

Quarterly Report

Real Earth Element (REE)/Critical Mineral (CM) Extraction Technique

Goal and scope

Life-Cycle Analysis: Life-cycle analysis including energy and material analysis, environmental impact assessment, scalability assessment and detailed economic analysis shall be conducted to the current REE and CM supply chain and investigate the potential upgrading of the REE and CM process industry, in order to establish pathways toward net neutral carbon emission and the process engineering and design requirements to accomplish this.

Life Cycle Inventory (LCI)

To undertake the LCI the processes within the boundary of analysis requires a detailed description. This ensures all key units, energy and material flows are well analyzed. This work looks at both the traditional/current production technique and then the recent innovation of critical metal extraction by Sandia National Lab. The proposal from this is to use supercritical CO₂ (sCO₂)-H₂O-Chelator solvent system for in-situ and ex-situ mining.

The study area consists of coal fields, active mines, and abandoned mine sites Figure 1 and they include the San Juan and Raton Basins in San Juan, Rio Arriba, Sandoval, McKinley, Cibola, Catron, Socorro, and Colfax Counties.

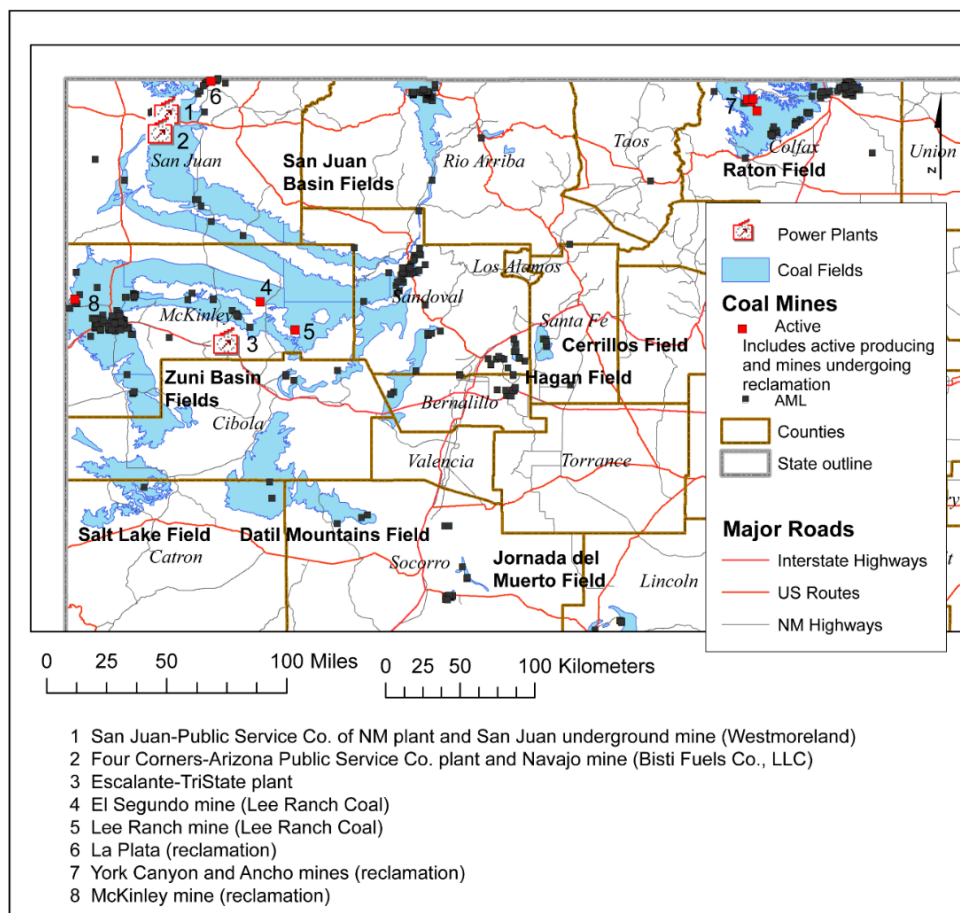


Figure 1

Traditional/current

Process	Brief description
Mining	Excavation, hydraulic digging, crushing etc.
Beneficiation	After mining, the ores are crushed and processed to increase their REE concentration. This step is normally undertaken at, or close to, the mine site. Using a range of physical and chemical processes, REE bearing minerals are separated from iron oxide and other gangue minerals. The concentrate is then subjected to six conditioning treatments with steam and different reagents (Krishnamurthy and Gupta 2005). Common reagents used in this process are either fatty acids or hydroxomates which collect the REE minerals in the slurry. Sodium silicate disperses the silicates and allows the fatty acid to attach better to the REE concentrate (Jordens et al. 2013) (Zhi Li 2014). The resulting final concentrate is 60% REE oxide with recovery rate of 65 to 75% (Krishnamurthy 2005).
Roasting/Cracking	the mineral concentrate from beneficiation is roasted with sulfuric acid. Sulfuric acid is a common reactant to dissolve carbonatite minerals, such as the bastnäsite ore. This high-temperature acid-roasting process is relatively simple but generates potentially hazardous exhaust gases (Zhang and Zhao). When bastnäsite is treated with sulfuric acid, REE precipitates as double sulfates.
Leaching	This relatively simple process consists of an acid-base extraction in two steps: (1) diluted HCl and an alkaline treatment are used to selectively precipitate the undesired metal concentrates and leave in a residue (2) concentrated HCl is used to transform the REE sulfates into REE chlorides.
Solvent Extraction	During the process, leachate containing REE ions produced from the leaching operation is blended with an organic extractant and as a result, REE ions in the aqueous phase produce more soluble compounds in the organic solution (Krishnamurthy 2005) (Vahidi and Zhao 2016). In general, one of the liquid phases is an aqueous phase, whereas the other one is an organic phase (that is, kerosene, toluene, etc). The solute distribution depends on solute-solvent interactions such as metal-water interactions in the aqueous phase, or reactions of the solute with other species in the organic or aqueous phase (Hoogerstraete et al, 2013) Subsequently, during the stripping reaction, which reverses the extraction reaction in the solvent extraction process, by using hydrochloric acid or oxalic acid, the REE ions are ultimately transported from the loaded organic extractant to a fresh aqueous medium in which the REE ions are more soluble. Eventually, the REE ions concentration in the aqueous medium after the solvent extraction process is 10–100 times of the REE ions concentration after the leaching process (Preez and S Preston 1992) (Krishnamurthy 2005) (Vander Hoogerstraete et al. 2013).
