RARE EARTHS OCCURRENCE IN FLORIDA PHOSPHATE ORE AND THEIR FATE DURING MINING AND CHEMICAL PROCESSING

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Phosphate minerals have been identified as significant unconventional rare earths resources. World’s identified phosphate resources total about 300 billion tons, representing 90 million tons of rare earth elements (REE), assuming an average REE content of 300 ppm. Under a project funded by the Critical Materials Institute (CMI), the Florida Industrial and Phosphate Research Institute (FIPR Institute) conducted detailed chemical and mineralogical characterization of REE in different phosphate mining and processing streams. The research project includes three major parts. Part I covers chemical analysis and some basic properties of different samples. Part II is a detailed process mineralogy study of the amine flotation tails. The third part focuses on isolation and characterization of REE mineral particles in three samples using two advanced techniques, dual energy (DE) rapid scan radiography and high resolution X-ray microtomography (HRXMT).

Five samples were collected from a central Florida phosphate operation, including amine flotation tails, waste clay, phosphate rock, phosphoric acid, wet phosphogypsum (PG), and phosphoric acid sludge. These samples were analyzed for rare earth elements, uranium, thorium, routine chemical compositions, and radioactivity. Results show total REE of 70-500 ppm in the samples with uranium ranging from 25-120 ppm. Radium-226 analyzed about 20 pCi/g in phosphogypsum, 28 in phosphate rock, and 0.2 in phosphoric acid, and the corresponding uranium-238 numbers are 2.8, 20 and 36 pCi/g. Simple sizing and chemical analysis of phosphogypsum revealed an extremely encouraging piece of information on REE in PG. About 65% of the REE in PG is concentrated in the minus 500 mesh (approximately 30 microns) fraction that represents less than 10% of the total PG mass. Another fact is that the finest fraction also contains most of the thorium but little uranium.

A detailed process mineralogy study was conducted on the amine flotation tails sample using a Mineral Liberation Analyzer, the most advanced instrument for this type of study. Two major rare earth minerals were detected in the amine tails including monazite and xenotime. The monazite monomers average 1.27% CaO, 13.73% La\textsubscript{2}O\textsubscript{3}, 29.28% Ce\textsubscript{2}O\textsubscript{3}, 12.26% Nd\textsubscript{2}O\textsubscript{3}, 0.63% UO\textsubscript{2}, 6.2% ThO\textsubscript{2}, 3.55% Pr\textsubscript{2}O\textsubscript{3}, 0.46% Al\textsubscript{2}O\textsubscript{3}, 1.69% SiO\textsubscript{2}, and 30.92% P\textsubscript{2}O\textsubscript{5}. Xenotime is composed of the following chemicals: 46.44% Y\textsubscript{2}O\textsubscript{3}, 2.29% Gd\textsubscript{2}O\textsubscript{3}, 5.24% Dy\textsubscript{2}O\textsubscript{3}, 3.93% Yb\textsubscript{2}O\textsubscript{3}, 0.31% Nd\textsubscript{2}O\textsubscript{3}, 4.61% Er\textsubscript{2}O\textsubscript{3}, 0.66% Sm\textsubscript{2}O\textsubscript{3}, 1.06% UO\textsubscript{2}, 0.19% CaO, and 35.26 P\textsubscript{2}O\textsubscript{5}. Other major minerals in the amine tails include quartz, fluoapatite, feldspar, rutile, pseudorutile and zircon.

In Part III, dual energy (DE) rapid scan radiography was used to first identify potential RE particles, followed by a more detailed quantified liberation analysis by high resolution X-ray microtomography (HRXMT). Three sample streams, Shaking Table Concentrate, Acid Plant Feed, and Phosphogypsum, were separated into three size classes: >106 μm, 75-106 μm, and 53-75 μm. DE radiographs were taken at two energy levels and the ratio calculated. The images were thresholded to show only potential rare earth particles and then those particles were removed to prepare HRXMT samples. The samples were digitally reconstructed and the concentration of rare earth particles found using digital processing software. Based on the degree of liberation, the best particle size to find fully liberated monazite particles is 75-106 μm, although other sizes can reasonably be considered for Acid Plant Feed and Phosphogypsum.

Based on chemical analyses and minerals characterization, the following conclusions may be made about the occurrence and fate of REE in phosphate mining and processing: 1) REE in the flotation tails exist primarily in monazite with some in xenotime and heavy minerals such as zircon; 2) In the phosphoric acid manufacturing process over 70% of the REE in phosphate rock is dissolved, but a majority (about 70%) of which is either re-precipitated with PG or get absorbed onto PG; 3) the REE in phosphoric acid is mostly precipitated as the acid is concentrated from about 30% P2O5 to 54%; 4) REE in the waste clay occur in two major forms, xenotime and calcium substitution in phosphate crystals.