

Rare Earths in Phosphate: Characterization & Extraction

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SUMMARY

Much of this chapter is based on results from a multi-year research project supported by the Critical Materials Institute (CMI), an Energy Innovation Hub funded by the US Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office. It also draws substantial materials from two projects funded by the Florida Industrial and Phosphate Research (FIPR) Institute, Florida Polytechnic University. Under the CMI project, FIPR Institute was engaged in three major activities: 1) chemical and mineralogical characterization of rare earth elements (REEs) in different phosphate processing streams, 2) concentration of uranium and REE (rare earth element)-containing materials from the various processing streams, and 3) extraction of REEs and uranium from the concentrated materials. This chapter covers the main findings of those three efforts, and is divided into four parts. Part I covers chemical analysis and basic properties of different samples. Part II is a detailed process mineralogy study of the amine flotation tails. Part III focuses on isolation and characterization of rare earth (RE) mineral particles in three samples using two advanced techniques, dual energy (DE) rapid scan radiography and high resolution X-ray microtomography (HRXMT). Part IV presents process development work on the concentration of REE-containing materials and extraction of REEs.

In Part I, six samples were collected from a central Florida phosphate operation, including 2000 pounds of amine flotation tails, 5 full 5-gallon buckets of waste clay, 100 pounds of ground phosphate rock, 2 full 5-gallon buckets of phosphoric acid, 50 pounds of wet phosphogypsum, and several barrels of phosphoric acid sludge. These samples were analyzed for rare earth elements, uranium, thorium, routine chemical compositions, and radioactivity. Results show total REEs of 70-2600 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 (PG) revealed an extremely encouraging piece of information on REEs in PG. About 65% of the REEs 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.

In Part II, 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 rare earth minerals were detected in the amine tails including monazite and xenotime. The monazite monomers average 1.27%

CaO, 13.73% La₂O₃, 29.28% Ce₂O₃, 12.26% Nd₂O₃, 0.63% UO₂, 6.2% ThO₂, 3.55% Pr₂O₃, 0.46% Al₂O₃, 1.69% SiO₂, and 30.92% P₂O₅. Xenotime is composed of the following chemicals: 46.44% Y₂O₃, 2.29% Gd₂O₃, 5.24% Dy₂O₃, 3.93% Yb₂O₃, 0.31% Nd₂O₃, 4.61% Er₂O₃, 0.66% Sm₂O₃, 1.06% UO₂, 0.19% CaO, and 35.26 P₂O₅. Other major minerals in the amine tails include quartz, fluorapatite, 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, a 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 the 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.

In Part IV, technically feasible processing flowsheet was developed for phosphate clay, flotation tails, phosphogypsum and phosphoric acid sludge. The flowsheet for phosphate clay involves removal of clay minerals using small hydrocyclones, upgrading of phosphate as well as REE-containing materials from the cyclone underflow product, selective leaching of the concentrate to remove magnesium, and stage wise leaching of the Mg-free product for REE recovery and phosphoric acid production. REEs in PG can be recovered by countercurrent leaching using dilute phosphoric acid. Gravity separation followed by flotation could recover up to 65% of the REEs from flotation tails. High recovery of both REEs and phosphoric acid was achieved by decantation, washing, and filtration.

INTRODUCTION

1.1 Rare Earth Elements in Phosphate

Rare earth elements (REEs) have earned their reputation for being “rare” not because they are scarce in the Earth’s crust but because they “rarely” exist in mineral forms that can be mined and extracted economically. For example, the average concentration of the rare earth elements in the Earth’s crust (ranging from 150 to 220 ppm) is much higher than that of copper (55 ppm).

Although there are over 200 minerals known to contain appreciable amounts of rare earth elements, only three of them are economically significant, they include bastnaesite, monazite and xenotime, with bastnaesite and monazite accounting for about 95% of the current sources for light rare earths. Some rare-earth-bearing clays are also significant sources for REEs. Xenotime is the primary mineral for heavy REEs and yttrium.

Rare earth elements may also be extracted as a byproduct from processing of minerals, such as copper, gold, uranium, and phosphate ores, with phosphate perhaps having the greatest potential. Certain phosphate deposits, specifically the fluorapatite ores, contain significant amounts of the rare earths (Jorjani et al, 2008; Becker, 1983; Preston et al, 1996). Table 1 shows lanthanide content in some phosphate rock (Altschuler et al, 1967a, 1967b; Bliskovskii et al, 1969).

Table 1

Lanthanide Content in Selected Phosphate Rock

Phosphate rock source	Ln ₂ O ₃ (%)
Kola, Russia	0.8 -1.0
Florida, USA	0.06 – 0.29
Algeria	0.13 – 0.18
Morocco	0.14 -0.16
Tunisia	0.14

Some phosphate ores or processing streams contain much higher REEs than what is shown in Table 1. A Canadian phosphate deposit near Quebec, for example, contains about 1800 ppm of rare earth elements. Another Canadian phosphate deposit in Ontario has an estimated content of 1.59% $\text{La}_2\text{O}_3 + \text{Ce}_2\text{O}_3$. In some recently discovered phosphate deposits in northern China (Xia, 2011), rare earth element (REE) concentration (total R_2O_3) ranges from 1.5% to 6.41%.

1.2 Rare Earth Elements in Florida Phosphate

The Florida phosphate ore (matrix) is mined in open pits using large draglines. Phosphate matrix is first transported to the beneficiation plant, and after several washing and separation steps, is turned onto four streams, pebble product, flotation concentrate product, sand tailings, and waste clay. In the chemical processing plant, the combined pebble/concentrate rock product is reacted with sulfuric acid producing phosphoric acid and phosphogypsum byproduct.

Published analyses, decades old, of trace elements in Florida phosphate rock have shown that many of these vital rare earth elements are present. Though only present in trace amounts, because of the tonnage of phosphate produced, these elements are still significant in aggregate mass and have not been recovered. A relatively detailed investigation of REEs in Florida phosphate was conducted by Kremer and Chokshi (1989) of Mobil Research & Development Corporation. The total REEs in Florida phosphate matrix analyzed 282 ppm (88 ppm neodymium, 68 ppm cerium, 57 ppm yttrium, and 49 ppm lanthanum, accounting for 90%). Distributions of REEs in the mining and chemical processing streams were also determined, showing 40% in waste clay, 37.5% in PG, 12.5% in phosphoric acid, and 10% in sand tailings. Data further indicated that REEs were concentrated in fine phosphate particles, as the pebble product analyzed 284 ppm REEs versus 575 ppm in the flotation concentrate. The high REE concentration (336 ppm) in waste clay is other evidence of REEs concentrating in fine phosphate particles. Another set of data by the USGS (Altschuler et al, 1967) showed that Florida phosphate rock contained about 500 ppm REEs, with 150 ppm lanthanum, 120 ppm cerium and 110 ppm yttrium. According to a report by the former USBM (May and Sweeney, 1983), Florida phosphogypsum contained 300 ppm REEs, with 130-170 ppm gadolinium, 49 ppm cerium and 39 ppm lanthanum.

1.3 The CMI Efforts

As stated in the Summary, The Critical Materials Institute (CMI) is an Energy Innovation Hub funded by the US Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office. Phase 1 of CMI officially began July 1, 2013, and concluded June 30, 2018, with a total DOE funding of \$120 million. CMI entered its Phase 2 on July 1, 2018, for another 5 years with slightly less funding than Phase 1. Figure 1 shows the logos of the CMI team members as of February 2020.



Figure 1. Logos for CMI Team Members, February 2020.

CHEMICAL AND PHYSICAL CHARACTERIZATIONS OF PHOSPHATE PROCESSING STREAMS

Much of this chapter is based on analysis of development work for phosphate processing streams from phosphate operations in central Florida, USA. In order to understand the fate of REEs during the phosphate mining and chemical processing steps, a simplified processing flowchart is needed. Figure 2 shows a block diagram of the overall phosphate mining and processing flowsheet in Florida.

2.1. Sample Collection

The following samples were collected for this multi-year project:

- 2000 pounds of amine flotation tails – in 3 - 55 gal drums
- 5 full 5-gallon buckets of primary slime (slurry) – 10% thickened clay plus secondary clay
- 100 pounds of acid plant rock feed (ground and wet) – ball mill product
- 2 full 5-gallon buckets of phosphoric acid – 30% clarified acid
- 150 pounds of wet phosphogypsum – three 5-gal buckets of gypsum from an active stack
- 95 pounds of phosphoric acid sludge – 3 barrels.

Element

2.2. Chemical Analysis of Head Samples Chemical analysis covered the following components: P_2O_5 , CaO, Mg, Fe_2O_3 Standard 1 (digest) 20ml digestion acid, 10ml pt A, 10ml pt B, 9ml Ca std in 100ml volumetric, cool and add 2 ml of mixed

Quality assurance and Quality control

1. Run the 100% standard as a sample in each batch, since it has a known concentration, thus assuring accuracy of the ICP readings.
2. A reference apatite concentrate with rare earth values (0.5000g) and a duplicate of a random sample are prepared and run with each batch.
3. The QC range should be 2-5% depending on the sample nature.

2.2.1.2. ICP-MS

To maintain total dissolved solids at less than 0.5 % for ICP-MS, the standards with the same matrix as used for ICP-OES are diluted ten times, and the sample weight is adjusted to less than 0.5 % total dissolved solids level. The preliminary results indicate that for the less sensitive elements, such as thorium and uranium, the results from ICP-MS are more stable and re-producible than those from ICP_OES. ICP-MS has a lot lower detection limits than ICP-OES, which are required for the low concentrate elements analyses.

2.3. Chemical Analysis Results

A routine chemical analysis of phosphate rock covers six (6) components. Table 2 shows chemical analysis results on the first set of samples

Table 2

Routine Chemical Analysis of Head Samples (wt%)

Sample ID	P_2O_5	Insol	MgO	Fe_2O_3	Al_2O_3	CaO
Phosphate Rock	27.36	15.84	0.50	1.19	1.19	38.84
Phosphate Rock*Dup	27.39	16.30	0.48	1.18	1.17	38.80
Phosphoric Acid	27.81	0.00	0.40	0.83	0.72	0.80
Phosphoric Acid Dup	27.70	0.02	0.41	0.83	0.78	0.82
Phosphogypsum 1	1.33	47.82	0.02	0.15	0.17	15.87

Sample ID	P ₂ O ₅	Insol	MgO	Fe ₂ O ₃	Al ₂ O ₃	CaO
Phosphogypsum 1 Dup	1.45	45.06	0.03	0.16	0.20	20.25
Phosphogypsum	1.47	45.03	0.02	0.14	0.18	19.71
Phosphogypsum 2 Dup	1.37	44.06	0.02	0.13	0.15	19.48
Phosphogypsum 3	1.42	46.40	0.02	0.13	0.13	17.70
Phosphogypsum 3 Dup	1.43	41.42	0.02	0.13	0.12	18.00
Amine Tail	2.49	86.11	0.03	0.29	0.28	4.25
Amine Tail Dup	2.72	90.07	0.03	0.29	0.28	4.12
Waste Clay	5.64	51.04	2.33	2.16	7.84	9.55
Waste Clay Dup	5.55	51.75	2.13	1.86	6.48	9.40

*Dup represents a duplicate digestion and analysis of the same sample.

Radioactivity analysis was conducted by the Department of Health of the State of Florida, see Table 3.

Table 3

Radioactivity Analysis of Head Samples (pCi/g)

Sample	Radium-226	Radium-228	U-235	U-238
Phosphogypsum 1	19.4 ± 0.8	0.5 ± 0.1	0.4 ± 0.1	2.8 ± 0.1
Phosphogypsum 2	21.7 ± 0.9	0.5 ± 0.1	0.4 ± 0.1	2.9 ± 0.2
Phosphogypsum 3	17.5 ± 0.6	0.5 ± 0.1	0.4 ± 0.1	2.8 ± 0.3
Phosphoric acid	0.2 ± 0.2	0.1 ± 0.1	2.7 ± 0.1	36.0 ± 1.4
Amine tails	5.5 ± 0.3	2.8 ± 0.1	0.3 ± 0.1	4.2 ± 0.3
Waste clay	14.9 ± 0.6	0.9 ± 0.1	0.8 ± 0.1	12.9 ± 0.6
Phosphate rock	27.9 ± 2.5	1.0 ± 0.1	2.0 ± 0.1	20.3 ± 0.7

Analysis of REE, Thorium and Uranium in Head Samples (ppm)

Sample ID	Pr	Eu	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sc	Gd	Sm	Th	U
Phosphate Rock	7.92	3.48	2.17	13.81	3.25	9.62	1.22	8.69	1.34	4.90	16.46	12.04	9.15	87.77
Phosphate Rock Dup	8.23	3.39	2.13	13.48	2.91	9.28	1.10	8.51	1.37	4.80	16.34	11.45	9.69	89.25
Phosphoric Acid	0.00	0.00	0.00	0.54	0.11	1.92	0.57	3.18	0.56	4.37	0.91	0.00	6.21	119.88
Phosphoric Acid Dup	0.00	0.00	0.00	0.49	0.06	1.81	0.60	3.19	0.58	4.36	1.03	0.00	5.26	123.33
Phosphogypsum 1	5.30	0.87	0.07	4.04	1.16	2.22	0.10	1.49	0.00	0.07	1.84	4.27	0.00	30.64
Phosphogypsum 1 Dup	5.44	0.85	0.12	4.15	1.21	2.29	0.32	1.50	0.00	0.11	1.88	4.06	0.00	31.57
Phosphogypsum 2	5.41	0.84	0.03	4.12	0.99	2.41	0.35	1.47	0.00	0.04	1.73	4.10	0.00	30.17
Phosphogypsum 2 Dup	5.78	0.96	0.10	4.53	1.07	2.51	0.14	1.60	0.00	0.06	2.32	4.46	0.00	31.79
Phosphogypsum 3	6.41	1.04	0.38	4.84	1.13	2.60	0.34	1.70	0.00	0.04	2.67	4.89	0.00	32.41
Phosphogypsum 3 Dup	6.70	1.03	0.33	4.82	1.28	2.67	0.57	1.69	0.00	0.02	2.64	5.04	0.00	32.10
Amine Tail	5.72	0.96	0.18	4.72	0.99	2.81	0.43	2.26	0.07	1.48	4.03	4.97	6.58	25.16
Amine Tail	5.69	0.95	0.23	4.77	1.19	2.82	0.56	2.27	0.08	1.50	3.87	4.88	6.50	24.42
Waste Clay	2.55	1.92	1.02	7.26	0.55	4.77	0.60	4.41	0.84	6.05	10.42	6.07	5.24	37.12
Waste Clay Dup	2.63	1.82	0.95	7.11	0.80	4.49	0.52	4.27	0.79	6.16	9.82	6.47	6.61	37.49

In this table, “Dup” represents a duplicate digestion and analysis of the same sample. The phosphogypsum (PG) samples from the three different buckets were sampled and analyzed separately in order to determine

whether the samples were homogenized in the collection process. The three PG samples show small variations in chemical analysis, but can be considered to be representative of the same source.

