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FOSSIL ENERGY – EXTRACTION OF REEs FROM ACID MINE DRAINAGE

Rare Earth Elements (REEs) make a group of seventeen chemical elements, including fifteen lanthanides, scandium, and yttrium. Due to their unique physiochemical properties, REEs have become materials of capital importance in modern society, serving as the basis in the manufacture of magnets, batteries, catalysts, lasers, etc. Global demand of REEs has steadily increased over the last decade, with China dominating the market. China's REE exports represent approximately 85% of the global transaction, with 90% of US imports credited to China. This represents an issue of national security, as well as an area of great scientific interest.

Significant attention and research is being devoted to the extraction and separation of REEs from various sources. Conventional mining extraction of REEs involves the use of environmentally challenging methods. Advanced methods of REE extraction are, thus, in demand. Both physical beneficiation and chemical/thermal separation approaches are being investigated in the development of novel REEs extraction technologies. One potential approach suited for REE recovery is supercritical fluid extraction (SFE). SFE separation with supercritical carbon dioxide (sCO2) is attractive for REE due to the advantageous/benign characteristics of this medium.

The Lehigh University Energy Research Center (ERC), in collaboration with Applied Separations of Allentown, PA, is conducting research to investigate the feasibility of a chelate-enhanced sCO2 method for REE extraction from acid mine drainage (AMD). AMD is a metal-rich acidic wastewater byproduct from the coal mining industry. The project is carried out with support from Blaschak Coal Corporation and Ben Franklin Technology Partners (BFTP). The team from Lehigh University is led by Prof. Jonas Baltrusaitis from the ChBE Department and includes Drs. Xingchao Wang and Carlos Romero, Zheng Yao and graduate students. Al Kaziunas and Rolf Schlake participate from Applied Separations. The Blaschak team includes Greg Driscoll, Boyd Kreglow, Tom Lowe and Harold Schobert. Connie Faylor manages the BFTP side of the project. Greg Driscoll, CEO of Blaschak Coal says, "Extracting REEs from AMD from the Pennsylvania Anthracite region presents the dual opportunity to finding

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RENEWABLE ENERGY – THERMAL ENERGY STORAGE RESEARCH

Due to the inherent variability of solar energy, deep penetration of solar thermal power would need to rely on the availability of efficient, reliable and affordable thermal energy storage (TES). Concentrated Solar Power (CSP) is well suited for adaptation in schemes that include TES. Available concepts for CSP-TES include solid media storage such as rocks and sand, steam accumulators, and two-tank sensible storage based on molten salts. Due to its dual use as a storage media and heat transfer fluid, the two-tank molten salt storage technology is the commercial standard for tower and parabolic trough power plants with TES, working in the 300-500°C temperature range. However, Prof. Sudhakar Neti of the Energy Research Center (ERC) says, "The thermal properties, energy density and cost of molten salts systems, warrant development of alternative, more cost-effective concepts to make TES more competitive for solar thermal applications, as well as industrial processes."

An interdisciplinary team at Lehigh University, led by the ERC, is researching different TES concepts. The collaborative team includes faculty from Mechanical Engineering and Mechanics (Alp Oztekin and Ganesh Balasubramanian), Chemical and Biological Engineering (Mark Snyder and Kemal Tuzla), Civil and Environmental Engineering (Clay Naito, Spencer Quiel and Muhannad Suleiman), and the Energy Research Center (Sudhakar Neti and Carlos Romero). According to the operating principle, TES can be classified as sensible heat storage, latent heat storage and thermochemical energy storage (TCES). The TES team at Lehigh is working on all three forms of TES.

One project being carried out by the TES team is for a sensible heat TES concept that utilizes cementitious materials with enhanced thermo-mechanical properties for this type of application. Prof. Clay Naito says, "Dissimilar thermal expansion between thermosiphons, which charge the media, and concrete can result in the formation of high tensile

