specific conditions can increase its concentration five-fold, from 0.5-61 ppm to 90-320 ppm [76, 77]. Indium is currently obtained only as a by-product of zinc refining. In 2010, the total worldwide output of indium was 574 tonnes [25 “Indium”].

Lead is no longer used as an anti-knock additive to gasoline, nor for paint, but it is still used in a few applications where density is important (e.g. in shotgun pellets or as a shield around X-ray

¹ In zinc production, Gallium is generated during the smelting process and deposited in the slag. The increase on energy prices has forced zinc producers to shift from pyrometallurgical to hydrometallurgical routes. As result of such change, gallium is not longer recovered from zinc.

machines or radioactive materials.) The main use of lead is in lead-acid starting-ignition-lighting (S.L.I) storage batteries for cars and trucks. It is found in nature as galena (PbS) which is its primary sulfide and in some oxidized ores: anglesite (PbSO₄) and Cerussite (PbCO₃). World production is supplied 44% from sulfides and 56% from secondary sources (scrap from lead-acid batteries). In 2010, global lead production was 3.32 million tonnes [25 “Lead”]. Lead ore often contains iron, copper and zinc sulfides or sulfates, as well as “hitch-hiker” metals such as silver and gold. Although the world production of gold and silver is not particularly high in mass terms (2,500 and 22,200 tonnes, respectively), they are not classed as critical metals [25 “Gold” “Silver”].

Other important industrial metals include chromium, cobalt, manganese, molybdenum, nickel and tin. Chromium and nickel are alloying elements for stainless steel, while cobalt, molybdenum and niobium are components of “super-alloys” for jet engines and gas turbines. The major nickel resources in the world are in the form of laterites (70% of the world resources) but the nickel sulfide ores are more valuable [78]. Historically, nickel has been mostly supplied from sulfide deposits as pentlandite (Ni,Fe)₉S₈ since the concentration of nickel is higher, compared to that of laterites as nickeliferrous limonite ((Fe,Ni)O(OH)) and garnierite (Ni,Mg)₃Si₂O₅(OH)₄. In 2003, as the demand for nickel - and its price - continue to grow, nickel production from laterite ores increased to 42 % and is expected to rise to 51 % by 2012 [79, 80]. Producing nickel from laterite ore requires from two to three times as much energy as reduction from sulfide ores, but the downside is the quantity of sulfur dioxide emissions [27]. In modern plants the sulfur dioxide can be captured and converted into sulfuric acid. The current price for nickel makes production from laterite ores economically feasible. However if the price declines production would be affected.

Nickel sulfides are usually associated with copper and/or iron sulfides, and some of the sulfide deposits also contain cobalt, platinum group metals, selenium and tellurium [81]. Laterite ores can co-produce iron in the form of ferro-nickel, or ferro-cobalt. Presently, laterites supply 50% of world cobalt production, while 35% is produced from copper sulfide ores and 15% from cobalt arsenides [72]. In 2010, the total production of cobalt was 88,000 tonnes [25].

Other critical metals with marginal recovery rates that are contained in some nickel ore are platinum associated metals (PGMs). In 2010, the total production of PGMs was 689 tonnes, only about 11 tonnes² were by-products of nickel. The total world production of platinum and palladium was 609 tonnes, of which 215 tonnes were obtained from recycling. From such platinum and palladium, there were 73 tonnes of other PGMs metals produced [30, 31].

Tin is still used for plating (tin cans), but the critical use is for solder to connect wires and electronic components. The only mineral of commercial importance as a source of tin is cassiterite (SnO_2), which is also associated with tantalum, tungsten and gold in some deposits, in the African Republic of the Congo. Small quantities of tin are recovered from complex sulfides such as stannite ($\text{Cu}_2\text{FeSnS}_4$), cylindrite ($\text{Pb}_3\text{Sn}_4\text{FeSb}_2\text{S}_{14}$), franckeite ($\text{Pb}_5\text{Sn}_3\text{Sb}_2\text{S}_{14}$), canfieldite (Ag_8SnS_6) and teallite (PbSnS_2). In 2010, the total world tin production equals 274,000 tonnes. About 10% of the production was supplied from the manufacturing from scrapped alloys of tin and recycled by those same alloys industries [25 “Tin”]. Niobium and tantalum are two critical metals sometimes co-produced by tin. A mineral known as “coltan” currently mined in the African Republic of the Congo, consists of a combination of columbite (niobium oxide) and tantalite. In 2010, world niobium output was 63,000 tonnes. World production of tantalum was 1,016 tonnes, over 65% from tantalite (coltan, a co-product with niobium), 24% from recycling and 10% from tin slag [25 “Niobium & tantalum”].