2.3. Sizing Analysis of Phosphogypsum

Simple sizing and chemical analysis of phosphogypsum (PG) revealed an extremely encouraging piece of information on REE in PG. As shown in Table 5, about 65% of the REE is concentrated in the minus 500 mesh (approximately 30 microns) fraction that represents 10% of the total PG. Another fact is that the finest fraction also contains most of the thorium. Distributions of other chemical species are shown in Table 6.

Table 5

Size Distribution of Rare Earths in PG

Screen size mesh	Major REE, ppm	Major REE, ppm	Major REE, ppm	Major REE, ppm	Major REE, ppm	Total REE ppm	REE Distribution %
	La	Ce	Pr	Nd	Y		
+200	23.02	41.22	6.83	28.53	27.52	141.69	26.08
-200+270	43.63	71.85	11.28	50.92	51.02	256.17	2.19
-270+325	55.09	87.13	12.90	59.30	60.49	306.47	3.37
-325+400	65.79	103.47	14.95	69.28	74.33	366.30	0.70
-400+500	88.81	135.32	18.07	90.21	90.74	467.96	2.28
-500	579.13	954.51	63.29	630.41	559.53	2981.29	65.39

Table 6

Size Distribution of Major Chemical Components in PG

Screen size mesh	Yield, wt%	Major Chemical components, wt%	Major Chemical components, wt%	Major Chemical components, wt%	Major Chemical components, wt%	Major Chemical components, wt%	U ppm	Th ppm
		Insol	P ₂ O ₅	Fe ₂ O ₃	Al ₂ O ₃	CaO		
+200	79.24	59.94	0.15	0.04	0.12	13.06	34.25	0.00
-	3.68	19.23	0.60	0.09	0.19	29.83	35.87	0.89
200+270								
-	4.73	7.44	0.63	0.10	0.34	31.02	34.33	0.20
270+325								
-	0.82	6.13	0.72	0.11	0.41	33.82	35.44	0.37
325+400								
-	2.10	7.10	0.62	0.11	0.59	31.90	34.68	0.91
400+500								
-500	9.44	6.40	3.52	2.04	3.84	27.62	0.00	10.93

2.4. Sizing Analysis of Phosphate Clay

Phosphate beneficiation in Florida generates over one ton of phosphatic clay (slime) per ton of phosphate rock produced. Since the beginning of the large scale washing and desliming practice for phosphate beneficiation, over two billion tons of such slime have been accumulated, which contain approximately 600 million tons of

phosphate rock, 600,000 tons of rare earth elements (REE), and 80 million kilograms of uranium. However, recovery of these valuable elements from the phosphatic clay may well be the most challenging subject in mineral processing, because the clay is very dilute (averaging 3% solids) and extremely fine in size (Zhang et al.,). Under the CMI project, two slime samples were analyzed using a Horiba laser scattering particle size distribution analyzer, LA-960, with a scale from 0.01 μm to 3000 μm for dry and wet samples. The medium nozzle was set with data acquisition times of the sample as 50000 and data acquisition times of the blank as 5000. The air pressure is set at 0.3 MPa (3 Bar, 45 psi). The instrument is set at the right standard refractive index. Particle size distribution default is the volume which shows the volume ratios of particles for each particle diameter with 100 representing the total volume of all particles. For analytical testing of the wet samples, the instrument initially was run on blank. The samples were stirred well and a very small amount (about 0.25 ml) of the stirred clay was then transferred to a recirculation system for measurements.

Figure 3 shows a size distribution graph for a phosphate clay sample Four Corners (FC) mine. The mean size of the sample is 8.30 μm and the mode size is 8.23 μm . The size distribution follows a bimodal distribution with 10% of the particles having diameters averaging 0.32 μm , 50% averaging 6.96 μm , and 90 % averaging 16.67 μm . Figure 4 shows a size distribution graph for phosphate clay sample from South Fort Meade (SFM) mine. The mean size of the sample is 5.33 μm and the mode size is 4.79 μm . The size distribution follows a bimodal distribution with 10% of the particles having diameters averaging 0.13 μm , 50% averaging 3.45 μm , and 90 % averaging 9.04 μm .

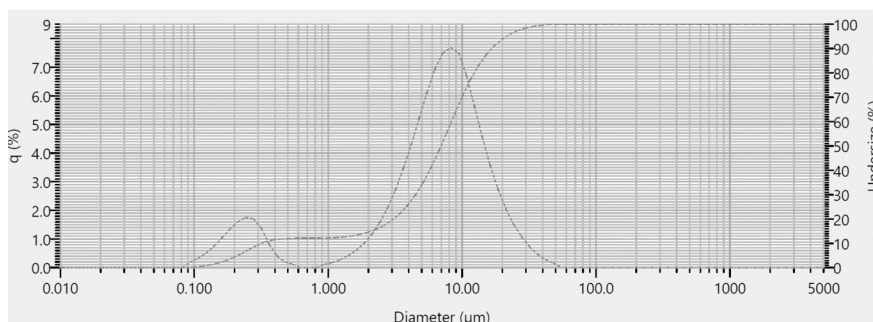


Figure 3. Particle Size Distribution of Phosphate Clay Sample FC.

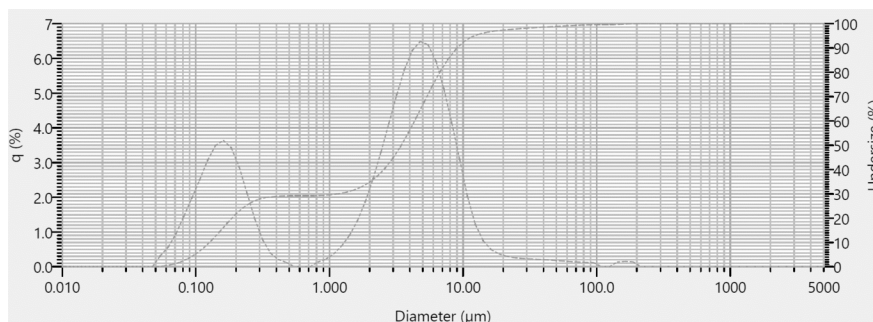


Figure 4. Particle Size Distribution of Phosphate Clay Sample SFM.

2.5. Rare Earths Mass Balance in Phosphate Mining and Processing Streams

2.5.1. Case 1, Plant A

The comprehensive investigation of REE in Florida phosphate conducted by Kremer and Chokshi (1989) showed that about 50% of the REE in the phosphate matrix reported to the final rock product, 40% to waste

clay, and 10% to flotation tailings. Since the current waste clay contains significantly less phosphate than that in the past, and that the portion of the pebble product is lower in the current phosphate ore, the percentage of REE distribution in the various streams could be very different. FIPR therefore undertook a major effort to sample and analyze two sets of samples for REE mass balance calculations. Table 7 summarizes the total REE concentrations in various samples from plant A.

Table 7

Total REE Concentrations (ppm) in Plant A Samples

Sample ID	Total REE
Final concentrate	608
Intermediate pebble	229
Regular pebble	163
Flotation feed	160
Cleaner tail +50	265
Cleaner tail -50+100	168
Cleaner tail -100+230	114
Rougher tail +50 a	61
Rougher tail -50+100	19.6
Rougher tail -100+230	18.2
Primary slime head	102
Phosphogypsum	119

Based on weight distribution in the different size fractions shown in Table 8, REE in the head samples of rougher tails and cleaner tails can be calculated as 39.68 and 152.78, respectively.

Table 8

Sizing Analysis of Rougher and Cleaner Tails from Plant A

Sample	Size Range (mesh)	Wt%
Rougher tail	+50	48.69
	-50+100	45.54
	-100+230	5.76
	-230	0.00
Cleaner tail	+50	2.91
	-50+100	63.62
	-100+230	33.38
	-230	0.09

A typical plant's mass flow rates are shown in Table 9.

Table 9

Plant Mass Flow Rates (Ton/Hour) for Plant A

Stream	Flow rate, TPH
Flotation feed	1850
Flotation concentrate	350
Regular pebble	160

Stream	Flow rate, TPH
Intermediate pebble (to bin)	90
Rougher tails (cell underflow)	1300
Amine tails (cell overflow)	200
Primary clay (to ISA)	750

By simple calculations based on the data in Tables 8-10, REE distributions in different streams can be derived, as follows:

$$\% \text{ REE distribution in the product} = 100 \times (608 \times 350 + 229 \times 90 + 163 \times 160) / (160 \times 1850 + 102 \times 750 + 229 \times 90 + 163 \times 160) = 61.9$$

$$\% \text{ REE distribution in the flotation tailings} = 100 \times (39.68 \times 1300 + 152.78 \times 200) / (160 \times 1850 + 102 \times 750 + 229 \times 90 + 163 \times 160) = 19.6$$

$$\% \text{ REE distribution in the waste clay} = 100 \times (102 \times 750) / (160 \times 1850 + 102 \times 750 + 229 \times 90 + 163 \times 160) = 18.2$$

Assuming that 5 tons of phosphogypsum (PG) are generated for each ton of P_2O_5 in the final product, and that the average P_2O_5 content in the final product is 30%, REE distribution in PG can then be estimated, as follows:

$$\% \text{ REE distribution in PG} = 100 \times 5 \times 0.3(350 + 160 + 90) \times 119 / (160 \times 1850 + 102 \times 750 + 229 \times 90 + 163 \times 160) = 25.88$$

The above total distribution of REE in PG represents 42.15% of the REE in the overall product, derived, as follows:

$$\% \text{ distribution of the product REE in PG} =$$

$$100 \times 5 \times 0.3(350 + 160 + 90) \times 119 / (350 \times 608 + 160 \times 163 + 229 \times 90 + 163 \times 160) = 42.15$$

The total REE in the matrix can be back calculated, as follows:

$$\text{REE concentration in the matrix (ppm)} = (160 \times 1850 + 102 \times 750 + 229 \times 90 + 163 \times 160) / (1850 + 750 + 90 + 160) = 145.$$

To better understand the REE mass balance numbers, one may refer to Figure 2 showing a flowsheet schematic of phosphate mining and processing.

2.5.2. Case 2, Plant B

Table 10 summarizes total REE concentrations in various samples from Plant B.

Table 10

Total REE Concentrations (ppm) in Samples from Plant B .

Sample	Total REE
Concentrate	901
Feed averaged	217
Pebble	262
Rougher tail +50	26.5
Rougher tail -50+100	17.9
Rougher tail -100+230	19.5
Rougher tail calculated	20.07
Amine tail -50+100	290
Amine tail -100+230	354
Amine tail calculated	335.0
Waste clay (CF Clay)	346
Gypsum	112

A typical plant mass distribution for this plant is shown in Table 12.

Table 11

Sizing Analysis of Rougher and Cleaner Tails from Plant B

Sample	Size Range (Mesh)	Wt%
Rougher tail	+50	22.51
	-50+100	63.00
	-100+230	14.20
	-230	0.29
Cleaner tail	+50	2.00
	-50+100	33.81
	-100+230	61.25
	-230	2.94

Table 12

Plant B Mass Distribution (tons)

Stream	Tons
Fine flotation feed	451000
Fine fatty acid tails	342000
Fine amine tails	22700
Coarse flotation feed	78500
Coarse fatty acid tails	47800
Coarse amine tails	7011
Concentrate	111400
Pebble	40100
Waste clay	240000

By simple calculations based on the data in Tables 11-13, REE distributions in different streams can be estimated, as follows:

% REE distribution in the product = $100 \times (901 \times 111400 + 262 \times 40100) / [217 \times (451000 + 78500) + 262 \times 40100 + 346 \times 240000] = 53.19$

% REE distribution in the flotation tailings = $100 \times ([335 \times (22700 + 7011) + 20 \times (342000 + 47800)] / [217 \times (451000 + 78500) + 262 \times 40100 + 346 \times 240000]) = 8.50$

% REE distribution in the waste clay = $100 \times (346 \times 240000) / [217 \times (451000 + 78500) + 262 \times 40100 + 346 \times 240000] = 39.83$.

