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Critical Elements Recovery from Phosphatic Clay

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Rare earth elements (REE) are important components in the field of modern technology, particularly for permanent magnets used in motors, generators, and superconducting systems. Supply concerns, driven by China's export restrictions, has led to the search for US domestic sources. Phosphate fertilizer production byproducts in Florida are considered potential REE resources, especially phosphogypsum. However, clay slimes generated during phosphate beneficiation also contain appreciable REE concentrations and may represent an underexplored alternative resource.

This study focuses on the valorization of phosphatic clays. We analyzed (1) phosphatic clays derived from the Peace River Formation within the Hawthorn Group, and (2) samples collected directly from clay impoundments of phosphate production facilities. LA-ICP-MS analysis of samples from the Peace River Formation yielded total REE concentrations of 100–500 ppm, comparable to the phosphate ore concentrates. X-ray diffraction confirmed the presence of apatite by reflections at ~25.9° and ~32° 2θ. The primary host of REE is expected to be fluorapatite, $Ca_5(PO_4)_3F_2$, where REE^{3+} substitutes for Ca^{2+} via coupled substitution mechanisms. Bulk compositions show a large range for Ca = 33–54 wt. % and Mg = 4–16 wt. %, indicating the presence of abundant dolomite. The presence of dolomite, $CaMg(CO_3)_2$, confirmed by its diagnostic peaks at ~30.9° and ~41.1° 2θ, is a challenge for REE and phosphate extraction from phosphatic clays.

Sequential soft leaching experiments were conducted at ambient temperature to selectively remove the dolomite without removing phosphates and REE. In low-dolomite clay (4 wt.% MgO), acetic acid (CH_3COOH) leaching removed >80 % Mg while dissolving <15 % phosphate, confirming selective carbonate attack. Subsequent sulfuric acid (0.5N and 2N) leaching at ambient temperature dissolved ~50 % of phosphate, liberating structurally bound REE. Stronger acid at higher temperatures could enhance phosphate dissolution rates. XRD shows dolomite peak removal after acetic acid treatment and reduced phosphate peaks after sulfuric acid, yielding an aluminosilicate-rich residue. Hot, concentrated sulfuric acid could mobilize Ga and other cations, while the remaining porous silica framework has potential absorbent applications.

Billions of tons of phosphatic clay accumulated in Florida offer opportunities for sequential leaching to recover critical elements, while generating valuable byproducts.