

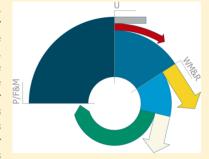
Lost by Design

Luca Ciacci,* Barbara K. Reck, N. T. Nassar, and T. E. Graedel

Center for Industrial Ecology, School of Forestry and Environmental Studies, Yale University, 195 Prospect Street, New Haven, Connecticut 06511, United States

Supporting Information

ABSTRACT: In some common uses metals are lost by intent—copper in brake pads, zinc in tires, and germanium in retained catalyst applications being examples. In other common uses, metals are incorporated into products in ways for which no viable recycling approaches exist, examples include selenium in colored glass and vanadium in pigments. To determine quantitatively the scope of these "losses by design", we have assessed the major uses of 56 metals and metalloids, assigning each use to one of three categories: in-use dissipation, currently unrecyclable when discarded, or potentially recyclable when discarded. In-use dissipation affects fewer than a dozen elements (including mercury and arsenic), but the spectrum of elements dissipated increases rapidly if applications from which they are currently unrecyclable are considered. In many cases the resulting dissipation rates are higher than 50%. Among others, specialty metals (e.g., gallium, indium, and thallium) and some heavy rare earth elements are



representative of modern technology, and their loss provides a measure of the degree of unsustainability in the contemporary use of materials and products. Even where uses are currently compatible with recycling technologies and approaches, end of life recycling rates are in most cases well below those that are potentially achievable. The outcomes of this research provide guidance in identifying product design approaches for reducing material losses so as to increase element recovery at end-of-life.

INTRODUCTION

The dictionary definition of "dissipate" is "to scatter or disperse, to drive or cause to go off in all directions, to disappear, to disintegrate, or to vanish". In the context of anthropogenic material cycles, dissipative losses are the flows of materials from the anthroposphere (i.e., human systems) to the biosphere (i.e., environment) in a manner that makes their future recovery extremely difficult, if not impossible. These flows may be desirable or undesirable, intentional or unintentional, ^{2–4} and can occur during any stage of a material's life cycle (e.g., tailings and slag from the production stage or outputs to air, water, and soil during waste treatment). Efforts are ongoing to raise the performance of current technologies to that of best practices toward a theoretical ideal of optimal material extraction and recovery. ^{5,6}

With respect to other dissipative flows, dissipative uses differ in that element loss is planned by design: the selection of materials made by designers and engineers to increase product performance depends on the intrinsic chemical and physical properties of elements, but the use of these elements in dissipative applications constrains any chance of secondary resource recovery. In some applications, such as sacrificial anodes and fertilizers, scattering and dispersion into the environment is part of the function itself. In others, loss is unintentional and undesired because of the toxic properties or market value of materials: for instance, catalysts lost into products (e.g., antimony-based catalysts into polyethylene terephthalate (PET) bottles), or platinum and cerium released from autocatalytic converters during on-road buffeting. Most elements are commonly employed in applications in their

metallic form, either as pure metals or alloys. Ideally, these elements would be recovered and reused. However, societal, economic, and technical challenges pose practical limits to the concept of the infinite recyclability of metals.^{7,8} In contrast, other applications use elements in compound forms in which their fate is often unknown once they enter into use,⁹ with several end-uses that have a potential for in-use dissipation (e.g., pyrotechnics and explosives).

Regardless of the intent, dissipative losses decrease the quantity of a material that is potentially available for future recovery and reuse, resulting in an increased dependency on primary sources. Dissipative uses of elements have come under increased scrutiny due to eco-toxicological effects of metals in the environment and long-term sustainability of metal supplies. The latter has been the focus of recent research from a materials "criticality" perspective. And 10 Nonetheless, a comprehensive approach to the study of dissipative losses of elements during the use phase has not been accomplished, with the result that dissipation's influence in limiting end-of-life recycling rates or increasing metal criticality is not fully understood. In response to this need, we have investigated and categorized the main causes for dissipation of elements during use, and measured the degree to which they are currently "lost

Special Issue: Critical Materials Recovery from Solutions and Wastes

Received: November 11, 2014 Revised: January 29, 2015 Accepted: February 18, 2015 Published: February 18, 2015



Table 1. Material Streams and Metrics Considered in the Study

material stream	corresponding metric	example of applications
in-use dissipated	in-use dissipation rate (IUDR)	selenium and manganese in fertilizers; aluminum, magnesium, copper, and barium in pyrotechnics; zinc in sacrificial anodes.
currently unrecyclable	current unrecyclability rate (CUR)	rare earth oxides in glass polishing powder; deoxidizing aluminum and desulfurizing manganese in steelmaking.
potentially recyclable unspecified	potential recyclability rate (PRR)	alloying elements technically recoverable or recyclable along with the carrier metal. miscellaneous uses that can be divided among in-use dissipated, currently unrecyclable, and potentially recyclable material streams were suitable information to be available.

