CMI

Critical Materials Institute

AN ENERGY INNOVATION HUB

Annual Report – August 2016

U.S. DEPARTMENT OF ENERGY

Welcome to the Critical Materials Institute. CMI has been in operation for three years, and this report is a summary of what we have achieved so far, as we strive to assure supply chains of the materials manufacturers need to sustain production of clean energy technologies.

Our approach is strictly limited to research and development efforts leading to technologies that can diversify the sources of critical materials; provide substitutes for materials that are in short supply; or improve the utilization of existing resources through enhanced efficiency in manufacturing and improved recycling.

We work hard at developing technologies to overcome specific barriers to commercial viability in these three areas. We measure our progress by the advancement of the relevant technologies, and our success by the adoption of our technologies by the commercial sector.

In this report you will find lists of the projects CMI conducted in year three, and the inventions that have resulted. You will be able to read summaries of the work under way in each of the areas described above, and also in supporting crosscutting areas of basic scientific research and economic analysis. A few specific R&D projects will be highlighted; for the entire scope of work done by a program of the scale of CMI, please refer to our website cmi.ameslab.gov or contact us directly.

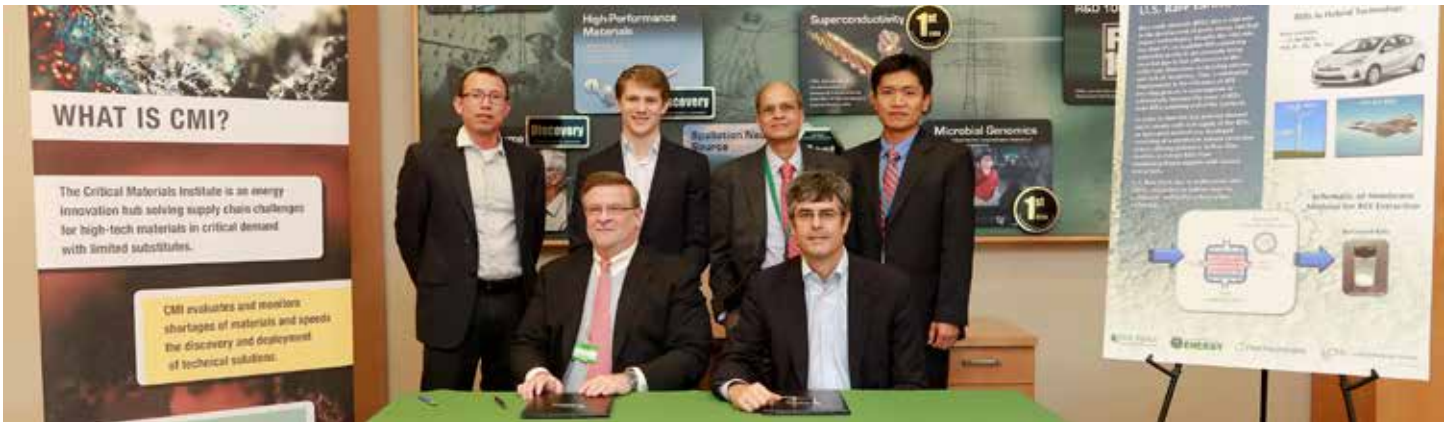
All of the work reported here is carried out by a dedicated team of researchers and support staff across a wide range of institutions. It is funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office, along with contributions from our various partner institutions.

Alex King
CMI Director
The Ames Laboratory

Rod Eggert
CMI Deputy Director
Colorado School of Mines

Technology Transfer

A key goal for CMI is to develop and deploy technology to the commercial sector. The first license, granted during year three, is for a CMI invention that aids in the recycling, recovery and extraction of rare earth minerals. The membrane solvent extraction system, invented by CMI partners Oak Ridge National Laboratory and Idaho National Laboratory, was licensed to Momentum Technologies, a subsidiary of U.S. Rare Earths, Inc. The official signing was held Nov. 19, 2015, at Oak Ridge National Laboratory.



Front row: Kevin M. Cassidy, president and CEO, U.S. Rare Earths, and Thom Mason, Director, Oak Ridge National Laboratory (ORNL). Back row: Nestor Franco, ORNL; Preston Bryant, U.S. Rare Earths; Ramesh Bhave, ORNL; and Daejin Kim, ORNL.

CMI Research and Development

CMI research and development efforts are moving rapidly toward commercialization.

Key technical successes have been achieved:

- A membrane solvent extraction system for rare earth elements has been licensed to Momentum Technologies, a subsidiary of U.S. Rare Earths, Inc.
- A substitute for Eu-based red phosphor materials is approaching the required performance characteristics.
- A new Al-Ce-X alloy exhibits better performance than current casting alloys.

CMI Five-Year Goals

Within its first five years, CMI will develop at least one technology, adopted by U.S. companies, in each of three areas:

- Diversifying and expanding production,
- Developing substitutes, and
- Reducing wastes.

CMI's aggressive timeframe to develop and deploy new technology requires new methods. We are pioneering the use of 3D printing to create and test new alloys.

Planning for Success

To accomplish goals with a tight timeframe for technology transfer, CMI collaborates with industry to select projects and conduct research.

> *"Going from an idea to a licensed technology in just two years is exactly what CMI is intended to do, and we've proven we can do it,"*
> said CMI Director Alex King.

Diversifying Supply

CMI efforts to diversify supply help reduce supply risk for critical materials. Significant progress has been made within three thrusts corresponding to developing new rare earth and lithium supply, improving the efficiency of processing, and finding new uses for cerium. These thrusts address gaps in the supply chain, each decreasing supply risk by making a unique type of economic impact.

Progress has centered on ways to concentrate rare earth minerals from different ore types; to recover rare earths from an abundant but dilute unconventional resource, namely phosphate rock; and to recover lithium from geothermal brine. CMI is making strides toward closing gaps in the rare earth supply chain with new, efficient technologies that could make domestic industry competitive.

Results include more efficient separations of adjacent lanthanides, and initial progress in developing entirely new processes for conversion of rare earth oxides to metal. An indirect but substantial impact on the supply chain would occur if the demand for cerium could be increased, since cerium accounts for approximately half the rare earth content of typical ores and is in oversupply.

Bruce Moyer, ORNL,
Leader, Diversifying Supply

Three Ways to Diversify Supply

CMI is at work on three ways to diversify supply. One is new sources of critical materials, including recovering rare earth elements from phosphate ore processing.

The second is transformational processing. This includes finding better ways to separate rare earth elements from each other and better ore processing methods, because rare earth elements tend to be found together and are difficult to separate.

