



environmental systems. A complete list of the SEES suite of funding opportunities can be found on the NSF Web site.<sup>4</sup>

In 2011, President Obama signed H.R. 5116, the reauthorization of the America COMPETES Act (ACA), into law. Section 509 directed NSF to establish a “Green Chemistry Basic Research program” to provide “sustained support” for “research into green and sustainable chemistry which will lead to safe, clean, and economical alternatives to traditional chemical products and practices”, as well as green chemistry education and technology transfer.<sup>5</sup> Following feedback received through workshops,<sup>6,7</sup> webinars, and meetings with the scientific community, NSF responded to the ACA by creating a new initiative within the SEES portfolio: Sustainable Chemistry, Engineering, and Materials (SusChEM). SusChEM’s mission is to support the discovery of new science and engineering that will provide humanity with a safe, stable, and sustainable supply of chemicals and materials sufficient to meet future global demand.<sup>8</sup> Recognizing the need for holistic, systems-level approaches in sustainability research, the SusChEM program involves five different divisions at NSF in fiscal year 2013, and more divisions may be added in the future.

Although NSF has long supported research in sustainability-related topics, to achieve a truly sustainable civilization, more research is required in both disciplinary fields and in areas that transcend traditional disciplinary boundaries. The “OneNSF” approach, which aims to enable seamless operations across organizational and disciplinary boundaries, will increase interaction among disciplines to identify innovative and effective approaches to better tackle complex problems in sustainability. This approach will leverage resources for maximum impact, promote innovative practices, and meet national needs. The initial introduction of SusChEM is focused primarily on the mathematical, physical, and geological sciences and engineering. However, NSF recognizes the importance of social, behavioral, and economic science to any comprehensive long-term risk mitigation strategy, as well as the need to transform education to train scientists in the systems-based approaches required to make interdisciplinary research successful. SusChEM may therefore be expected to involve additional disciplines in future years.

### ■ THE SUSCHEM CHALLENGE IN PERSPECTIVE

The elements in the Earth’s crust, oceans, and atmosphere are the fundamental building blocks of all molecules and materials. With the exception of helium, they do not escape from the planet as a result of human activity but rather are extracted, processed, used, and eventually converted into another form or dispersed, making them difficult to recover. The combustion of coal, for example, does not cause carbon to disappear from the planet; it simply converts carbon from a concentrated solid into carbon dioxide dispersed in the atmosphere. The use of phosphate ion-based fertilizer does not deplete the planet of phosphorus but rather it converts solid concentrated “phosphate rock,” typically mined in North Africa, into phosphate ions dispersed, for example, in the waters of the Chesapeake Bay, Mediterranean Sea, or the Gulf of Mexico, with subsequent nutrient pollution of these waters.

The supply of many key elements can become “critical” due to low Earth abundance or because the world has become dependent on a single supplier that is susceptible to supply disruption due to natural disasters, conflict, or political manipulation. As but one example, the world’s supply of the so-called “rare earth elements” (REEs) is currently dependent

almost solely on China. Although REE reserves are dispersed throughout the world (China only has 36% of reserves; the United States has 13%<sup>9</sup>), China has a near-monopoly on the production process.<sup>10,11</sup>

There are predictions, some controversial, that world production of the following elements and natural resources will “peak”<sup>12</sup> later this century:<sup>13</sup> lithium (for batteries), gallium (for LEDs and solar panels), germanium and tellurium (for solar panels), indium (for computer touch screens and solar panels), petroleum (for manufacturing agricultural, commodity, and pharmaceutical chemicals), phosphorus (in the form of phosphate ion for fertilizer), and REEs (for electronics, communications, national defense, lighting, TV monitors, incandescent lighting, cars, and water purification). Continuing increases in human population and the rising percentage of humanity with “middle class” spending power will dramatically increase demand for natural resources over the coming decades; thus, “peak” production may increasingly fail to satisfy world demand for critical elements.