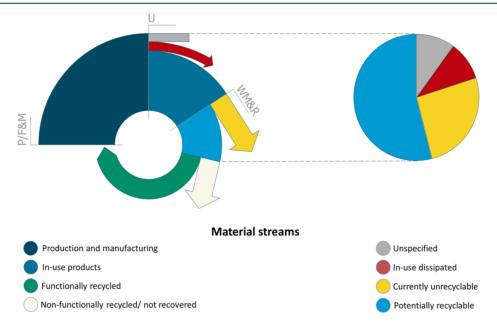


Figure 1. Scope of the study and main material streams investigated. P/F&M, production/fabrication and manufacturing; U, use; WM&R, waste management and recycling.

by design". We expect that the results will strengthen sustainability assessment methodologies for decision making, as promoted by the international life cycle assessment community. $^{14-17}$

■ MATERIALS AND METHODS

A model has been developed for measuring the contemporary dissipation of elements. It addresses all the common forms in which elements are used, from metals and alloys to chemical compounds, and it assigns on a global market share basis the allocation of a given element entering the use phase to one of four material streams: in-use dissipated, currently unrecyclable, potentially recyclable, and unspecified (Table 1). In a few cases we divide a use into more than one category because of dissipation or partial constrains on recycling. A first distinction between inherently and noninherently dissipative uses is made with the intention of providing estimates for the dissipation of elements during use. To this end, the "in-use dissipated" stream accounts for material flows that are not accumulated into anthropogenic stocks, and a lack of collection prevents any form of recovery at end-of-life (e.g., sacrificial anodes, fertilizers), in which scattering and dispersion into the environment is planned by design. The "currently unrecyclable" stream accounts for material flows into use for which technological and/or economic barriers prevent elemental recycling, such as in the case of deoxidizing aluminum in steelmaking or the recovery of rare earth elements from

exhausted glass polishing powders. An unequivocal distinction between technical and economic reasons hindering element recycling is not always clear, because related variables are often strongly correlated. Ultimately, high market value is an incentive for recovery, and if the market value is high enough it is more likely that recycling will occur. 18 "Potentially recyclable" flows, in turn, are those for which today's technology is compatible with their recovery, enabling them to be functionally or nonfunctionally recycled/not recovered according to the United Nations Environment Programme definition.¹⁹ A fourth material stream, named "unspecified", groups those miscellaneous applications that cannot be divided among the previous material streams because of lack of data. The four metrics associated with dissipation and recovery are sketched in Figure 1. Flows of a given element enter use at point U, with a flow magnitude of 100%. Three or four principal uses generally exist for an element, together with a number of minor miscellaneous uses. The latter defy simple characterization, and are not further analyzed. One or more principal uses may be dissipated during use (examples given above); the rest are eventually discarded to the waste management and recycling (WM&R) stage. Some of the material in those discards may be currently unrecyclable, the remainder being potentially recyclable. As a graphical depiction of the results of our analyses, we show in Figure 1 a pie chart of dissipation and recycling potential for a generic element x. In this case, more than half of current element x use (by mass) is

Environmental Science & Technology

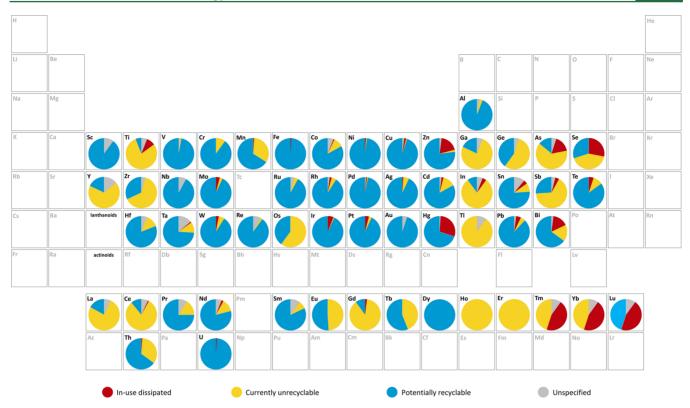


Figure 2. Percent distribution of elements among the four material streams.

potentially recyclable (the blue wedge). Between 20% and 30% is currently unrecyclable (the yellow wedge), with the remaining fraction lost by design (the red wedge) or unspecified.

Material flows into applications having a useful lifetime of one year or less do not accumulate in use and are thus assumed to exit use in their entirety in the same year (many inherently dissipative uses fall within this situation). For applications with useful lifetimes longer than one year, the degree of dissipation is calculated over the entire lifetime. An extensive data collection has been carried out from the scholarly literature and institute and association reports. Data apply to recent years, with 2008 as the average year of reference. A detailed description of the data inventory for each of the 56 metals is reported in the Supporting Information. In light of the intended goal and scope, we believe that the data used for the analysis are reasonably consistent and reliable. It is, of course, true that some level of uncertainty is associated with any estimate. We regard market shares, end-use lifetime distributions, and element release dynamic models as the main sources of uncertainty in this study. Although decreasing this uncertainty may improve the accuracy of our estimates in the future, we do not expect that a higher level of accuracy will significantly change the main conclusions of the study.

■ RESULTS AND DISCUSSION

Metal Dissipation and Recycling Potential. Mass flow percentages into the four material streams for all 56 elements are shown in Figure 2. Elements belonging to the same chemical group are often applied in the same end-use markets, and similarities in uses emerge more along groups than along chemical periods. However, some exceptions are noticeable in groups III and IV (e.g., yttrium, titanium), and for some of the

elements at the metal-metalloid boundary (e.g., aluminum, gallium, antimony, and bismuth).

Inherently dissipative uses account for more than 10% of total flow into use for only eight elements (zinc, arsenic, selenium, thulium, ytterbium, lutetium, mercury, and bismuth). The end uses responsible for this in-use dissipation include medical imaging applications (mainly for thulium, ytterbium, and lutetium), agriculture, biocide products (e.g., fungicides and pesticides), pharmaceutical uses for elements such as zinc, arsenic, selenium, bismuth, and to a lesser extent, antimony and tellurium; sacrificial anodes or galvanic protection applications (zinc, cadmium, tin, and lead), minor corrosion losses (e.g., iron and copper in architectural and building applications), zinc oxide used as a vulcanizing agent and released during tire wear, and tool abrasion (tungsten and cobalt). Mercury in-use dissipation mostly derives from its use in small scale artisanal gold mining (ASGM). 20,21 Other inherently dissipative applications include pyrotechnics to generate light, colors, and sound effects for entertainment, signaling (e.g., emergency), and military applications.²²

