

# 5th CS3 2013

Efficient Utilization of Elements

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# The Chemical Sciences and Society Summit (CS3)

## The CS3

The annual Chemical Sciences and Society Summit has brought together some of the most accomplished chemists from around the globe and has challenged them to propose meaningful approaches to solving society's most pressing needs in the areas of health, food, energy, and the environment. This unique event has been conducted in a highly constructive format, and has rotated each year among the participating countries. The Efficient Use of Elements summarizes the fifth CS3 meeting, which was held in Narita, Japan in September 2013. Over 30 chemists representing the five participating countries worked together to identify and clarify problems associated with the rapid increase in demand for scarce elements and propose rational, meaningful approaches to resolving these serious problems facing society. This report presents a summary of the resource problems we face and what must be done to find effective solutions as discussed by the participating scientists.

The CS3 initiative is a collaboration between the Chinese Chemical Society (CCS), the German Chemical Society (GDCh), the Chemical Society of Japan (CSJ), the Royal Society of Chemistry (RSC) and the American Chemical Society (ACS). The symposia are supported by the National Science Foundation of China (NSFC), the German Research Foundation (DFG), the Japan Society for the Promotion of Science (JSPS), the UK Engineering and Physical Sciences Research Council (EPSRC), and the USA National Science Foundation (NSF).

## Executive Summary

The past few decades have brought forth advances in technology, particularly with respect to communications, information technology, and consumer products. This has led to unprecedented levels of comfort and convenience, improved medical diagnostics and treatment, more efficient transportation, and rapid access to quantities of information that were unimaginable a generation ago. This however, has been accompanied by considerable depletion of resources,

compounded by increases in population and fully legitimate efforts by many in non-industrialized countries to obtain the material comforts of the industrialized world.

Much of this technological progress has been realized because of advances in our understanding of chemistry, physics, and materials science. The ability to harness the unique characteristics of certain elements that until recently were little more than laboratory curiosities has brought into being stronger magnets, smaller microprocessors, more efficient solar cells, lighter structural materials, and a plethora of advanced technology. These innovations have enabled great progress towards fulfilling societal needs and desires.

However, much of this new technology is heavily dependent on scarce elements. It has been reported that industrial giant General Electric uses 72 of the first 82 elements in its product line, and many of these elements are rare or are difficult to obtain.<sup>1</sup> The popularity of smart phones, tablets, and other consumer electronics has caused a dramatic increase in the demand for rare earth elements such as europium, terbium, and lanthanum, on which these current technologies are dependent.

Many energy technologies are dependent on scarce elements that limit their applicability. Photovoltaic devices offer potential as a sustainable, versatile energy source, however next-generation devices typically contain rare elements such as indium, gallium, germanium, tellurium, and rhodium. Development of high performance devices without the use of these expensive metals would greatly reduce cost and increase the economic viability of solar power. Fuel cells are another area in which scarce materials are necessary in current devices, such as cerium in high temperature fuel cells, and platinum in low temperature devices. One other area of particular concern is the use of rare earth elements like neodymium and dysprosium in high performance magnets. Significant quantities of these critical elements are needed for magnets that can be used in high temperature applications such as electric automobiles, including hybrids, as well as wind turbines for

electricity generation. The need for more efficient use as well as alternatives is a serious problem that must be solved.

Precious metals like palladium, rhodium, osmium, platinum, and iridium are frequently used as catalysts in the manufacture of pharmaceuticals and commodity chemicals as well as household consumer goods. And automobile catalytic converters account for a large portion of the demand for platinum and rhodium.

There are many approaches to resolving problems of material scarcity, and a multi-faceted strategy will be necessary to avoid serious disruptions. In some cases scarce elements can be replaced by earth-abundant alternatives, and this is desirable, however not always possible. Often the unique physical and chemical characteristic of one particular element or a small group of elements are indispensable for a particular application, and in cases where a substitution can be made, there is often loss of performance. However in other cases it may be possible to decrease the amount of the critical element or elements by optimizing structure or operating conditions, or by the presence of other common elements to achieve the desired performance. Because elements are *de facto* a strictly limited resource, it is important to focus on recovery and recycling. It is crucial that these critical resources be used with consideration of the entire utilization cycle, from mining, to manufacturing, to recovery, and to reuse.

Solving many of these problems will require a coordinated, global approach. Public support for training scientists and engineers, public and private investment in research facilities including universities, and pre-competitive collaboration and communication among industry and academia are vital to resolving the serious resource problems facing society. Additionally, clear public policy and science-based regulations are necessary to insure a coordinated, coherent, and international effort. These are not issues that will be solved by any one country, corporation, or institution.

One compelling example of the need for action is the case of peak phosphorus. Phosphorus, although not scarce, is absolutely necessary for life as we know it on earth, and there is absolutely no substitute for it. It is currently mined at a rate of 20 million tons per year as phosphate rock, 90% of which is used as fertilizer, on which approximately two-thirds

of agricultural production is dependant. It is expected that shortages of phosphate will occur in the next 50 to 150 years, which assuming the status quo, would lead to serious famine. The case of phosphorus is not unsolvable; it is a plentiful element, and changes in agricultural practices, improved phosphorus use and recovery, and addressing the population issue, when combined, could lead to a reasonable solution. Inaction however, could lead to dire consequences. It must be stressed that critical element depletion has potential consequences more serious than the already serious problems of peak oil and global warming, and that clear, comprehensive actions must be taken now to avoid future disruption.