² The amount produced as by-product might be higher as the yearly production from Russia did not specify the amount produced from nickel and that from platinum sulfides and arsenides.

Appendix 2. Rare earth elements embodied in intermediate and end-products

In this appendix, an estimation of the amount of rare earth elements used in different functions and embodied in intermediate and end products is done. The main functions of rare earth are as dopants for semiconductors, catalysis, electrical storage, alloying elements, additive in glass and ceramic and as abrasives. All these functions are used in intermediates and end-products. For example, lanthanum is used as dopant for semiconductors in phosphors (intermediate product), and phosphors are used in liquid crystal display, plasma flat panels and lighting, all of them end-products.

This supporting information describes how the amount of rare earth in each intermediate and end product has been estimated. All information was based on market share given for 2008 and extrapolated to 2010 [7].

a2.1. Rare earth metals as dopants in phosphors

The principal applications for rare-earth phosphors are in display screens (cathode ray, liquid crystal and plasma) and in low-energy fluorescent lighting tubes. Each of the different display technologies requires somewhat different types and compositions of phosphors, as do fluorescent tubes in which the phosphors reduce energy consumption and provide specific colors. The composition of phosphors varies depending on the color required for the end product. For red, the RE oxides used includes yttrium, europium and gadolinium. For green, the hosts used are lanthanum, cerium and yttrium while terbium and gadolinium are used as activators. For blue, it is mainly used europium oxide. The combination of red, green and blue gives white color. Phosphors are largely used for lighting (84%), followed by LCDs (12%) and plasma displays (4%) [7].

a2.2. Rare earth metals as catalysts

The amount of rare earths used as catalyst in 2010 (22,920 tonnes) was estimated based on their use in 2008 [63, 82]. About 70% are used in fluid catalytic cracking and 30% in auto catalyst converters [7].

a2.2.1. Auto catalyst converters.

Auto catalyst converters are a part of the exhaust system used to reduce the emission of harmful pollutants, such as carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NO_x). A converter typically consists of one or more honeycomb, generally made of alumina, which has three principal components: wash-coating, active elements (such as platinum group metals) and additives such as rare earth oxides. The efficiency of catalysts is strongly determined by the thermostability of alumina-based wash-coating. Rare earth oxides are added to the wash-coating to improve the thermostability of alumina and ensure the activation of catalyst under high temperature [41].

In 2010, the manufacturing of 78 million units of cars required a total of 6,980 tonnes of REE, which gives an estimate of 90 g of REE per vehicle [44], one third the amount reported in 2003 [43]. The composition of REE in converters is 90% cerium, 5% lanthanum, 3% neodymium and 2% praseodymium. In 2010, 6,280 tonnes of cerium, 350 tonnes of lanthanum, 210 tonnes of neodymium and 140 tonnes of praseodymium were used in internal combustion vehicles.

a2.2.2. Fluid Catalytic Cracking

Fluid catalytic cracking (FCC) is mainly used in petroleum refining to break down long complex organic molecules as kerosene and heavy hydrocarbons, into simpler and lighter molecules as gasoline and liquefied petroleum gas. In this process, catalysts are used to improve the yield to light hydrocarbons. The most widely used catalysts in FCC are the synthetic zeolites: Faujasite-type (also called zeolite Y), and ZMS-5 zeolites [45]. Both of these zeolites contain rare earth elements (REE), generally lanthanum and cerium, to improve the stability at high temperature (catalytic stability) and increasing catalyst activity and gasoline selectivity [27, 46]. Each liter of hydrocarbons feedstock requires about 4.66 kg of catalyst. Commercial catalysts are composed by 85% amorphous silica-alumina cracking catalyst and 15% of zeolites [83, 84]. The content of rare earth can vary from less than 1% to 3% [49, 50, 85]. In 2010, the annual production of feedstock from FCC was 1,668 million liters. FCC containing primarily Y zeolites account for more than 95% of total consumption [52]. Assuming that production of REE for FCC requires 15,940 tonnes of REE, for each liter of feedstock it is required an average of 9g of REE, not far from the 0.2% REE content estimated by some authors