The situation is more complex for end-uses from which elements are currently unrecyclable. In this case, more than half of the 56 elements have unrecyclable rates higher than 10%, including most rare earths (yttrium, lanthanum, cerium, praseodymium, neodymium, europium, gadolinium, terbium, holmium, erbium, thulium, ytterbium) and specialty metals (gallium, germanium, arsenic, cadmium, indium, antimony, thallium), plus titanium, manganese, selenium, zirconium, hafnium, bismuth, thorium, and some precious metals (ruthenium, osmium, iridium). In the case of rare earth elements, recycling programs exist for praseodymium, neodymium, samarium, europium, terbium, and, dysprosium from permanent magnets, phosphors (i.e., fluorescent lamps), and rechargeable batteries (e.g., NiMH), 23-25 but not yet for

holmium, erbium, and gadolinium. Thus, complete unrecyclability characterizes these end-uses for these elements. Lanthanum and cerium have high dissipative losses due to their use in applications such as glass additives and glass polishing. Thulium and ytterbium in medical applications are regarded as unrecyclable when they are not inherently dissipated (i.e., when used as beta emitters in nuclear medicine). Yttrium's unrecyclable end-uses include phosphors, with the exception of fluorescent lamps, ²⁶ and ceramics.

Gallium, indium, and thallium, all belonging to the same chemical group, are challenging to recycle due to their use in electronics in very low concentrations. However, the development of recycling processes for indium recovery in liquid crystal displays has been a recent focus, and a significant increase in indium recycling from the electronics sector can be expected over time. ^{27,28}

Pigments cover a wide range of applications in which many elements are used in the form of compounds to apply color to paint, plastic, paper, glass, and other materials, with little or no chance for recovery at end-of-life. In this context, titanium is representative of issues that must be addressed in consideration of dissipation by design. Titanium is not generally characterized as a critical material, ^{3,29,30} but it has been recently identified as a metal that should be further investigated.²⁸ The largest market for titanium is the pigment sector, where it is mostly utilized in the form of titanium dioxide to provide white pigment for paint, plastic, and paper. The amount of titanium that is not dispersed into the environment from cracking and flaking processes due to oxidation, physical wear, and ultraviolet degradation is very likely deposited into landfills along with construction and demolition waste or reused in aggregates with low market value, 11 resulting in an unsustainable picture for this element in the long term. Apart from pigments, titanium is used in glass, ceramics, and catalysts production,³¹ in which cases it is also currently unrecyclable. Minor but increasing inherently dissipative uses of titanium include toothpaste, sunscreens, and similar products: from 2005 to 2010, nanoscale titanium dioxide used in products for personal care grew from 1 to 5 mg,³² raising further challenges for titanium recovery.

Dissipation in pigments also occurs with selenium, cadmium, and lead. Glass manufacturing is the main end-use for selenium, which is employed to decolorize green and yellow glass and to obtain pink glasses for artistic purposes, 33 while pigments based upon cadmium sulfate are used in plastics (for instance, nylon, acrylonitrile butadiene styrene, polycarbonates, high density polyethylene, silicone resins, and other thermoplastics), glass, ceramics, and artist paints (e.g., in red and yellow colors). Lead pigments have been historically used in paints for coloration and to improve drying. Although lead in paint has been restricted in many regions (e.g., United States and Europe), lead-based paints are still in use in some developing countries. 34,35

Other applications from which elements are currently unrecyclable include chemical additives and catalysts. The largest market sector for antimony is as an additive to various materials to prevent the release of flammable gases. ^{36,37} A combination of antimony trioxide with halogens (e.g., chlorinated alkyd resin) is used as a flame-retardant in adhesives, plastics (e.g., polyvinyl chloride (PVC), polyethylene, polypropylene, and polystyrene), rubber, textiles, paper, and pigments (e.g., in chromate pigments manufacturing). Tin is used as a stabilizer in PVC production, while the market for wood preservatives based on arsenic (e.g.,

chromated copper arsenate, CCA) grew after arsenic was banned for agricultural uses.³⁸ The U.S. Environmental Protection Agency has classified CCA as a restricted use product, and CCA-containing wood is no longer being produced for residential applications;³⁹ a similar restriction was also applied by the European Commission.⁴⁰ Further restrictions for the use of arsenic in wood preservatives and pesticides have been debated, but the arsenic put into use in past years will remain in in-use stocks until its final disposal, which considering the long lifetimes of buildings and constructions will not occur for many years.³⁶

Catalyst loss into products is relevant in the case of the antimony and germanium used in the production of PET bottles. Germanium oxide is a recommended substitute for antimony or titanium catalysts in this regard, although high cost has limited the use of germanium to 10% of total PET production.⁴¹ The use of germanium is due to its property of avoiding undesired coloring in the final product, and germanium oxide catalysts are designed to remain in PET bottles to enhance their brightness and transparency. Similarly, iridium and ruthenium losses derive from electrochemical applications, while tellurium is used as catalyst for the oxidation of organic compounds, hydrogenation of oils, chlorination, as a vulcanizing agent and accelerator in the processing of rubber, and as a catalyst in synthetic fibers. Due to high dispersion and scattering, tellurium recycling is not currently performed from these end-uses.^{6,42} Significant catalyst losses occur even for metals with high market value and with well-established recycling infrastructures, such as the platinum-group metals. For instance, rhodium, palladium, and platinum used in automobile catalytic converters are subjected to corrosion losses due to abrasive action, vibration, improper maintenance, and poor road conditions.4

Reducing Loss by Design. Reducing Dissipative Losses by Minimizing Problematic Uses. "Reduce, reuse, recycle" is the strategy commonly proposed for a hierarchic management of materials, an approach that would ideally provide products with less input of resources and less environmental impacts. This concept has been debated widely with regard to bulk materials, 44 but the solutions are complicated when that strategy is applied to dissipative uses. As discussed above, dissipation of elements is caused by scattering and dispersion into the environment at concentrations that prevent any form of recovery. In many cases, reducing the amount per unit of product used in applications such as pyrotechnics, pigments, or flame retardants would result in only minor improvements, if any, because the potential for further elemental reduction is limited. In other cases, the functionality of products is strictly dependent upon properties of a given element present at specific concentrations. This is the case, for example, of pharmaceuticals for which a desired dose-response effect is reauired.