The third way CMI research is working to diversify supply is to find new uses for co-products. This research focuses on cerium.

CMI Researchers Use Supercomputing to Find Rare-Earth Refining Alternatives

We have identified agents for the separation of rare earth metals that will perform better and reduce costs as compared with those now used. Currently, many solvent-extraction processes rely on ligands—molecules that act to bind with and separate the metals.

Through the use of computer–aided molecular design, a collaboration of researchers from the Supramolecular Design Institute, Oak Ridge National Laboratory and The Ames Laboratory identified several new ligands predicted to be highly effective once synthesized and tested.

"Development of each ligand by industry can take up to five years and cost millions of dollars," said Vyacheslav Bryantsev (ORNL). "Guiding the design computationally prior to experimental testing allows us to really narrow down and focus only on the very promising ligands, ones that are very strong and very selective."

The researchers developed a program called Host Designer, a molecule-building software program that can quickly prescreen millions of possibilities. Millions of potential molecules were reduced to about 3,000. Then, successively more complex computational analyses were used to narrow the number of potential ligands to a handful.

The research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility at Lawrence Berkeley National Laboratory.

Our Partnerships are Keys to Success

The strength of CMI and the Hub concept lies in bringing the best science together with industrial innovation. In a remarkable CMI partnership, high-level computer calculations, X-ray beam-line tomographic imaging, metallurgical mechanical property determination, and alloy castings approaching a hundred kilograms per shot in an industrial foundry are all happening in a single research project.

The unique combination of resources is accelerating development of a new aluminum-cerium alloy for high-temperature applications from concept to an expected product on the market–and jobs–in less than four years.

The CMI Team members partnering on this research include The Ames Laboratory, Lawrence Livermore National Laboratory, Eck Industries and Oak Ridge National Laboratory.

Rare Earth Innovation to Improve Nylon Manufacturing

CMI created a new catalyst that makes use of the widely available rare earth metal cerium to improve the manufacture of nylon. The process uses a cerium-based material made into nanometer-sized particles with a palladium catalyst to produce cyclohexanone, a key ingredient in the production of nylon. With the new catalyst, the temperature of the traditional method of producing nylon can be reduced while increasing the selectivity.

What to Do with All the Cerium?

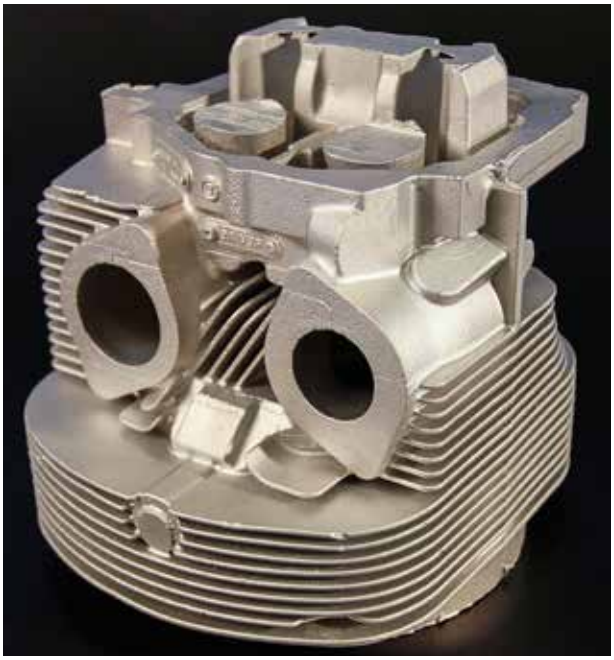
Cerium is the most abundant rare earth, constituting 36% of the global rare earth reserves, but its value is only 4% of the total. If new high-volume uses for cerium can be developed, then the increased demand will drive increased production of the less abundant rare earths critical for clean energy. CMI research to develop new uses for cerium has led to an improved catalyst for the high-throughput manufacture of nylon and a new aluminum alloy for the transportation industry.

New Casting Alloys Use Cerium

"Our customers are waiting in line for aluminum alloys that perform well at high temperatures and that are cheaper to produce," says Dave Weiss of Eck Industries. They seek:

- Increased alloy strength at high temperature,
- Reduced the weight of an engine,
- Increased fuel efficiency,
- Eliminated heat treatment,
- Decreased foundry costs, and
- Reduced machining costs with near net-shape casting.

A new aluminum alloy containing cerium, developed by CMI, could use very large amounts of cerium: 4 billion pounds of aluminum are used annually in transportation. The alloy with approximately 12% cerium delivers 30 ksi tensile strength as cast, with a fine microstructure that persists to 400°C. Casting methods are comparable to industry standard aluminum alloys, and the need for heat treatment may be eliminated.



A new Al-Ce-X alloy exhibits better performance than current casting alloys.

Developing Substitutes

CMI work in developing substitutes focuses on strong permanent magnets with reduced or no rare earth content and alternate phosphors for lighting technologies. Project teams are highly interactive within our magnet and lighting thrust areas, as well as with other CMI projects.

The magnet team achieves its objectives through both materials discovery efforts and process improvements. CMI researchers in the magnet team engage industry through workshops and discussions to solicit input to develop and refine performance targets and benchmarks for potential substitutes for high performance magnets and magnets with intermediate performance that could reduce demand for neodymium-iron-boron magnets.

The lighting team has developed several new substitutes for fluorescent lamps within the first three years and these are undergoing manufacturing trials. The team has now set its sights on LED technology to discover and develop new rare-earth free phosphors with better color renditioning characteristics. The identification of lamp phosphors is challenging because of the numerous simultaneous requirements that must be met while reducing the rare earth content.

Tom Lograsso, Ames, Leader, Developing Substitutes

Recycling Magnets through Advanced Processing

CMI demonstrated binderjet printing of near-net-shape magnets using Sm-Co powders recovered from recycling swarf. Additive manufacturing produces bonded gap magnets at near net shape.

- Multi-step process developed for reclaiming Sm-Co magnet swarfs *(see story on page 8)*
- Successfully printed near-net-shape bonded gap magnets

Work continues to address the effect of impurities during printing, and optimize the magnetic properties.

Accelerating Materials Discovery

CMI researchers developed the Material Design Simulator (MDS) to accelerate materials discovery and development. The MDS was applied on the phase equilibria in the Sm-Co system to evaluate search phase stability space and identify compositions for the stabilization of high Fe-bearing magnet formulations. The team is working with the CMI rapid assessment team to provide experimental benchmarks for the MDS. The MDS has also been applied to Al-Ce alloy development, and is being used to predict the most favorable phase distributions and volume fractions for optimum strength of the alloy.

