

Integrating LA-ICP-ToF-MS mapping with alpha autoradiography and EDX to determine the host phases for radionuclides and REE in phosphogypsum waste

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Phosphogypsum (PG) is an industrial waste by-product from the wet process manufacture of phosphoric acid (H_3PO_4). Gypsum has potential applications in drywall, cement, road aggregate, in addition to being a cheap thermal insulator and fire retardant. With the world's reliance on phosphate-based fertilizers, the remediation of PG is a necessity complicated by the fact that the wastes contain U-series radionuclides (mostly ^{226}Ra and daughters), fluoride and heavy metals/metalloids.

Phosphogypsum has also been explored as a source of economic quantities of rare earth elements (REE), elements essential for modern technology. However, the valorization of PG is contingent on radionuclide remediation. Yet, the mineralogical control on the distribution of REE, radionuclides and elements regulated under the Resource Conservation and Recovery Act (RCRA) and their potential heterogeneity within the phosphogypsum is poorly understood. Here, we integrate energy-dispersive X-ray spectrometry (EDX), laser ablation inductively coupled plasma time-of-flight mass spectrometry (LA-ICP-ToF-MS) and alpha autoradiography to constrain the host phases of radionuclides, RCRA elements and REE in PG from the Piney Point phosphogypsum stack, USA.

Mineralogically, the PG waste comprises light (gypsum + quartz) and dark (quartz + iron phosphate + chukhrovite-meniaylovite in a Si-rich amorphous or nanoparticle matrix) lithologies. Alpha autoradiography demonstrates that radionuclides are concentrated in the dark lithology with hotspots of alpha emission often related to areas dominated by the Si-rich matrix, where trace element maps also show enrichment in some RCRA elements (e.g., As, Se, Ba and Pb). Chukhrovite and/or meniaylovite is a major host of REE within the dark lithology whilst Ba, and presumably Ra, is hosted in nanoparticle barite-celestine agglomerates up to tens of micron in size. By contrast, the light (gypsum-dominated) lithology is relatively free of RCRA, radionuclides and REE suggesting targeted removal of the light lithology from the phosphogypsum could be a viable purification strategy. Finally, selective removal of chukhrovite/meniaylovite from dark lithologies could concentrate REE in economic quantities.