The inability to collect products and materials at end-of-life also constrains reuse and recycling strategies. However, a distinction between temporary and permanent stocks of elements might reveal some opportunities for future recovery. In many inherently dissipative uses or unintentional material releases, such as in the case of marine paints, elements will accumulate into permanent environmental deposits (e.g., the ocean floor) with no potential for recovery. In other cases, the elements will be dispersed into the environment but the possibility for collection remains. This is the case for iron and copper compounds released from architectural and building

applications, and road dust containing metal particles from frictional/abrasion corrosion (e.g., zinc oxides from tire wear or copper from brake linings), 45-47 which generally do not travel very far from the source of emission and accumulate in soil. Some of these releases may be washed into municipal sewage waters. 11 The low concentrations of elements in these media appear to be not recoverable by conventional processes, but the exploration of novel collection methods has been discussed in connection with the management of future urban deposits.⁴⁸ In addition, biogeochemical cycles and undesired material releases from unintentional uses of a given element in anthropogenic cycles (e.g., outflows of lead, copper, and vanadium as trace contaminants from fossil fuel combustion and from iron and steel production)^{4,49,50} can influence the spatial and temporal magnitude of elemental accumulation in temporary and permanent deposits,⁵¹ and thus the amount potentially recyclable. The characterization of biogeochemical cycles and of unintentional uses of elements is out of the scope of this study and not further analyzed here.

Finally, many dissipative applications involve materials for which recycling is not a feasible route because of a loss of quality, a lack of appropriate technology, higher energy input than for virgin materials, and lower economic incentives compared to recycling costs. Examples in this sense include elements dispersed in plastics, paints, papers, glass, and ceramics.⁴⁴ Thus, one can ask how dissipation can be reduced and what actions would be most effective?

Restrictive measures (e.g., bans or taxations on raw materials) and the adoption of substitutes have been previously proposed as initiatives to discourage inherently dissipative uses of elements. ^{2-4,11-13} Over time a better understanding of exposure to toxic metals has resulted in a significant reduction of some harmful substances released in the environment. Typical examples are lead used as an additive in petrol or the employment of tributyl tin as an antifouling agent in marine paint. Although many bans are in force in many countries, the use of these substances cannot be entirely excluded due to lack of legislation or illicit utilization into products, 34,35 for instance, the use of arsenic compounds to create a bright blue color in pyrotechnics.⁵² Even excluding the presence of arsenic, however, pyrotechnics are recognized as transient events responsible for increasing metal accumulation in the environment and biota; 22 they constitute a signal example of in-use dissipation that has inspired research to develop alternative pyrotechnics. Compared to traditional compositions nitrogenbased pyrotechnics are smokeless, so that they do not need to compensate for the release of particle matter by adding supplemental constituents and can therefore provide colored flares with fewer amounts of additives. 52-54

Social and cultural perspectives can also be significant drivers for reducing inherently dissipative uses.⁷ For instance, a practical guide published by a United Nations panel highlighted the importance of a better awareness of governments, miners, and civil society upon technology and approaches for reducing the use of mercury in ASGM.²⁰ Some of the more promising solutions and best practices, many of them based on zero-mercury processes (e.g., gravity methods, direct smelting, and chemical leaching), would allow for environmental improvements, cost savings, and enhanced gold extraction efficiencies.²⁰

Economic incentives have historically driven material recovery and the research for substitutes. For example, among the major end-uses of cobalt, tungsten, vanadium, and rhenium is their employment in catalysis. In these applications

process losses and flows into products often resulted in significant material dissipation rates until the increasing cost of replacement resulted in efforts to recycle the catalysts as a source of secondary metals.⁵⁵ In other uses, the range of potential substitutes is limited by the intrinsic functionality of a given end-use such as for nuclear applications in which radioactive properties of certain elements are exploited,⁵⁶ or for sacrificial anodes that provide galvanic protection from corrosion to some metals.

Surface coatings containing pigments can extend the life of products such as galvanized steel. ^{57,58} However, these pigments are generally unrecyclable. In a few cases, potential for recovery may derive from the collection of single waste streams that concentrate discards with similar compositions for functional recycling. Such is the case in some countries with colored glass, in which elements such as selenium, lanthanum, and cerium are used as color additives. Due to the wide range of applications in which pigments are used, the adoption of separate collection streams based only on their color is not always consistent with efficient recycling. For instance, in the case of thermoplastics the technical feasibility of recycling is determined by compatibility with polymeric composition. 44 Thus, adopting basic design for recycling and design for resource efficiency procedures in the manufacturing of new products 42,59 may be among the most effective way to improve the potential recyclability of embodied elements.