[53]. In fluid catalyst cracking, cerium is used in zeolites as a thermal and hydrothermal stabilizer to extend the life and increase the activity of catalyst.

a2.2.3. Other industrial processes

Although not quantified in the present work, cerium is also used on other non-cracking catalyst processes as: ammonia synthesis, hydrogenation, dehydrogenation, polymerization, isomerization, oxidation and in automobile emissions control [27]. Rare earth salts compared to transition elements are high polymerization temperatures, reducing the cooling stage of the polymer, and substituting toxic aromatic solvents by aliphatic ones. This leads to a significant industrial development of the use of neodymium salts for rubber manufacturing.

a2.3. Rare earth metals as electrical storage in NiMH batteries

A nickel metal hydride (NiMH) battery is a type of rechargeable battery composed by cathode, anode, electrolyte and separator all assembled in a steel case. The cathode is generally made of nickel coat or nickel oxyhydroxide (NiOOH). The anode consists on a hydrogen-absorbing alloy based on a mischmetal, made of rare earths elements (REE), and nickel. The electrolyte is a potassium solution and the separator is either polyamide or polypropylene based [86]. REE are mainly contained in the anode of NiMH batteries as a mischmetal. In 2010, 12,670 tonnes of REE were used in NiMH battery alloys [7]. Pillot estimated 65% of the batteries were used for HEV vehicles, 18% for retail (toys and household tools), 9% for cordless phones and 8% in other electrical and electronic devices [87].

As a way to select the best estimate of the amount of REE in NiMH batteries, we accounted for the amount of cobalt and nickel used for them. For misused NiMH batteries³, Xu estimated the following content of metals: 33% of REE, 50% of nickel, 10% of cobalt, 2% of aluminum and 6% of manganese [61]. In 2008, China used 6,200 tonnes of RE for NiMH which represents 50% of the world market. Based on that amount, we estimate the amount of nickel (9,450 tonnes) and cobalt (1,890 tonnes) for NiMH in 2008.

³ Rodrigues and Mansur estimated the following metal content in NiMH batteries: 50% nickel, 5.1-5.5% cobalt and 15.3-29% rare earths elements.

In 2010, the world cobalt production was estimated in 44,000 tonnes. About 16,000 tonnes of cobalt was used in NiMH and Li-ion batteries [88]. The market share for NiMH and Li-ion is 3 and 97%. The amount of cobalt used in NiMH is 2 times higher than the amount used for Li-ion. Thus the amount of cobalt used in NiMH batteries is about 960 tonnes compared to the 1,890 tonnes estimated for China. In NiMH batteries, nickel is used in the positive and negative electrodes, and in the foam electrode substrate. In 2010, the world production of nickel was 1.45 million tonnes being about 43,560 tonnes used in NiCd and NiMH batteries [88]. Since the amount of nickel used in each type of battery is about the same; we use the market share for each type to estimate the amount of nickel used. Pillot suggests that about 34% of nickel for batteries is used for NiMH. Thus the amount of nickel for NiMH batteries equals 14,810 tonnes. Considering that China has about 50% of world NiMH production, the amount of nickel used by China is 7,400 tonnes which is not far from the 9,450 tonnes given by Xu for 2008 [61].

After this short discussion about the amount of REE in NiMH batteries, we estimated the amount of REE, nickel and cobalt as 12,400, 18,900 and 3,780 tonnes respectively. The amount of REE is not far from that given by Lynas: 12,670 tonnes. For HEV which represent 65% of the end use of NiMH batteries, the total amount of RE equals 8,060 tonnes. According to Pillot, the remaining 4,610 tonnes are used for retail (toys and household tools), cordless phones and in other electrical and electronic devices [87].