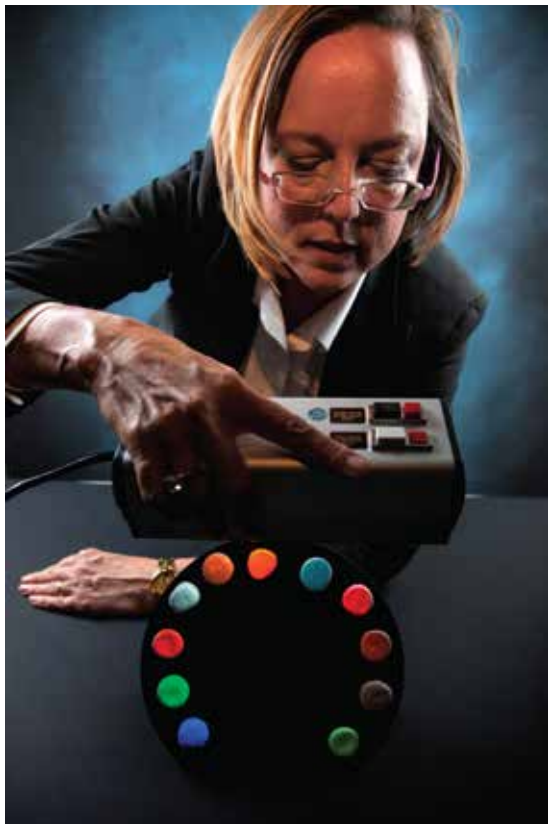
Two materials have been discovered that may be competitive with $Nd_2Fe_{14}B$ at high temperatures (> 150°C) and have reduced critical material content. These may be suitable for applications where high temperatures are common, such as regenerative braking. The magnet team has made significant steps toward solving technological challenges inhibiting the development of exchange spring magnets. They have succeeded in applying salt matrix annealing to increase the coercivity of both mechanically milled and chemically synthesized $SmCo_5$ nanoparticles, avoiding the coercivity loss normally exhibited when $SmCo_5$ is synthesized in nanocrystalline sizes.

Phosphor Substitutes: Green

CMI researchers discovered a new type of phosphor, based on decorating a host with nanoparticles. This discovery will help replace phosphors that provide the color green. The goal of 10x critical rare earth reduction while completely eliminating the lanthanum content is close to being achieved.

Phosphor Substitutes: Red

CMI's leading candidate for replacing Eu-bearing red phosphors has reached the luminescence performance goals to meet manufacturing requirements. Working closely with GE, this material shows great promise for replacing current red phosphors for the remainder of the lifecycle of long-tube fluorescent lighting.



Above left, the CMI lighting team members at LLNL include (from left) Paul Martinez, Nerine Cherepy, Zach Seeley, Kiel Holliday, Ich Tran, Nick Harvey and Steve Payne. Above, Cherepy displays commercial phosphors (six samples from bottom left of semi-circle) and phosphors being developed as replacements (five on right).

Better Fluorescent Lighting

CMI researchers at General Electric, Lawrence Livermore National Laboratory, The Ames Laboratory and Oak Ridge National Laboratory have created new kinds of fluorescent lighting phosphors that have far lower rare earth content than current technologies. These candidate phosphors are close to meeting stringent requirements for longevity, efficiency, color rendition and cost.

"The fundamental physics of these phosphors is compelling, and we are taking the next steps to assess their feasibility for commercial lighting by evaluating chemical issues such as slurry compatibility and improving the synthetic procedures," said Steve Payne (LLNL), the leader on the project. The principal investigators are Nerine Cherepy (LLNL), Lynn Boatner (ORNL) and Alok Srivastava (GE).

Phosphors in fluorescent lighting consume more than 1,000 tonnes of rare earth oxides per year. While LED lighting will eventually replace fluorescent tubes, low-cost linear fluorescent lighting is expected to remain a dominant feature in U.S. infrastructure for more than a decade. The current triphosphor blend was developed more than 30 years ago. That mixture of blue, green and red emitters includes green and red from rare earth elements. CMI researchers identified a green phosphor that reduces Tb content by 90 percent and eliminates La, and a new red phosphor that eliminates Eu and Y, and is free of rare earths.

Interactions

Interacting with other CMI researchers is vital in identifying candidate materials and processes with potential impact, and accelerating the pace of R&D efforts, particularly for Al-Ce thermodynamic properties and magnet recycling.

Reuse and Recycling

Eric Peterson, INL,
Leader, Reuse and Recycling

CMI reuse and recycling activities have made strong progress toward developing new technologies that improve the recovery and reuse of critical materials in manufacturing and product streams, and getting industry to adopt them.

Source preparation projects address three major challenges for recycling:

- Being able to economically move the resource to recycling centers,
- Extracting critical materials from their very complex matrices that are much different from the naturally occurring ores, and
- Being able to sell the products back into the markets at competitive prices.

Affecting recycling requires careful component logistical coordination and economic pre-treatment processes coupled with different extractive methodologies than those applied to naturally occurring ores.

Extraction and materials production efforts focus on developing novel beneficiation and metal reduction systems with a range of processing methods with characteristics including reduced energy use, lower environmental impact and higher throughput. We work on product streams that contain magnets, lighting phosphors, electronics, and thermal barrier coatings. These efforts have led to CMI's first commercial license.

Thermal Barrier Coating Revert Process

Yttrium-bearing Thermal Barrier Coatings (TBCs) are used to improve the operating efficiency of gas turbines and aircraft engines by protecting metal alloy components and enabling higher operating temperatures. During application, however, as much as 80% of the material can be oversprayed and end up as waste in dust collectors. CMI has developed a simple and cost-effective method to reuse the overspray.

Ikenna Nlebedim,
The Ames Laboratory

New Method for Recycling Magnets

A new recycling method developed by CMI scientists recovers valuable rare earth magnetic material from manufacturing waste and creates useful magnets out of it. The process inexpensively processes and directly reuses samarium-cobalt waste powders as raw material. It can be used to create polymer-bonded magnets that are comparable in performance to commercial bonded magnets made from materials, and also virgin sintered magnets.

This project is one way CMI is developing and deploying methods for recovery and reuse of rare earth magnets. Other projects consider end-of-life consumer products. Together, these types of projects require understanding logistics, economics and regulation.

CMI is developing strategies to reintroduce recycled rare earths into the supply stream, as well as developing and deploying designs that enable cost-effective disassembly of devices and components.