Environmental challenges related to older pigments (for instance, those containing arsenic, lead, chromium, and mercury) have inspired efforts to substitute inorganic pigments that utilize lead and cadmium³¹ with organic compounds or biobased pigments. 60 The major barriers that limit the large scale production of these alternatives are the high cost of manufacturing, the use of fossil sources (e.g., petroleum and gas), the large quantities of solvents that are often involved in organic pigment production, and the lack of thermal stability of some biobased pigments. 31,60 Furthermore, many organic and biobased compounds show rheological properties (e.g., light scattering capacity) that are not always comparable with those of inorganic pigments. An alternative approach to address the potential toxicity of older pigments involves a new generation of inorganic pigments based on encapsulation into a silica or zircon matrix which serves as a lattice host for chromophores.31,61

Reducing Dissipative Losses by a Systems Approach. The research for substitutes has been traditionally carried out on an elemental basis: that is, when market price, environmental burdens, or criticality issues related to a given element were unsustainable, the most common approach was to look for other elements or materials that could replace that specific element at lower economic or environmental cost. This approach helped to reduce the use of toxic substances, but failed to decrease material loss and transferred dissipation from one element to another. This is in essence what happened when zinc oxide pigments were largely replaced by those of titanium dioxide. In this application, more than 80% of titanium is lost with no chance for recovery. A more comprehensive approach would be to adopt a systems perspective by concentrating on the desirable services that a product provides to the user: that is, by shifting the attention from materials to products⁵⁹ or, better yet, to the function provided. Green pyrotechnics (nitrogen substituting for metal powder) are a good example of this approach. In energy systems the spectrum of choices may include different sources (e.g., renewables). In **Environmental Science & Technology**

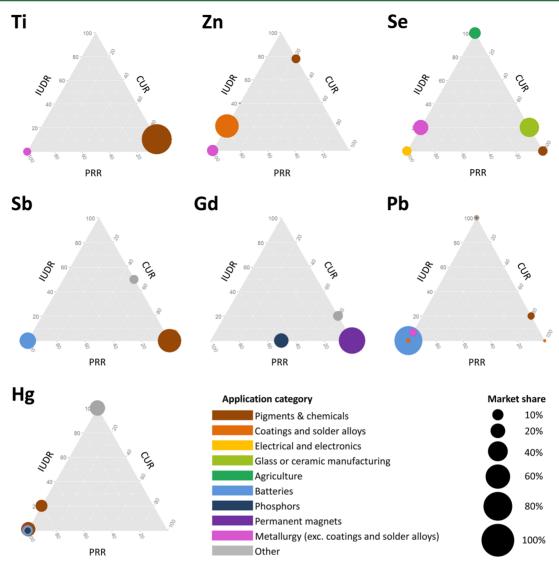


Figure 3. Ternary charts for several selected elements, displaying the application results for three metrics: IUDR, in-use dissipation rate; CUR, current unrecyclability rate; PRR, potential recyclability rate.

the case of titanium-based pigments, because of the high cost of titanium dioxide production there has been a continued research effort to identify potential alternatives. Among others, talc is a potential substitute, and a novel class of products having kaolin or calcite as a core material and titanium dioxide as the shell have been proposed as a means to reduce the amount of titanium in pigments while preserving the desired rheological properties of the final products. 63,64

Systems thinking can be of particular value in connection with complex products such as automobile catalytic converters. In this application, mixed oxides of cerium and zirconium have replaced pure cerium oxide as an oxygen-exchange coating on the ceramic support to increase the thermal stability of the alumina layer and the catalytic activity of noble metals. 65,66 However, the resulting in-use dissipation of zirconium due to vibration and corrosion now adds to ceramic applications from which zirconium is currently unrecyclable. Similarly, to reduce the losses of platinum and rhodium during nitric acid production palladium catchment gauzes were introduced in 1968. Platinum loss (in the form of platinum dioxide) is about 30%, but with the help of these gauzes some 80% of the vaporized platinum and 50% of the rhodium can be

recovered.^{68,69} A further benefit of using palladium gauzes is that they decrease greenhouse gas emissions by reducing nitric oxide (formed during the process) to nitrogen. However, 30% of the palladium is lost during the platinum recovery process.⁶⁹

Reducing Dissipative Losses during the Design of Products. A lack of precision in defining elemental dissipation has been previously highlighted.^{3,4} This has made it difficult for product designers to anticipate the resource benefits possible from minimizing dissipation. We believe that an improved understanding of loss by design will provide guidance to industry in investigating routes for reducing material losses and supporting the development of options for increasing element recovery at EOL. To this aim, Figure 3 displays the results by use for several selected elements for in-use dissipation rate (IUDR), the current unrecyclability rate (CUR), and the current potential recyclability rate (PRR). These metrics correspond to the three material streams identified in Table 1, but have been rescaled to 100% of flow into principal uses after excluding unspecified applications. Figure 3 can thus be used to provide a reference as to how far off-target each current application is. A transition toward more sustainable use of a metal over time requires the shift of the spectrum of its uses toward the lower

left corner of the ternary diagram, such that all principal uses are potentially recyclable (i.e., ideally to 100% PRR, 0% CUR, and 0% IUDR).

A detailed example will demonstrate the understanding provided by Figure 3 diagram. The ternary chart for selenium displays 100% potential recyclability only for selenium applications in electronics (the main source of selenium old scrap). Negligible selenium emissions during use are assumed from electronics because they exist in protected environments. The remaining four selenium market sectors have various rates of selenium losses. With the exception of the agricultural sector, in which selenium is applied as an essential and irreplaceable nutrient, 56 new approaches to the use of selenium in glass manufacturing, metallurgy, and pigments have the potential to reduce selenium's "loss by design". In glass manufacturing selenium is used to reduce solar heat transmission in architectural applications and for color purposes. Elemental selenium was previously added to glass, but losses due to vaporization were greater than 50%. To decrease this unintentional release, selenium compounds (e.g., sodium selenite and selenate) are now used instead, although some losses remain.³³ Additional in-use dissipation of selenium derives from its employment in metallurgy due to volatilization losses. Because glass manufacturing and metallurgy are the largest market sectors for selenium, actions aimed at reducing these losses would have the greatest effect on decreasing selenium in-use dissipation. Selenium's minor end-uses include its employment as a thermal stabilizer in rubber production, as a catalyst for hydrocarbons, as an additive in the preparation of dental fillings, and as a red pigment for plastic and paints. The selenium that remains embodied in finished products, either as glass, rubber, or plastic goods, is currently unrecyclable. 13A small amount of the selenium used in photocopiers, electrical rectifiers, and solar cells is recovered and reprocessed into a secondary input material. 70 Overall, the sum of in-use dissipation and current unrecyclability for selenium reduces its potential recyclability to 30% of the element flow into use, 70 but recycling process inefficiencies shrink that potential to 1% or less.