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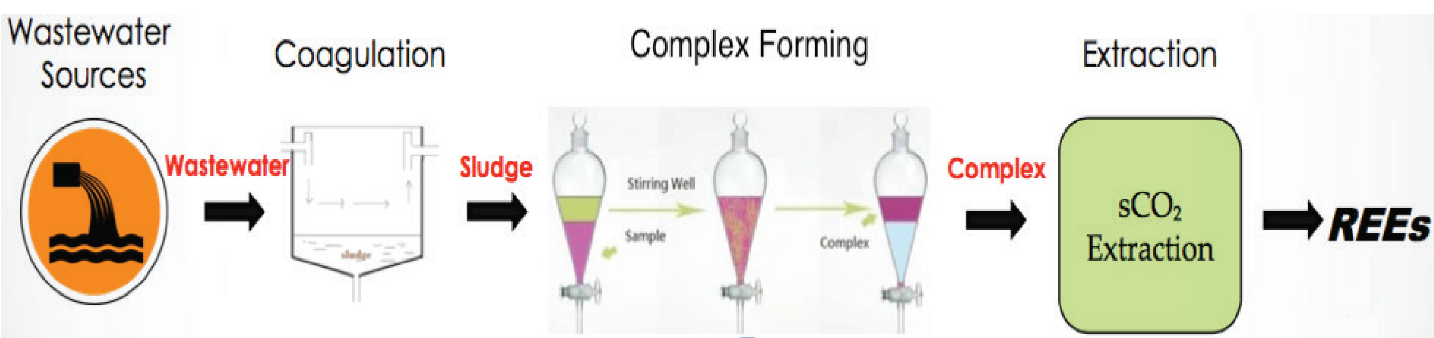
non-energy uses of our coal, as well as providing an avenue for AMD environmental compliance.”

AMD samples from four different locations were provided by Blaschak. They include materials from Centralia, Washington, the Big Mountain Mine Pool in Western Pennsylvania, the Sayre Penn Scott Mine Pool in Eastern Pennsylvania, and the St. Nicholas Breaker Mine Pool in Schuylkill County, Pennsylvania. Tom Lowe from Blaschak indicates that “pH values of the material samples range from 4.3 to 5.9, with REE concentrations of Ce ranging from 0.005 to 0.08 mg/L. The lowest pH samples resulted in larger total REE content in the liquid samples.”

The extraction method developed in this study is a hydrometallurgic process that consists of a coagulation process, where metallic compounds and REE compounds are precipitated with an aluminum-based coagulant from AMD samples; a complex forming process, where precipitates are complexed with organic ligands; and a CO2 separation stage, where sCO2 was used to extract REEs from the complex product. “Direct extraction of metal iron is inefficient in sCO2 because the requirement of charge neutralization and the low ability of the interaction between the solute and the solvent,” says Jonas Baltrusaitis. As part of this study, a range of solid and aqueous ligands have been investigated, resulting in complexes that are quite soluble in sCO2, and that enhance the extractability of REEs in sCO2.

“Simulated and actual material samples were prepared for the different steps of experimentation. Liquid solubility tests were carried out using a 50 mL pressurized test apparatus, with CO2 pressurized to 200 bar and up to 80°C. Process conditions were optimized to achieve the highest level of REE recovery efficiencies, including saturation solubility,” explains Al Kaziunas of Applied Separations. “REEs extraction efficiencies in sCO2 reached 88.4% for Ce, 94.1% for La, and 94.8% for Nd, as measure by ICP-OES,” says Dr. Xingchao Wang of the ERC. “The effect of [H+] concentration on sCO2 extraction efficiency was confirmed in this study, with nitration being the rate-limiting step in the complexing step,” adds Wang.

Rolf Schlake of Applied Separation concludes, “This study has demonstrated the initial feasibility of utilizing sCO2 in extracting REEs from AMD sources. Process optimization and scale-up are still outstanding areas of improvement. Experimentation with other ligands and designing specific equipment to improve the separation are the next steps to be undertaken. Some of this may allow direct separation of REEs by atomic number.” Discroll adds, “Blaschak envisions the process to be engineered to also work on coal sources, which would allow our company to find other applications and added value to our product.”