Recycling Rare Earth Magnets from Hard Disk Drives

Addressing one of the major cost-barriers to recycling rare earth magnets from hard disk drives (HDDs), CMI has designed an automated system capable of extracting voice coil magnets from approximately four HDD units per second. Work on this system is proceeding under a Cooperative Research and Development Agreement with Oddello Industries, LLC, while further design refinements are made. Several corporations have expressed interest in acquiring the system.

Functional Thin Film Recovery

CMI is developing an economic, environmentally friendly process for recycling functional thin films and recovering indium and rare earth oxides. Acid bake tests of both indium tin oxide powder and rare earth phosphors have proven technical feasibility. Constituents of interest were found to have been converted to sulfates and soluble in water. REEs were precipitated as oxalates, and indium was recoverable *via* solvent extraction and precipitation as a hydroxide. These results suggest selective separation will be possible.

CMI's First Commercially Adopted Technology: Membrane Solvent Extraction

CMI has created a membrane solvent extraction method, and licensed it to Momentum Technologies *(see signing photo on page 3)*. Dispersion-free membrane solvent extraction, operating under non-equilibrium conditions, with or without the inclusion of aqueous strip dispersion, overcomes the stability issues that usually arise due to the gradual loss of extractant. Membrane-based solvent extraction can now deliver better performance than traditional solvent extraction, minimizing costly extractant losses while delivering higher efficiency and productivity in a continuous operation mode. *(See diagram on page 16.)*

New CMI Process Recycles Used Rare Earth Metals

CMI scientists developed a two-step recovery process that makes recycling rare earth metals from magnets easier and more cost effective.

"Recycling rare earth metals out of consumer waste is problematic, and there are multiple obstacles in the entire chain from manufacturing to collection infrastructure to sorting and processing," said CMI scientist Ryan Ott (Ames). "We're looking at ways to make the processing part of that chain—removing the rare earths from scrap magnet material—better."

The researchers developed a two-stage liquid metal extraction process that uses differences between the solubility properties of different elements to separate rare earth metals. "Magnesium has good solubility with rare earths, particularly with neodymium, and poor solubility with the other components of magnets, like iron and boron," said Ott.

When the scrap metals are melted with magnesium, the lighter atomic weight rare earths bind with the magnesium and leave the iron scrap and other materials behind. Then rare earths are recovered from the magnesium through vacuum distillation. In the second step, another material is used to bind with and extract the heavier atomic weight rare earths, like dysprosium. Finding the best way to do the second step was the important breakthrough, as that was key to making it more economically viable as a large-scale recycling method.

Magnesium is melted with magnet scrap in an induction furnace.

Crosscutting Research

Eric Schwegler, LLNL, Leader, Crosscutting Research

Crosscutting research enhances CMI research and development, enabling project teams to start sooner through forward-looking assessments that include the environmental, social and economic aspects of materials criticality and technology commercialization, and to work faster by providing access to key tools and capabilities that are common across CMI.

The main objectives for crosscutting research are to: 1) provide validated predictive tools and materials databanks to enable CMI to develop timely, alternative solutions for advanced materials and processing; 2) assess the potential environmental impact of the new technologies being developed by CMI and develop strategies for mitigating deleterious effects; and 3) evaluate the supply chain and criticality of materials by developing an analytical framework for forward-looking assessments of raw materials that are, or may become, critical to the deployment of clean energy technologies.

Crosscutting research teams have made progress on each of these objectives, and have had a profound impact on CMI research. Some key achievements include:

- Developing a novel computational method for predicting the magnetic properties of disordered alloy systems as a function of temperature and composition, and validated by comparing the response of a series of alloys, formed using a rapid prototyping system, against their experimentally measured properties. This code makes it possible to design magnet alloys *in silico,* increasing the speed and lowering the cost of the design process for magnet materials.
- Completing a new criticality assessment of materials essential to clean energy technologies. The new assessment includes both updating the 2011 DOE evaluation and specific methodological refinement.
- Completing project level roadmaps for all CMI research teams that include quantitative milestones and key decision points. In addition, three new clean energy technology application-specific roadmaps have been completed for wind power, energy efficient lighting and electric vehicles. These roadmapping efforts highlight CMI's collective impact on key clean energy markets and demonstrate that a combination of reduced REE demand and increased domestic supply are needed to achieve target goals for green energy.

Technology Adoption is in Sight

Recurring themes in technology adoption include:

- Projects span a wide range of Technology Readiness Levels (TRL),
- Economic analysis drives and guides projects, and
- Synergy with other parts of CMI accelerates research progress.

Below, Jeffery D. St. Jeor is on a Science Undergraduate Laboratory Internship (SULI) at Idaho National Laboratory.

Rare Earth Effects on Biological Wastewater Treatment Systems

Expanding rare earth element (REE) recycling and production is likely to result in growing volumes and new compositions of wastewater. In some cases, discharge to a municipal wastewater treatment plant may be an attractive disposal option. However, the biological performance of the treatment plant cannot be jeopardized.

Data regarding impacts of REE and REE processing wastewaters

Rapid Assessment Methodologies

Addressing the United States' critical materials challenges requires rapidly accelerating the development of new alloys and processes.

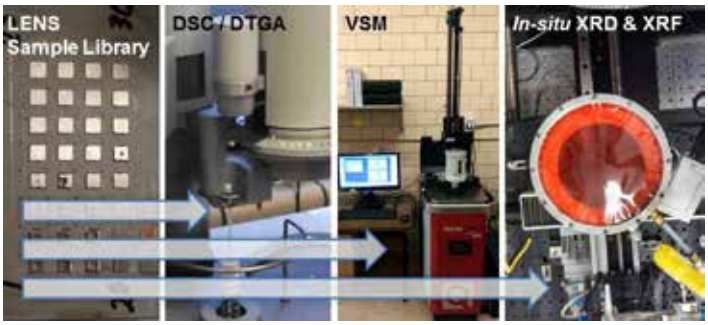
Ryan Ott (Ames) has been working to realize this goal by developing a diverse set of combinatorial synthesis and high-throughput characterization capabilities.

An example of these new capabilities is shown below. Bulk combinatorial synthesis is performed using additive manufacturing (a 3D printing process) *via* a specially adapted Laser Engineered Net Shaping (LENS) system.

This is used to rapidly screen for potential permanent magnet alloys that exhibit a high energy product and good elevated temperature coercivity, along with decreased content of critical elements Dy and Nd. Bulk samples of $(Nd_{1-x}Ce_x)_2(Fe_{1-y}Co_y)_{14}B$ alloys were printed by LENS, which were then characterized using autosampler DSC/DTGA and VSM and *in situ* synchrotron XRD.