Maintaining a stable and affordable supply of critical elements is necessary but insufficient to achieve a sustainable world. The 12 principles of green chemistry, as defined by Anastas and Warner, provide a framework for a new paradigm for chemical and materials production.<sup>14</sup> This approach emphasizes (but is not limited to) waste prevention; atom economy; safer chemicals and processes; energy-efficient design; improved catalysis; and the recycling, reuse, and repurposing of chemicals and materials. All of these concepts are fundamental to the SusChEM mission.

As an example, the Division of Chemistry (CHE) at NSF is currently supporting green chemistry research to develop reactions involving the combination of two or more building blocks, with all other reagents required only in catalytical quantities.<sup>15</sup> In such reactions, the product is simply the sum of the reactants, and no stoichiometric byproducts are produced.

Achieving a safe and sustainable world means that critical elements must be harvested and converted into chemicals and materials in an environmentally benign manner. The extraction, use, and manufacture of chemicals, materials, and devices should minimize waste, environmental pollution, and energy consumption. Whenever possible, toxic chemicals and their byproducts must be replaced with safer alternatives. Thus, a comprehensive view of sustainability also considers the full life cycle of chemicals and materials, from their extraction from the Earth’s crust to their incorporation into engineered products and their fate after end use. Ideally, chemicals and materials will be reused, recycled, and repurposed indefinitely after initial usage. NSF has historically supported research in this area, but SEES, and in particular the SusChEM effort, elevate this interest to a priority.

Through SusChEM, NSF will support the discovery of new science and engineering that will (1) improve the harvesting and processing of natural resources, (2) replace and substitute scarce, toxic, and/or expensive chemicals and materials with Earth-abundant, benign, and inexpensive alternatives with comparable functionality, (3) extend the lifetime of materials through improved durability, (4) reduce energy consumption through improved catalysis, and (5) discover low-energy means of recycling, repurposing, recovering, and reusing chemicals and materials.

## ■ IMPROVE THE HARVESTING AND PROCESSING OF NATURAL RESOURCES

Sustainable harvesting begins with extracting resources from Earth systems using cost-effective techniques that minimize negative impacts on the environment and human health. This includes new extraction methods that use less energy, water, and chemical solvents. Any new methods of resource extraction must be developed in the context of a deep understanding of the Earth systems from which the resources originate.

Geoscientists are well positioned to play a critical role in fundamental research regarding harvesting raw materials using less energy, fresh water, and organic solvents than current practice, working in collaboration with chemists and engineers, who are well poised to translate discoveries into technology. The geosciences provide a rich and deep understanding of topics such as elemental cycling (how resources we extract are used and eventually reincorporated into the planetary system) and the complex systems in nature, which are critical to handling life cycle issues and resource extraction.

Geoscientists have developed an impressive array of methods for tracking materials and elements in complex Earth systems. Such methods can be used to understand the supply chain and life cycle of a material. For example, mineralogical and isotopic characterization are used to trace the provenance of the tantalum ore coltan (columbite–tantalite), given problems with its use as a “conflict mineral” to fund wars in the Democratic Republic of the Congo.<sup>16</sup> Continued development of chemical methods is still needed to enable more effective identification and monitoring of critical elements in the natural environment.

Potential areas for further exploration include understanding the interactions of biological systems with minerals and critical resources in the environment. For example, biomining is a relatively new approach to extraction that uses microorganisms to leach minerals from ores rather than relying on extreme heat or toxic chemicals.<sup>17</sup> Bacteria also have the potential to assist applications such as shale gas generation through biostimulation and the biological recovery of critical elements from waste.<sup>18</sup> Additionally, the sediment at the bottom of oceanic systems is rich in critical elements,<sup>19</sup> although concerns regarding their extraction with existing technologies have yet to be addressed.

## ■ REPLACE RARE, TOXIC, AND/OR EXPENSIVE CHEMICALS AND MATERIALS WITH EARTH-ABUNDANT, BENIGN, AND INEXPENSIVE ALTERNATIVES WITH COMPARABLE FUNCTIONALITY

In 1956, M. King Hubbert proposed what is now called the “Hubbert Curve” describing the life cycle of the production of petroleum.<sup>12</sup> This analysis is now routinely (and controversially) applied to the production of other chemicals that must be extracted from the Earth.<sup>20</sup> Hubbert analysis correctly predicted that the U.S. production of petroleum would peak around 1970 and predicts that world petroleum production will peak between 2010 and 2020, followed by a swift decline.