The above distributions can be normalized as 52.40% to the product, 39.23% to the waste clay, and 8.37% to the flotation tails.

MINERALOGY STUDIES

3.1. Amine Tails

3.1.1. Elemental and Chemical Components Analysis of Amine Tails

Table 13 shows concentrations of major compounds in the as-received amine tails, and Table 14 lists contents of the rare earth elements.

Table 13

Chemical Compositions (wt%) of the Amine Flotation Tails

Compound	SiO ₂	Al ₂ O ₃	TFe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O
Content	86.36	2.51	0.88	0.10	3.56	0.11	0.81
Compound	TiO ₂	P ₂ O ₅	MnO	H ₂ O	LOI	[?]	
Content	1.07	2.31	0.039	0.08	1.44	99.269	

Table 14

Analysis (ppm) of Rare Earth Elements in the Amine Tails

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Content	29.36	65.77	5.71	39.65	4.92	0.95	3.93	0.20
Element	Dy	Ho	Er	Tm	Yb	Lu	Y	[?]REE
Content	4.75	1.10	0.50	0.50	2.26	0.08	36.02	195.70

Corresponding analyses for gravity separation concentrate and tails from the amine tails are shown in Tables 15-17. Gravity separation was conducted using a jig. The jiggling concentrate was sized into three fractions, +70 mesh, 70 by 100 mesh and -100 mesh. Results show that the -100 mesh fraction contains a higher concentration of REE totaling about 618 ppm. Another interesting fact is that REE content has no obvious correlation with the P₂O₅ concentration, indicating that REE in the amine tails is not associated with the phosphate minerals.

Table 15

Chemical Compositions (wt%) of Jiggling Products from the Amine Tails

Sample ID	P ₂ O ₅	MgO	Fe ₂ O ₃	Al ₂ O ₃	CaO	Insol
Jig Concentrate	3.84	0.03	0.32	0.4	4.99	88.38
Jig Tails	3.12	0.03	0.4	0.31	3.98	90.42
+70 mesh jig concentrate	3.61	0.03	0.36	0.24	4.41	90.08
-70+100 jig concentrate	5.07	0.05	0.25	0.54	6.77	85.09
-100 jig concentrate	3.11	0.05	0.24	1.23	4.21	88.65

Table 16

Analysis (ppm) of REE in the Jiggling Products from the Amine Tails

Sample ID	Pr	Eu	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sc
Concentrate	5.62	0.99	0.65	4.7	0.88	3.55	0.91	2.51	0.27	2.09
Tails	6.09	0.94	0.61	4.62	0.83	3.19	0.83	1.96	0.09	2.44
+70 M conc.	3.91	0.62	0.56	3.32	0.73	2.54	0.68	1.62	0.09	1.36
-70+100 conc.	6.65	1.5	1.02	7.06	1.65	5.25	1.06	3.72	0.42	2.53
-100 conc.	16.29	1.69	1.8	7.97	1.28	5.29	1.05	3.37	0.5	4.21

Table 17

Analysis (ppm) of U and REE in the Jiggling Products from the Amine Tails

Sample ID	Gd	Sm	Th	Ce	Y	La	Nd	U	[?]REE
Concentrate	6.02	3.85	9.04	63.59	38.67	27.64	40.2	32.11	211.18
Tails	5.05	6.84	0	55.45	29.89	23.7	38.48	33.76	181.01
+70 mesh concentrate	3.27	5.2	0	36.92	24.86	15.29	26.2	33.48	127.17
-70+100 concentrate	7.78	7.36	0	66.16	53.42	32.44	46.65	25.96	244.67
-100 conc.	13.21	11.44	18.09	209.9	48.14	86.02	187.6	6.95	617.85

3.1.2. Sizing Analysis of Amine Tails

Table 18 shows detailed sizing analysis of the amine tails.

Table 18

Size Distribution of the Amine Tails Head Sample

Mesh Size	Wt.%	Cumulative wt.%
-200	7.01	7.01
-140+200	53.60	60.61
-100+140	14.09	74.7
-60+100	25.18	99.88
+60	0.12	100

3.1.3. Mineral Components and Their Concentrations

Quantitative mineral analysis was conducted using a Mineral Liberation Analyzer (MLA). The MLA is perhaps the most advanced analyzer on today's market for mineral identification, mineral quantification, mineral liberation, and grain size. It is an automated, X-ray based analyzer coupled with smart software modules, and analyzes mineral samples in polished sections of drill core, particulate or lump materials. MLA can produce vast information, invaluable to geologists, mineralogists and process engineers. Two rare earth minerals were identified by MLA, they are monazite and xenotime, both at very low concentrations. Major non rare earth minerals include quartz, fluorapatite, feldspar, zircon, and rutile, Table 19.

Table 19

Quantitative Mineral Analysis of Amine Tails Using MLA

Mineral	Wt%%	Mineral	Wt%%	Mineral	Wt%%
Monazite	0.053	Tourmaline	0.353	Pseudo- rutile	1.125
Xenotime	0.003	Garnet	0.477	Rutile	0.450
Zircon	0.614	Epidote	0.119	Leucoxene	0.148
Apatite	8.703	Kyanite	1.174	Sphene	0.337
Wavellite	0.512	Staurolite	0.329	Limonite	0.016
Woodhouseite	0.009	Kaolin	0.048	Siderite	0.143
Quartz	80.011	Pyrite	0.047	Zinc spinel	0.003
Feldspar	5.294	Sphalerite	0.009	Others	0.003
Biotite	0.004	Calcite	0.003	Total	100.000

3.1.4. Size Distribution of Major Minerals

The size range of the mineral particles was also analyzed using MLA. Results show that the major rare earth minerals are relatively fine with 100% of the xenotime particles smaller than 40 microns and 88.93% of the

monazite particles below 80 microns. The particle sizes of other minerals ranged from 0.02 to 0.16 mm. Table 20 shows the size analysis details.

Table 20
Size Distribution Analysis for the Major Minerals in Amine Tails

Size range, mm	Weight distribution, %	Weight distribution, %	Weight distribution, %	Weight distribution, %	Weight distribution, %
	Apatite	Monazite	Xenotime	Zircon	Rutile
-0.32+0.16	3.32				
-0.16+0.08	44.68	11.07		24.96	30.1
-0.08+0.04	34.60	78.29		62.83	63.2
-0.04+0.02	12.13	8.54	86.71	10.21	5.95
-0.02+0.01	3.97	1.98	5.20	1.47	0.55
-0.01	1.30	0.12	8.09	0.53	0.17
Total	100.00	100.00	100.00	100.00	100.00

3.1.5. Dissemination Characteristics of Major Minerals

Monazite

Micro-area chemical analysis of monazite was performed using Energy Dispersive X-ray Spectroscopy (EDS), and the results are shown in Table 21. The monazite particles contain the rare earth elements La, Ce, Nd and Pr, with Ca, U and Rh substitutions. Other impurities include Si and Al. Figure 5 shows a clear monomer monazite particle while Figure 6 indicates inclusion of monazite within quartz.

Table 21
Chemical Components of Monazite Analyzed Using EDS

Spectrum	Chemical components, %	Chemical components, %	Chemical components, %	Chemical components, %
	CaO	La ₂ O ₃	Ce ₂ O ₃	Nd ₂ O ₃
1	1.38	13.69	28.62	12.00
2	1.49	12.73	29.41	12.65
3	1.26	17.69	31.45	9.09
4	1.45	9.93	26.81	15.33
5	1.14	13.40	28.10	12.59
6	1.67	13.81	28.76	11.76
7	1.22	14.24	29.50	11.27
8	0.90	13.84	29.76	12.05
9	0.95	13.95	30.81	13.38
10	1.25	14.04	29.57	12.43
Average	1.27	13.73	29.28	12.26

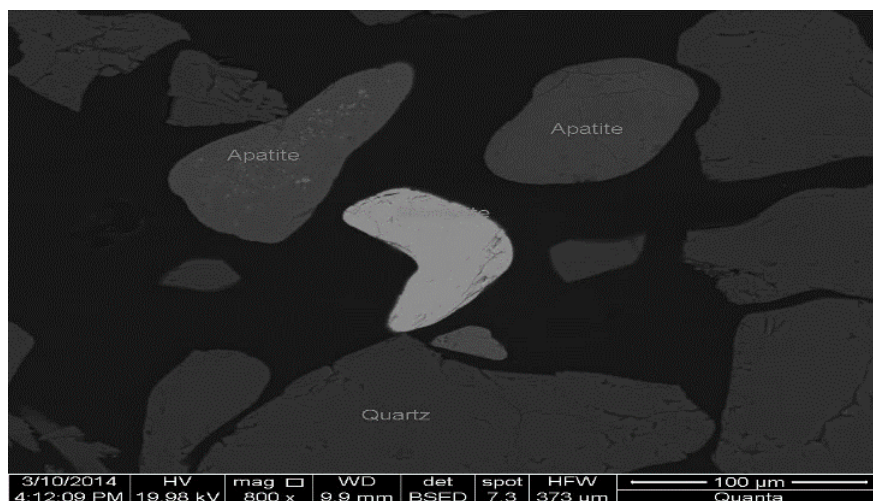


Figure 5. SEM-BSE Image Showing Monazite Monomer.

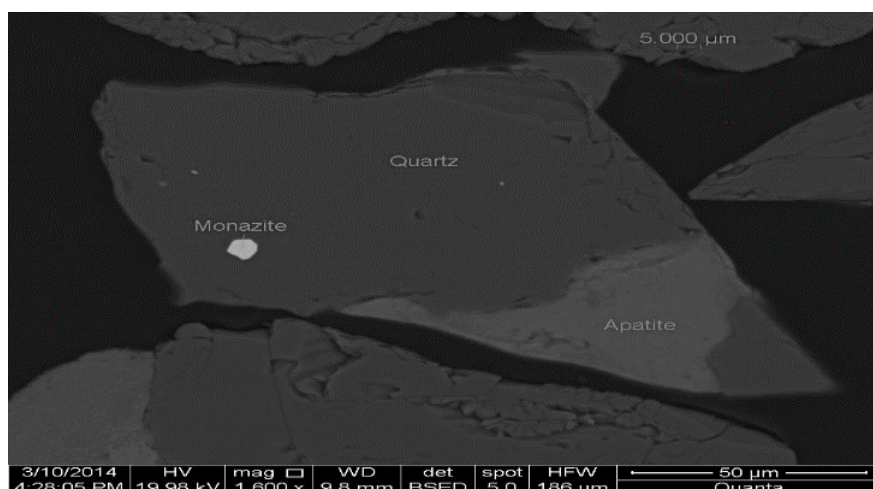


Figure 6. SEM-BSE Image Showing Monazite Inclusion in Quartz.

Xenotime

Micro-area chemical analysis of xenotime was also performed using Energy Dispersive X-ray Spectroscopy (EDS), and the results are shown in Table 22. The xenotime particles contain the rare earth elements Y, Gd, Dy, Yb, Nd, Er and Sm, with Ca and U substitutions. Figure 7 shows a clear monomer of a xenotime particle while Figure 8 indicates inclusion of xenotime within apatite.

Table 22

Chemical Components of Xenotime Analyzed Using EDS

Spectrum	Chemical components, %	Chemical components, %	Chemical components, %	Chemical components, %
	Y ₂ O ₃	Gd ₂ O ₃	Dy ₂ O ₃	Yb ₂ O ₃
1	44.18	2.66	5.90	4.89
2	47.67	2.04	4.93	3.31

Spectrum	Chemical components, %	Chemical components, %	Chemical components, %	Chemical components, %
3	47.48	2.17	4.89	3.60
Average	46.44	2.29	5.24	3.93

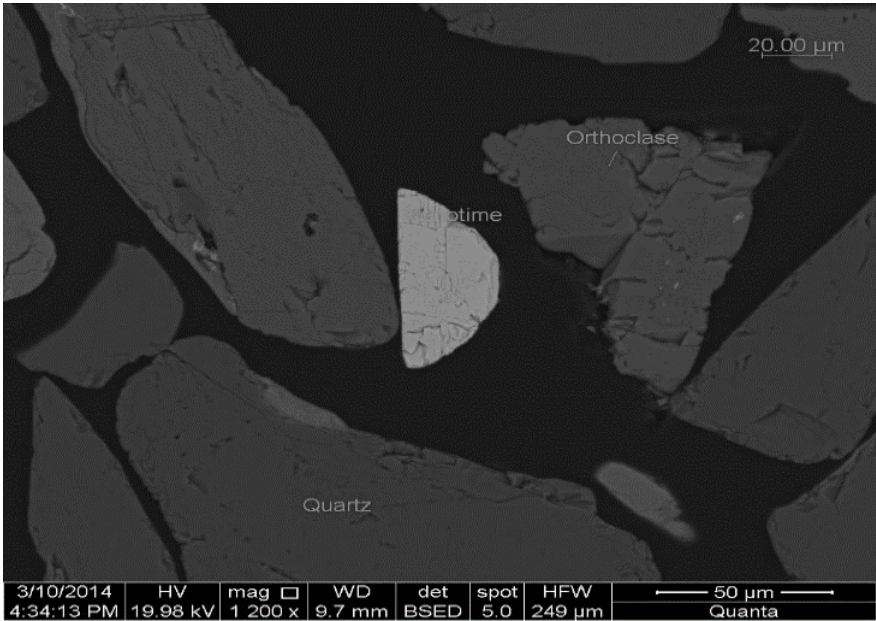


Figure 7. SEM-BSE Image Showing Xenotime Monomer.

