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Environmentally Benign Extraction of Critical Metals from Coal and Coal byproducts

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The U.S. imports 100% of many of its strategic metals, including rare earth elements (REE). Each year ~45 million tons of coal ash is generated from coal-burning power plants, and two-thirds of that ash is not reused. Much of this unused coal ash has high contents of REEs; typically, around 300-900 ppm (Kolker et al. 2017, International J. of Coal Geol., 184: 1-10). Traditionally the REE extraction process involves mining and beneficiation followed by chemical treatment using acids to dissolve ores/minerals. These steps are not only labor-intensive but take a devastating toll on the environment. Similarly, the current state-of-the-art for industrial REE separations utilizes solvent extraction with phosphonic acids, a complex process notorious for its excessive chemical consumption, and wastewater effluents.

Citric acid, with seven potentially O–donor atoms, is an asymmetric ligand that can self-assemble around metal ions in diverse arrangements such as a chelating and bridging spacer. Supercritical CO_2 ($scCO_2$) fluid is an excellent solvent to extract metals due to its low toxicity. In addition, the solubility of metals in $scCO_2$ varies with pressure, permitting selective extractions. Through the combination of basic chelating chemistry and the unique property of $scCO_2$ we developed environmental benign extraction technology using a $scCO_2$-water-citrate solvent to remove valuable critical metals along with toxic metals from coal and its byproducts. This fluid, with an appropriate chemical modification, can provide high enough acidity and solubility to release metals from coal and coal byproducts.

Extraction experiments on coal ash from the Central Appalachian basin, SRM 1633C with 685 ppm total REEs, were conducted using citric acid solution with and without supercritical CO_2 solvent, respectively. Results show that up to 42% total REEs contained in the coal ash were extracted into citric aqueous solution within days. The leachate is 3.5% higher in critical REEs fraction compared with the original coal ash. During this extraction process, no new waste is generated, whereas the original coal ash is becoming less hazardous to the environment via the removal of toxic metals such as selenium and arsenic.