## Introduction

Securing resources has always been a central activity of human society, and as technology changes, the demand for resources also changes. With the industrial revolution, in addition to agricultural commodities like timber, wool, and cotton, the demand for mineral resources and fossil fuels increased dramatically with telling political and environmental consequences. Industrial advances in the 20<sup>th</sup> century led to even greater demand and consumption. In the beginning of the 21<sup>st</sup> century, the appetite for resources remains voracious, and in fact has grown to include a desire for many elements that are scarce or difficult to obtain, and/or leave a large environmental footprint when they are extracted. Many of these elements are not found in deposits of sufficient concentration to mine as a primary target, and in fact are obtained as by-products of refining other minerals. These scarce elements generally occur as atomic substitutes in common ores, and thus do not exist as a distinct mineral, but rather as an impurity. Two examples of this are tellurium, a by-product of copper refining, and indium, which occurs with zinc and lead ores. As a result, the availability of a scarce element can be directly related to the demand for a common commodity.

There are a significant number of elements that are often described as critical. For example, because of their high activity and chemical selectivity, precious metals like palladium, rhodium, osmium, platinum, and iridium are frequently used as catalysts in the manufacture of pharmaceuticals and commodity chemicals as well as household

consumer goods. The high power-density magnets used in electric motors in hybrid cars and modern electric generators require rare earth metals such as neodymium, terbium, dysprosium, and promethium in order to operate at high temperature. And automobile catalytic converters account for a large portion the demand for platinum and rhodium. Furthermore, modern electronic devices such as computers and smart phones contain a complex mixture of elements such as indium, many of which are scarce, and little of which is recovered.

#### A few elements that could be in a smart phone



It is important to distinguish the difference between scarce and critical. A scarce element is one that exists in low abundance on earth, for example, platinum or tellurium, and a scarce element might not be critical if the demand is either low or highly elastic. A critical element, on the other hand, might not actually be rare, but demand is high and availability may be limited or at risk due to technical, political, or social factors, or obtaining the element may create a large environmental burden. Determining which elements are critical is beyond the scope of this report, and detailed discussion of criticality and scarcity can be found elsewhere.<sup>2</sup>

The looming crisis of resource depletion is not limited to precious metals. Although vast reserves of lithium are known, particularly in Argentina and Bolivia, the huge increase in demand for lithium batteries suggests that recycling strategies should be seriously considered in addition to developing batteries with extended service life. With current technology, there are sufficient reserves of lithium to provide batteries for 12 billion cars, and it can be recycled when the batteries fail. Nevertheless, because of the high demand, lithium use should be thought of in terms of economic efficiency, environmental compatibility, and stable supply.

Table 1: Examples of Critical Elements

Element	Use	Current Reserves
Rhodium	Manufacturing fine and commodity chemicals, pharmaceuticals, exhaust catalyst	At current consumption 160 years
Platinum	Manufacturing fine and commodity chemicals, pharmaceuticals, exhaust catalyst	At current consumption 160 years
Indium	Electronics, touch screens, LEDs	At current consumption 24 years
Tellurium	Solar cells	Unclear, occurs with copper ore
Neodymium	High performance magnets, lasers	As of 2010, 420 years. Demand is rapidly increasing.
Dysprosium	High performance magnets	209 years but demand is rapidly increasing

Halada, Katagiri. *Proc. Of EcoBalance 2010*, pp 609

Table 2: Energy and Elements

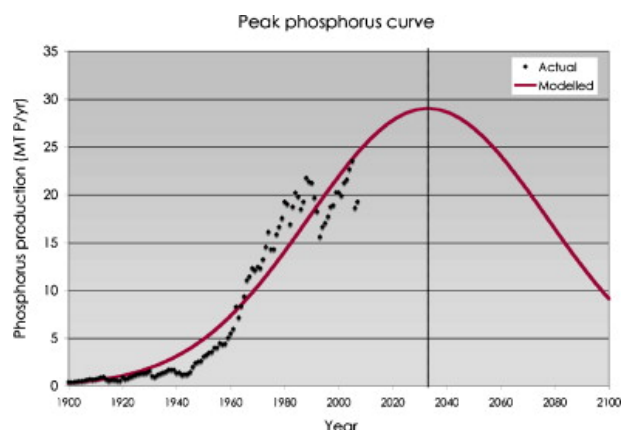
Technology	Applications	Critical Elements
Batteries	Transportation, electronics, generation systems	Currently lithium
Photovoltaic devices	Solar power	Indium, gallium, germanium, tellurium, ruthenium
Magnets	Generators (wind turbines), motors	Neodymium, dysprosium, terbium
Superconductors	Chemical and medical imaging, transportation, potential use in computers and power transmission	Helium, lanthanides
Thermoelectrics	Power generation	Tellurium, ytterbium, cerium
Fuel cells	Power generation, transportation, mobile power sources	Yttrium, scandium, platinum

Many of the new approaches to increased efficiency require a variety of critical resources, and the technologies being developed may reduce pressure on one or more resources, yet at the same time rely heavily on elements that are scarce and/or difficult to obtain. For example, modern LCD televisions are significantly more energy efficient than the older cathode ray tube devices, however, they require additional rare elements. It is therefore absolutely necessary to view efficient use of elements both at a systemic level as well as on a specific application level in order to achieve balanced solutions.

