

Rare-earth elements separation technology licensed to Marshallton

November 30 2021



Oak Ridge National Laboratory scientists Santa Jansone-Popova, left, and Ilja Popovs quantify rare-earth element concentrations in liquid samples using a spectroscopy instrument. Credit: Genevieve Martin/ORNL, U.S. Dept. of Energy

A new technology for rare-earth elements chemical separation has been

licensed to Marshallton Research Laboratories, a North Carolina-based manufacturer of organic chemicals for a range of industries.

Developed by scientists from Oak Ridge National Laboratory and Idaho National Laboratory in the Department of Energy's Critical Materials Institute, or CMI, the technology provides insight into how to cost-effectively separate in-demand rare-earth elements, which could dramatically shift industry to benefit producers in the United States.

The unique electronic properties of rare-earth elements, or REEs—a group of 17 metallic elements that includes 15 lanthanides plus yttrium and scandium—make them critical for producing electronics, optical technologies, alloys and high-performance magnets. These powerful, permanent magnets are vital to clean energy technology and defense applications.

Individual REEs do not occur in minable concentrations in the Earth's crust, but are naturally mineralized together and must be chemically separated to use for technological applications. Their physical and chemical similarities make them extremely difficult and costly to separate while generating a lot of waste. Extraction and separation of REEs for technological applications occurs largely overseas.

To meet the growing need for these materials and to limit the nation's reliance on foreign sources, ORNL and INL scientists working under the banner of CMI, a DOE Energy Innovation Hub led by Ames Laboratory, have applied their deep expertise in chemical synthesis, separations, and engineering to design and produce new extraction agents based on diglycolamide, or DGA, ligands and a corresponding process for separating lanthanides that outperforms current technology.

"At Marshallton, our purpose is to become a domestic, strategically reliable supplier of DGA extractants for rare-earth elements. We expect

to service pilot-plant and commercial operations in ore processing, recovery from mining tailings and recycling," said Mac Foster, co-owner of Marshallton and a collaborator on the technology. "We're excited to further explore what these new extractants can achieve."

REEs are commercially separated using liquid-liquid extraction, which uses ligands—organic molecules composed of carbon, hydrogen, oxygen, and nitrogen atoms—as extractants to selectively bind the REE ions. An oily solvent containing the extractant is vigorously mixed with an REE-rich aqueous solution, then allowed to separate in the same manner as oil and vinegar for salad dressing. During this process, the REEs get transferred into the organic solvent forming complexes with the extractant molecules. DGAs show higher affinity for lanthanides with smaller ionic radius, which allows individual REEs to be separated from one another in multiple stages.

"Our goal was to identify an extractant that surpasses the performance of the state-of-the-art ligands that are currently used in industry," ORNL's Santa Jansone-Popova said. "The compound widely used is a phosphorous based extractant, called PC88A, and since its selectivity is relatively low, a lot of separation stages are required along with generation of additional waste throughout the process."

Selectivity refers to the degree to which a solvent prefers one metal over another and is described by a unit called separation factor. For example, when seeking to separate adjacent lanthanides neodymium and praseodymium—both used in high-powered magnets—the phosphorus-based extractant's separation factor is around 1.2, which is very low.



Jansone-Popova, right, uses an automated chromatography system to purify diglycolamide—an extractant used for rare-earth element separation. Popovs prepares samples for the analysis using a pipetting robot. Credit: Genevieve Martin/ORNL, U.S. Dept. of Energy

"You have to run the extraction many, many times to separate adjacent lanthanides completely. We need to improve the economics of the process, reduce the waste, reduce the complexity—limit the steps it takes to achieve separation," Jansone-Popova said.

ORNL's Chemical Science Division had been experimenting with an alternative DGA called TOGDA, which has a separation factor of 2.5—already a big improvement over the phosphorus-based extractant. However, a key variable in the economics of the process is loading

capacity—how many grams per liter of extractants can be held in the organic solvent without adverse reactions. TODGA could only handle about one-fifth of what the phosphorous-based extract could.

