# Energy Critical Elements: The Rare Earths

## Introduction

The rare earth elements, comprising of scandium (Sc), yttrium (Y), and the lanthanides [the most important ones regarding this theme are: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), erbium (Er), ytterbium (Yb), and lutetium (Lu)], are vitally critical to both our military and energy securities.

In the military sector, all of our weapon systems are especially dependent on: Nd, Pr, Sm and Dy in permanent magnets which are utilized in electric motors, computers, guidance systems, etc.; Y, Ce, and Nd in sensors, electronic materials, e.g. capacitors, resistors; Y, La, Nd, Eu, Tb, and Dy in phosphors for optical displays and lasers, etc.; Y and Gd in aircraft engines and turbines; Y and Gd in communication devices such as filters, tuners, phase shifters, radar antennas; and Y, La, Gd, and Lu in optical devices, camera lenses, fiber optics.

In the energy sector: Nd, Pr, Sm, and Dy are used in permanent magnets for electric motors (cars, trucks, wind turbines); La and mischmetal in nickel-metal-hydride batteries; Ce, La, and mixed rare earths in petroleum refining catalysts; Y, Ce, Eu, Tb, and Dy in fluorescent and LED lighting; Y, Ce, and Nd in oxygen and electrical sensors to control combustion in automobiles to improve the efficiencies of fuel consumption and reduce the environmental pollution; Y, La, and Ce in high temperature alloys for turbines for generating electricity; and Gd as a nuclear reactor moderator.

## Rare Earth Research at the Ames Laboratory

### *History*

The Ames Laboratory has a long tradition of research on the rare earth related elements, going back to World War II when the Ames Laboratory developed a low cost process for preparing uranium (U) metal for the first atomic nuclear fusion reactor in Chicago. The process is still being used today. The Ames Laboratory also supplied two tons of U (1/3 of the fuel needed) for the reactor to be self sustaining. Subsequently scientists at the Ames Laboratory developed the ion exchange process for separating and purifying the rare earth elements, which is still utilized today to produce the highest purity individual elements. They also contributed together with other Department of Energy laboratories to the commercialization of the liquid-liquid solvent extraction processes which are used today for separating the rare earth elements on a large scale; tens of thousands of tons per year per mine, or about 140,000 tons in 2010 worldwide, 90% coming from China. In the late 1940s to early 1950s Ames Laboratory scientists developed processes for making pure rare earths by the metallothermic process, and during the 1950s through 1970s developed new processes for purifying the metals from 99 to 99.99 wt.% pure by casting, zoning, sublimination, distillation and solid state electrolysis methods. During this same period they studied the fundamental properties of the elementary metals – magnetic, electrical, thermal, elastic, mechanical, chemical, etc. – and prepared and discovered many new intermetallic, inorganic and organic compounds. Much of this new information contributed to the eventual discovery of the electrical properties of the $LaNi_5H_x$ battery electrode; the magnetic behaviors of Terfenol-D ($Tb_{0.3}Dy_{0.7}Fe_{1.9}$) a giant magnetostrictive material; the magnetically very strong $Sm_2Co_{17}$, $SmCo_5$, $Nd_2Fe_{14}B$ and $Pr_2Fe_{14}B$ permanent magnets; and the electrical conductivity of yttria-stabilized zirconia $(Zr_{1-x}Y_x)O_2$ electrical sensors. One of the co-discoverers of the $Nd_2Fe_{14}B$ permanent magnets carried out his Ph.D. graduate research at the Ames Laboratory.

Analytical chemists devised new schemes, techniques and procedures for analyzing the purity of individual rare earth elements for other rare earths, and also non-rare earth impurities. Modifications of these methods are still utilized today.

*Current Research Activities*

Most of the research on rare earth carried out at the Ames Laboratory is funded by the U.S. Department of Energy through the Office of Basic Energy Sciences (BES), with some lesser support from Energy Efficiency and Renewable Energy (EERE), and Advanced Research Projects Agency-Energy (ARPA-E). Other research is supported by CRADAs (Cooperative Research and Development Agreements) and work for industry.

The BES research includes several projects (7) and these are as follows. (1) Extraordinary Responsive Magnetic Rare Earth Materials, such as $R_5(Si_{1-x}Ge_x)_4$, $RAl_2$, and $RCo_2$, which exhibit unusual magnetic, electric, thermal, and elastic behaviors when stimulated by external changes of temperature, applied magnetic fields, or pressure. These include the giant magnetocaloric effect, colossal magnetoresistance and giant magnetostriction (Pecharsky and Gschneidner). (2) Novel Materials Preparation and Processing Methodologies research includes quasicrystals $(Cd_{84}Yb_{16})$, $RFeAsO_{1-x}$ superconductors (polycrystalline and single crystals), reactive metal crystal growth (GdNi)(Lograsso, McCallum, Anderson and Jones). (3) Work in the Innovative and Complex Metal-Rich Materials Project has a small rare earth component, which includes (R,M)-M′X giant multiply endohedral clusters (Miller and Corbett). (4) Complex States, Emergent Phenomena and Superconductivity in Intermetallic and Metal-like Compounds research involves correlated electron systems (Yb-based materials), superconductors ($RNi_2B_2C$, RFeAsO), and ferromagnets ($Nd_2Fe_{14}B$, $CeAgSb_2$) (Canfield and Prozorov). (5) Research in the Correlations and Competition between Lattice, Electrons and Magnetism Project involves X-ray and neutron scattering of various materials including $Gd_5(Si_{2-x}Ge_x)_4$, $RNi_2B_2C$, GdBiPt, and RFeAsO (McQueeney, Kreyssig, Goldman). (6) The Magnetic Materials Discovery research on $LaNi_2Ge_2$ and $LaNi_2P_2$ mixtures, $RV_4O_8$, and $EuM_2Sb_2$ (M = Pd, Rh) was carried out in this Project by David Johnston. (7) In addition to these experimental efforts there is a considerable amount of theoretical work going on overlapping several of the condensed matter physics research projects tying this research together (Harmon, Duane Johnson).