Similar considerations can be extended to elements other than selenium. For most base and precious metals the goal of 100% potential recyclability has been achieved, or nearly so. For others, particularly the specialty metals and rare earth metals, much remains to be done. ^{19,71} Improved recycling rates for these elements will not be possible so long as their IUDR and CUR values are significantly above zero. In addition to addressing dissipation, it is important to remember that losses can and do occur after use. This is of most concern for elements that have relatively small geological reserves and that are used for short periods of time. It is therefore important not only to reduce in-use dissipation but also to convert the "potentially recyclable" fraction into "currently recyclable".

In conclusion, in this study a comprehensive perspective on the uses of materials in modern society has been used to measure the degree to which elements are currently lost by design, or because of the absence of any potential for recovery at end-of-life. The complexity of today's materials and the demands of product performance lead to a wide range of applications in which elements are commonly used. As a consequence, dissipative uses are present throughout the periodic table. What may be most surprising is that in many cases the use of elements in dissipative or currently unrecyclable applications represents more than 50% of the

annual input flow, thus already constraining progress toward a circular economy. Among others, specialty metals and heavy rare earths are representative of modern technology, ⁷² and their dissipation rates provide a measure of their levels of unsustainable use in contemporary materials and products. The continuing miniaturization of products and the increasing integration of materials in products suggest that the future of metal recovery and recycling may be even more problematic in coming years than is now the case.

In this sense, the metrics investigated in this work (i.e., IUDR, CUR, and PRR) identify pathways toward the development of technologies that may modify current patterns of inherently dissipative uses and currently unrecyclable applications. However, because material dissipation is often by design, it is precisely in the design and manufacture of products that the most effective actions can be undertaken to avoid or reduce material losses. We thus advocate a transition from approaches that involve loss by design to those striving instead for retention by design. Such actions will likely go far in improving the long-term sustainability of the metals that are crucial to modern technology.

ASSOCIATED CONTENT

Supporting Information

A detailed description of sources of data, assumptions, and proxy data is reported in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Phone: 203.432.4246; fax: 203.432.5556; e-mail: luca.ciacci@yale.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was funded by the United States National Science Foundation and by the "Wealth from Waste Cluster", a research collaboration between the Australian Commonwealth Scientific and Industrial Research Organisation (CSIRO), University of Technology Sydney (UTS), The University of Queensland, Swinburne University of Technology, Monash University, and Yale University. We gratefully acknowledge the contribution of each partner and the CSIRO Flagship Collaboration Fund. The Wealth from Waste Cluster is part of the Minerals Resources Flagship and is supported by the Manufacturing Flagship.

REFERENCES

- (1) Oxford English Dictionary (OED). http://www.oed.com/(accessed October, 2014).
- (2) Ayres, R. U., Industrial metabolism: Theory and policy. In *The Greening of Industrial Ecosystems*; Allenby, B. R., R, D., Ed.; National Academy Press: Washington, D.C., 1994; pp 23–37.
- (3) Zimmermann, T.; Gößling-Reisemann, S. Critical materials and dissipative losses: A screening study. *Sci. Total Environ.* **2013**, *461*–462, 774–780.
- (4) Lifset, R. J.; Eckelman, M. J.; Harper, E. M.; Hausfather, Z.; Urbina, G. Metal lost and found: Dissipative uses and releases of copper in the United States 1975–2000. *Sci. Total Environ.* **2012**, 417–418, 138–147.
- (5) Allwood, J. M.; Cullen, J. M. Sustainable Materials with Both Eyes Open; UIT Cambridge Ltd.: Cambridge, UK, 2012.