REO product finishing	The chlorides from the solvent extraction processes undergo oxalate or carbonate precipitation; some are sold as carbonates, and some are sent to final calcination for further treatment. The precipitation is done under low atmospheric pressure and there are no fumes. The oxalate slurry is washed with hot water to remove liquid residue. The clean slurry is pumped to a centrifuge to separate liquid from solid and then is transferred to a tunnel furnace for calcination. Product finishing processes such as calcination are included in the solvent extraction process.
Tailing, Flue gas and Waste treatment	The waste water treatment process in the HDS includes the following stages: Neutralisation with hydrated lime, which in turn involves; Milk of lime production (mixing hydrated lime with water); Three stage neutralization with the hydroxide ion from milk of lime production; Thickening; Solids filtration (producing neutralization underflow). Water recovered from solids thickening and filtration then proceeds to biological treatment; Nutrition addition, Aeration and biological oxidation, Settling and Discharge.

Proposed Technology

Process	Brief description
Fracking	The solvent will be injected into an ore deposit as a fracking fluid. This operation will increase rock permeability by up to four orders of magnitude. The sCO ₂ - chelator fluid will dissolve surrounding minerals along the flow pathway to create new transport route and more porosity.
Reaction	The sCO ₂ solvent with a chelator, such as citric acid, reacts with the host minerals to extract critical metals.
Mineralization	CO ₂ can be either recycled or converted into carbonate minerals. As the ore minerals react with the solvent mixture, the divalent cations (Ca ²⁺ , Mg ²⁺ and Fe ²⁺) will release from the ore minerals, the pH value of the system increases and eventually the system reaches the solubility limit of minerals, leading to the carbonate mineral formation.
Pump back	Pregnant solution is pumped back and with further addition of chelator group separation the solution is separated into REE and other cations.
REE separation	REE ore is separated into individual REEs.

Ongoing/Future work

- Complete Inventory analysis
- develop a spreadsheet model for LCA and TEA analysis

Selected References

1. Gwendolyn Bailey, P. James Joyce, Dieuwertje Schrijvers, Rita Schulze, Anne Marie Sylvestre, Benjamin Sprecher, Ehsan Vahidi, Wim Dewulf, Karel Van Acker, Review and new life cycle assessment for rare earth production from bastnäsite, ion adsorption clays and lateritic monazite, *Resources, Conservation and Recycling*, Volume 155, 2020, 104675, ISSN 0921-3449,
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3. N. A. Azzolina, J. A. Hamling, W. D. Peck, C. D. Gorecki, D. V Nakles, and L. S. Melzer, "A Life Cycle Analysis of Incremental Oil Produced via CO₂ EOR," *Energy Procedia*, vol. 114, pp. 6588–6596, 2017.
4. ISO 14041: Environmental Management - Life Cycle Assessment - Goal and Scope Definition and Inventory Analysis. 199
5. Navarro J and Zhao F (2014) Life-cycle assessment of the production of rare-earth elements for energy applications: a review. *Front. Energy Res.* 2:45. doi: 10.3389/fenrg.2014.00045