From this combined high-throughput approach that spans both the synthesis and characterization of the material, Ott was able to rapidly determine the composition ranges of viable alloys based on the measured saturation magnetizations and Curie temperatures.

Based on these results, CMI is working on substitute materials to optimize the compositions, structures and extrinsic properties of the alloys to develop permanent magnets with decreased critical materials.



Left: CMI has assembled a suite of unique, high-throughput synthesis and characterization capabilities for rapid assessment of new alloy materials.

"Project priorities are guided by techno-economic analysis."
— CMI Director Alex King

Crosscutting Research Helps CMI Achieve Its Goals Faster

Working faster helps CMI accelerate achievement of goals in other focus areas.

- CMI is identifying materials that may become critical, and accessing the technical and economic potential of CMI research, allowing work to start sooner.
- CMI has improved computational and experimental tools, allowing R&D to go faster.

on biotic systems in general are scant, and wastewater pretreatment standards do not exist. Environmentally benign REE processing technologies (e.g., beneficiation or recycling) will have a significant advantage over technologies with high environmental costs.

Yoshiko Fujita (INL) is examining the effect of the new flotation agents being developed by CMI on the health of activated sludge obtained from an operating wastewater treatment plant. The metric used to gauge microbial activity was the specific oxygen utilization rate (SOUR), a measure of aerobic respiration and indicative of the microbial consortium's ability to degrade pollutants. Fujita's observation of SOUR inhibition suggests that further evaluation of the ecotoxicity of this compound may be warranted as part of the overall assessment of its potential for widespread industry adoption.

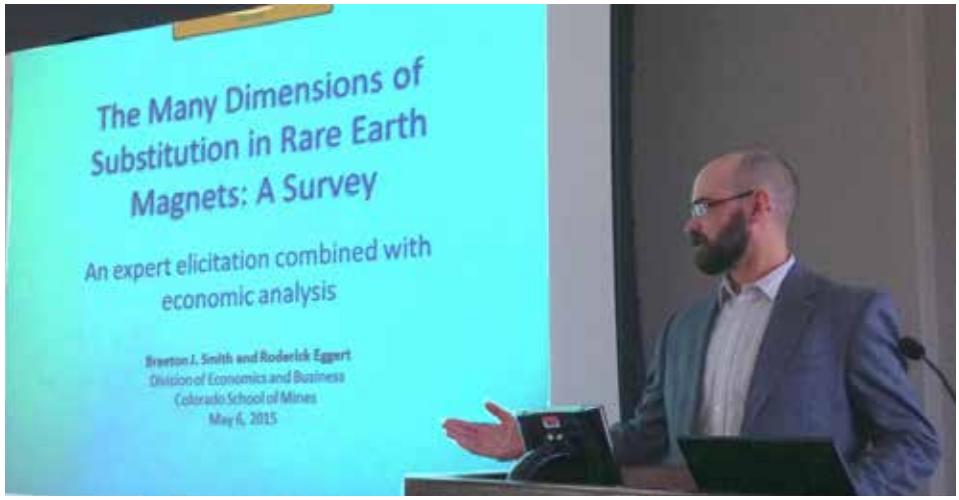
Substitution is Multifaceted

Materials substitution is an important response to criticality. When a material becomes less available or more expensive–or experiences greater price volatility–its users have an incentive to reduce or eliminate its use.

Consider the case of neodymium-iron-boron (NdFeB) magnets and the dramatic increase in rare earth prices in 2010-11 and the equally dramatic, subsequent fall in prices. In the face of this volatile market environment, magnet manufacturers had the incentive to reduce the use of rare earths in the magnets they produce, and users of NdFeB magnets had the incentive to use fewer or smaller magnets. How and to what extent did substitution occur?

Colorado School of Mines graduate student Braeton Smith and CMI Deputy Director Rod Eggert shed light on this issue in a recent paper. The study highlights that substitution takes a number of forms:

- ***Element for element,*** in which one element substitutes for another within a given magnet grade (for example, the possibility of using terbium in place of dysprosium in a N42SH magnet, one of a number of grades of NdFeB magnet);
- ***Technology for element,*** in which the content of an element is reduced within a specific magnet grade by using an improved production method (for example, using diffusion technology to optimize and reduce the amount of dysprosium by 50% or more in an N42SH magnet);
- ***Grade for grade,*** in which a user replaces one grade of a NdFeB magnet with another;
- ***Magnet for magnet,*** in which a user replaces one type of magnet with another (for example, a samarium-cobalt instead of a neodymium one); and
- ***System for system,*** in which a user replaces one system for achieving a desired outcome for another (for example, a windfarm designer choosing a turbine with an induction generator and gearbox, requiring no rare-earth magnets, rather than a more-efficient direct-drive turbine using NdFeB magnets).



Colorado School of Mines graduate student Braeton Smith presents his research.

Substitution in any of these forms can occur quickly only if off-the-shelf technology exists. Moreover, the final three forms of substitution typically require (often significant) re-engineering of a component or system to accommodate changes in material performance associated with using a different magnet grade, type of magnet or system.

For NdFeB magnets over the relatively short time period 2010-15, Smith and Eggert find that technology-for-element, grade-for-grade and system-for-system substitution were more important than element-for-element and magnet-for-magnet substitution. Perhaps the most-used form of substitution was technology for element, reducing the use of dysprosium in high-temperature NdFeB magnets by half or more through the use of diffusion production technology.

In many cases, no substitution occurred at all, and instead increased costs either were absorbed by a magnet manufacturer or passed on to customers.

Longer term, more extensive substitutions will become possible from innovations stimulated by the 2010-11 price increases but not fully developed until long after the price increases are forgotten.

Reference

Smith, B.J., and R.G. Eggert, 2016. "Multifaceted Material Substitution: The Case of NdFeB Magnets, 2010-2015," JOM, vol. 68, no. 7, pp.1964-1971. doi:10:1007 /s11837-016-1913-2.

Working with CMI

CMI Team Members

Team members have research subcontracts from CMI or provide cost-share funds. Requirements include specific research project deliverables within the entity's areas of expertise, based on a scope of work and a negotiated budget, as approved by CMI. This level of participation is required to sign CMI's Master Non-disclosure Agreement and the Intellectual Property Management Plan.

CMI Affiliates

Affiliates are companies and organizations interested in being informed about CMI research outcomes and in providing ongoing input to CMI. Foreign entitites must be approved for membership by the U.S. Department of Energy. CMI revised its Affiliate program in December 2015, resulting in doubling the number of Affiliates.