- (6) Graedel, T. E.; Harper, E. M.; Nassar, N. T.; Reck, B. K. On the materials basis of modern society. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, DOI: 10.1073/pnas.1312752110.
- (7) Reck, B. K.; Graedel, T. E. Challenges in metal recycling. *Science* **2012**, 337 (6095), 690–695.
- (8) Eckelman, M. J.; Reck, B. K.; Graedel, T. E. Exploring the global journey of nickel with markov chain models. *J. Ind. Ecol* **2012**, *16* (3), 334–342.
- (9) Izard, C. F.; Müller, D. B. Tracking the devil's metal: Historical global and contemporary U.S. tin cycles. *Resour. Conserv. Recyl.* **2010**, 54 (12), 1436–1441.
- (10) Gordon, R. B.; Bertram, M.; Graedel, T. E. Metal stocks and sustainability. Proc. Natl. Acad. Sci. U.S.A. 2006, 103 (5), 1209-1214.
- (11) Ayres, R. U. Toxic heavy metals: Materials cycle optimization. *Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89* (3), 815–820.
- (12) Peiró, L. T.; Méndez, G. V.; Ayres, R. U. Material flow analysis of scarce metals: Sources, functions, end-uses and aspects for future supply. *Environ. Sci. Technol.* **2013**, *47* (6), 2939–2947.
- (13) Ziemann, S.; Schebek, L.; Weil, M. Dissipative application of lithium—Lost for the future? *Metall. Res. Technol.* **2012**, *109* (05), 341–347.
- (14) Azapagic, A.; Perdan, S. Indicators of sustainable development for industry: A general framework. *Process Saf. Environ. Prot.* **2000**, 78 (4), 243–261.
- (15) Heijungs, R; Huppes, G; Guinée, J Scientific Framework for LCA. Deliverable (D15) of CALCAS Project. Institute of Environmental Sciences; Leiden University (CML), 2009; http://www.calcasproject.net.
- (16) Jeswani, H. K.; Azapagic, A.; Schepelmann, P.; Ritthoff, M. Options for broadening and deepening the LCA approaches. *J. Clean. Prod.* **2010**, *18* (2), 120–127.
- (17) Ciacci, L.; Eckelman, M. J.; Passarini, F.; Chen, W.-Q.; Vassura, I.; Morselli, L. Historical evolution of greenhouse gas emissions from aluminum production at a country level. *J. Clean. Prod.* **2014**, *84*, 540–549.
- (18) Dahmus, J. B.; Gutowski, T. G. What gets recycled: An information theory based model for product recycling. *Environ. Sci. Technol.* **2007**, 41 (21), 7543–7550.
- (19) United Nations Environment Programme (UNEP). Recycling Rates of Metals—A Status Report, A report of the Working Group on the Global Metal Flows to the International Resource Panel; Graedel, T. E. et al., 2011.
- (20) United Nations Environment Programme (UNEP). A Practical Guide—Reducing Mercury Use in Artisanal and Small-Scale Gold Mining; Telmer K., Stapper D. et al., 2012.
- (21) Eckelman, M. J.; Anastas, P. T.; Zimmerman, J. B. Spatial assessment of net mercury emissions from the use of fluorescent bulbs. *Environ. Sci. Technol.* **2008**, 42 (22), 8564–8570.
- (22) Moreno, T.; Querol, X.; Alastuey, A.; Cruz Minguillón, M.; Pey, J.; Rodriguez, S.; Vicente Miró, J.; Felis, C.; Gibbons, W. Recreational atmospheric pollution episodes: Inhalable metalliferous particles from firework displays. *Atmos. Environ.* **2007**, *41* (5), 913–922.
- (23) Rhodia to Recycle Rare Earths from Magnets; Rhodia, 2011.
- (24) Umicore, Umicore and Rhodia Develop Unique Rare Earth Recycling Process for Recheargeable Batteries; Rhodia, 2011.
- (25) Rollat, A. How to satisfy the Rare Earths Demand—Rhodia Rare Earth Systems Initiatives; Rhodia, 2012
- (26) Burridge, E. ICIS Innovation Award 2012: Closing the Loop on Rare Earths; ICIS, 2012
- (27) Caffarey M., Umicore Precious Metals Refining. 2012. http://www.serdc.org/Resources/Documents/Summit%20Presentations/SERDC%20Summit%20Presentation%20-%20Mark%20Caffarey.pdf (accessed October 2014)..
- (28) Buchert, M.; Schüler, D.; Bleher, D. Critical Metals for Future Sustainable Technologies and Their Recycling Potential; United Nations Environment Programme (UNEP), 2009
- (29) Critical Raw Materials for the EU. Report of the Ad-Hoc Working Group on Defining Critical Raw Materials; European Commission: Bruxells, 2010.

- (30) Gunn, G. Critical Metals Handbook, British Geological Survey; Wiley & Sons: Keyworth, Nottingham, UK, 2014.
- (31) Swiler, D. R. Pigments, inorganic. In Kirk-Othmer Encyclopedia of Chemical Technology; John Wiley & Sons, Inc., 2000.
- (32) Weir, A.; Westerhoff, P.; Fabricius, L.; Hristovski, K.; von Goetz, N. Titanium dioxide nanoparticles in food and personal care products. *Environ. Sci. Technol.* **2012**, *46* (4), 2242–2250.
- (33) Langner, B. E. Selenium and selenium compounds. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
- (34) Adebamowo, E. O.; Scott Clark, C.; Roda, S.; Agbede, O. A.; Sridhar, M. K. C.; Adebamowo, C. A. Lead content of dried films of domestic paints currently sold in Nigeria. *Sci. Total Environ.* **2007**, 388 (1–3), 116–120.
- (35) Anne, H. Lead-Laden Paint Still Widely Sold around the World; Reuters, 2009.
- (36) Grund, S. C.; Hanusch, K.; Breunig, H. J.; Wolf, H. U. Antimony and antimony compounds. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA, 2008.
- (37) Carlin, J. F. J. Antimony recycling in the United States in 2000; U.S. Geological Survey, 2006
- (38) Loebenstein, J. R. Materials Flow of Arsenic in the United States, 1994.
- (39) Chromated Copper Arsenate (CCA); U.S. Geological Survey, 2011.
- (40) Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE); European Commission2013.
- (41) Melcher, F., Buchholz, P. Germanium; John Wiley & Sons, Ltd, 2014.
- (42) Geological Survey (U.S.)Tellurium. In *Minerals Yearbook*; U.S. Geological Survey, 2014.
- (43) Nassar, N. T. Anthropospheric losses of platinum group elements. In *Element Recovery and Sustainability*, Chapter 7; The Royal Society of Chemistry, 2013; pp 185–206.
- (44) Allwood, J. M., Squaring the circular economy: The role of recycling within a hierarchy of material management strategies. In *Handbook of Recycling*; Ernst Worrell, M. A. R., Ed.; Elsevier Inc.: Waltham MA, 2014.
- (45) Burkhardt, M.; Rossi, L.; Boller, M. Diffuse release of environmental hazards by railways. *Desalination* **2008**, 226 (1–3), 106–113.
- (46) Adachi, K.; Tainosho, Y. Characterization of heavy metal particles embedded in tire dust. *Environ. Int.* **2004**, *30* (8), 1009–1017. (47) Councell, T. B.; Duckenfield, K. U.; Landa, E. R.; Callender, E. Tire-wear particles as a source of zinc to the environment. *Environ. Sci. Technol.* **2004**, *38* (15), 4206–4214.
- (48) Wittmer, D.; Lichtensteiger, T. Exploration of urban deposits: Long-term prospects for resource and waste management. *Waste Manage Res.* **2007**, 25, 220–226.
- (49) Elshkaki, A.; Voet, E. v. d.; Holderbeke, M. V.; Timmermans, V. Long-term consequences of non-intentional flows of substances: Modelling non-intentional flows of lead in the Dutch economic system and evaluating their environmental consequences. *Waste Manage* **2009**, 29 (6), 1916–1928.
- (50) Soldi, T.; Riolo, C.; Alberti, G.; Gallorini, M.; Peloso, G. F. Environmental vanadium distribution from an industrial settlement. *Sci. Total Environ.* **1996**, *181* (1), 45–50.
- (51) Klee, R. J.; Graedel, T. E. Elemental cycles: A status report on human or natural dominance. *Annu. Rev. Env Resour* **2004**, 29 (1), 69–107.
- (52) Sterba, J.; Steinhauser, G.; Grass, F. Illicit utilization of arsenic compounds in pyrotechnics? An analysis of the suspended particle emission during Vienna's New Year fireworks. *J. Radioanal Nucl. Chem.* **2013**, 296 (1), 237–243.
- (53) Fischer, N.; Klapötke, T. M.; Peters, K.; Rusan, M.; Stierstorfer, J. Alkaline earth metal salts of 5,5'-Bistetrazole—From academical interest to practical application. *Z. Anorg. Allg. Chem.* **2011**, 637 (12), 1693–1701.