Fossil fuels are burned to power airplanes and automobiles, to heat buildings, and to generate electricity. Fossil fuels are also used to supply the building blocks of the chemical industry for manufacturing consumer products, agricultural chemicals, and pharmaceuticals. An increase in the price of petroleum will lead to an increase in the price of many chemicals and the products they form. Shortages in the supply of petroleum have

the potential to cause significant disruption in the manufacturing sector. To mitigate this volatility, we must discover abundant, less expensive alternatives to replace petroleum.

Research is underway to develop biofuels as an alternative to fossil fuels. For example, NSF’s Emerging Frontiers in Research and Innovation (EFRI) Office is supporting research on photosynthetic biorefineries. This strategy aims to achieve the sustainable production of transportation fuels and industrial chemicals by harnessing solar energy to drive the conversion of atmospheric CO<sub>2</sub> and water into carbon-based fuels and chemicals. For example, photosynthetic processes in single-celled algae,<sup>21–24</sup> diatoms,<sup>25</sup> or bacteria such as cyanobacteria<sup>26</sup> use sunlight as the energy source to convert atmospheric CO<sub>2</sub> to energy-rich metabolites such as lipids, hydrocarbons, or other specific chemicals, which can be processed into diesel or gasoline substitutes or converted into biochemicals. Further awards in these areas are highlighted in NSF award announcements.<sup>27,28</sup>

Research is also needed to discover “green” chemical reactions that will convert biorenewable sources of chemicals into building block chemicals for manufacturing. The CHE and Chemical, Bioengineering, Environmental, and Transport Systems (CBET) divisions at NSF currently support research in this area. For example, microbial catalysis and chemical catalysis are being used to convert renewable nontoxic sugar starting materials into chemicals currently derived from the benzene–toluene–xylene stream of petroleum and gas refining,<sup>29</sup> and new routes to commodity and fine chemicals are being designed through, for example, coupling renewable methanol and allenes to complex alcohol building blocks in a direct and byproduct-free method.<sup>30,31</sup>

CBET has embraced this area of research through many awards. For instance, research is being supported to sustainably generate fuels, other hydrocarbons, or intermediates through the catalytic conversion of abundant and/or naturally occurring substances, like CO<sub>2</sub> or lignin, the substance that gives plants their structural integrity.<sup>32–35</sup> Improvements are also being sought in enzymatic catalysis to convert biomass to chemicals and fuel components typically derived from petroleum.<sup>36</sup>

In addition to replacing petroleum with renewable sources of carbon, a sustainable future must also include the replacement of many other rare, toxic, and expensive chemicals and materials. Metals such as iridium, platinum, and rhodium are used as catalysts in the manufacture of products from plastics and pharmaceuticals to fuel cells and clothing dyes. These metals come with a high price tag (\$22,000 per pound for platinum and \$16,000 per pound for iridium) and obtaining them is often environmentally detrimental or politically challenging.

An example of this type of research supported by CHE shows that iron can be used as a cheap Earth-abundant substitute for platinum in the preparation of many common household materials such as silicone for envelope glue and the soles of shoes, as well as in shampoo.<sup>37,38</sup> This research has shown that the geometry around the metal center plays a key role in determining the reactivity patterns of the new catalysts.