NiMH batteries are described as AB_5 batteries where A is generally for lanthanide metal and B for nickel. Although their starting point is $LaNi_5$, in practice lanthanum is substituted by lanthanum rich mischmetal containing cerium, neodymium, praseodymium and samarium [89]. Mischmetal varies widely in composition; it might be lanthanum rich, cerium rich and may contain several other rare earths. Table a1 shows the different composition of mischmetals in NiMH batteries found in the literature.

Table a1. Composition of mischmetal in NiMH batteries.

	Percentage of each rare earth				
	La	Ce	Nd	Pr	Sm
Xu (1999) [90]	65	4	3	28	
Ying (2006) [89]	78	15	6	1	-
Mueller (2006) [86]	42	36	6	16	
Morgan (2010) [7]	50	33	3	10	3
Eriksson (2011) [91]	60	10	10	20	

In this paper, we assumed as average composition the given by Morgan [7]. Thus the amount of each RE in NiMH is equals to 6,330 tonnes of lanthanum, 4,230 tonnes of cerium, 1,270 tonnes of neodymium, 420 tonnes of praseodymium and 420 tonnes of samarium.

Amount of RE in electric vehicles: There are several estimations of the amount of REE in NiMH of HEV:

- Estimation 1: 1 kg NiMH battery contains an average of 0.06 kg of REE. A Toyota Prius with a 53.3 kg NiMH battery contains 3.2 kg of REE [2, 86, 90, 92, 93]. The total amount of RE elements in NiMH is 1,535 tonnes, far from the 8,236 tonnes estimated based on Pillot [7].
- Estimation 2: 1 cell contains 0.051 kg of REE. A Toyota Prius with a battery containing 38 NiMH modules, each of them containing 6 cells of 1.2 V, and has a total of 12 kg of REE. Eriksson estimates 9 kg of REE for a NiMH of 37 kg of weight [91]. Xu et al. estimate that a NiMH battery contains 13 kg of RE and reports 6,200 tonnes of RE for NiMH batteries in China (China represents about 50% of the total NiMH market) [61]. Morgan also estimates 13 kg of RE per NiMH battery for HEV [7]. Assuming 13 kg of REE and using the worldwide annual production of HEV (533,000 units), the amount of RE is 6,930 tonnes.

Due to the high discrepancy between both methods of estimation, we decided to estimate the amount of RE in NiMH batteries of HEV using data of 2008 from Pillot, Lynas and Roskill [7, 82, 87, 94]. For 2010, 4,030 tonnes of lanthanum, 2,690 tonnes of cerium, 206 tonnes of praseodymium, 805 tonnes of neodymium and 206 of samarium, totaling 8,060 tonnes were used in NiMH batteries for HEV.

Amount of RE in electrical and electronic devices: the amount of RE in NiMH batteries used in electrical and electronic devices was calculated as the difference between the total annual use of RE for NiMH and the amount used by NiMH batteries in HEV. In 2010, 2,300 tonnes of lanthanum, 1,540 tonnes of cerium, 150 tonnes of praseodymium, 460 tonnes of neodymium and 150 tonnes of samarium, totaling 4,610 tonnes of RE were used.

a2.4. Rare earth metals as alloys

Almost all the published estimation of the amount of rare earth elements for metallurgy agrees on giving an estimate of 32,025 tonnes of REE produced [63, 82]. From this production, 75% are used in magnets and 25% in alloys with iron and aluminum [7].

a2.4.1. Rare earth metals as alloys in magnets

It is assumed that the usage of rare elements in magnets given by Morgan 2010 (Lynas corporation), corresponds to the composition of rare elements in neodymium-iron-boron (NIB) magnets [7]. In the three main NIB formulations ($\text{Nd}_2\text{Fe}_{14}\text{B}$, $\text{Pr}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_{10}\text{Dy}_4\text{F}_{80}\text{B}_6$), the rare earth metal content varies from 26.7 to 31.6%, the iron content is 67.4-72.8% and the boron content 1.0%. Table a2 shows the amount of each rare earth metal and their total amount in NIB magnets.