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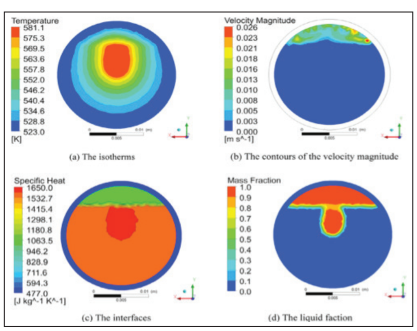
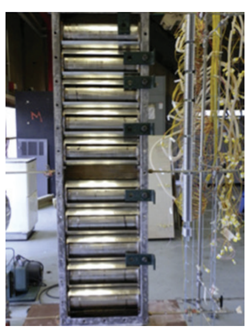
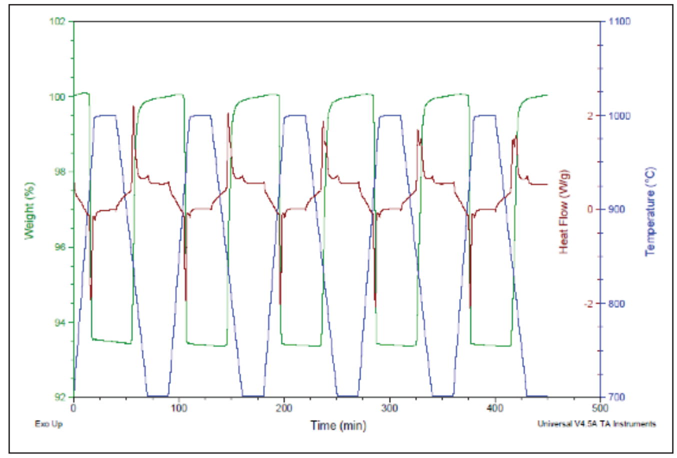
stress in the concrete near the interface, and the formation of global cracking of the system. We will be exploring compliant materials with high thermal conductivity, as well as steel reinforcement and proper distribution of fibers to minimize the size of cracking if incompatible expansions were to occur. This can be supplemented with pre-stressing methods in which the concrete is pre-compressed using embedded steel under tension. These approaches are regularly used to minimize crack sizes in concrete structures subjected to harsh environments." This project will ultimately aim at developing a thermal energy storage prototype designed and built for up to 400°C operation, 100 kWhth, 90% round-trip efficiency and cost no more than $25/kWhth.

A second project consists of embedding eutectic salt mixtures into graphite foam to gain significant improvements in material thermal conductivity. Dr. Xingchao Wang, an ERC researcher working on the project explains, "Graphite foam is a highly porous, carbon-based material with a high thermal conductivity. By embedding a chloride salt into the porous structure of the foam, the foam would serve as an additional heat transfer surface area for the salt. This additional heat transfer surface area would increase the effective conductivity, which would reduce overall system-level costs." Profs. Tuzla and Oztekin add, "This project extrapolates research by the TES team on inclusion of nano-diamond, Al_2O_3, and SiC nano-particles for improvement in heat transfer capabilities of heat transfer fluids for solar applications; and on encapsulated phase change materials (EPCMs) for high-temperature TES. The latter latent heat TES project included experiments and computer simulations with a range of EPCMs in a high temperature thermocline, operating at 500°C, 120 kWhth. The following binary systems were studied: $NaNO_3$-KNO_3, $LiNO_3$-$NaNO_3$, and $LiNO_3$-KNO_3."







A third project focuses on TCES using the REDOX reaction of metal oxides capable of storing thermal energy at temperatures in excess of 900°C. Nasser Vahedi, a graduate student in Mechanical Engineering, and Prof. Snyder say, "We have been performing experiments, using TGA/DSC/XRD/SEM instrumentation, on the $2\ Co_3O_4(s) + \Delta H_r \leftrightarrow 6\ CoO(s) + O_2(g)$ and the $CaCO_3(s) + \Delta H_r \leftrightarrow CaO(s) + CO_2(g)$ reactions and have been able to identify and work on the challenges with these materials in relation to material and thermal stability, process/reactor design, scalability and cost reduction." One important aspect that was identified was the coarsening and grain growth after cyclic operation of the system, which would result in operational issues related to O_2 or CO_2 diffusion into the solid reactant, during the thermal discharge part of the cycle.

Dr. Romero adds, "Another important dimension with TES is related to flexible operation of conventional fossil power plants. With the fast penetration of renewable energy in the power generation matrix, fossil power plants are forced to comply with fluctuating grid imbalances between available generation and demand. These new dispatch conditions demand flexible plant operation, which is constrained by technical limitations of the conventional units. TES offers a large bulk energy management advantage for addressing flexible plant operation and provides additional thermal reserve that could be used for extended load range (peak power benefit)."

IN MEMORIAM

This edition of the Lehigh Energy Update is dedicated to Prof. Edward K. Levy. Prof. Levy dedicated his life to pursuing studies in energy topics of critical importance to the research community, government agencies, and the power generation industry. His 40+-year illustrious career covered advancements in combustion, fluidization, thermal sciences, environmental research, and power plant technologies. Under his supervision, more than 200 graduate students started their careers at the Energy Research Center (ERC). His colleagues and friends at the ERC and Lehigh University are grateful for his dedication and valuable work.

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