Toxicity is also a primary concern, and worldwide demand is growing for materials that are benign to the environment and human health. Lead can still be found in many consumer products, including toys, and in solder and electronic devices such as actuators, sensors, and transducers. Regulations restrict the use of lead because of its adverse impact on public health. For example, the 2006 European Restriction of Hazardous



Substances Directive (RoHS) restricts hazardous substances, including lead, used in electrical and electronic equipment. Other related legislative acts passed by the European Union include End-of Life Vehicles (ELV) in 2003 and Waste from Electrical and Electronic Equipment (WEEE) in 2004. Current NSF-supported research in the Division of Materials Research (DMR) includes the development of lead-free piezoelectrics and solders.<sup>39–43</sup>

Even technologies that already aim to address sustainability challenges can be improved. A solar panel converts solar radiation into electricity and is an alternative to burning fossil fuels. However, the cadmium commonly used in commercial solar panels is extremely toxic, while another main component, tellurium, is rather scarce. Thus basic research is needed to discover more efficient methods of locating and harvesting tellurium and/or to create solar panels that replace or minimize the use of toxic and scarce components. A current project co-funded by DMR and CHE targets using more Earth-abundant materials for solar conversion.<sup>44</sup> Another multidisciplinary, collaborative project seeks to develop organic solar cells with a power conversion efficiency that is competitive with amorphous inorganic solar cells,<sup>45</sup> which would result in alternative solar energy harvest materials and devices that can be manufactured in an environmentally friendly way and at low cost.

### ■ EXTEND THE LIFETIME OF MATERIALS THROUGH IMPROVED DURABILITY

Resources may also be conserved by extending the working lifetime of a product, particularly when it is operating in extreme or harsh environments. Research into improved durability may include enhancing the performance of a material or material system by increasing its resistance to oxidation or corrosion, improving its mechanical properties, or increasing its resistance to radiation. A 2011 National Research Council report estimates that the aggregate cost of corrosion consumes at least 2–4% of the U.S. gross national product and outlines four corrosion grand challenges deserving attention.<sup>46</sup> These challenges include developing cost-effective and environmentally friendly corrosion-resistant materials and coatings and developing modeling, forecasting, and testing methods that can accurately predict and reflect long-term behavior in service environments. NSF currently supports several research projects aimed at tackling the problem of metal alloy corrosion.<sup>47–51</sup> These projects address only a small fraction of this large and complex problem, which spans a wide range of materials.

Fundamental materials science research aimed to discover and develop new and improved materials or materials systems is also needed to extend the operational range of materials and to increase their efficiency or efficacy. We need to better understand the triggers that degrade materials properties, so we may control the trigger events and/or reactions to them. Additionally, new materials may be designed that are able to self-heal or self-repair. For example, the seals for solid oxide fuel cells are exposed to very high temperatures and are susceptible to cracking in service. NSF-supported ceramics research is expected to develop a new class of glass and glass composites that self-repair damage, thereby extending their lifetime and cost effectiveness.<sup>52</sup> Another example of NSF-supported research in this area is in polymers, where an unconventional biomimetic approach is under investigation to design self-healing elastomers that can spontaneously repair themselves under ambient conditions after mechanical damage.<sup>53</sup>

### ■ REDUCE ENERGY CONSUMPTION THROUGH IMPROVED CATALYSIS

As mentioned previously, an “ideal” green chemical reaction requires minimal energy input, among other considerations. Two examples for achieving this are the use of enzyme catalysts for *in vivo* systems and the use of metal catalysts in synthetic chemistry systems. The Haber–Bosch process, for example, produces ammonia for use as fertilizer by reacting nitrogen and hydrogen over a catalyst at high temperature and pressure. The hydrogen used in this process is produced by “cracking” natural gas over a catalyst at high temperature and pressure. The Haber–Bosch process feeds a significant fraction of the Earth’s people, but it is also responsible for 1–2% of the world’s energy utilization.<sup>54</sup> Clearly, reducing energy consumption in this process will have significant benefits.