Table a2. Composition of NIB magnets.

	Percentage of each rare earth				% rare earth in NIB magnets
	Nd	Pr	Dy	Tb	
Xu (1999) [95] (NIB scrap)	18	1.82	5.3		25.12
Hong (2007) [96]	24		5.4	0.87	30.27
Xu (2009) [61]	22.5-30	7.5	1.2		30-31.2
Morgan (2010) [7]	20.97	7.17	1.65	0.21	30
Schueler (2011) [6]	30		3	un.	33
Du (2011) [97]	20	5	5	1	31
Gutfleisch (2011) [98]	21.77		9.81		31.58

In our estimation, we assumed an average amount of 30% of rare earth, 69% iron and 1% boron in NIB magnets, as deducted from Morgan [7]. For 2010, we estimated that 24,060 tonnes of rare earth were used in NIB magnets.

Amount of RE in wind turbines: In 2010, the new wind turbine installation was 36 GW [99]. Only about 14% of the total new installation used NIB magnets [6]. Table a3 shows the amount of rare earth, given as kg of NIB magnets or as kg of neodymium, found in different sources. Based on this information, we estimated the amount of REE used in new wind turbines.

Table a3. Amount of NIB magnet and neodymium used in wind turbines given by different authors.

	kg NIB	kg Nd	Total RE (tonnes)	% of total REE
Constantinides (2010) [100]	600	<i>126</i>	680	3%
Lifton (2009) [101]	700	<i>147</i>	794	3.6%
	1000	<i>210</i>	1,135	5.1%
Schueler (2011) [6]	400	<i>84*</i>	454	2%
Morgan (2010) [7]	<i>1,600</i>	<i>333**</i>	1,800	8%
Du (2011) [97]			3,345	15%

Numbers in cursive have been calculated based on 20.97% Nd and 30% REE content in NIB respectively.

*Schüler et al. assume 30% content of Nd in NIB. Schüler et al. estimate a demand of 1,512 tonnes of NIB and 450 tonnes of Nd for wind turbines in 2008.

** 3 MW require 1 tonne of neodymium that is 0.333kg of Nd per MW.

For our estimation, we use the average content of 860 kg of NIB per MW of wind turbine. Based on the composition given by Morgan, 910 tonnes of neodymium, 310 tonnes of praseodymium, 70 tonnes of dysprosium and 10 tonnes of terbium were used for NIB magnets in wind turbines.

Amount of RE in electric vehicles: In 2010, the number of new hybrid cars registered reached 533 thousand units [94]. Table a4 shows the amount of rare earth, given as kg of neodymium per motor, found in different sources. Based on this information, we estimated the amount of REE used in hybrid vehicles. Assuming each electric vehicle requires 1 electric motor per wheel, we obtain the amount of neodymium per vehicle:

Table a4. Amount of neodymium used in electric and hybrid electric vehicles given by different authors.

	kg Nd (motor)	kg Nd (vehicle)	% total REE
Lindegger (2009) [102]	1.5-2.3	6-9	19-28%
Lifton (2009) [101]	1	4	12.3%
Constantinides (2010) [100]	1.25	5	15.4%
Kingsnorth (2009) [63]	1.9	7.6	23.3%
Du (2011) [97]			15%

* Lindegger et al. 2008 estimate a content of 0.222-0.328 kg of NIB for a 3kW motor. The desired motor sizes are 90 and 100 kW.

For our estimation, we use the average amount of 6.3 kg of neodymium per electric vehicle which gives a total of 4,800 tonnes of REE. The amount of each rare metal used was: 3,358 tonnes of neodymium, 1,148 tonnes of praseodymium, 264 tonnes of dysprosium and 34 tonnes of terbium.

Amount of RE in magnetic resonance imaging (MRI): In 2010, there were 2,500 new MRI units produced [103]. Table a5 shows the amount of rare earth, given as kg of NIB magnets per unit, found in different literature sources.