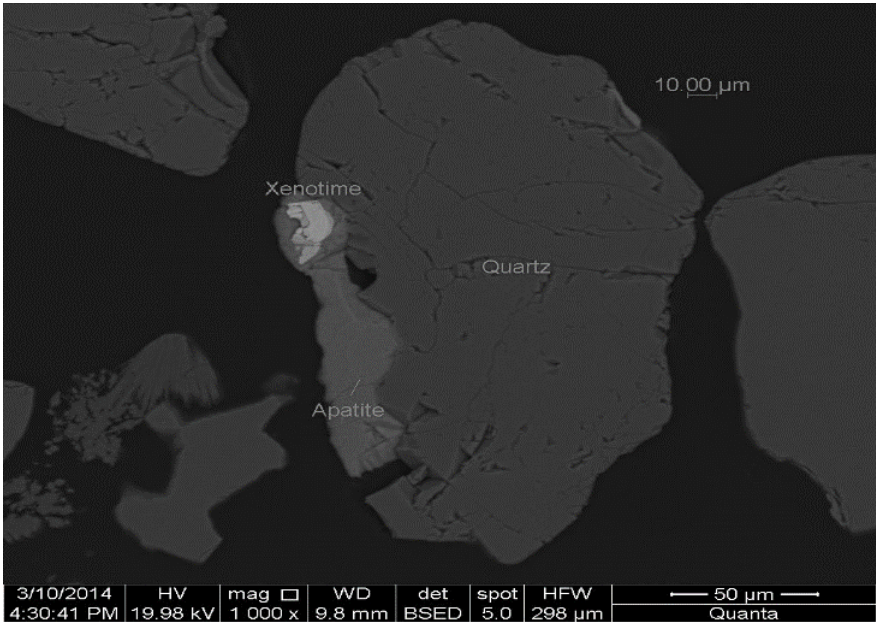


Figure 8. SEM-BSE Image Showing Xenotime Inclusion In Quartz.

Zircon

Micro-area chemical analysis of zircon was also performed using Energy Dispersive X-ray Spectroscopy (EDS), and the results are shown in Table 23. The zircon particles do not contain many rare earth elements, but some particles contain a minute amount of iron. Figure 9 shows clear zircon monomers.

Table 23

Chemical Components of Zircon Analyzed Using EDS

Spectrum	Chemical components, %	Chemical components, %	Chemical components, %	Chemical components, %
	ZrO ₂	HfO ₂ *	FeO	SiO ₂
1	66.20	1.15	0.00	32.65
2	66.40	1.25	0.00	32.35
3	65.93	1.14	0.03	32.90
4	66.15	1.40	0.06	32.39
5	66.17	1.42	0.00	32.40
6	65.11	1.74	0.00	33.15
7	66.45	1.05	0.00	32.50
8	66.35	1.22	0.00	32.43
9	66.37	1.27	0.00	32.35
10	65.98	1.59	0.00	32.44
Average	66.11	1.32	0.01	32.56

*Hafnium (Hf) analysis may have higher errors

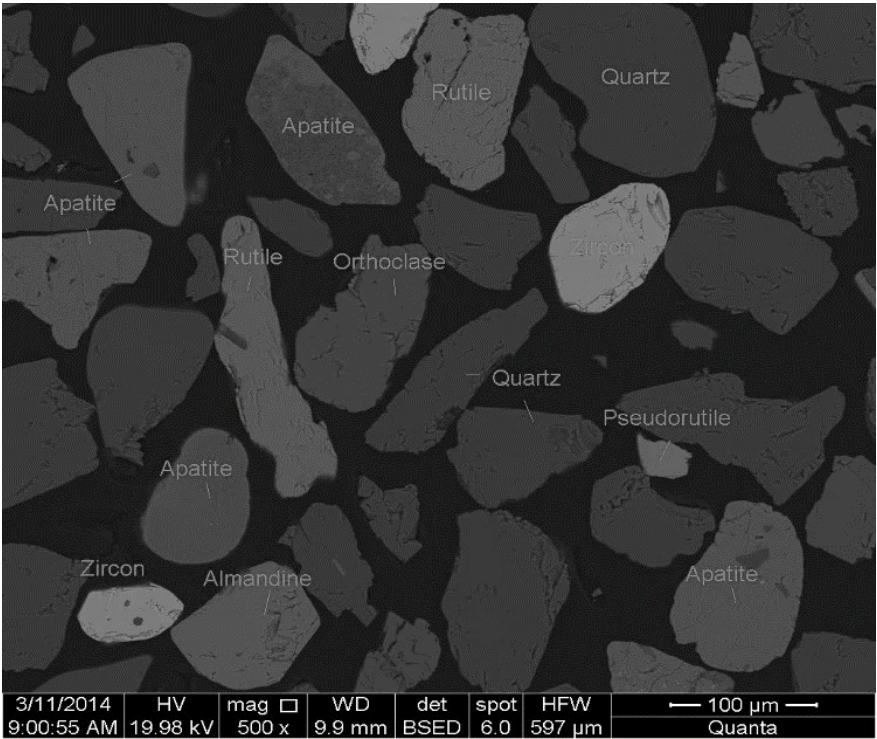


Figure 9. SEM-BSE Image Showing Zircon Monomer.

Rutile, Pseudorutile, Leucoxene

Major titanium oxide minerals in the sample include rutile, pseudorutile, and leucoxene with pseudorutile being the most abundant. Again, micro-area chemical analysis of these three minerals was performed using Energy Dispersive X-ray Spectroscopy (EDS), and the results are shown in Figure 10 and Tables 24-26.

Table 24

Chemical Components of Rutile Analyzed Using EDS

Spectrum	Chemical components, %	Chemical components, %	Chemical components, %	Chemical components, %
	Nb ₂ O ₅	TiO ₂	FeO	Al ₂ O ₃
1	0.47	98.83	0.13	0.08
2	0.33	98.63	0.46	0.13
3	0.08	98.58	0.54	0.16
4	0.44	98.85	0.17	0.08
5	1.08	97.71	0.53	0.16
6	0.00	99.05	0.42	0.08
7	0.00	94.58	1.26	2.05
8	0.23	95.82	0.53	0.78
9	0.21	98.40	0.12	0.54
10	0.28	98.95	0.11	0.20
11	0.24	98.90	0.12	0.38
12	1.08	97.10	0.95	0.24
13	0.77	98.03	0.58	0.22
14	0.51	98.42	0.51	0.20
Average	0.41	97.99	0.46	0.38

Table 25

Chemical Components of Pseudorutile Analyzed Using EDS

Spectrum	Chemical components, %	Chemical components, %	Chemical components, %	Chemical components, %
	TiO ₂	FeO	MgO	P ₂ O ₅
1	60.59	37.50	0.00	0.01
2	67.29	30.82	0.07	0.11
3	75.16	21.27	0.12	0.66
4	61.90	33.58	1.05	0.00
5	62.94	33.55	0.04	0.08
6	69.09	28.64	0.03	0.07
7	63.58	32.64	0.14	0.02
8	62.49	34.56	0.37	0.00
9	71.38	25.70	0.18	0.19
10	64.28	32.39	0.07	0.06
11	59.56	37.94	0.38	0.10
12	65.94	31.25	0.07	0.00
13	66.89	29.96	0.14	0.10
Average	65.47	31.52	0.20	0.11

Table 26

Chemical Components of Leucorene Analyzed Using EDS

Species	Chemical components, %	Chemical components, %	Chemical components, %	Chemical components, %	Chemical components, %
	Nb ₂ O ₅	TiO ₂	MnO	FeO	CaO
1	0.28	67.18	2.20	25.82	0.52
2	0.00	72.73	3.85	20.97	0.38
3	0.00	78.88	0.64	17.74	0.26
4	0.00	72.03	3.75	22.75	0.47
5	0.09	78.75	0.61	17.62	0.53
6	0.07	85.57	0.11	11.39	0.85
7	0.00	68.00	0.31	4.58	13.11
8	0.00	63.60	2.59	30.95	0.35
9	0.03	77.23	0.52	19.86	0.86
10	0.00	68.76	0.26	3.88	13.11
11	0.00	67.26	3.45	25.95	0.94
Average	0.04	72.73	1.66	18.32	3.13

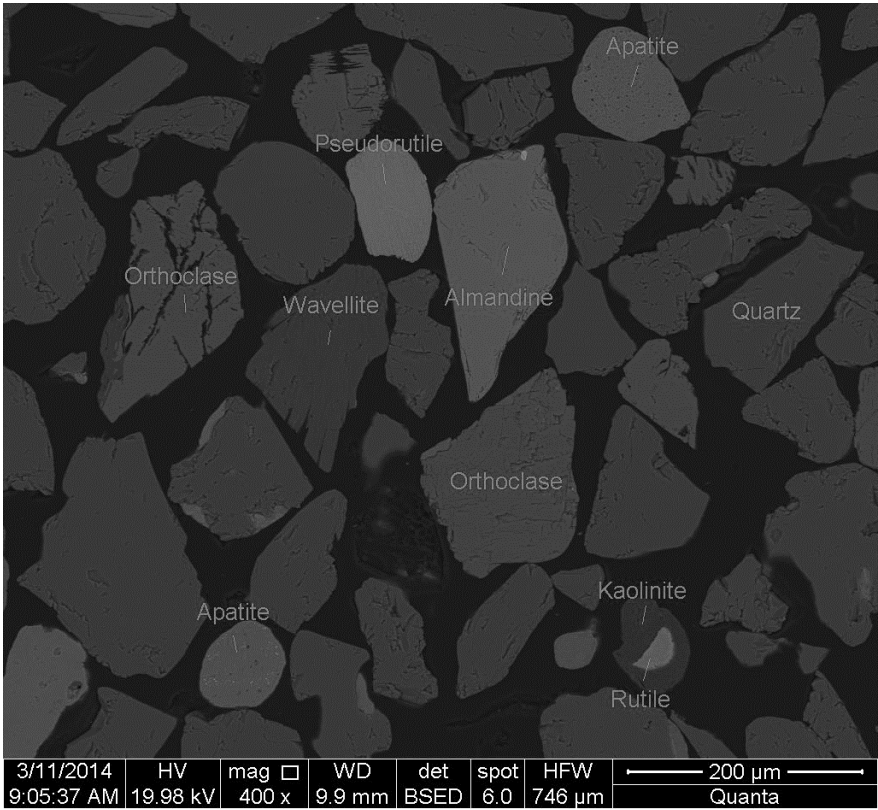


Figure 10. SEM-BSE Image Showing Rutile And Pseudorutile Monomers.

Phosphate Minerals

Francolite is the primary phosphate mineral with apatite being the minor one. However, MLA measurement identifies minerals based on chemical components, thus is unable to distinguish francolite from apatite. Micro-area chemical analysis of the phosphate was performed using Energy Dispersive X-ray Spectroscopy

(EDS), and the results are shown in Table 27. All phosphate particles contain fluorine and substantial amounts of impurities such as silica, aluminum and iron. A small number of francolite particles contain rare earth elements.

In addition to francolite monomers, substantial amounts of francolite exist as shell shaped particles covering quartz surfaces, as is shown in Figure 11.

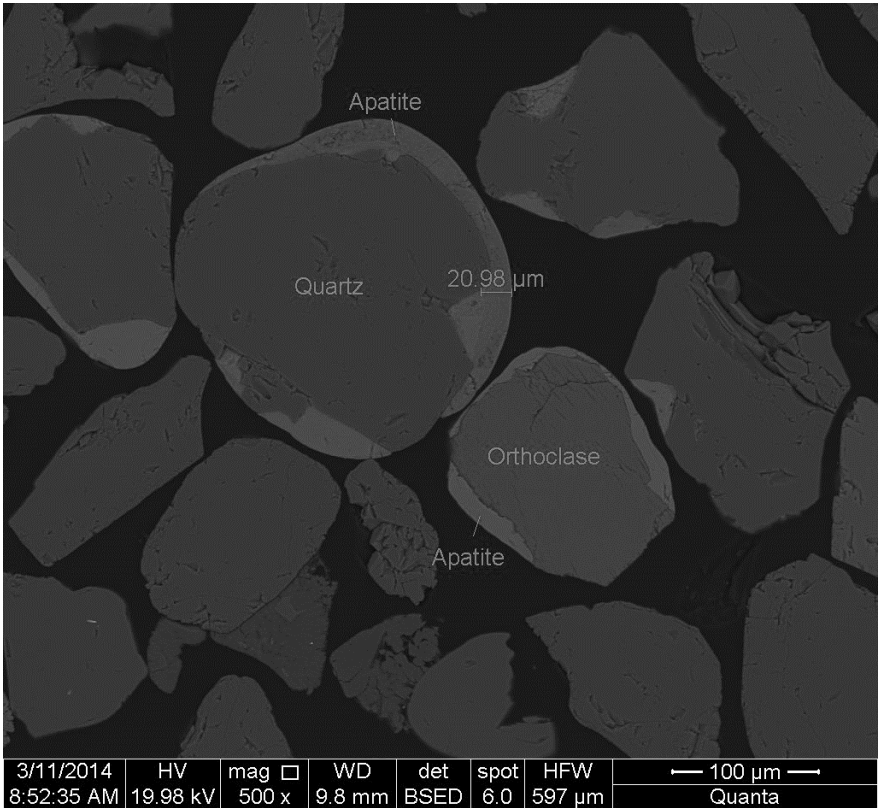


Figure 11. SEM-BSE Image Showing Wrapping of Quartz by Phosphate.

