

Microanalytical Perspectives on REEs and RCRA Elements from Ore to Waste in the Phosphate Cycle

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Florida's phosphate deposits supply over 70% of U.S. phosphate fertilizer. In the wet-process, phosphate rock is reacted with sulfuric acid to produce phosphoric acid, creating the waste-product of phosphogypsum (PG), stored in engineered stacks. PG could serve as a substitute for natural gypsum in construction or in agriculture, but the observed levels of radionuclides, fluoride, and heavy metals make most of it unsuitable for reuse. However, PG also contains several desired elements, with the rare earth elements (REEs) representing a promising target for valorization. The leachability of RCRA elements (As, Ba, Cd, Cr, Pb, Hg, Se, Ag) that are also present needs to be assessed further. Yet, the mineralogical factors controlling the distribution and mineralogical pathways of REEs and RCRA elements in PG remain incompletely understood.

We obtained cores of phosphatic sediments and from the Piney Point PG stack in Central Florida. Samples were analyzed for mineralogy and composition using X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDX) and laser ablation inductively coupled plasma time-of-flight mass spectrometry (LA-ICP-ToF-MS). These methods allowed us to investigate the geochemical and mineralogical behavior of REEs and RCRA elements from ore to PG.

The phosphate ore is dominated by carbonate (fluor)apatite with quartz and Ca-Mg carbonate in a clay matrix. REEs are mainly incorporated into carbonate apatite, while among the RCRA elements, As, Ba, and Cr were above the detection limit. The clay matrix exhibited negligible levels of REE content. In the PG stack, two distinct lithologies, light and dark, were identified. The light fraction consists predominantly of gypsum with minor quartz, whereas the dark fraction is enriched in iron-phosphate along with chukhrovite/meniaylovite ($\text{Ca}_{4.5}\text{Al}_2(\text{SO}_4)\text{F}_{13} \cdot 12\text{H}_2\text{O}$ / $\text{Ca}_4\text{AlSi}(\text{SO}_4)\text{F}_{13} \cdot 12\text{H}_2\text{O}$). Notably, REEs preferentially partition into the chukhrovite/meniaylovite, substituting for Al^{3+} , whereas As, Ba, Pb and Se are predominantly hosted by other phases within the dark fraction.

These results highlight the distinct mineralogical controls on the distribution and mobility of REEs and RCRA elements from ore to PG stack. Understanding these partitioning mechanisms is critical for assessing the potential for REE recovery and developing remediation strategies to mitigate the environmental risks posed by PG waste.