CMI Associates

Associates may use CMI expertise *via* DOE-approved contractual mechanisms, such as Cooperative Research and Development Agreement (CRADA) or Strategic Partnership Projects (SPP).

External Collaborations

CMI engages in a wide range of collaborations to accelerate progress toward meeting goals. It has ongoing interactions with program offices and research projects within DOE, with other federal agencies, with individual corporations, associations and industry groups within the United States and internationally. CMI also maintains connections with foreign funding agencies and researchers who have interests in critical materials. These interactions are facilitated by a variety of instruments, such as CRADAs, memoranda of understanding (MOUs), non-disclosure agreements (NDAs), and others, as appropriate.

During year three,
CMI added two Team members,
increasing momentum
toward commercialization.

Eck Industries, Inc.
Specialists in Premium Aluminum Castings

United Technologies Research Center

TEAM

- The Ames Laboratory
- Idaho National Laboratory
- Lawrence Livermore National Laboratory
- Oak Ridge National Laboratory
- Brown University
- University of California-Davis
- Colorado School of Mines
- Florida Industrial and Phosphate Research Institute (FIPR)
- Iowa State University
- Purdue University
- Rutgers, The State University of New Jersey
- Advanced Recovery
- Cytec
- Eck Industries, Inc.
- GE
- Molycorp
- OLI
- Simbol Materials
- United Technologies Research Center

AFFILIATES

- ABB
- ASTM International
- Barr Engineering Co.
- EEC
- Etrema Products, Inc.
- Infinium
- Montana Tech
- Mosaic
- Native American Mining Solutions (NAMS)
- NASA Glenn Research Center
- Niron Magnetics, Inc.
- Phinix, LLC
- Printspace
- Rare Element Resources
- REEcycle
- Rio Tinto
- Simplot
- Tasman Metals, Ltd.
- Urban Mining

CMI Projects

CMI started with about three dozen projects. Each project is reviewed regularly, and over time, some have been completed, dropped, redirected or merged. A total of 44 projects have been undertaken over three years, and in its third year, CMI scientists conducted research in 36 distinct projects. Titles are listed below.

Rare earths and other critical materials play a vital role in many modern clean energy technologies. These include

- Wind turbines,
- Solar panels,
- Electric vehicles, and
- Energy-efficient lighting.

CMI research targets three goals:

- Diversifying supply,
- Discovering substitute materials, and
- Developing tools and processes for recycling materials.

CMI Projects Active in Year Three

Diversifying Supply

- Advanced Beneficiation Techniques
- Recovery of REEs and Uranium from Phosphate Ore Processing
- Improved Methods for Lithium Extraction
- Enhanced Separation of Adjacent Rare Earth Elements
- Conversion to Metal, Alloys, and Materials
- Computational Prescreening of Ligands
- Development of High Cerium Content Aluminum Alloys

Developing Substitutes

- Reduced Rare Earth Content High Performance Magnets
- Additive Manufacturing of Permanent Magnets
- Optimization of Grain Boundaries and Interfaces in Fine Particle Magnets
- Thermo-Magnetic Processing of Rare Earth Magnets
- Direct Conversion of Sm_2O_3 to $SmCo_x$ Permanent Magnets
- Materials Design Simulator
- New Efficient Phosphors Without Critical Material Content for Lighting
- Nano-AlN-Mn *via* Mechanochemistry (new start)
- Energy Efficient Lighting (new start)

CMI projects are designed to include industrial partners, which ensures the research is on target with industry needs.

Improving Reuse and Recyling

- Recovery and Reuse of Rare Earth Metals from Phosphor Dusts
- Beneficiation of Photovoltaic (and Other) Functional Coatings
- Transforming Reuse and Recycling of Rare Earth Magnets
- Thermal Barrier Coat Revert and Future Opportunities
- Laser Induced Breakdown Spectroscopy (new start)
- Supercritical Fluid Beneficiation of Waste Streams
- Membrane Solvent Extraction for Rare Earth Separations
- Bioleaching for Recovery of Recycled REE
- Recovery of Critical Materials from Consumer Devices
- Beta-Diketonoate Complexes (new start)

CMI's rigorous project management system includes quarterly updates and annual reviews of each R&D effort.

Crosscutting Research

- *Ab initio* Theory of Temperature Dependent and Multi-Scale Phenomena in Magnets
- Predicting, Controlling and Tailoring Crystal Electric Field Splitting for Magnetic Anisotropy in REE Systems and d-impurities in Phosphors
- Fundamental Properties and Phase Diagrams
- Rapid Assessment Methodologies
- Treatment of Mineral Processing Waste Streams and Recovery of Clean Water Using Sorption, Passive, and Active Microfiltration Systems
- Rare Earth Effects on Biologial Wastewater Treatment Systems
- Criticality and Sustainability Assessment
- Economic Analysis of CMI Research and Global Material Supply Chains
- National Technology Roadmap for Critical Materials