Table a5. Amount of neodymium used in MRI units given by different authors.

	kg NIB (MRI)	Total RE (tonnes)
Tasman [104]*	700	525
Stratfor Global intelligence [105]	880	660
Bubar (2011) [106]	1,000	750
	3,000	2,250
Average	860	2,150

* <http://www.tasmanmetals.com/s/PrincipalUses.asp>

For our estimation, we use average estimate (860 kg of NIB magnets). To calculate the amount of each metal, we use the composition for NIB given by Morgan [7]. In 2010, 450 tonnes of neodymium, 5 tonnes of terbium, 155 tonnes of praseodymium, 35 tonnes of dysprosium were used in NIB magnets for MRI.

Gadolinium is used in the magnet sector as a as a magnetic resonance imaging contrast agent and as magnet component in research for magnetic cooling. As an MRI agent, it improves the visibility of internal body structures by altering the relaxation times of tissues and body cavities where it is present. The amount of Gadolinium used as an agent can be estimated based on its amount in doses and the number of exams performed during 2008. Gadolinium is mainly used in the form of gadolinium complex like diethylenetriamine pentaacetic acid (Gd-DTPA: $C_{28}H_{54}GdN_5O_{20}$) in doses of 0.1-0.2 mmol per kg of body mass, that is about 0.01-0.03 g of Gd [107]. In 2010, there were about 80 million

MRI exams [103]. By assuming an average patient body mass of 70⁴ kg, the amount of gadolinium required is about 88 tonnes.

Gadolinium is also used in magnetic cooling research. Gschneidner et al. use gadolinium powder in the form of wheels for creating magnetic refrigeration. Gadolinium has a high magnetocaloric effect; it heats up when exposed to a magnetic field, and then cools down when the magnetic field is removed (generating in overall a cooling effect) [108]. We estimated that its remaining production (390 tonnes) is used for magnetic cooling.

a2.4.2. Rare earth metals as alloys in metallurgical alloys.

In 2010, there were 7,965 tonnes of RE used in alloys with iron and aluminum [7]. The amount of REE was 4,140 tonnes of cerium, 1,315 tonnes of neodymium, 2,070 tonnes of lanthanum and 440 tonnes of praseodymium. The amount of mischmetal in alloys is estimated on the range of less than 1% to 2-4% depending on alloy. Mischmetal are used as minor alloys for controlling inclusions and improving the performance for steel and iron. For instance, cerium combined with sulfide form particles more rounded that are less likely to generate cracking. Mischmetal is also used in zinc galvanizing applications as for Zinc-Aluminium alloy named Galfan (Zn-5Al-MM). Galfan is composed by 95% Zinc, 5% Aluminum and less than 1% of mischmetal. It is often used to be as the coatings for steel, to enhance the product life for certain applications [69].

Mischmetal also acts as a grain-refining agent in some steel compositions improving the mechanical properties and fatigue resistance, and to increase the heat strength of super-alloys containing nickel, chromium, molybdenum and iron. They increase the plasticity of refractory metals vanadium, tantalum and tungsten and strengths aluminum, magnesium, copper and titanium alloys [27].

⁴ The average women and men mass are 60 and 80 kg respectively. Assuming that the patients are 50% women and 50% men, the average mass for a patient is 70kg (http://www.articleworld.org/index.php/Human_weight).

Addition of REE has also been used to improve mechanical properties and reduce fatigue in aluminum alloys, especially aluminum-lithium alloys used for the construction of airframes, and also for aluminum-iron-vanadium-silicon and aluminum-silicon alloys used for cylinder liner.