Table 27

*Chemical Components of Phosphate Analyzed Using EDS**

Spe- ctrum	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %
	F	Cl	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	FeO	MnO	SrO
1	2.21	0.00	0.44	0.27	0.94	3.42	38.91	2.29	0.50	49.56	1.47	0.00	0.00
2	2.41	0.00	0.09	0.04	0.62	2.22	41.56	0.40	0.36	51.63	0.67	0.00	0.00
3	2.65	0.00	0.44	0.24	1.50	3.18	39.41	0.74	0.38	50.74	0.45	0.27	0.00
4	2.37	0.00	0.37	0.13	1.15	0.83	42.11	0.47	0.22	51.73	0.63	0.00	0.00
5	2.47	0.00	0.39	0.24	1.69	1.94	37.50	4.68	0.36	48.10	2.64	0.00	0.00
6	2.57	0.00	0.59	0.29	1.36	3.12	39.22	1.14	0.15	50.96	0.60	0.00	0.00
7	2.50	0.00	0.27	0.19	1.94	3.20	40.76	0.64	0.13	49.89	0.47	0.00	0.00

Spe- ctrum	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %	Chemical Com- po- nents, %
8	2.17	0.00	0.85	0.27	1.52	1.04	40.62	1.04	0.16	48.91	0.94	0.05	2.44
9	2.34	0.00	1.03	0.70	1.10	1.45	40.72	2.14	0.19	49.56	0.76	0.00	0.00
10	2.56	0.00	0.42	0.16	0.44	1.39	40.61	0.91	0.27	52.40	0.84	0.00	0.00
11	2.51	0.10	0.87	0.17	0.59	0.81	39.98	2.10	0.30	50.41	0.31	0.00	1.84
12	2.53	0.00	0.47	0.18	1.74	1.37	40.94	1.07	0.29	50.91	0.50	0.00	0.00
13	2.33	0.00	0.30	0.26	2.14	4.03	37.89	2.90	0.46	48.02	1.66	0.00	0.00
14	2.08	0.00	0.29	0.13	0.77	1.75	40.10	2.47	0.39	48.21	1.50	0.07	1.81
15	2.47	0.00	0.40	0.26	1.46	3.69	39.77	0.68	0.22	50.49	0.55	0.00	0.00
16	2.30	0.00	0.42	0.30	1.29	2.36	36.32	6.25	0.41	46.48	3.88	0.00	0.00
17	2.44	0.00	0.61	0.43	2.19	5.17	37.19	1.14	0.62	49.54	0.67	0.00	0.00
18	2.45	0.00	0.34	0.19	0.36	1.43	41.59	0.69	0.09	52.43	0.43	0.00	0.00
19	2.44	0.00	0.62	0.21	0.58	1.40	39.06	2.54	0.32	51.23	1.60	0.00	0.00
20	2.45	0.00	0.81	0.20	0.62	2.90	38.33	2.57	0.07	50.81	1.25	0.00	0.00
21	2.42	0.00	1.32	1.29	0.98	5.16	35.62	2.80	0.39	47.97	2.06	0.00	0.00
22	2.32	0.00	0.15	0.09	0.67	2.34	41.66	0.43	0.04	51.66	0.66	0.00	0.00
23	2.75	0.00	0.58	0.25	1.19	1.35	40.30	1.10	0.17	51.97	0.33	0.00	0.00
24	2.44	0.00	0.28	0.10	1.44	1.00	42.26	0.97	0.05	51.01	0.45	0.00	0.00
Avg	2.42	0.00	0.51	0.27	1.18	2.36	39.68	1.76	0.27	50.19	1.06	0.02	0.25

*MLA could not tell the difference between francolite and apatite

3.2. Mineralogical Examination of Phosphate Clay

Phosphate mining in Florida has accumulated more than 2 Gt of phosphate clay (slime), containing approximately 600 Mt of phosphate rock, 600 kt of rare earth elements (REEs) and 80 million kilograms of uranium (Zhang et al., 2017). However, the recovery of these valuable elements from the phosphate clay is not easy for the following reasons; 1) the waste clay coming from the beneficiation plant is very dilute, with an average solids

concentration of 3% ; 2) the material is extremely fine in size, with more than 50% having a particle size smaller than 2 μm ; 3) about 50% percent of the material are clay minerals; and 4) large amounts of magnesium, iron and aluminum are present in the phosphate clay.

X-ray diffraction analysis shows that the slime sample contains over 60% clay minerals, making it extremely challenging to recover the rare earths and phosphorus values (see Table 28).

Table 28

Mineralogical Composition of a Clay Sample

Phase	Chemical Formula	Weight %
Quartz	SiO ₂	10.7
Apatite	Ca ₅ P ₃ O ₁₂ (OH, F)	15.6
Wavellite	Al ₃ P ₂ O ₁₆ H ₁₃	1.2
Dolomite	CaMgC ₂ O ₆	5.4
Kaolinite	Si ₂ Al ₂ O ₉ H ₄	8.8
Montmorillonite	Al ₄ Si ₈ CaO ₂₄ H ₂	2.0

Phase	Chemical Formula	Weight %
Illite	$\text{Al}_4\text{Si}_2\text{KO}_{12}\text{H}_3$	0.6
Amorphous Content (mainly clay)	Amorphous Content (mainly clay)	55.7

3.3. Mineralogical Examination of Phosphoric Acid Sludge

The solid fraction of phosphoric acid sludge is mainly gypsum with rare earth elements existing as monazite and xenotime. Figure 12 shows an XRD graph of the sludge solids.

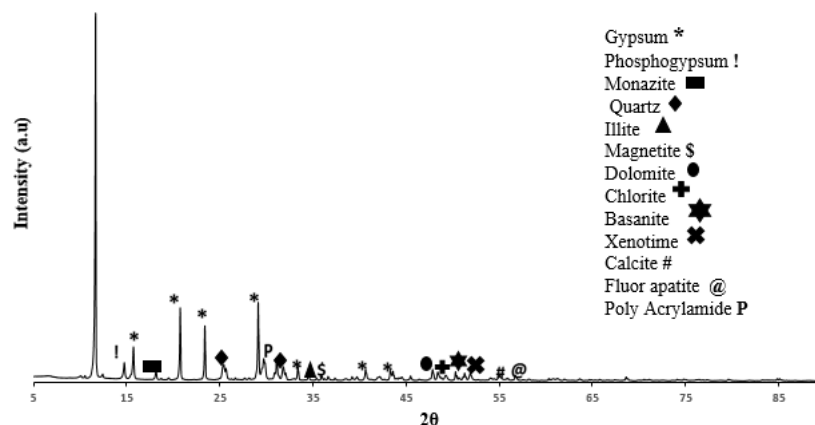


Figure 12. XRD Peaks of Phosphoric Acid Sludge Solids.

ISOLATION AND CHARACTERIZATION OF RE MINERAL PARTICLES IN FLORIDA PHOSPHATE ROCK BY DE RAPID SCAN RADIOGRAPHY AND HRXMT

4.1. Sample Collection and Characterization

4.1.1. Particle Size Separation

The first two samples shipped to University of Utah were the Shaking Table Concentrate and the Acid Plant Feed. There was about a kilogram of each sample that needed to be separated into size classes. To do this, three sieves were chosen: 140 mesh (106 μm), 200 mesh (75 μm), and 270 mesh (53 μm). A vibrating sieve shaker was used to do this separation of each sample, first as dry sieving then again as a wet sieving for thorough and effective separation. Four size classes were prepared: >106 microns, 75-106 microns, 53-75 microns, and <53 microns. Because the last class was so small, no further testing was done on this portion, which left three size classes to be examined for each sample.

Because of the length of time required for the double separation of dry sieving followed by wet sieving, when the third sample (Phosphogypsum) arrived, a different method was applied. Coning and quartering was used instead of dry separation, reducing the bulk sample in content from approximately one kilogram to a bit more than 100 grams. The 100 gram sample was then separated into size classes using the same wet sieving on the vibrating sieve shaker as was used for the other two samples.

4.1.2. Chemical and Mineralogical Characterization

Before proceeding to DE radiography and HRXMT, an idea about what was present in the samples was necessary. A chemical analysis of the Acid Plant Feed was provided, as can be seen in Table 29, and an approximate estimation for the Shaking Table Concentrate, as in Table 30. To get a more exact concentration for the Shaking Table Concentrate, a portion of the >106 microns sample was further separated using gravity

separation by hand panning. The heavy particles were separated out from the lighter ones and taken for X-ray diffraction (XRD) and HRXMT. The minerals identified in the sample were zircon (ZrSiO_4), apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$), and monazite ($(\text{Ce},\text{La})\text{PO}_4$).

Table 29

Chemical Analysis of Acid Plant Feed

ICP	Lachat	Lachat	Lachat	Lachat							
P_2O_5 %	P_2O_5 %	P_2O_5 %	P_2O_5 %	P_2O_5 %	Insol	Insol	Insol	Insol	MgO	MgO	MgO
26.46	27.36	27.36	27.36	27.36	15.84	15.84	15.84	15.84	0.50	0.50	0.50
Pr ppm	Eu ppm	Eu ppm	Eu ppm	Tb ppm	Tb ppm	Tb ppm	Tb ppm	Dy ppm	Dy ppm	Dy ppm	Dy ppm
7.92	3.48	3.48	3.48	2.17	2.17	2.17	2.17	13.81	13.81	13.81	13.81
Yb ppm	Lu ppm	Lu ppm	Sc ppm	Sc ppm	Sc ppm	Gd ppm	Gd ppm	Gd ppm	Gd ppm	Gd ppm	Sm ppm
8.69	1.34	1.34	4.90	4.90	4.90	16.46	16.46	16.46	16.46	16.46	12.0
Ce ppm	Y ppm	La ppm	La ppm	La ppm	La ppm	La ppm	Nd ppm	Nd ppm	Nd ppm		
131.16	132.06	77.58	77.58	77.58	77.58	77.58	85.26	85.26	85.26		

Table 30

Provided Estimated Chemical Analysis of Shaking Table Concentrate

ICP	Lachat	Lachat	Lachat	Lachat						
P_2O_5	P_2O_5	P_2O_5	P_2O_5	P_2O_5	Insol	Insol	Insol	Insol	MgO	MgO
6-9	6-9	6-9	6-9	6-9	70-80	70-80	70-80	70-80	0.03-0.08	0.03-0.08
Pr ppm	Pr ppm	Eu ppm	Eu ppm	Eu ppm	Eu ppm	Tb ppm	Tb ppm	Tb ppm	Tb ppm	Dy ppm
10-16	10-16	2-3	2-3	2-3	2-3	0.5-0.7	0.5-0.7	0.5-0.7	0.5-0.7	5.0-7.5
Tm ppm	Tm ppm	Tm ppm	Yb ppm	Yb ppm	Yb ppm	Yb ppm	Lu ppm	Lu ppm	Lu ppm	Lu ppm
1.0-1.5	1.0-1.5	1.0-1.5	4.0-6.0	4.0-6.0	4.0-6.0	4.0-6.0	0.10-0.15	0.10-0.15	0.10-0.15	0.10-0.15
Th ppm	Th ppm	Th ppm	Th ppm	U ppm	U ppm	U ppm	U ppm	Ce ppm	Ce ppm	Ce ppm
8.0-10.0	8.0-10.0	8.0-10.0	8.0-10.0	30-50	30-50	30-50	30-50	130-150	130-150	130-150

4.2. Dual Energy Calibration

4.2.1. Materials and Methods

Plastic plates, 3"x1", and double-sided sticky tape were used to prepare the samples for DE radiography. Pure samples were placed on double-sided sticky tape, which was attached to a plastic plate, and then were stabilized with a second plate. For this case, two types of samples were prepared for mineral identification which are shown in Figure 13. The image on the left shows the first sample with minerals used for calibration and the image on the right shows the second sample with minerals used for calibration verification. Table 31 shows more detailed information about the minerals used for verification.

Hosted file

image13.emf available at <https://authorea.com/users/622355/articles/645744-rare-earths-in-phosphate-characterization-extraction>

Figure 13. Radiographs of the Pure Reference Minerals and Minerals in Cu-Mo Flotation Tailing for DE Calibration.

