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RECOVERY OF RARE EARTH ELEMENTS FROM AMD SLUDGE

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Recovery of rare earth elements from coal mine drainage

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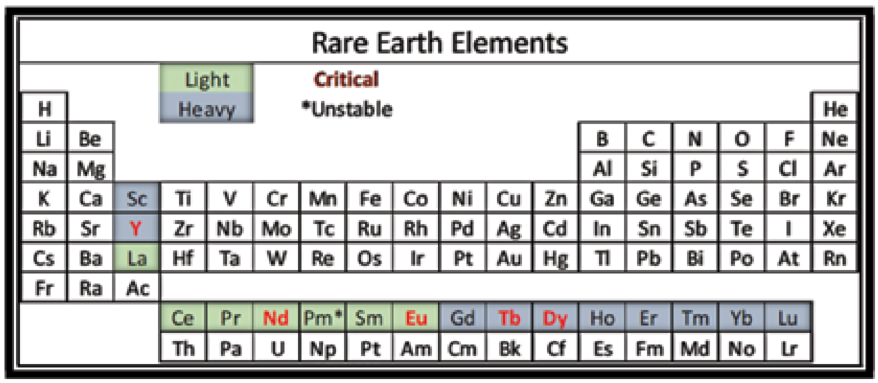
Rare earth elements (REEs) are critical in today's technology-driven world. These elements are used in electronics such as smart phones, magnets, computers, televisions and most notably in national defense technologies. The REEs are located at the bottom of the periodic table (Figure 1) and include 17 different elements (Table 1). The elements listed as REEs are not really "rare," but they rarely occur in concentrations that make them economically attractive to mine and process.

Figure 1. The rare earth elements typically include the 15 lanthanides, plus Yttrium and Scandium. They are further classified as light, heavy and critical (See Tables 1 and 2). Promethium does not occur naturally.*



These elements occur in a wide variety of geologic formations but are rarely found in concentrations to facilitate extraction and refinement. Where they are found in significant concentrations, the ore body is often contaminated with radioactive thorium and uranium, which causes problems with handling and disposal of ores and processing wastes. As such, the U.S. currently imports 90 percent of its REEs from China. With increasing demand for REEs for technology and defense uses, U.S. mining companies have invested time and capital to discover and secure REE resources outside of China. Unfortunately, many of these companies entered bankruptcy or lost interest due to unpredictability in demand and shifting prices.

TABLE 1. List of 17 rare earth elements (REE) with their atomic number and symbol. Table from Thermofisher.com.

*Promethium is unstable and does not occur naturally.

**Scandium and Yttrium are classified as rare earths, although not lanthanides.

Atomic #	Element	Symbol
21	Scandium**	Sc
39	Yttrium	Y
57	Lanthanum	La
58	Cerium	Ce
59	Praseodymium	Pr
60	Neodymium	Nd
61	Promethium*	Pm
62	Samarium	Sm
63	Europium	Eu
64	Gadolinium	Gd
65	Terbium	Tb
66	Dysprosium	Dy
67	Holmium	Ho
68	Erbium	Er
69	Thulium	Tm
70	Ytterbium	Yb
71	Lutetium	Lu

Only two REE mines started production outside of China in response to this demand. The Mount Weld deposit in Australia began production in 2013. The ore from Mount Weld is processed in Malaysia, whose operating permit has come under scrutiny because of unsafe practices for disposing of radioactive waste, and hence their production of REEs has ceased. The second mining operation, Mountain Pass located in the U.S., has experienced instability in reaching full-scale production due to lower REE prices and uneven distribution of light versus heavy REEs in the ore body.

There continues to be a strong need to find domestic, predictable supplies of these critical elements, regardless of their pricing. Many industrial processes rely on REEs for their products, including catalysts, metallurgy, petroleum refining, catalytic converters, ceramics, phosphors and electronics. The availability of heavy REEs are of particular concern because identifying geologic sources of these elements in the U.S. have been unsuccessful. Of the 15,000 tons of REEs used by the U.S. every year, approximately 800 tons (five percent) are required for the defense industry. To develop secure, predictable, domestic supplies, the U.S. Department of Energy's National Energy Technology Laboratory (USDOE NETL) initiated a national competition in 2015 to develop economical and environmentally safe methods for extracting REEs from domestic material sources.