- (54) Steinhauser, G.; Klapötke, T. M. Using the chemistry of fireworks to engage students in learning basic chemical principles: A lesson in eco-friendly pyrotechnics. *J. Chem. Educ.* **2010**, 87 (2), 150–156.
- (55) Eijsbouts, S.; Battiston, A. A.; van Leerdam, G. C. Life cycle of hydroprocessing catalysts and total catalyst management. *Catal. Today* **2008**, *130* (2–4), *361*–373.
- (56) Enghag, P. Encyclopedia of the Elements—Technical data, History, Processing, Applications; Wiley-VCH: Weinheim, Germany, 2004.
- (57) Karlén, C.; Odnevall Wallinder, I.; Heijerick, D.; Leygraf, C.; Janssen, C. R. Runoff rates and ecotoxicity of zinc induced by atmospheric corrosion. *Sci. Total Environ.* **2001**, 277 (1–3), 169–180.
- (58) Duplex System—Painting Over Hot-Dip Galvanized Steel; American Galvanizers Association (AGA): Centennial, CO, 2012.
- (59) Metal Recycling: Opportunities, Limits, Infrastructure. A Report of the Working Group on the Global Metal Flows to the International Resource Panel; Reuter, M. A., Hudson, C., van Schaik, A., Heiskanen, K., Meskers, C., Hagelüken, C., Eds.; United Nations Environment Programme (UNEP), 2013.
- (60) Shen, J.; Song, Z.; Qian, X.; Ni, Y. Carbohydrate-based fillers and pigments for papermaking: A review. *Carbohydr. Polym.* **2011**, 85 (1), 17–22.
- (61) Jaffe, E. E., Pigments, Organic. In Kirk-Othmer Encyclopedia of Chemical Technology; John Wiley & Sons, Inc., 2000.
- (62) Levitt, T. Marketing Myopia; Harvard Business Review, 1960.
- (63) Ahmed, N. M.; Selim, M. M. Innovative titanium dioxide-kaolin mixed pigments performance in anticorrosive paints. *Pigm. Resin Technol.* **2011**, 40 (1), 4–16.
- (64) Karakaş, F.; Çelik, M. S. Effect of quantity and size distribution of calcite filler on the quality of water borne paints. *Prog. Org. Coat.* **2012**, 74 (3), 555–563.
- (65) Kašpar, J.; Fornasiero, P.; Hickey, N. Automotive catalytic converters: Current status and some perspectives. *Catal. Today* **2003**, 77 (4), 419–449.
- (66) Helmers, E. Elements accompanying platinum emitted from automobile catalyst's. *Chemosphere* **1996**, 33 (3), 405–419.
- (67) Johnson Matthey. Nitric acid manufacture and uses. http://www.platinum.matthey.com/about-pgm/applications/industrial/nitric-acid (accessed October 2014).
- (68) Holzmann, H. Platinum recovery in ammonia oxidation plants. *Platinum Metals Rev.* **1969**, *13* (1), 2.
- (69) Hagelüken, C.; Buchert, M.; Stahl, H. Materials Flow of Platinum Group Metals—systems Analysis and Measures for Sustainable Optimization of the Materials Flow of Platinum Group Metals; GFMS, Ltd.: London, 2005.
- (70) George M. W.; Wagner L. A. Selenium Recycling in the United States in 2004; U.S. Geological Survey, 2009; Circular 1196-T, p 12.
- (71) Graedel, T. E.; Allwood, J.; Birat, J.-P.; Buchert, M.; Hagelüken, C.; Reck, B. K.; Sibley, S. F.; Sonnemann, G. What do we know about metal recycling rates? *J. Ind. Ecol* **2011**, *15* (3), 355–366.
- (72) Greenfield, A.; Graedel, T. E. The omnivorous diet of modern technology. *Resour. Conserv. Recyl.* **2013**, 74 (0), 1–7.