Scandium-aluminum alloys are suitable for light weight construction, as in military aviation. Scandium is used for hardening other metals, especially in aluminum-scandium (Al-Sc), titanium-scandium (Ti-Sc) and Beryllium-scandium (Be-Sc) alloys for the aerospace industry. Yttrium added to steel in small amounts improves the granular structure; added to cast iron in fractions of a hundredth of a percent it doubles the hardness and increases wear-resistance by a factor of four. However, none of the reports quoted above mention the uses of yttrium in alloys. The amount of RE used for electrical and electronic devices can be further disaggregated the following share: 57.4% in retail, 23.4% in cordless phones and 19.2% in others [87].

a2.5. Rare earth metals as additives

In 2010, the total amount of REE used as additives was 17,425 tonnes [63]. From this production, 37% are used as additives in ceramic and 63% in glass [7].

a2.5.1. Rare earth metals as additives in glass

The major glass additives are cerium and lanthanum oxides. Adding cerium to glass helps overcome the decolorizing to yellow green caused by iron oxide, always present as an impurity in glass. Cerium is also a good UV and IR absorbent and thus used in protective glasses, as for example in quantities of 2-4% for glass blowing and welding goggles [64]. Lanthanum is used in silica glasses to give a high index of refraction and low dispersion in lenses for autofocus single-lens reflex (SLR) cameras and video cameras.

Other REE used in lower amounts are neodymium, yttrium and praseodymium. Neodymium and praseodymium are used for coloring glasses. Neodymium colors glass bright red, praseodymium colors glass green, and their combination blue [19]. Yttrium is used in the form of yttrium-aluminum garnets ($Y_3Al_5O_{12}$) to form synthetic crystals that are widely used as an active laser medium in solid-

state lasers [18]. YAG lasers use neodymium for its optimal absorption and emitting wavelength to be used in various medical applications, drilling, welding and material processing [19].

Other metals used as additives are erbium, ytterbium and holmium are used in luminescent solar concentrators and light sources for fiber optics and in laser materials [64]. There is no published data disclosing the amount of these metals in glass industry. Rare earth elements contained in optical glass must be of 99.9-99.995% purity [19]. In 2010, 10,560 tonnes of REE were used as additives in glass: 7,260 tonnes of cerium, 2,640 tonnes of lanthanum, 330 tonnes of neodymium, 110 tonnes of praseodymium and 220 tonnes of yttrium.

a2.5.2. Rare earth metals as additives in ceramics

The total amount of REE for ceramics industry is 6,865 tonnes [63]. The main REE used are yttrium (3,495 tonnes), lanthanum (1,190 tonnes), cerium (980 tonnes), neodymium (800 tonnes) and praseodymium (400 tonnes). Yttrium is used combined with silica for turbine blade applications. Rare earths are becoming important for new zirconia ceramics. Yttrium and cerium are used in partially stabilized zirconia (PSZ) and tetragonal zirconia polycrystals (TZP), both high performance ceramics with excellent toughness and strength properties at low and intermediate temperatures. End products of these ceramics containing yttrium are components for adiabatic diesel engines, cutting tools, wire drawing dies and furnace elements for use up to 2,000°C in oxidizing atmosphere. Lanthanum is used in lead zirconate-titanate (PLZT), a transparent ferroelectric ceramic material.

Cerium is used as phase stabilizer in zirconia based products and in various ceramics including dental compositions [19]. Neodymium is used in ceramic glazes to produce blue to lavender colors. Praseodymium incorporated in zirconium silicate lattice is used for the production of high temperature resistance lemon yellow pigments for the ceramic industry.

a2.6. Rare earth metals as abrasive

Rare earth oxides are excellent abrasives for glass polishing in the manufacture of LCD, optical glass, mirrors, photomasks, plate glass, lenses and cut glass. Rare earth powders apart from providing a high mechanical abrasion react with the surface of glasses providing a high quality finishing [61]. There are various grades of rare earth oxide polishing powder. They can be fully composed by cerium

oxide, or with a content of 45-75% cerium with the remaining of other rare earth oxides [109]. Tao estimated the composition of waste polishing powder as: 0-35% lanthanum, 50-99% of cerium, 0-15% neodymium and 0-5% of praseodymium [61]. We have estimated Morgan's as the average composition for polishing powder: 32% lanthanum, 65% cerium and 4% of praseodymium [7]. Morgan does not report any amount of neodymium in REE polishing powders.

In 2010, 13,750 tonnes of REE were used for polishing powder in the glass industry. About 40% of which was consumed in LCD industry and the rest for other glass products.

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