Table 31

Detailed Information for Main Minerals in Cu-Mo Flotation Tailing

	Mineral	Mineral	Effective atomic number, Z_{actual}	Density, g/cm ³
	name	formula		
1	Molybdenite	MoS ₂	36.87	4.6-4.7
2	Galena	PbS ₂	78.96	7.2-7.6
3	Chalcopyrite	CuFeS ₂	25.00	4.1-4.3
4	Bornite	Cu ₅ FeS ₄	26.58	4.9-5.3
5	Barite	BaSO ₄	48.73	4.3-5.0
6	Malachite	Cu ₃ (CO ₃) ₂ (OH) ₂	24.78	3.6-4.0
7	Azurite	Cu ₂ CO ₃ (OH) ₂	24.85	3.7-3.8
8	Chalcocite	Cu ₂ S	27.40	5.5-5.8
9	Quartz	SiO ₂	11.85	2.6-2.7
10	Hematite	Fe ₂ O ₃	23.56	5.1-5.2
11	Sphalerite	(Zn, Fe)S ₂	27.18	3.9-4.2
12	Pyrite	FeS ₂	22.06	4.9-5.1

4.2.2. Reference Samples for Calibration

Reference samples were prepared for the estimation of reconstruction coefficients for effective atomic numbers using DE radiography measurements. In this case, aluminum, copper and lead were selected as known materials. These three elements can represent the three different mineral phases usually present in samples from metal mining operations having low attenuation coefficients (gangue, quartz/silicates), medium attenuation coefficients (copper, most base metal minerals) and high attenuation coefficients (molybdenite, galena, lead or other precious metals).

Coefficients k_1 , k_2 , k_3 and k_4 were then calculated according to Equation 8 using $p = 3.8$. Yielding and .

Then, the calculated effective atomic number is compared to the actual effective atomic number to determine the accuracy in data correlation and verify calibration, shown in Figure 14.

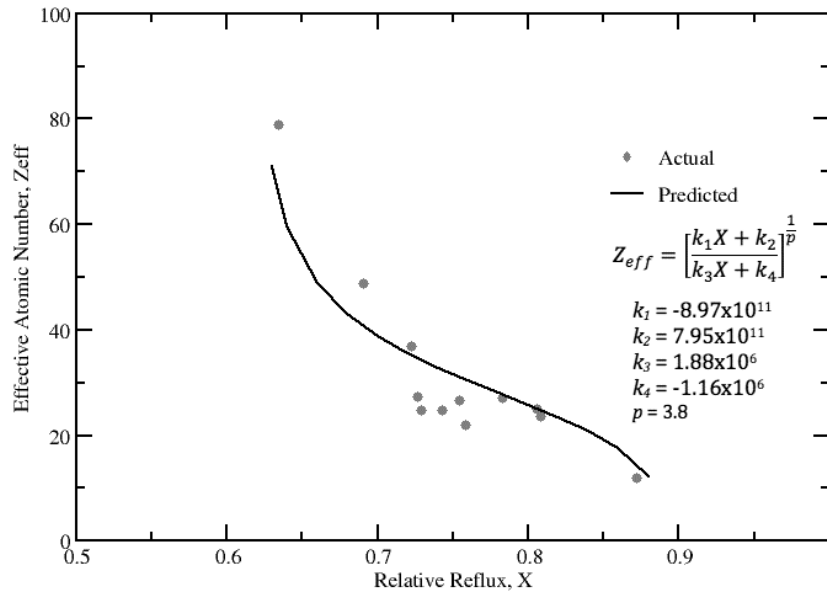


Figure 14. Comparison between Calculated and Actual Effective Atomic Numbers.

4.3. High Resolution X-Ray Microtomography Calibration

4.3.1. Estimation of Mineral Attenuation Coefficients

It is important to estimate the linear attenuation coefficient before the scan has been taken in order to use the proper settings for the scans. The mass attenuation coefficient has a linear relationship with energy according to Beer's law. Scans for heavy materials with high density and high atomic number require a high-level X-ray energy source in order to get enough X-ray photons to the detector. Therefore, it is very important to determine which level of X-ray energy is sufficient to pass through high atomic number and high-density RE samples. A preview of the linear relationship of X-ray mass attenuation coefficient and energy, using XMuDat software, is shown in Figure 15.

From the estimation of mineral attenuation coefficients, it is evident that the lower the photon energy, the greater the attenuation coefficient difference between minerals. This will make it easier to apply a threshold to radiograph scans and identify only potential RE particles. Additionally, the photon energy should be large enough to pass through the high atomic number and high-density minerals; for example, monazite and zircon. Taking both of those factors into consideration, an energy voltage 70 kV was selected to scan the samples. Other parameters are defined by considering the projection quality and include an exposure time of 10 seconds for each projection image and a magnification level of 4X.

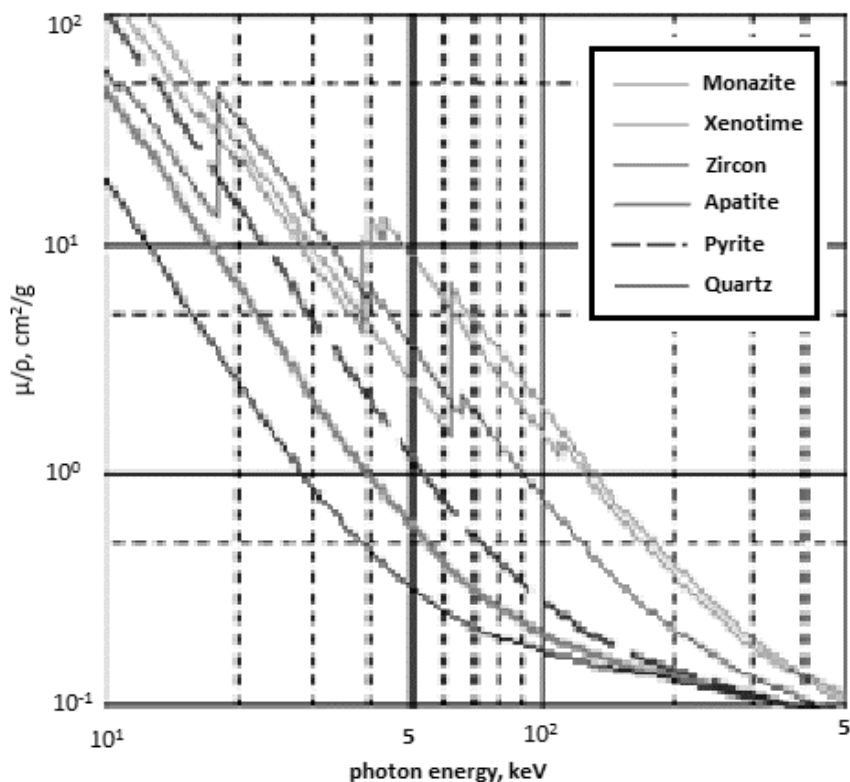


Figure 15. Mineral Attenuation Coefficients Estimated Using XMuDat.

4.4. Calibration of Mineral Standards

In order to obtain an accurate analysis of the RE sample, usually the CT standard has to be set for the mineral characterization. Here, from the initial XRD analysis, monazite, zircon, apatite and quartz minerals are expected to be present in the samples. Monazite is the mineral of interest as the RE mineral. Therefore,

monazite and zircon standards were scanned using the same conditions as the RE sample, which are 4X magnification level, 70 kV energy voltage, and 10 seconds exposure time per projection.

After the reconstruction of CT standards, the CT number distribution map can be exported and transformed into an extension .txt file, which can then be plotted using EXCEL or XMGrace. The CT number distribution map of minerals is shown in Figure 16. From the CT number distribution map of CT standards, it can be seen that monazite has the highest attenuation coefficient and apatite has the lowest. There is a big difference between the high-density and high atomic number minerals and the gangue mineral, apatite. The minerals are clearly distinguished based on their attenuation coefficient. There is some overlap between monazite and zircon, but this is not a serious problem.

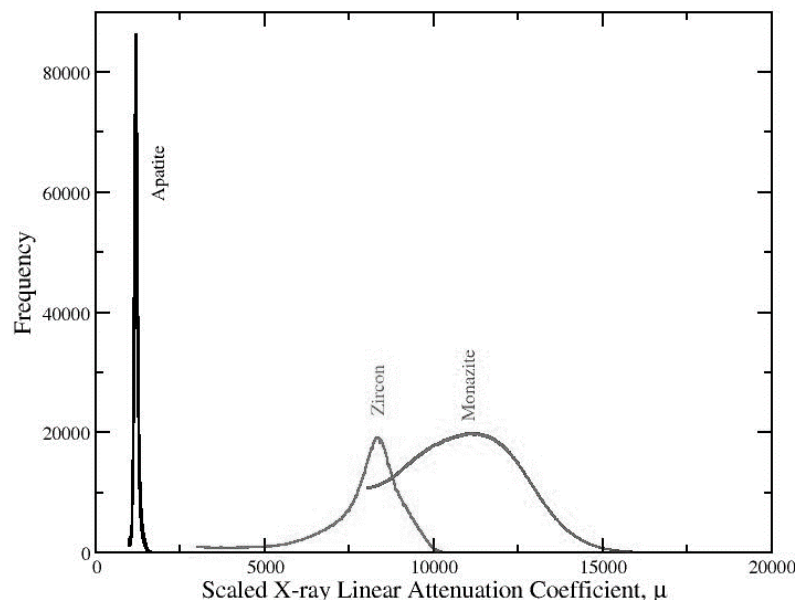


Figure 16. Scaled CT Number Distribution Map for Mineral Phases.

4.5. Calibration of Rare Earth Phosphate Sample

Since the CT standards of pure monazite, zircon, and apatite samples have been made, it is possible to generate CT scaled data from the software XMController. This was done for the heavy fraction of the Shaking Table Concentrate after scanning and the reconstruction with scaled data using the standards. The same scaling has been applied to the HRXMT samples of this project.

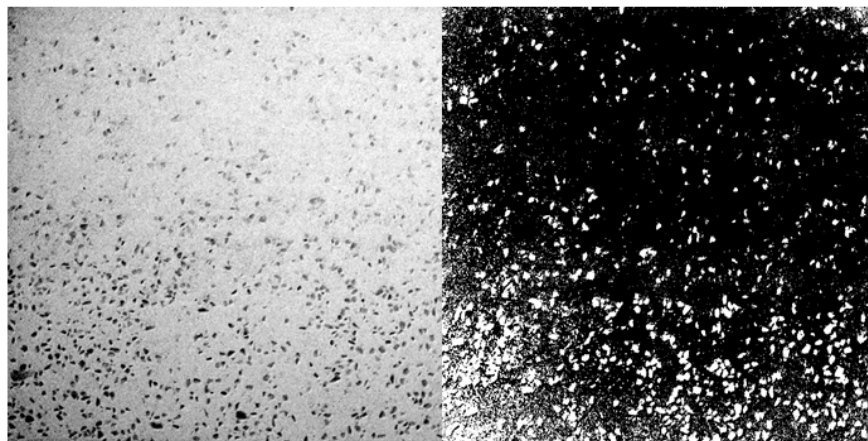
4.6. Dual Energy (DE) Radiography

In order to begin the DE radiography scans, a vibrating riffler was used to separate out a representative portion from each size class of each sample and the subsample was attached to a slide (glass plate) using double sided sticky tape and secured using a second slide. Three slides were prepared from each size class for each sample, making a total of nine slides per sample and 27 slides in total. Each slide has roughly 34,000 particles attached to it, so a total of 102,000 particles from each size class for each sample were then imaged.

The DE radiography scans were completed by splitting the slide into 40 sections, making a 4x10 grid, and scanning each section at a low energy level (80 kV) and a high energy level (140 kV).

The attenuation coefficients recorded from the DE radiography were used to find the relative reflex, R, which

then gave an effective atomic number using the calibration curve completed in Section 5.2.3. To do this, Matlab was utilized to read each radiograph at both high and low energies and compare the two scans, which gave the relative reflex (X) pixel by pixel. Once the relative reflex was calculated, a threshold was applied to identify the potential rare earth (RE) particles. Thresholding discards all the relative reflex values above a given point and accepts those below it. The threshold number used was $X = 0.70$, which corresponds to $Z_{\text{eff}} = 38$. This means that all of the values where $X < 0.70$ were accepted, giving particles with $Z_{\text{eff}} > 38$. This threshold was chosen based on the calibration curve (see Figure 16), and tested on a sample of pure bastnasite, seen in Figure 17.



(a) (b)

Figure 17. Bastnasite (a) Radiograph and (b) Resulting Thresholded Image Used for Threshold Verification.

Looking at the calibration curve, 0.70 might seem a little high when looking for RE particles. However, as the particle density increases, the 80 kV and 140 kV energies that were used might have some difficulties penetrating the particles. Due to this effect, the accuracy of the calibration curve as it nears higher atomic numbers decreases. Therefore, 0.70 was utilized to make sure all the potential RE particles were gathered. Examples of the DE radiography scans taken at high and low energies, their corresponding relative reflex image, and the image after thresholding can be seen in Figures 18, 19, and 20. Note that the dark particles in the DE scans correspond to the white portions in the thresholded images and are potential RE particles.