In addition to solving technical challenges, it is equally important to consider social, political, and economic challenges as well. While free market economic mechanisms and social tradition may be effective means for responding to some aspects of a changing world, resource depletion has reached a level of seriousness at which policy, and direct cooperation between governments, corporations, universities, and other social institutions is vital.

The results of inaction could be serious. Our dependence on the latest modern technology has become so great, particularly dependence on computers, that a lack of a few key elements could prevent not only the manufacture of new devices, but also the replacement of equipment that has exceeded its usable lifetime. This is not a hypothetical problem, there are a number of elements crucial to current technology for which known reserves will be exhausted within several decades at current consumption, and not all of them are generally thought of as exotic. Based on current consumption trends and known reserves, silver, lead, and tin are all expected to be in short supply within 30 years.<sup>3</sup> This is not to say that new reserves will not be discovered, however, new reserves may be difficult to access and hence economically unviable. Much more troubling is the prospect of phosphorus depletion. Global demand for phosphorus is roughly 20 million tons per year, and growing at a rate of 2.5% per year. Current reserves are not clearly known, as they are reported by the producers and have not been confirmed officially. This element is of particular concern because currently two thirds of global food production relies on fertilizers containing mineral phosphorus, and without it, two thirds of the human population, or more than 4 billion people, would go hungry. The sudden disappearance of minable

phosphate ore is of course an unlikely scenario, however, fairly rapid depletion of readily accessible ore to a point where availability is significantly reduced is likely at current rates of consumption, and agricultural practices as well as population issues must be addressed in order to avoid serious food shortages. It must be stressed that phosphorus is absolutely essential for life as we know it, and there is absolutely no substitute for it.



*D. Cordell, J-O. Drangert, S. White. Global Environmental Change 19 (2009) pg 298*

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## Where does Chemistry fit in?

Chemistry is concerned with what constitutes materials, how they change and react, and how they can be created and controlled by humans. It is also concerned with the energy released or consumed through these changes, and how to control it. Chemistry is fundamental to all science and technology. This is particularly true for technology that requires new materials, for example, solar and fuel cells, batteries, and microprocessors.

The efficient use of elements can be divided into several components. Substitution of critical elements with more abundant elements is a primary goal, for example, replacing palladium with iron as a catalyst in a cross-coupling reaction. These types of replacements, however, require sustained effort in basic research. Replacement is however, not always possible. Often it is easier to just reduce the amount of critical elements used by optimizing reaction conditions or by use of a co-catalyst. There are numerous examples of this approach, however, these advances often require significant research effort. Efficient recycling can, in some cases,

partially relieve supply issues. For example, iron and lead are extensively recycled. Because the properties of elements are not changed by use, if a desired element can be recovered from a product at the end of use, it can be further used and can reduce pressure on natural reserves. Recycling as well is not always simple and can require applied research. In many applications critical elements are used in small quantities, which can make separation quite difficult. Where substitution is not possible, an alternate and often more challenging approach is to develop completely new materials and systems to achieve the same goal. This can often require not only applied development but also fundamental research. And finally, providing research based rational for regulation and public policy may be necessary. In addition to ensuring sufficient resources are available for research, governments need to vigorously encourage change on a societal scale through legislation and regulation. For example, manufacturers should be encouraged, or perhaps in some cases compelled, to include full life-cycle analysis in product design, including recycling and resource recovery, and consumers should be encouraged to return items at the end of their service life for proper treatment.

In this report, areas in which chemical research and development are central to both technological advances as well as efficient use of elements are divided into three groups. Materials for energy production and storage, that is, materials used to construct solar and fuel cells, batteries, magnets, and other devices, often contain critical elements. Catalysts are absolutely critical in many areas of manufacturing, particularly commodity chemicals, and often contain precious metals. And recovery, reuse, and recycling are important in the short term, and critical in the long term, because we do live on a finite planet. Because the chemistry world is economically global and many elements are unevenly distributed geographically, it is important to approach availability questions in all of these areas as a joint international effort.

## Materials for Energy

The need for reliable energy sources and effective means of power generation has been a focus of human attention since the beginning of the industrial revolution. Despite dramatic increases in efficiency and reduction of

relative environmental burden, continued heavy reliance on fossil fuels has led to environmental consequences, such as pollution and global warming. In order to maintain the current standard of living, better ways of generating power and storing energy are indispensable, and as population increases, a more dramatic improvement in technology will be necessary. Among the various technologies being explored to address power needs, many of them require the use of critical elements, and in order to fully exploit them, efficient use or replacement issues must be resolved.