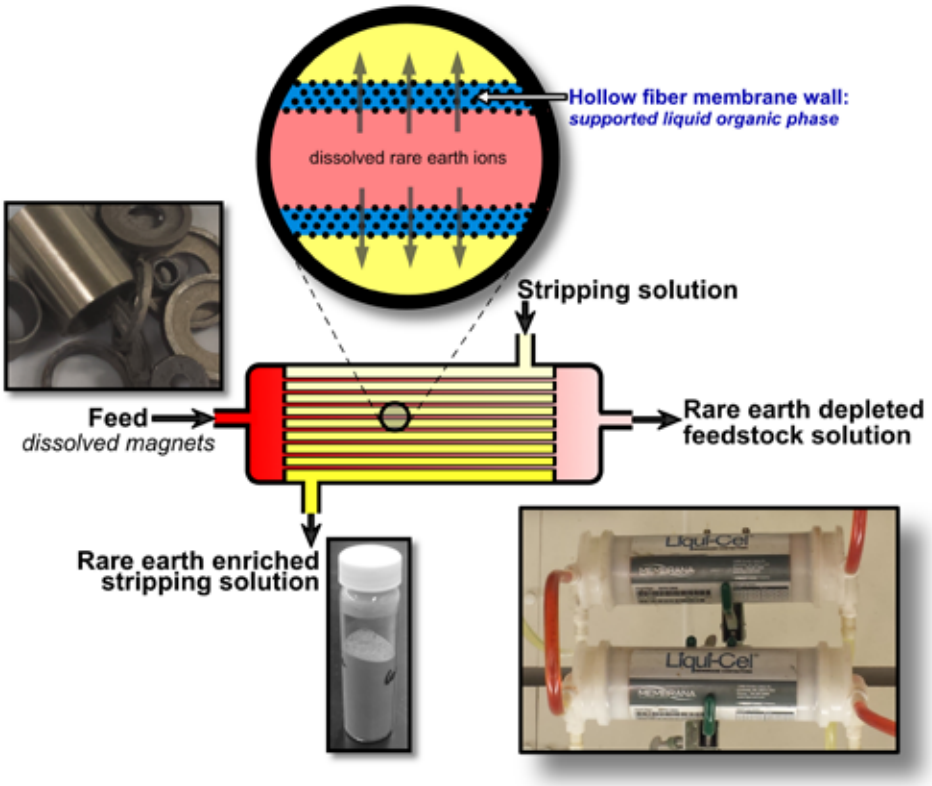
Intellectual Property

Success is defined for CMI by how well it meets its mission to assure supply chains of materials critical to clean energy technologies. To enable innovation in U.S. manufacturing and to enhance U.S. energy security, CMI must develop, demonstrate, and deploy clean energy technology. To direct research in a way to minimize the time to discovery and the time between discovery and deployment, the CMI Team includes both research and industrial partners.

Invention disclosures measure progress and highlight areas where research may lead to a patent and licensing of a technology or progress. CMI researchers have created more than 40 invention disclosures, filed 16 patent applications (listed below), and licensed one technology. All the technologies are available for licensing.

CMI Invention Disclosures with Patent Applications

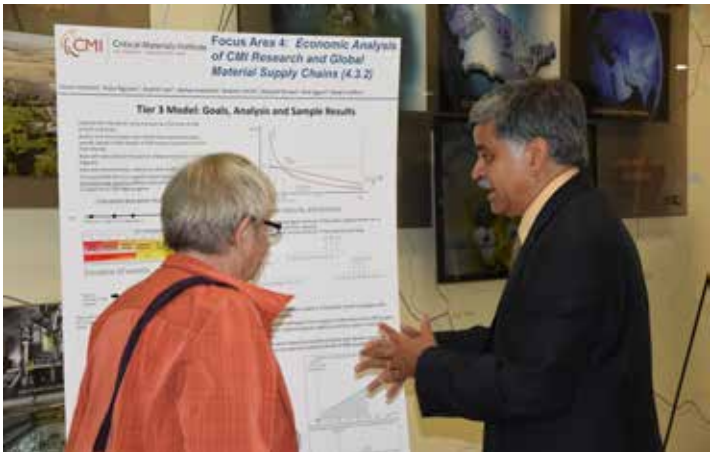
- Membrane Solvent Extraction for Rare Earth Separations ***Licensed***
- Extraction of Rare Earth Elements from Phosphoric Acid Streams
- Selective Composite Membranes for Lithium Extraction from Geothermal Brines
- Extraction of Rare Earths from Fly Ash
- Recovery of Dy-enriched Fe Alloy from Magnet Scrap Alloy *via* Selective Separation of Rare Earth Elements
- Aluminum Nitride Phosphors for Fluorescent Lighting
- Task Specific Ionic Liquids Extractive Metallurgy or Rare Earth Minerals
- Recycle of FeNdB Machine Swarf and Magnets
- Chemical Separation of Terbium Oxide (SEPTER)
- Automated Printed Circuit Board Disassembly by Rapid Heating
- Electrochemistry Enabled Recovery of Value Metals from Electronics
- A One Step Process for the Removal of Nickel/Nickel Copper Surface Coating from the $Nd_2Fe_{14}B$ (neo) Permanent Magnets
- Castable High-Temperature Ce-Modified Al Alloys
- High Command Fidelity Electromagnetically Driven Calorimeter (High-CoFi EleDriCal)
- The Separation of Ancylite by Way of Magnetic Separation and Froth Flotation
- Recovering Rare Earth Metals Using Bismuth Extractant



CMI issued its first license for a membrane solvent extraction system that can help recover and recycle rare earth elements found in electronic waste. This license was non-exclusive, so the technology is available for additional licensing.

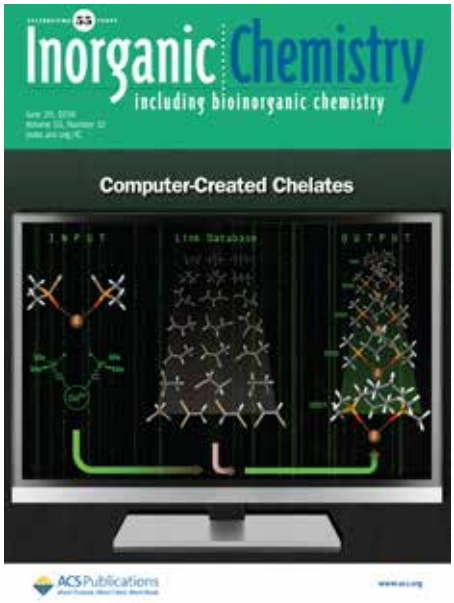
CMI Team members have first right of refusal to CMI Award Intellectual Property.

All invention disclosures listed here are available for licensing outside of CMI Team members.



CMI Invention Disclosures Available for Licensing

- Recovery of Neodymium from Neodymium Iron Boride Magnets
- Methods of Separating Lithium-Chloride from Geothermal Brine Solutions
- Novel Surface Coatings to Improve the Functional Properties of Permanent Magnets
- Additive Manufacturing of Bonded Permanent Magnets Using a Novel Polymer Matrix
- Ceria-based Catalyst for Selective Phenol Hydrogenation under Mild Reaction Conditions
- Recycling and Conversion of Samarium Cobalt Magnet Waste into Useful Magnet
- Catalysts for Styrene Production
- Separation of Neodymium from Praseodymium
- High Throughput Cost Effective Rare Earth Magnets Recycling System
- Directly Printing Rare Earth Bonded Magnets
- Procedure for Concentrating Rare-earth Elements in Neodynium Iron Boron-based Permanent Magnets for Efficient Recycling/Recovery
- Enhancing Consumer Product Recycling *via* Rapid Fastener Eradication
- Synthesis of High Surface Area Mesoporous Ceria
- Self-Assembly of Low Surface Colloidal Nanoparticles into High Surface Area Networks
- Selective Chemical Separation of Rare Earth Oxalates (CSEREOX)
- Carbothermic Preparation of $SmCo_x$ (x=5 to 8.5) Permanent Magnets Directly from Sm_2O_3
- Engineering Caulobacter Surface Protein for Rare Earth Element Absorption
- Novel Methods toward Selective Surface Modification of $Nd_2Fe_{14}B$ Magnets to Achieve High Performance Permanent Magnets
- Mesoporous Carbon and Methods of Use
- 3D Printable Liquid Crystalline Elastomers with Tunable Shape Memory Behaviors and Bio-derived Renditions
- Structural Optimization of Complex Materials Using High-throughput Hierarchical Decomposition Methods
- Novel 3D Printing Method to Fabricate Bonded Magnets of Complex Shape
- Rare Earth Free High Performance Doped Magnet
- Acid-free Dissolution and Separation of Rare Earth Metals



Journals Highlight High-impact CMI Research

CMI scientists publish their research in peer-reviewed journals and present at conferences. Several journals have featured CMI research on their covers. Also, *Applied Physics Letters* featured CMI research by Williams *et al.* as an AIP Editor's Choice.