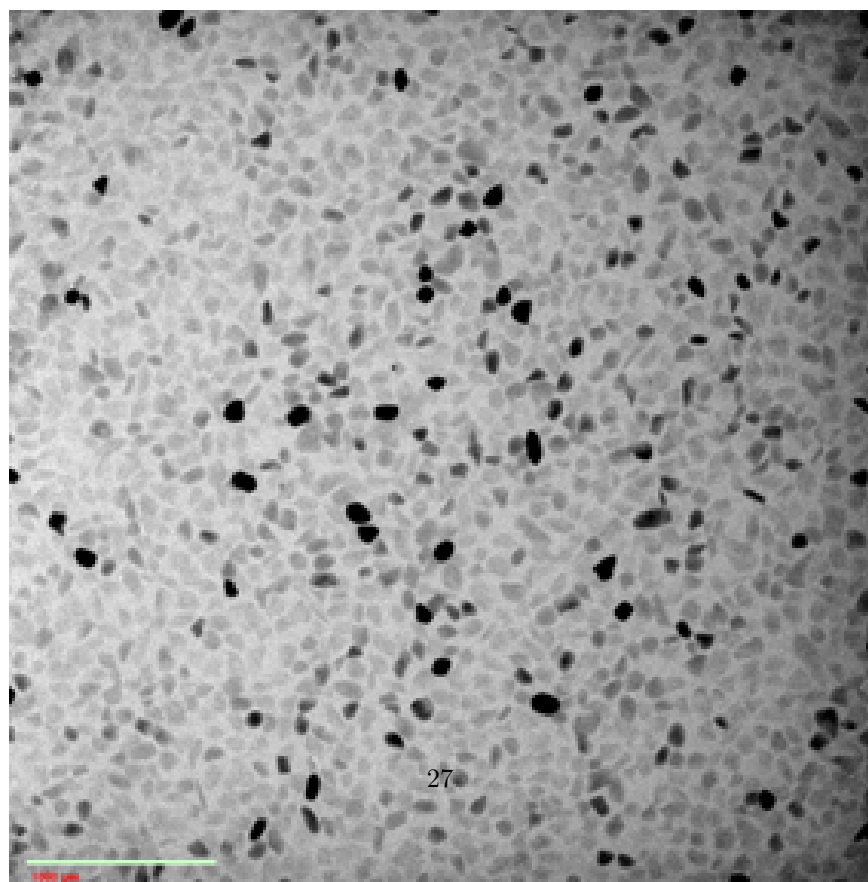
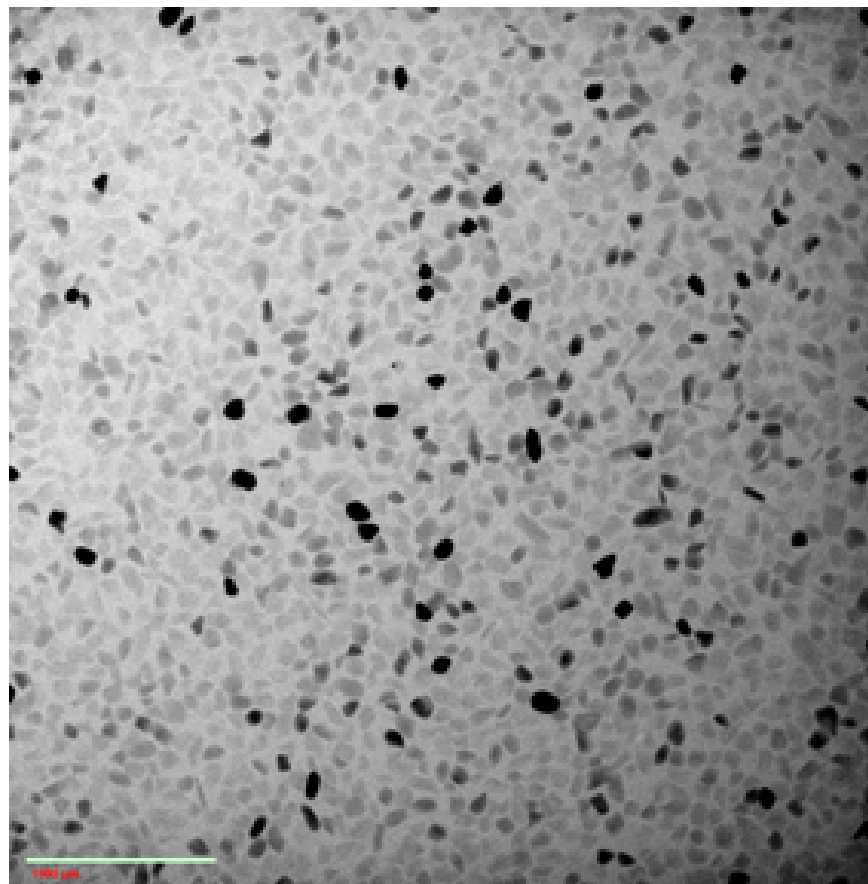


Figure 18. DE Scans, Relative Reflex, and Thresholded Image of A Section from Shaking Table Concentrate.

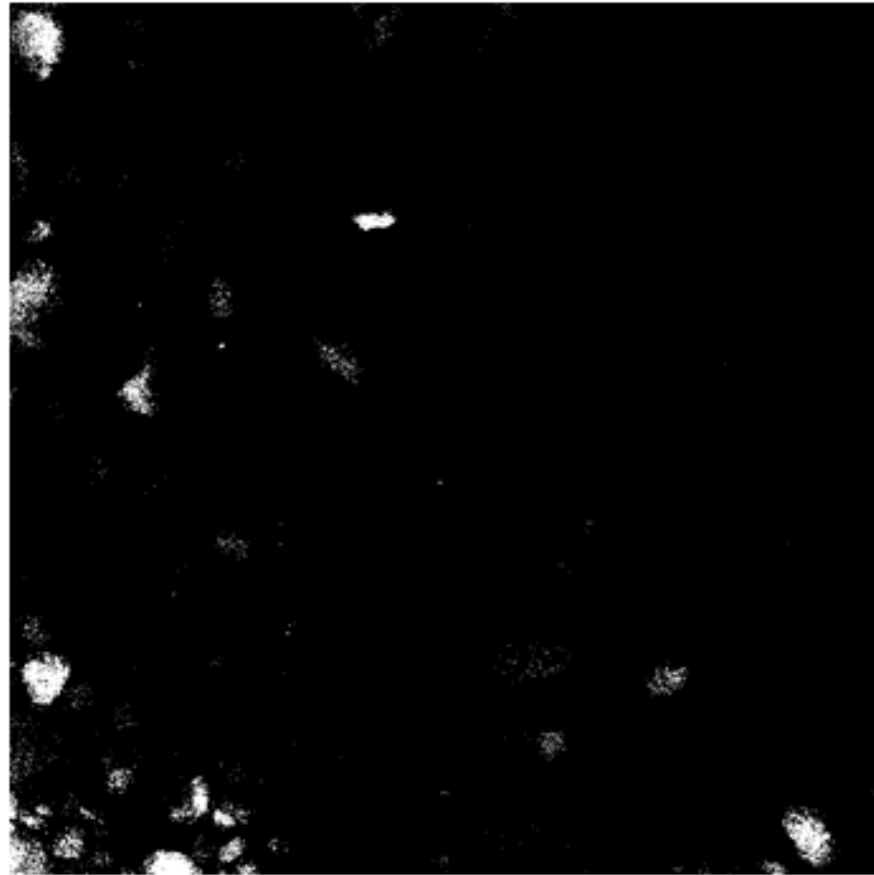


Figure 19. DE Scans, Relative Reflex, and Thresholded Image of A Section from Acid Plant Feed.

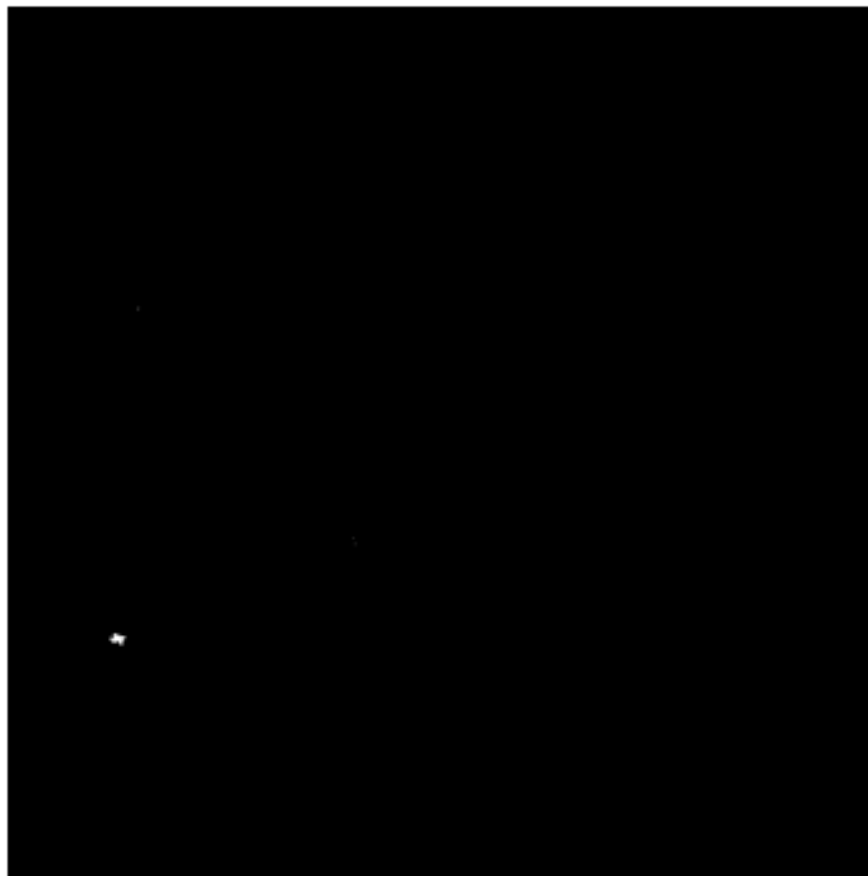


Figure 20. DE Scans, Relative Reflex, and Thresholded Image of A Section from Phosphogypsum.

While some of these thresholded images appear to have a good number of potential rare earth particles, it is important to remember that each image is only one of 120 possible images for each size group of each sample, and the majority of the other images have no potential particles shown.

4.7. High Resolution X-Ray Microtomography (HRXMT)

The particles that were identified and isolated using DE radiography were removed and prepared for HRXMT scanning. For this portion of the test, the samples were secured in a plastic cylindrical tube. Samples from different slides were separated by a circular paper, as can be seen in Figure 21. The final prepared samples can be seen in Figure 22.

The samples were then scanned using the conditions determined in Section 5.4, that is, 70 kV energy and 10 seconds per image. 1000 projection images were taken while rotating the samples 360°. This created a series of projection images, several of which can be seen in Figure 23, which were then used to reconstruct a 3D digital copy of each sample using the phosphate rare earth standard created and used for calibration. These can be seen in the Results section.