In line with the objectives of reducing energy consumption, improved catalysts would allow operation at lower temperatures and pressures, ultimately aiming for a process as close to atmospheric pressure and room temperature as possible. One approach under investigation is to use a nitrogen-selective inorganic membrane to transport nitrogen atoms to surface catalytic sites to achieve low-pressure synthesis of ammonia.<sup>55</sup> Fundamental properties of novel metal nanostructures are under investigation, with the aim of developing catalysts such as molybdenum nanostructures for the effective conversion of natural gas to various fuels and chemicals.<sup>56</sup> Another example is research that aims to develop catalytic carbon–hydrogen (C–H) amination reactions as a means of preparing new carbon–nitrogen (C–N) bonds without the need to prefunctionalize the reactive sites, leading to reduced cost, energy consumption, and environmental impact.<sup>57,58</sup> Computational modeling also plays a role, through, for example, research on promising copper catalysts for hydrocarbon amination. In these studies, calculations have guided experimental modifications to first-generation catalysts providing enhanced activity, selectivity, and substrate scope.<sup>59</sup>

The potential for adapting nature-inspired systems for technological use is also being considered. Two NSF-supported projects on catalysis examine the photocatalyzed generation of hydrogen by minerals<sup>60</sup> and mineral-catalyzed water oxidation.<sup>61</sup> For example, from studies of different processes associated with early Earth geology, insights are being gained into unusual catalytic mechanisms that might be harnessable as efficient fuel sources from long-lasting Earth-abundant resources.

### ■ DISCOVER LOW-ENERGY MEANS OF RECYCLING, REPURPOSING, RECOVERING, AND REUSING CHEMICALS AND MATERIALS

Despite continuously improving chemical processes and new materials research, critical chemicals and materials will still be required for the foreseeable future, and some potentially critical elements may never be replaced. For example, it is difficult to imagine how the magnetic properties of REEs can be replicated by alternative chemicals or materials, and there is no conceivable substitute for phosphorus as it is used by all life on the planet. Thus, a critical question is, how can we recycle these substances using less energy and more efficiently than current practice? Additionally, conservation and environmental stewardship require that we learn the fate of every chemical used and produced in chemical extraction and manufacturing. Ultimately, we must learn how we can reuse and repurpose

products at the end of what needs to be the first of many lifecycles.

Chemists and chemical engineers are interested in developing techniques for recycling chemicals that cannot be replaced, designing chemical processes to include recovery and recycling (“optimum atom economy”), and discovering new separation science that will facilitate recycling. Resource recovery needs to be developed in the context of the Earth systems from which the resources originate. For example, can we effectively recover critical elements, such as phosphorus, from soils and sediments by understanding the sorption of phosphates to mineral surfaces? One area for further exploration is developing a deeper understanding of the crystal chemistry of minerals, which plays an important role in resource recovery (e.g., through phosphate crystallization from wastes or the use of minerals for elemental sequestration).

Fundamental materials research is needed to discover or improve current materials and materials systems to enhance their recyclability, reuse, repurposing, and reclamation, including biodegradability. For example, conventional concrete production involves the use of Portland cement in a process that is one of two primary producers of carbon dioxide, a major greenhouse gas. Geopolymers, synthetic aluminosilicate polymers formed by chemical reaction between a solid precursor, such as metakaolin, and an alkali solution, are attracting attention, in part, for their promise to considerably reduce the amount of greenhouse emissions. NSF-supported research is exploring whether substitution of fly ash for clay in geopolymers might enhance environmental and structural benefits.<sup>62</sup> Fly ash is an attractive alternative to clay, as it is a waste material produced during coal combustion, for example, to generate electricity, and is often used as a replacement for some of the cement in concrete.

Finally, a paradigm shift is needed so that research is aimed, from the start, to envision the entire anthropogenic lifecycle of any chemical, material, or product used in manufacturing, where end-of-use is a primary consideration. Materials and products should be designed for more efficient reclamation, repurposing, recycling, and reuse. For example, how can a cell phone or computer be designed in such a way that critical components can be more efficiently removed and recycled or reused? Another area of interest is new materials or materials synthesis methods that minimize waste and/or emphasize the use of biorelated materials.