Power generation is generally thought of as being in the realm of engineering, yet chemistry has played and continues to play a crucial role in its development. Combustion of fuels, charge and discharge cycles of batteries, and the operation of fuel cells are all chemical reactions, and the design and construction of the materials used in modern devices rely on increasingly sophisticated knowledge of chemistry. The search for and synthesis of new materials requires consideration of both the reactivity of the starting materials and the desired functionality and possible applications of the product. Additionally, it is becoming increasingly necessary to also consider the availability and collateral impact of the elements utilized in constructing these new materials. Materials design using efficient utilization of elements as a parameter is a relatively new approach, and requires an added context in chemical education and research planning. Detailed discussion of critical elements specific to energy materials can be found in other reports.<sup>4</sup> Within the realm of energy materials, there are a number of areas that are of particular importance.

## Batteries

Batteries are becoming increasingly important in both the more conventional role in mobile applications as well as in stationary applications (household use, back-up in generating systems, stabilizing the electrical grid). There are many objectives involved in new battery design, including high energy density, power density, long-term stability, reduced cost, and enhanced safety. Improved battery designs require stable oxidation states of the active redox pairs, optimized electrolytes with respect to stability and ionic conductivity in an application specific temperature range, and searching for abundant light element combinations that can

be used as effective redox pairs. Replacing critical elements like cobalt and finding appropriate catalysts for metal air batteries is also necessary.

At present there are several battery chemistries available commercially, each with distinctive positive attributes, and each with distinctive weaknesses to be addressed with further research. One example, lithium ion batteries, with high energy density and demonstrated efficacy in consumer electronics, are the current battery of choice for powering most electric automobiles. Unfortunately, high battery cost, limited cycle life, limited range, and continued safety concerns have hindered general adoption of electric vehicles. One of the principle safety issues for current lithium ion batteries arises from the presence of liquid organic electrolytes. These volatile and flammable liquids pose a serious fire risk when exposed to severe conditions, such as high cell temperatures from external sources or to high voltage stress due to overcharging. Similarly, lithium polymer cells can suffer catastrophic failure when punctured or overcharged. Replacing the organic electrolyte with a solid, non-combustible electrolyte would eliminate this safety risk and provide additional important benefits such as substantially extended cycle life and a reduced self-discharge rate. Furthermore, recycling and reuse strategies need to be widely adopted to ensure reliable supplies of the elements necessary for these systems.

## Photovoltaic Devices

Because of the vast quantity of energy delivered to earth as sunlight, solar energy is viewed as a highly attractive source of power. Current photovoltaic technology is rapidly approaching the maximum expected efficiency, with silicon photovoltaic cells, the most common type of commercial photocell, providing 25% power conversion efficiency under laboratory conditions. Despite efficiency of commercial cells reaching nearly 75% of that in experimental cells, the cost of silicon-based units is still too high to compete with fossil fuel energy. Silicon itself is highly abundant, however, refining the element to the necessary purity is very energy intensive (and hence, expensive). Developing cheaper methods of production would greatly enhance the economic viability of current photovoltaic cell designs. Efforts to reduce the cost of solar cells have also been made with thin film 2nd

generation devices by incorporating absorber material(s) with improved optical properties such that the material used per module can be dramatically reduced. The cost of 2nd generation photovoltaic modules, however, remains high due to the necessity of high temperature fabrication, reducing the compatibility with inexpensive substrates, as well as the necessary use of expensive elements such as indium, gallium, germanium, tellurium, and ruthenium. One big goal is to discover new materials with desired properties but made of earth abundant elements, and the design of a system that exhibits minimized resistive losses as deposited, and that can achieve bulk type carrier transport through nanocrystal or polycrystalline thin films in a single deposition. More generally, better charge mobility and efficient charge separation is key.

## Magnets

Greater reliance on renewable energy sources and increased attention towards total energy efficiency over the entire energy lifecycle has accelerated research in energy related technology. Magnetic materials are ubiquitous in both energy production and energy use and play an important role in improving the efficiency and performance of many devices used in these applications. Hard magnets are key components in many consumer and industrial devices and are particularly important within the renewable energy sector. Motors and generators in electric vehicles and wind turbines require permanent magnets that remain stable at temperatures exceeding 120 °C. In order to meet this requirement, magnets containing rare earth elements such as neodymium and dysprosium are used, of which dysprosium is scarce. The need for more efficient use of rare earth elements in magnetic materials is urgent, and reduction and finally replacement of these elements with more abundant alternatives is necessary. Additionally, the rare earth balance needs to be addressed. These elements never occur alone in ore and demand for the scarce elements, for example dysprosium and terbium, needs to be reduced, while applications for the ubiquitous elements, such as samarium and cerium, need to be found. In order to develop resource efficient magnets that do not rely on scarce rare earths, it will be necessary to develop magnetic materials which are not necessarily the best in absolute performance, but provide the needed characteristics while



assuring a secure and inexpensive raw material supply. For example, magnetic anisotropy can be induced in high magnetization cubic 3d-based metals and alloys such as FeCo by tetragonal distortion of thin films by epitaxial growth. Chemistry can find solutions to stabilize these structures by interstitial and substitutional modification of bulk material.