The presence of REEs in coal was known as early as 1964. In 2014, the USDOE analyzed the economic feasibility of recovering REEs from coal, coal refuse and coal fly ash as material sources. In 2015, with a small startup grant from USDOE, researchers at West Virginia University sampled AMD precipitates from nine sites and found significant concentrations of REEs in these precipitates formed during acid mine drainage (AMD) treatment (Ziemkiewicz et al., 2016).

A detailed study of REE occurrence in the northern and central Appalachian Coal Basin was developed by Dr. Paul Ziemkiewicz, director of West Virginia University's Water Research Institute (WRI). He and his team at WVU collected AMD from both surface and underground mines and collected precipitates formed during AMD treatment with alkaline chemicals at these sites (Figure 2). The aqueous samples were acidified in two percent nitric acid and analyzed using ICP-MS by certified laboratories. The precipitate samples were digested using sodium peroxide and re-dissolved in hydrochloric acid and analyzed by ICP-MS.

Ziemkiewicz and his team found an average total REE concentration of 258 ug/L (or ppb) with a range of 8 to 1,139 ug/L in aqueous samples of AMD (Table 2). The REE concentration from AMD precipitates averaged 517 mg/kg (or ppm) with a range of 29 to 1,286 mg/kg, a concentration factor of more than 2,000 over aqueous AMD samples (Table 2). The AMD precipitates contain almost 10 times more REE concentrations than U.S. coal (66 mg/kg) (Vass et al., 2016). Another important finding was that REE concentrations were much higher in aqueous AMD samples with a solution pH of 5.0 or less (Figure 3).

Table 2 shows the concentrations of individual REEs in samples of untreated AMD and samples of AMD precipitates formed during AMD treatment. Elements highlighted in green are "light," those highlighted in blue are "heavy," and those with red lettering are termed "critical" elements. *Note: mg/kg (ppm) is 1,000 times greater than the unit ug/L (ppb). Therefore, the concentration of REEs in precipitates is more than 1,000 times greater than in raw, untreated AMD.

Given the high REE concentrations extracted from AMD precipitates, estimates of REE production from AMD treatment plants could produce from 800 to 2,200 metric tons (Mg) of REEs per year (Ziemkiewicz et al., 2016). The high concentrations of REEs in AMD sludge and their processing

Figure 2. Typical AMD treatment pond where precipitates are captured and allowed to settle from treated AMD.

TABLE 2. REE concentrations.

Element	Untreated AMD (ug/L)*	Precipitates (mg/kg)*
Sc	13	16
Y	70	125
La	11	62
Ce	42	108
Pr	7	15
Nd	39	74
Sm	14	21
Eu	4	5
Gd	19	28
Tb	3	5
Dy	17	26
Ho	3	5
Er	8	13
Tm	1	2
Yb	6	10
Lu	1	2
Total REEs	**258**	**517**

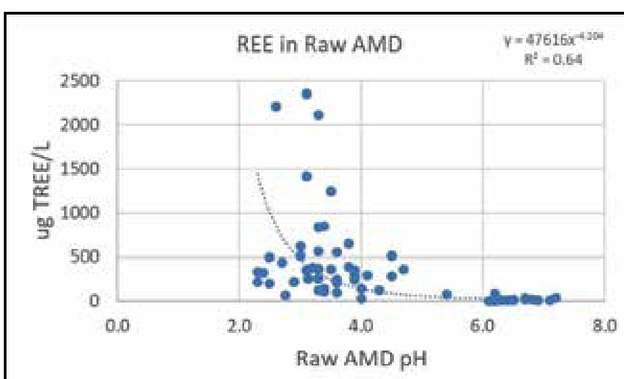


Figure 3. The relationship between the pH of raw AMD and the concentration of Total REEs (TREE) in the aqueous phase. Clearly, higher concentrations of TREEs occur in AMD at less than 5.0 pH.

and sale on the market provide an opportunity to recover some of the costs of treating AMD. This financial recovery would encourage companies to maintain AMD treatment which would improve the quality of streams and rivers in the region. AMD treatment is an environmental and costly obligation for mining companies; therefore, collecting and processing the REEs from these AMD treatment precipitates could create a revenue stream and provide a financial return from a costly treatment and disposal process. This process would promote a new industry for economic development and generate a secure domestic supply of REEs.