The EERE-Vehicle Technologies research project includes studies of anisotropic bonded and sintered $R_2Fe_{14}B$ (R=Nd+Y+Dy) permanent magnets with high temperature stability for automotive traction motors with little or no Dy content. Also this research was expanded to include scientists and engineers from University of Nebraska-Lincoln, University of Maryland, Brown University, Oak Ridge National Laboratory, and Arnold Magnetic Technologies to enable a fully coupled theoretical and experimental effort to develop non-rare-earth magnets for advanced traction motors (Anderson, McCallum, Kramer).

There is one funded ARPA-E project which involves developing high energy permanent magnets for hybrid vehicles and alternative energy. The lead organization for this effort is the University of Delaware (G.C. Hadjipanayis). The Ames Laboratory's research is headed by McCallum.

A new ARPA-E project on Ce-based permanent magnets for automotive traction motors was funded to begin in FY2012. The Ames Laboratory is the lead organization and there are three industrial partners – Molycorp Minerals, General Motors and Nova Torque. McCallum is the lead project manager and is joined by his Ames Laboratory colleagues Antropov, Gschneidner, Johnson, Kramer and Pecharsky.

CRADA rare earth related research is concerned with recycling magnetic materials and developing new low cost processes for making rare earth metals for various industrial uses. A work for other project involves research on magnetic refrigerant materials.

*Materials Preparation Center (MPC)*

The MPC was established in the 1970s to provide high purity rare earth metals, intermetallic compounds, inorganic compounds, alloys, etc. to research scientists, not only at the Ames Laboratory but also all over the world to promote and assist scientific investigations, both basic and applied; and under certain conditions to assist the commercialization of certain materials. In addition to supplying polycrystalline materials, they also grow single crystals and directional preferred oriented polycrystals of many of these materials, and also make very high purity rare earth and related metals by advanced metallurgical processing techniques. The MPC is a world-renowned national resource treasure. The MPC works on a cost recovery basis.

**Future Research and Other Needs**
(not just the Ames Laboratory but the entire USA)

*Magnets –* $Nd_2Fe_{14}B$

- Reduce the amount of Dy
- Improve the high temperature magnetic strength
- Improve the processing technology
- Lower cost Nd, Pr metals
- Reduce the rare earth content
- Non-rare earth magnets – new, improved existing ones

*Phosphors*

- Improved, lower cost, more efficient separation technologies
- New host materials – more efficient light emitting phosphors
- Reduce amount of activators (Eu, Tb) for same lumen output
- Development of up-conversion phosphors

*Production and Separation*

- New improved extractants and complexing reagents
- Design of better separation techniques, and/or equipment
- New advanced chemistries – combinational and biometric

*Catalysts*

- Improve the effectiveness of the rare earths in stabilizing the zeolite cracking catalysts
- New catalysts and catalytic processes – for bond-cleavage and for bond-formation of hydrocarbons
- New diesel exhaust catalysts

*Recycling*

- Design processes for recovering the metallic materials and placing them directly in production schemes as metallic materials without converting them to chemicals (oxides or halides), separating the rare earths, then reducing them to the metals and finally alloying; especially important for magnets, battery and metallic alloying agents.
- Better recovery techniques for rare earth phosphors from CFC (compact fluorescent lamps), long tubes, color TVs and monitors, color display units
- Design phosphor applications for reusing recycled, but unseparated rare earth phosphors
- Recovery of rare earths from cracking catalysts, especially the heavy lanthanides Tb and Dy
- Develop value-based lifecycle models

*Sustainability*

- Improve manufacturing efficiency – reduce waste.
- Design end-of-life products to easily recover the rare earth materials
- Develop green chemistry and environmentally friendly processing technologies

*New Advanced Energy Technologies*

- Fuel cells
- Magnetic refrigeration

*Rare-earth Information Center (RIC)*

- Re-establish RIC to help promote rare earth research and technology, and commercialization of these elements via the *RIC News* and *RIC Insight*, respectively, the quarterly and monthly RIC newsletters; and answering information inquiries.

*Rebuilding the Rare-Earth Industry Beyond Mining*

- Loan guarantees for small mining companies, producers of intermediate products (metals, magnets, phosphors, catalysts, etc.) and OEMs (Original Equipment Manufacturers) who manufacture hard drives, electric motors, cell phones, i-pods, CFLs, wind turbines, sensors, etc.
- Tax incentives for same.

*Replacing Rare Earth Intellectual Capital – It's Imperative to Educate and Train the Next Generation of Engineers, Scientists and Technical Business Managers*

- Requires 60 to 110 Ph.D., M.S., and B.S. degree students per year for the next ten years
- Promote rare earth courses at educational institutions – via distance learning; semester long courses, short courses
- Research projects funded by NSF, DOE, DoD, NIST
- National scholarships
- Establish a National Research Center of Rare Earths and Energy