## Superconductors

Superconductors are materials that conduct electrical current without energy loss below a critical temperature. Magnets constructed from superconductors can generate strong magnetic fields which find applications like Magnetic Resonance Imaging (MRI), Nuclear Magnetic Resonance (NMR) spectrometry, mass spectrometry, particle acceleration, and use in superconducting trains. Currently, these devices must be cooled with liquid helium in order to maintain subcritical temperature. Helium is a critical element, and is essentially non-recoverable once it escapes to the atmosphere. There are so-called high temperature superconductors, which can be effectively cooled with liquid nitrogen, however they are brittle and difficult to process. There are to date no room temperature superconductors.

A fundamental research challenge is to be able to predict or engineer superconducting materials with the desired characteristics, taking into account abundance and toxicity of the constituent elements, and if possible, discovering materials that can superconduct near room temperature. A close collaboration between theoreticians and chemists, taking into account chemical intuition can lead to an acceleration of materials discovery. Room temperature superconductors could greatly reduce global energy problems, provide for faster computers, and allow transportation of energy without loss, among other things. As an immediate goal however, developing easily processed liquid nitrogen temperature superconductors could provide significant benefit in the near term.

## Thermoelectrics

Thermoelectric generators are used to transform a heat gradient into electricity. These devices exploit a temperature dependent electrical potential between two conducting materials and require no moving

parts. In principle, these devices could be used to further harvest usable energy from hot exhaust streams from motor vehicles, turbines, fuel cells, or other heat generating devices. The known materials are insufficient in terms of efficiency, life expectancy, and use of critical elements. Several of the compounds that have been developed as thermoelectrics contain lead, bismuth, tellurium, cobalt, ytterbium, cerium, and antimony. These elements are not suitable for mass produced devices. As with superconductors, the ability to design and predict properties is highly desirable, and close collaboration between theoreticians, experimental chemists, and materials scientists taking into account chemical intuition, could lead to great progress.

## Fuel Cell Materials

There currently exist a number of different types of fuel cells, varying in operating temperature, fuel, size, and a number of other criteria, particularly structural. High temperature solid oxide electrochemical cells are used for efficient conversion of hydrocarbon fuels to electricity and production of hydrogen from steam. Because of several characteristics, they show high potential for stationary applications, and do not require platinum group metal catalysts. Lanthanide perovskites are widely utilized in both solid oxide fuel cell anodes and electrolyser anodes functioning as both electron conductors and as electrocatalysts, and reduction of use or replacement of lanthanides by more sustainable elements would be highly desirable. The current electrolyte of choice is based on zirconia, typically doped with yttria or scandia. Achievement of similar performance in new materials comprising more sustainable elements will significantly improve viability of these technologies. Catalytic electrolysis of steam or carbon dioxide to hydrogen or synthesis gas demands materials similar to those described above.

In addition to solid oxide fuel cells, which require high operating temperatures, low temperature fuel cells utilizing polymer electrolyte membranes are also being investigated and have found many applications. Unlike solid oxide fuel cells, polymer electrolyte membrane fuel cells

operate at much lower temperature, as well as being lighter and more compact, making them more desirable for mobile applications. There do remain however, challenges to the viability of these low temperature fuel cells. Currently, the best performing low temperature fuel cells utilize platinum, a critical metal, as a catalyst. Currently, core-shell nanostructures are being investigated for realization of ultralow platinum loading, as well as investigation of non-precious metal catalysts such as nitrogen-doped carbon and tungsten carbide, which has the same electronic structure as platinum. Alkaline polymer electrolytes can enable the use of non-precious metal catalysts, however the ionic conductivity and chemical stability of these polymers remains a challenge. Nevertheless, significant progress has been reported. In addition to the above issues, development of polymer electrolyte membrane fuel cells operable at 100-150 °C can offer a number of merits, including faster reaction kinetics and tolerance to fuel contaminants. The present exchange membranes only work under humid conditions below 90 °C.

## Hydrogen Storage

Hydrogen storage presents a rather unusual problem in that although the element has good energy density by weight, it has low energy density by volume. For example, one litre of gasoline contains about 64% more hydrogen than there is in one litre of pure liquid hydrogen. Therefore, in order to store hydrogen for applications where volume is important, for example in motor vehicles, alternate strategies are necessary. One possibility is storage as metal hydride complexes, such as  $\text{LaNi}_5\text{H}_6$  or  $\text{Mg}_2\text{NiH}_4$ . However, these compounds exhibit very slow kinetics for hydrogenation and dehydrogenation, which necessitates high temperatures and large pressure changes. One possible solution is to use catalysts to reduce the activation energies for these reactions. The challenge is that many of these catalysts are fairly rare. Earth abundant, light alternatives are required. Hydrogen storage technology will become increasingly important as fuel cells become more widely adopted.

In addition to hydrogen, generation of renewable transport fuels and development of storable forms of energy in the form of fuels will also be important in the post-fossil fuel age. The conversion of solar energy into a chemical fuel via artificial photosynthesis is a possible scenario and is currently in development in several laboratories around the world. The use of critical elements may be of concern here.

## Catalysts

Catalysis has been responsible for improvements in energy efficiency of processes and efficient use of elements. Many processes are only economic because of catalysis. By their very nature catalysts are often used in small quantities and in many cases are already recycled. For some processes the balance of energy efficiency and use of elements and other factors is already optimal. There are some areas where scientists continue to work towards optimizing even further.