Selected CMI Publications

- T. Alammar, J. Cybinska, P.S. Campbell, and A.V. Mudring, "Sonochemical synthesis of highly luminescent Ln_2O_3:Eu^{3+} (Y, La, Gd) nanocrystals," *Journal of Luminescence,* doi:10.1016/j.jlumin.2015.05.004
- N. Cherepy, S.A. Payne, N.M. Harvey, D. Aberg, Z.M. Seeley, K.S. Holliday, I.C. Tran, F. Zhou, H.P. Martinez, J.M. Demeyer, A.D. Drobshoff, A.M. Srivastava, S.J. Camardello, H.S. Comanzo, D.L. Schlagel, and T.A. Lograsso, "Red-Emitting Manganese-doped Aluminum Nitride Phosphor," *Optical Materials,* 54 14-21; doi:10.1016/j.optmat.2016.02.008
- J. Cybinska, C. Lorbeer, and A.V. Mudring "Ionic liquid assisted microwave synthesis route towards color-tunable luminescence of lanthanide-doped $BiPO_4$," *Journal of Luminescence,* doi:10.1016/j.jlumin.2015.06.051
- J. Cybinska, M. Wozniak, A.V. Mudring, and E. Zych, "Controllable synthesis of nanoscale YPO_4:Eu^{3+} in ionic liquid," *Journal of Luminescence,* doi:10.1016/j.jlumin.2015.07.008
- L.A. Diaz, T.E. Lister, J.A. Parkman, and G.G. Clark, "Comprehensive Process for the Recovery of Value and Critical Materials from Electronic Waste," *Journal of Cleaner Production,* doi:10.1016/j.jclepro.2016.03.061.
- P. Ghosh and A.-V. Mudring, "Phase selective synthesis of quantum cutting nanophosphors and the observation of a spontaneous room temperature phase transition," *Nanoscale,* doi:10.1039/c6nr00172f
- L. Huang, V. Taufour, T.N. Lamichhane, B. Schrunk, S.L. Bud'ko, P.C. Canfield, and A. Kaminski, "Imaging the magnetic nanodomains in $Nd_2Fe_{14}B$," *Physical Review B,* doi:10.1103/PhysRevB.93.094408
- U.S. Kaluarachchi, V. Taufour, A.E. Bohmer, M.A. Tanatar, S.L. Bud'ko, V.G. Kogan, R. Prozorov, and P.C. Canfield, "Nonmonotonic pressure evolution of the upper critical field in superconducting FeSe," *Physical Review B,* 2016, doi:10.1103/PhysRevB.93.064503
- B.W. McCann, N. De Silva, T.L. Windus, M.S. Gordon, B.A. Moyer, V.S. Bryantsev, and B.P. Hay, "Computer-Aided Molecular Design of Bis-phosphine Oxide Lanthanide Extractants," *Inorganic Chemistry,* doi:10.1021/acs.inorgchem.5b2995
- D.M. Park, D.W. Reed, M.C. Yung, A. Eslamimanesh, M.M. Lencka, A. Anderko, Y. Fujita, R.E. Riman, A. Navrotsky, and Y. Jiao, "Bioadsorption of Rare Earth Elements through Cell Surface Display of Lanthanide Binding Tags," *Environmental Science and Technology,* doi:10.1021/acs.est.5b06129.
- M. Redlinger and R. Eggert "Volatility of by-product metal and mineral process," *Resources Policy,* doi:10.1016/j.resourpol.2015.12.002
- T.J. Williams, A.E. Taylor, A.D. Christianson, S.E. Hahn, R.S. Fishman, D.S. Parker, M.A. McGuire, B.C. Sales, and M.D. Lumsden, "Extended magnetic exchange interactions in the high-temperature ferromagnet MnBi," *Applied Physics Letters,* doi:10.1063/1.4948933
- F. Zhou and D. Aberg, "Crystal-field calculations for transition-metal ions by application of an opposing potential," *Physical Review B,* doi:10.1103/PhysRevB.93.085123
- S.H. Zhou, M.J. Kramer, F.Q. Meng, R.W. McCallum and R.T. Ott, "Chemical partitioning for the Co-Pr system: First-principles, experiments and energetic calculations to investigate the hard magnetic phase," *Materials & Design,* doi:10.1016/j.matdes.2015.11.058

Meetings

CMI gathers to further collaboration among its partners. Examples in CMI year three included the annual meeting at Idaho National Laboratory, winter meeting at Colorado School of Mines with graduate/post-doc symposium, and a meeting at Florida Industrial and Phosphate Research Institute (FIPR).

Unique Facilities

CMI has developed several unique experimental and theoretical tools to support its research and development efforts.

- Bulk combinatoric library production facility
- Thin-film combinatoric library production facility
- High-throughput analysis
- Solvent exchange (SX) pilot scale test facility
- Electrophoretic deposition capability
- Filtration test facility
- Toxicology test capability
- Thermal analysis in high magnetic fields
- Rapid magnetic property assessment
- Rapid thermodynamic property assessment
- Micro-X-ray fluorescence analysis capability
- Metal reduction capabilities
- Robotic high-throughput catalyst development system

CMI Education and Outreach

CMI education and outreach programs focus on meeting the HR needs of the critical materials supply chain. Guided by industry input, we have:

- Created a critical materials exhibit in the Geology Museum at Mines.
- Convened a two-day research seminar for CMI graduate students and post-docs.
- Delivered monthly webinars on topics related to CMI objectives.

CMI scientists collaborate with industry partners to identify the most productive research paths.

CMI generates intellectual property at a high rate, and promotes it to industrial partners.

Collaboration Key to CMI Success

"Industrial collaboration is a strong indicator of future success for the institute. We have seen over and over again that participation and feedback from manufacturers about our research translates into marketable technologies in a much shorter time frame than traditional methods." — CMI Director Alex King.

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