### ■ PROPOSAL SUBMISSION TO NSF

SusChEM began in fiscal year (FY) 2013, and the NSF divisions currently participating are CHE<sup>63</sup> and DMR<sup>64</sup> in the Directorate for Mathematical and Physical Sciences (MPS); CBET<sup>65</sup> and Civil, Mechanical and Manufacturing Innovation (CMMI)<sup>66</sup> in the Directorate for Engineering (ENG); and EAR<sup>67</sup> in the Directorate for Geosciences (GEO) (<http://www.nsf.gov/pubs/2012/nsf12097/nsf12097.jsp>). The SusChEM initiative is expected to continue in future years.

CHE supports research that will (a) discover new chemistry to replace rare, expensive, and/or toxic chemicals with Earth-abundant, inexpensive, and benign chemicals, (b) discover new separation science to economically recycle chemicals that cannot be replaced such as phosphorus and the REEs, (c) discover new chemistry to facilitate the use of nonpetroleum-based renewable sources of organic chemicals, and (d) discover new environmentally friendly chemical reactions and processes

that require less energy, water, and organic solvents than current practice.

DMR research projects that target the discovery of new materials or make materials more sustainable through improved synthesis, enhanced applications, and/or advances in lifecycle management are encouraged (<http://www.nsf.gov/pubs/2012/nsf12095/nsf12095.jsp>). Broader impacts are sought that advance the field beyond traditional paradigms of materials optimization, and include educational and outreach activities aimed at broadening exposure, increasing awareness, and improving knowledge in the area of sustainability.

Sustainability in energy supply is a national priority and is a key area of research in a number of the individual programs in CBET. These programs further encourage proposals that address fundamental challenges in separation science and engineering to achieve a sustainable supply of critical materials through better extraction, refinery, and recovery processes; in catalysis and biocatalysis science and engineering to develop the improved catalysts that are an essential part of many of the sustainability and green chemistry efforts; and in biochemical and reaction engineering. Environmental sustainability and engineering are also programs in CBET that support these research efforts, particularly in those studying aqueous systems. In CMMI, the Materials Processing and Manufacturing program will participate through supporting research in sustainable materials processing, particularly research that aims to reduce the use of toxic components in processing, to develop processes that operate under ambient conditions rather than extreme temperatures, pressures, or other harsh conditions, and processes that conserve natural resources, such as water, raw materials, and energy. Additionally, the EFRI Office in ENG supports sustainability research on the topic of photosynthetic biorefineries, which aim to harness solar energy to drive the microbiological conversion of carbon dioxide and water into carbon-based fuels and chemicals.

The EAR division in GEO will accept SusChEM proposals concerning processes and materials of fundamental interest to the geosciences with implications for the design of sustainable materials, chemical processes, and engineering methods. Examples of topics include, but are not limited to, Earth processes relevant to sustainable harvesting, recovery, recycling, and management of limited resource elements; Earth materials with potential technological applications, particularly those that may serve to replace current technologies based upon nonrenewable, toxic, and/or limited resources; geochemical processes and systems of high potential relevance for novel green chemical synthesis methods; and understanding the role of geological cycles in the behavior of technological materials and byproducts in natural systems.

### ■ CONCLUDING REMARKS

The SusChEM challenge is enormous in its scope and potential impact. It affects the safe and sustainable manufacturing of commodity, agricultural, and pharmaceutical chemicals and is concerned with the safe and sustainable use of chemicals and materials that are critical for purposes as diverse as feeding humanity and defending the nation. It is important to note, however, that SusChEM interests are a necessary but insufficient component for achieving a sustainable world.

NSF is not alone in addressing this challenge. For example, the U.S. Department of Energy announced in May 2012 that it “plans to invest up to \$120 million over five years to launch a new Energy Innovation Hub, establishing a multidisciplinary

and sustained effort to identify problems and develop solutions across the lifecycle of critical materials.<sup>68</sup> Given the incredible scope of the SusChEM challenge, we can confidently predict that both the private sector and multiple federal agencies will have focused research priorities, as dictated by their respective missions. NSF looks forward to offering a complementary interdisciplinary program that will discover fundamental mathematical, physical, and geological sciences and engineering breakthroughs pertaining to SusChEM, support the development of the future workforce in this area, and offer valuable outreach to the general public and policy makers.

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### Notes

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