Catalysis relates to nearly every aspect of modern society, including clean air, clean water, food supply, energy production and storage, transportation, commodity chemicals and feedstocks. Catalysis plays an important role in many of the energy materials discussed in the previous section. A critical component in fuel cells is the catalyst that facilitates efficient oxidation of the fuel at low to moderate temperatures. And the success of solar-driven catalytic water splitting, an important research area, depends on developing complex tandem catalytic systems.

Many catalysts are based on critical elements, elements that may be rare or may be considered a near- or mid-term supply risk, and/or the extraction of which may represent a large environmental burden. To maintain current living standards and to extend this quality of life to more people, there is a need for more efficient use of elements in catalysis. Detailed discussion of the criticality of catalysis can be found in previous reports.<sup>5</sup> There are several challenges to be faced in catalysis development with respect to the betterment of society.

## Catalysts from Ubiquitous Elements

New catalysts must be designed based on ubiquitous, easily obtained elements. This

should include catalysts based on earth abundant, easily obtained metals as well as metal-free catalysts. Ubiquitous element catalysts are likely to be particularly useful in dissipative and highly distributed uses where the catalyst cannot be recovered and recycled. An example of this would be the platinum catalyst used in the production of cross-linked silicone.

Iron, a common and inexpensive element with excellent biological and environmental compatibility is just one example of a ubiquitous element catalyst, and is illustrative of the challenge of applying base metals to catalysis. The principle difficulty with using iron and other first row elements as catalysts is their tendency to undergo one-electron reactions, whereas precious metal catalysts such as palladium and rhodium typically undergo two-electron reactions. More explicitly, iron commonly exists in the oxidation states 0, I, II, and III, while rhodium commonly exists in the states I, III, and V. Because the oxidation states of rhodium typically change by two, reactions can be constrained to two-electron chemistry, that is, oxidative addition/reductive elimination. Iron, on the other hand, easily undergoes single-electron chemistry, for example, radical chemistry, which can be more difficult to control. This one-electron chemistry, however, may provide opportunities for new methodology. After all, metals used in biological reactions are principally first row elements, and Nature, by using multi-metallic active sites and/or biological ligands, is able to catalyze an impressive number of reactions efficiently. Pursuing this line of reasoning could lead to not only replacement protocols for currently used catalysts, but also new reactions and applications.

It is important to keep in mind that direct replacement of one element with another might not achieve the required efficiency, however, by discovering new chemistry with ubiquitous elements it may be possible to accomplish the desired processes through a different route. Over the past decade, significant progress has been made in organocatalysis, which may lead to alternate routes to produce fine chemicals and commodities that completely bypass the need for precious metal catalysts.

## Increased catalyst efficiency

Increasing the effectiveness and efficiency of catalysts can help reduce the demand for critical elements without requiring substitution or replacement. In addition to attention towards the metal centre, the environment around the active site and the oxidation state of the ligands should be considered. In solid catalysts, the number of active sites should be increased. This means that the catalytically active element should be concentrated at the surface of the support where it can react with the substrate. For homogenous catalysts, increasing the per-site activity is useful and is a fundamental metric for evaluating a catalytic system. For both homogeneous and heterogeneous catalysts, improved selectivity is desirable.

Catalysts should be more robust (particularly for more reactive base metal complexes) and resist deactivation. Self-healing catalysts (for example, perovskite-supported nanoparticles) should also be developed. This is particularly important for base metal catalysts because they are more susceptible to oxidation

Another application needing attention is the use of catalytic converters in motor vehicles. Although recovery of precious metals from automotive catalytic converters is extensively practiced, losses are inevitable and platinum group metals are rare and expensive. There is incentive to use platinum and rhodium more efficiently in this context.

## Total system design of catalysts

The total system architecture should be considered in the design, including ligand, outer-sphere, long range, and extended structures. Importantly, the fate of the catalyst should be included in the design. Removal, recovery, and reuse should be planned, as well as consideration of deleterious residuals such as ligands or supports. Recycling alone is not sufficient to solve the problem entirely, because there is inevitably some loss each cycle, and there are energy and resource costs associated with recycling as well. Many catalytic processes for commodity chemicals production have been highly developed, and in addition to being highly efficient, catalyst recovery has been included in the design.

## Fundamental understanding of catalysts

In order to accomplish these challenges, a new fundamental understanding of non-traditional catalysts must be created. As previously mentioned for the case of iron, to effectively use base metals as catalysts, learning to exploit the one electron chemistry of first-row transition metal complexes, including bio-inspired chemistry, will be important. Greater insight into reactions of non-metal catalysts, such as nitrogen-doped graphene, will be helpful, as well as learning to include and control the participation of ligands and supports in catalyst reactivity. Increased understanding of organocatalysis will also be highly beneficial. Furthermore, new metrics to assess the efficiency of catalyst use must be developed. Considerations like extraction efficiency (e.g. 1 ton of ore for 3 grams of platinum), energy use, carbon footprint, and distribution entropy need to be included. Catalyst lifetime, recycling cost, the impact of residues on the product as well as the fate of the ligand as well as metal must be considered. It must be recognized that the initial catalyst cost is usually not the main driver of catalyst choice.