To evaluate the monetary value of REEs in AMD, the average prices of REEs were compiled for the lanthanide series plus Yttrium from 2008 to 2015. Using a detailed pricing structure and analysis (see Vass et. al., 2016), a value of $89 per kg of total REEs was identified. (More information on the assumptions used for pricing is available from the authors and in the two cited papers). Using this value, a minimum estimate of the value of REEs in AMD precipitates is $3 million per year.

Now that REEs were identified and quantified in AMD precipitates and a monetary value placed on the precipitates if all the REEs could be extracted, additional work was needed to separate REEs from the other elements in AMD treatment precipitates (Fe, Al, Mn, Ca, Mg). Therefore, a procedure for economically recovering REEs from AMD precipitates was needed to realize this estimate of tonnage and monetary potential, and whether the process of recovery was economically viable at a production scale.

Figure 4. West Virginia University's REE Extraction Facility produces highly concentrated rate earth products from AMD precipitates. This sample is 87 percent rare earth oxide.

Separation technologies such as ion exchange, solvent extraction, or selective precipitation can be used to recover REEs in an oxide form. Once separated, the REE oxides could be packaged and sold to refiners with advanced capabilities to turn the oxides into metals (Figure 4). These processes utilize smelting or electrolysis to isolate REE metals that can then be sold on the open market.

In 2018 with NETL funding, a bench scale pilot plant was opened through a joint venture among WVU, Rockwell Automation and Shonk Investments LLC on West Virginia University's campus to test the technical and economic feasibility of scaling-up their extraction and refining technology with plans to rapidly commercialize the process.

In 2019, this project was successful in identifying economically attractive recovery of REEs from AMD such that USDOE Secretary Rick Perry announced the award of $5 million to the WVU team to expand their process to a full-scale field facility to be built into a new AMD treatment plant near Mt. Storm in northern WV. Figure 5 shows a conventional AMD treatment plant operated by the West Virginia Department of Environmental Protection where AMD precipitates will be generated and collected.

This phase of the project will be achieved by collaborating with the West Virginia Department of Environmental Protection's Office of Special Reclamation to design and build the treatment plant, Rockwell Automation to provide the sensor and control technology and TenCate Corporation to engineer materials to further concentrate REE-extracted materials. The on-site processing plant will reduce costs of operation significantly and pave the way for a new industry in Appalachia.

These collaborations are vital to the success and implementation of this pilot facility. Support of West Virginia's congressional leaders has been key. Senator Joe Manchin said, "These projects allow continued use of our domestic resources in an environmentally friendly way and will help reduce our vulnerability to foreign sources of rare earth elements."

Senator Shelley Moore Capito added, "REEs are essential to modern advanced manufacturing, and WVU's technology will help provide a domestic source of this material while cleaning up legacy mine waste. This is a win-win-win for our economy, our national security, and the environment."

Representative David McKinley stated, "WVU's work to develop a domestic REE source is critical and this funding will help to build an American supply chain and ensure that we are not dependent on other nations for our supply."

With this new funding, the WVU team will scale up and demonstrate how AMD treatment and watershed restoration can operate hand-in-hand with REE recovery. Success will generate a revenue stream that will offset stream restoration costs and point the way toward a new way of thinking about environmental cleanup – one that engages market forces while fulfilling a critical national need.

Figure 5. The West Virginia Department of Environmental Protection's Muddy Creek AMD treatment plant near Albright, WV, showing the lime silo and system control building in the lower left, two clarifiers and Geotubes across the creek for collection and dewatering of AMD precipitates.

In conclusion, this is a great opportunity to demonstrate the economics and environmental benefits of combining AMD treatment, watershed restoration and critical mineral recovery. The team at WVU has worked together for the past several years and are poised to move rapidly toward commercial development.

References:

Vass, C., A. Noble, P. Ziemkiewicz. 2016. The occurrence and concentration of rare earth elements in acid mine drainage and treatment byproducts. Mining, Metallurgy & Exploration. https://www.osti.gov/servlets/purl/1577094

Ziemkiewicz, P., T. He, A. Noble, X. Liu. 2016. Recover of rare earth elements (REEs) from coal mine drainage. In: 2016 West Virginia Mine Drainage Task Force Symposium, March 29-30, 2016, Morgantown, WV. https://wvmdtaskforce.files.wordpress.com/2016/04/2016-ziemkiewicz-etd30-amdtf-29mar16-a.pdf