"The extractant concentrations we were limited to were not adequate compared to the industry standard. At higher concentrations, we run into things like gelling or precipitation, which are detrimental to the process," said Kevin Lyon, an INL chemical engineer with expertise in applied solvent extraction who tested and developed the process design for the licensed technology. "If you think of the process as a conveyor belt, we want to be able to load that conveyor belt up as high as we can, or at least competitive with what industry does, to make it cost effective."

Jansone-Popova recognized that by chemically modifying the structure of DGAs, she might improve their properties and their efficiency in extracting REEs.

Her team at ORNL began a systematic approach to making structural changes to the DGA ligands by adding a range of substituents known as alkyls—fatty organic groups that exclusively contain hydrogen and carbon atoms. These groups can be arranged into different structural configurations. For example, their length and shape can be altered, branches created or linear chains transformed into cyclic arrangements.

The ORNL team passed the trial ligands off to Lyon to test under industrial operating conditions using a counter-current solvent extraction system—a series of vessels that mix and settle the materials to separate out REE compounds through a sequence of [liquid-liquid extraction](#) stages.

During the mixing, the ligands attract the metal ions using electron-rich donor groups, binding the metal ions in a coordinated manner. Extracting certain lanthanides over others depends on ligands having the right

number and arrangement of functional groups—atoms within a molecule that can maintain functionality independently of other atoms in the molecule—as well as the size of the ligands and their ability to mix with the oily organic solvent.

The ORNL team designed, synthesized and tested a library of chemically modified ligands, in collaboration with Lyon, narrowing the field of novel agents for industrial application that could potentially outperform state-of-the-art technology in REE selectivity. Each agent performs differently based on its physical arrangement and the electronic activity it prompts.

"The TOGDA extractant, when saturated with REE ions, would rapidly transform from the liquid phase into a gel or precipitate," Jansone-Popova said. "The new DGA ligands allow the system to remain homogenous even at higher extractant concentrations and maintain good selectivity."



Kevin Lyon, an Idaho National Laboratory chemical engineer with expertise in applied solvent extraction, operates a counter-current solvent extraction system for testing and developing the process design for the separation technology. Credit: INL, U.S. Dept. of Energy

In separating REEs, the new ligands achieved a selectivity range of 2.5–3.1, a staggering improvement for these critical materials.

The team then took on the challenge of scaling up the process to be viable for industry use.

"The process was very iterative; minute changes in the structures of these molecules have impact," Lyon said. "The bottom line is that a [new technology](#) has to be economically viable. We're very driven by input

from industry and the methods they use."

"Most REE extractants have a separation factor of about 1.5 for adjacent lanthanides across the series—if we get to 2, that's good. If we get to 2.5, that's really starting to save some money. If we can get to 3, we're really happy. We've gotten to 6.7 with one of Santa's ligands," said ORNL's Bruce Moyer, who leads the CMI focus area for diversifying supply and is a collaborator on the licensed technology.

The work of the CMI team was outlined in *Inorganic Chemistry*. Co-authors include ORNL's Santa Jansone-Popova, Bruce Moyer, Ilja Popovs, Camille Albisser, Vyacheslav Bryantsev, Mary Healy and Diana Stamberg; INL's Lyon; Argonne National Laboratory's Benjamin Reinhart; Foster of Marshallton Research Laboratories; and Alena Paulenova and Yana Karslyan, Oregon State University.

In his role at CMI, Moyer oversees a portfolio of research projects investigating how to expand the supply of REEs through innovative processes.

"CMI's goal is to provide the best separation technology to industry. We've selected these DGAs because they have the potential to reduce the consumption of chemicals and production of waste, thereby lowering costs. They're more selective, which reduces the number of stages needed, reducing the overall capital cost of building a plant," he said.

"We're creating better technology that will make the production of purified rare earths cheaper. By doing that, the U.S. industry will get more competitive and be able to deliver purified rare earths for magnet production and other applications."

More information: Diana Stamberg et al, Structure Activity Relationship Approach toward the Improved Separation of Rare-Earth

Elements Using Diglycolamides, *Inorganic Chemistry* (2020). [DOI: 10.1021/acs.inorgchem.0c02861](https://doi.org/10.1021/acs.inorgchem.0c02861)

Provided by Oak Ridge National Laboratory

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