Great progress has been made in applications of catalysis to clean energy and clean manufacturing, towards use of biorenewable feedstocks, generation of hydrogen from water, and use of CO<sub>2</sub> as a feedstock. The importance of catalysis in addressing these contemporary issues provides additional incentive to encourage efforts in this field. Catalysis remains a vital part of research and development and continued support is critical.

## Recovery, reuse, and recycling

Recycling for many elements, such as aluminium, iron, and lead is extensively practiced, and can in principle be established for critical elements as well. Because of their high cost and established use in manufacturing, recycling protocols have been developed for platinum group metals. Furthermore, they co-extract with copper in electronic waste recovery and can be further refined. There are however some applications in which the concentration of the noble metal is quite low and recovery is considered uneconomical. In current recovery protocols, however, rare-earth elements tend to form oxides and

partition with the slag, that is, the waste product of the process and are not recovered. As demand for these critical elements increases, these issues will need to be addressed. A detailed discussion of the recycling of critical elements from electronic waste can be found in previous reports.<sup>6</sup>

## Rare earth elements

As stated in the previous sections, rare earth elements are used in batteries, lighting, and magnets, particularly hard permanent magnets such as those used in wind turbines. Currently recycling and recovery of these elements is limited, with most activity occurring in pre-consumer waste, and overall, less than 1% of rare earth elements are recycled. Some rare earths are less abundant than others, in particular dysprosium, which is used sparingly in magnets to maintain strong magnetic fields at high temperatures. This low concentration however, is an impediment to widespread recycling and generally, because of the nature of the products and dispersion of the materials, it has been concluded that it is both difficult and expensive. Recovery methods including liquid-liquid technologies, hydrogen disproportionation, desorption and recombination, dissolution in molten magnesium, and acid leaching, have been attempted on a laboratory scale but there does not appear to be an established route. This is a pressing problem that needs to be solved.

## Actinides

There is an international recognition that nuclear energy is likely to be a part of an integral low carbon energy package to reduce global warming, at least in the near term. At present there are about 450 nuclear power stations in the world and over the next two decades used fuel will require reprocessing and the remaining radioactive elements will require safe disposal. Actinides are radioactive elements falling between actinium and lawrencium in the periodic table and only occur naturally in small quantities. These elements are produced through neutron capture by <sup>238</sup>U in nuclear reactors and it is important to recycle the uranium and, in order to achieve this, it is necessary to separate the actinides, notably plutonium, from the uranium. Separation can be achieved by the PUREX process (liquid-liquid extraction of plutonium with a solution of tri-*n*-butyl

phosphate in kerosene) but this process requires large volumes of solutions. Due to the similar properties of the actinides, separation is quite difficult. Electrochemical reactions in molten salts are being investigated as an alternative route to separation. It is important that better methods are developed in order to improve the safety, reliability, and economic viability of nuclear power.

## Phosphorus

Phosphorus has many industrial applications ranging from fine chemical synthesis to metallurgy and coatings. Most importantly, phosphorus is an essential nutrient required for life as we know it on earth. The global demand for phosphorus is roughly 20 million tons per year, and continues to grow. At this rate, shortages are expected to occur within the next one or two centuries. The greatest proportion of phosphorus is used in agriculture, with about 90% of mineral phosphorus production being used in fertilizer. Much of this fertilizer is lost as runoff, ultimately contributing to eutrophication of the marine environment. As a result, research investment should be made into the more efficient use and application of phosphorus fertilizer.

The depletion of phosphorus reserves and the associated environmental damage both from mining and agricultural runoff must be addressed through a multifaceted approach. New sedimentation and separation technology is needed to efficiently remove and recover phosphorus from municipal wastewater. Current refining technology provides a recovery rate from ore of only 40%, and this must be improved. Finally, sustainable farming and food systems are needed that reduce the amount of phosphorus lost as runoff and improve the recovery and reuse of phosphorus rich plant and animal waste. Failure to solve these issues could have dire consequences.

## Indium

Indium is a soft metal that occurs in low concentrations in zinc, lead, and tin ores, and is considered to be a rare element. The primary use of indium is as indium tin oxide thin coatings which account for about 84% of global consumption. These coatings are used as electrically conducting transparent films on flat panel devices such as liquid crystal displays. The amount of indium used per

device is generally small; a smart phone might contain a few milligrams while a large display may contain a few hundred milligrams. Despite the huge number of these devices produced, global production of indium as of 2011 was 640 tons annually.<sup>7</sup> Indium does not occur in sufficient concentrations to be economically mined as a primary metal at current prices, and supply is largely dependant on production of zinc, from which it is removed as a by-product. The supply of indium is fairly inelastic, and there is currently little capacity to increase production regardless of demand although in principle increased efficiency and further processing of zinc refining waste streams could increase output, however this would be a capital-intensive process.<sup>8</sup> The process commonly used to apply indium titanium oxide thin films is highly inefficient, and around 70% of the applied indium goes to waste material. Hence, recycling of pre-consumer waste is highly developed and widely practiced. Post consumer recycling is not practiced to any meaningful extent, and the quantity of indium in refuse landfills is significant. Because indium is present in small quantities in the devices in which it is used, research will be necessary to realize efficient post-consumer recycling. Graphene could be used as a substitute for indium tin oxide in conductive films and development of improved organic LEDs could potentially reduce the need for indium.

## Dysprosium

Dysprosium is a rare-earth element, and widely considered to be critical to clean energy technology. A major application of dysprosium is in high-performance permanent magnets, where the element increases resistance to demagnetization, particularly at high temperatures. There are a number of approaches towards reducing dysprosium content, one being reduction of operating temperature.<sup>8</sup> This would appear to be fairly straightforward for stationary applications where bulk and weight are not critical, however it would be a more formidable challenge in mobile applications. As stated previously in this paper, in many applications it is not necessary to develop alternatives as good as rare earth magnets, it is only necessary to develop sufficient alternatives constructed of earth-abundant elements. Efforts towards effective magnet recycling are underway, however robust financial and policy support are necessary.

## Helium

Helium is a monatomic, inert element and is the lightest of the noble gases. The largest single use of helium is in cryogenics, particularly in medical resonance imaging (MRI), as well as other applications requiring low-temperature superconducting magnets. Although helium is the second most abundant element in the universe, it is fairly rare on earth, because at ambient earth temperatures it has escape velocity, meaning that when released into the atmosphere, it escapes into space. Helium is produced on earth by the radioactive decay of mainly uranium and thorium, and is present in natural gas. In the short term, helium is expected to be in short supply, however facilities are being developed to capture helium during natural gas production as well as on-site recycling technology for both large and small-scale end users.

## Conclusions

The last several decades have witnessed remarkable advances in technology that have become widely adapted not only in science, medicine, and manufacturing, but also in end use consumer products. In particular, computerization and information technology have become such a fundamental part of modern society that disruption to the availability of these devices would have profound consequences. The rapid increase in demand for consumer electronics, high efficiency alternative energy systems, and specialty materials has led to a flourish of economic activity. Much of this technology, however, is heavily dependant on chemical elements that are either scarce or difficult to obtain, and under current practice is unsustainable. Other elements, for example phosphorus and lithium, are quite plentiful, but the rate of consumption, or the expected rate of consumption is rapid, and these vital materials are currently not being effectively conserved or recovered.

To face these challenges it will be helpful to find mechanisms to train researchers (especially junior researchers) in skill sets appropriate for developing energy materials and non-traditional catalysts and to develop pedagogical methods to lower barriers for acquiring this new expertise. Support for these areas of research should also include

incentives to encourage graduate students and early career scientists to move towards these important fields. Because of the great utility of large instrumentation such as cyclotrons in characterizing catalysts, magnets, superconductors, and other materials, it would be of great benefit to bring more national and international researchers to large user facilities. New lines of communication between academic researchers and end users, for example, chemical and pharmaceutical industries, to define important pre-competitive targets and opportunities for element substitution should be encouraged. And finally, international collaboration, communication, and researcher exchange to promote a view of element efficiency as a global issue should be fostered.

Comprehensive, coordinated action is urgently needed to address problems of critical element depletion. The problem is global in scope and requires attention from government, industry, and academia working together to forge a new approach to technology development that considers energy costs, environmental impact, and the complete use cycle of chemical elements required. Clear, rational public policy and regulations based on research, public and private support of research and education, and pre-competitive collaboration within industry and academia could facilitate great progress towards sustainable development.

## Recommendations & Challenges

### Energy Materials

- Batteries: Reduction of critical elements such as cobalt; improve service life; adopt recycling and reuse strategies for lithium ion batteries.
- Develop more efficient processes for producing PV grade silicon as well as new materials for solar cells that are made of other earth abundant elements.
- Develop more efficient use of rare earths in magnets and eventually replace with more abundant elements.
- Develop practical liquid nitrogen temperature superconductors and increase efficiency of thermoelectric devices.

- Fuel cells: Develop solid oxide fuel cells less reliant on rare earth elements and develop polymer electrolyte fuel cells less reliant on platinum group metals.

## Catalysts

- Improve the performance of catalysts containing scarce or critical elements.
- Develop catalysts made from ubiquitous elements for situations where the catalyst is not efficient or cannot be recycled.
- Improve robustness of ubiquitous element catalysts, which may be prone to deactivation on short timescales.
- Develop self-healing catalysts that regenerate and are therefore active for longer.

## Recovery, reuse, and recycling

- Incorporate total life cycle into the design and manufacture of new products and consider the impact of the comprising elements.
- Adopt recycling and reuse strategies for critical elements used in consumer electronics such indium
- Develop recycling and reuse strategies for rare earth elements, such as dysprosium, used in magnets.
- Improve the efficiency of both the mining and processing of phosphate, increase the efficiency of phosphorus containing fertilizers, and develop sedimentation and separation technology for recovering phosphorus from municipal wastewater.
- Develop systems to capture helium during natural gas production and for recycling.
- Develop separation techniques for actinides to enable recycling of uranium.

## Wider Challenges

- Encourage precompetitive cooperation among industry, academia, and national research institutes.

- Bring both national and international researchers to large central facilities equipped with powerful, advanced instrumentation.
- Find mechanisms to support and encourage emerging researchers entering these fields and develop pedagogical methods to prepare students for these areas.

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