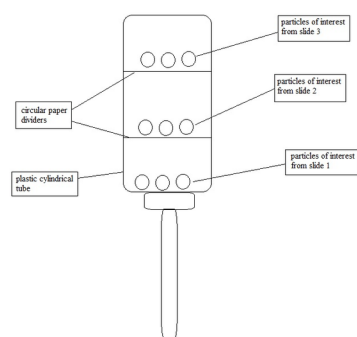
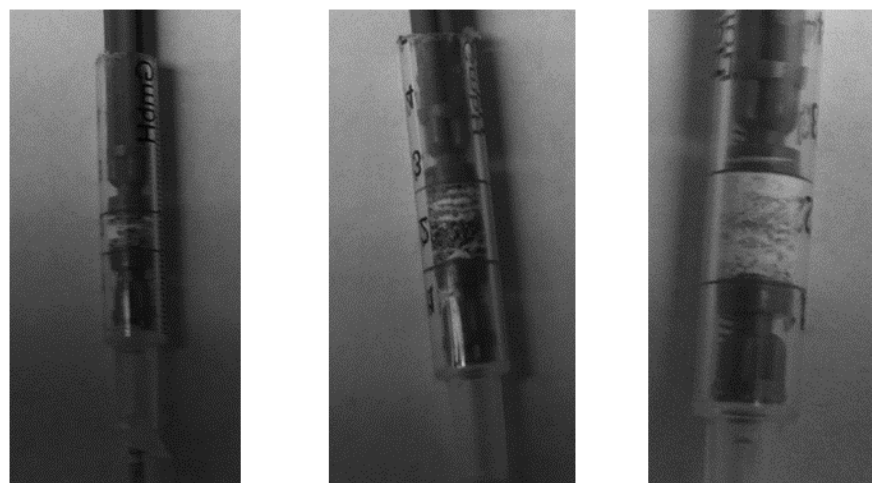
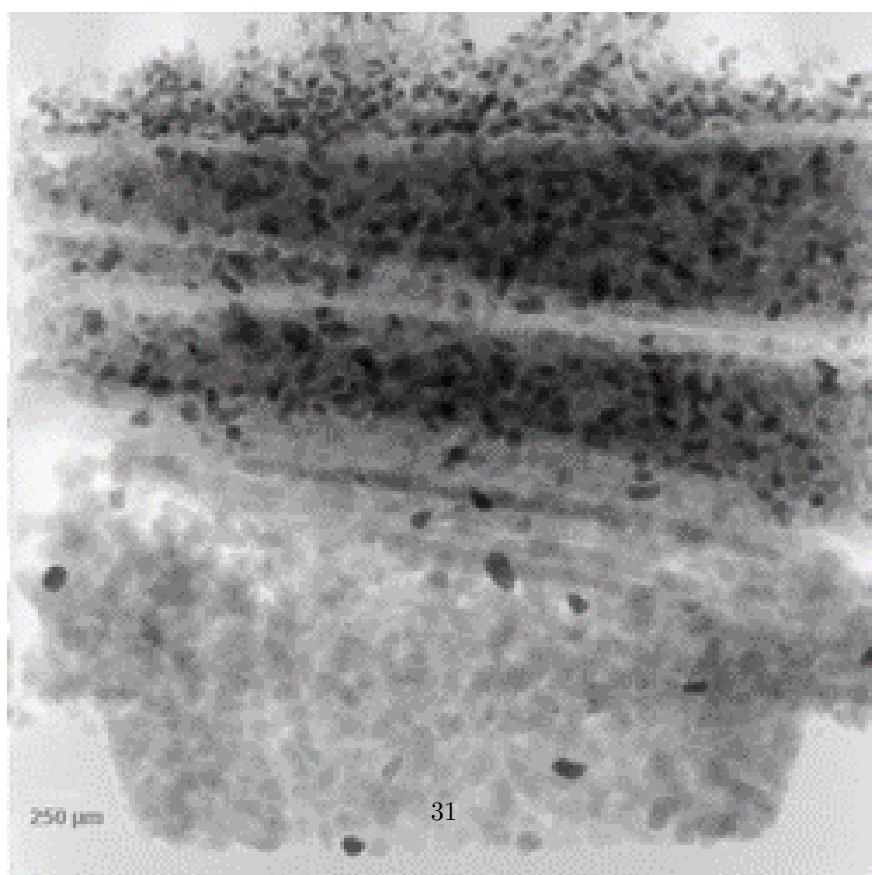
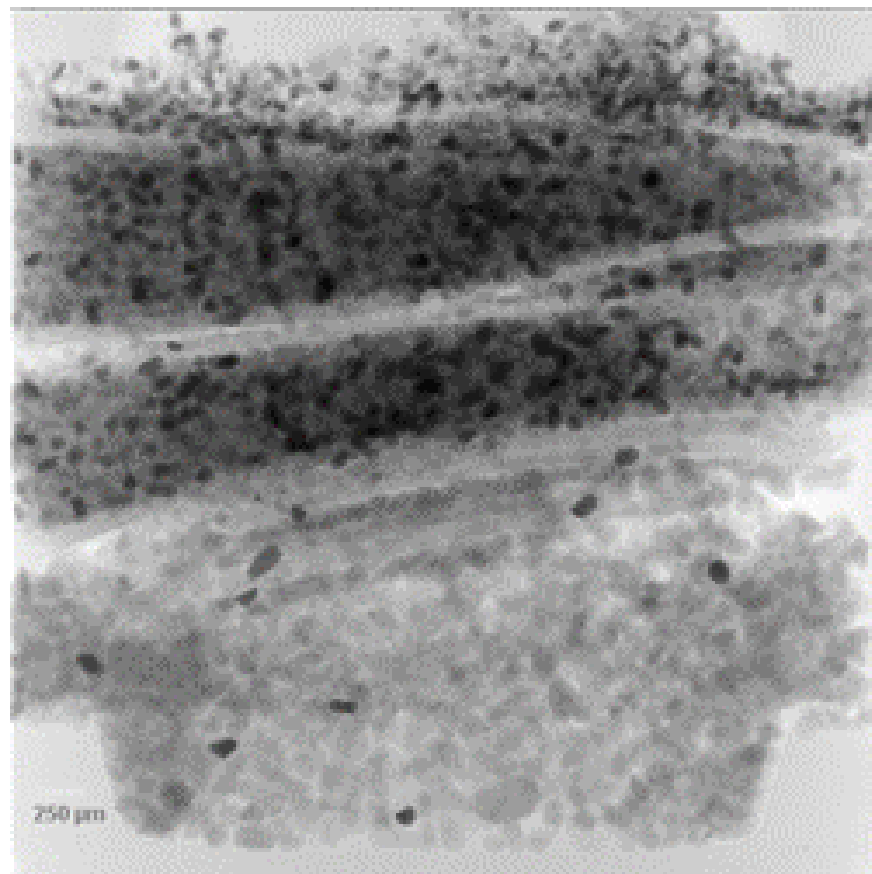


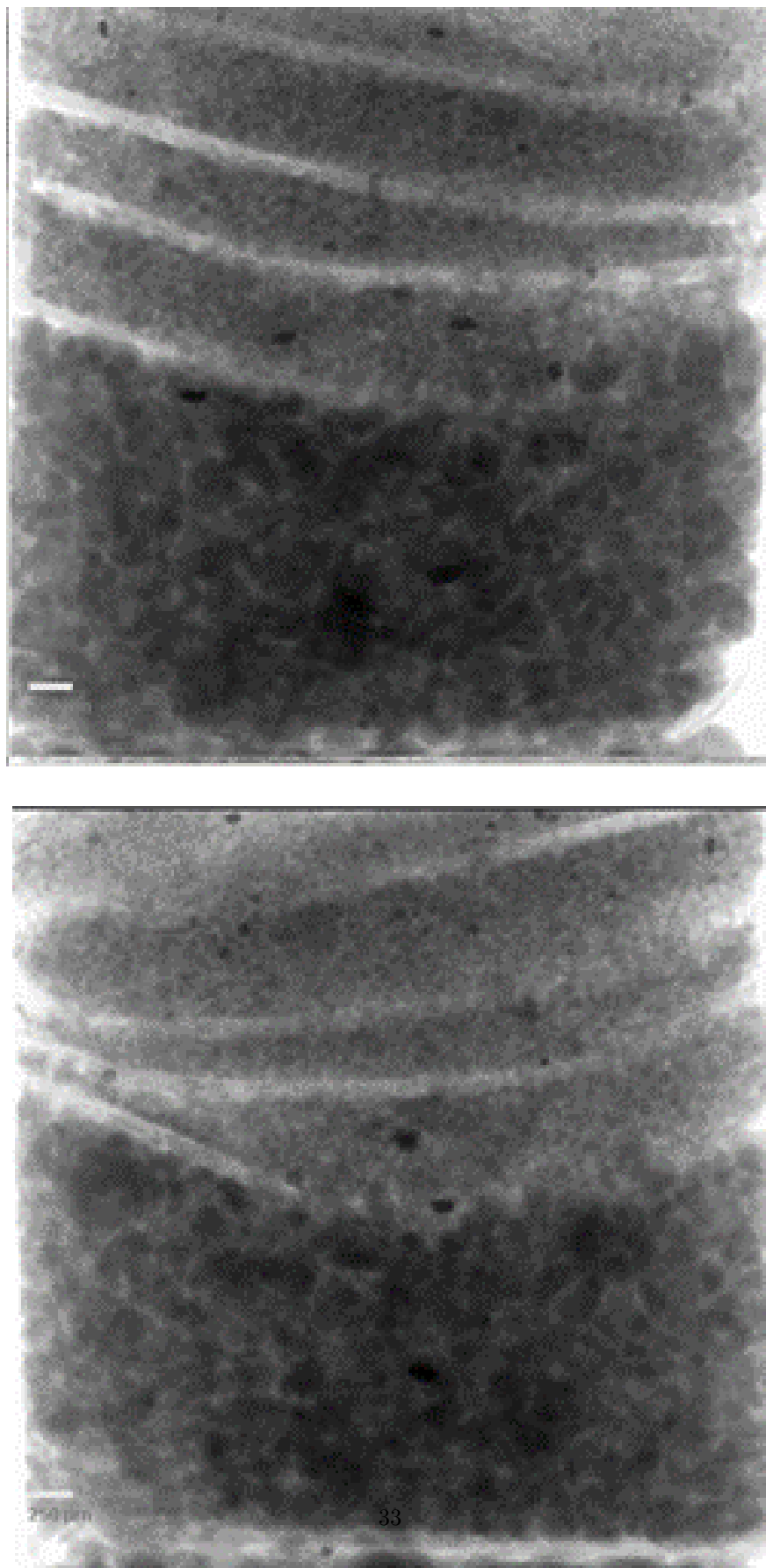
Figure 21. Sample Preparation Setup for HRXMT Scanning.

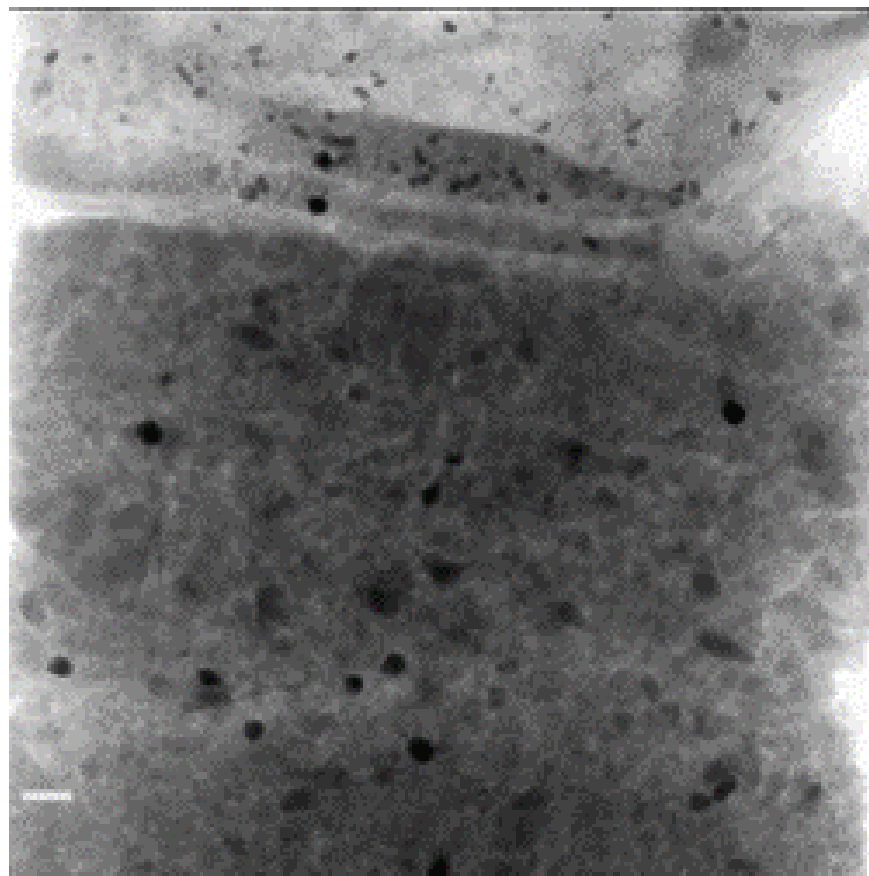
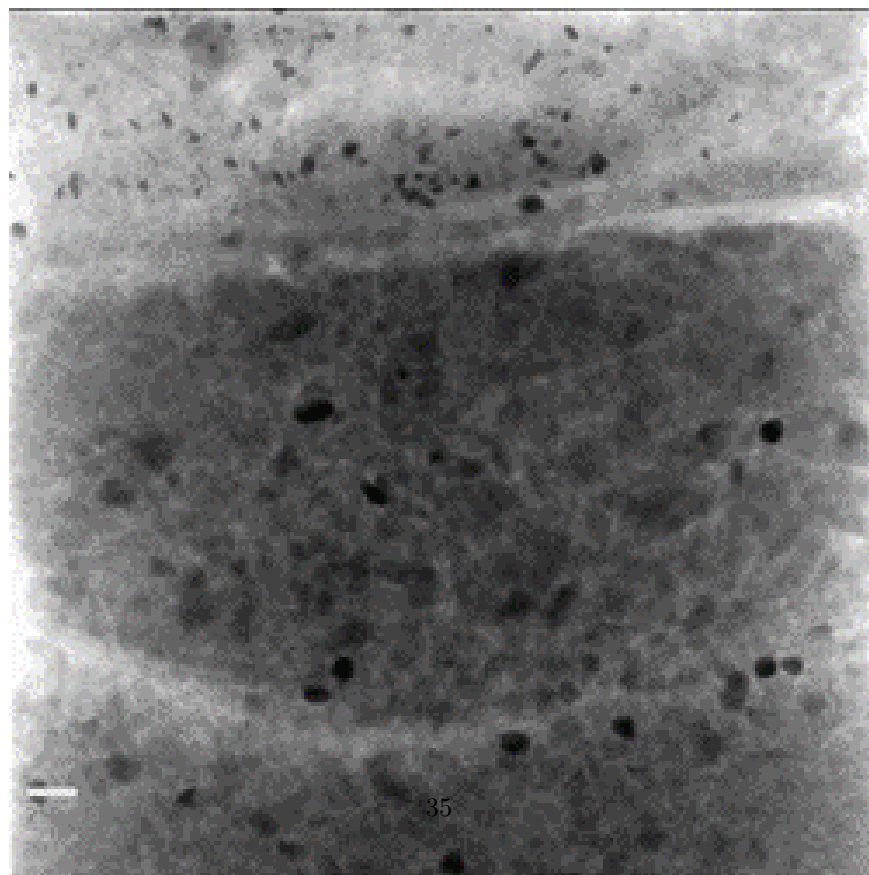


(a) (b) (c)

Figure 22. Final HRXMT Samples for Each (a) Shaking Table Concentrate, (b) Acid Plant Feed, and (c) Phosphogypsum.







(a) (b) (c)

Figure 23. Projection Images from (a) Shaking Table Concentrate, (b) Acid Plant Feed, and (c) Phosphogypsum before Reconstruction.

4.8. DE Radiography Results

Out of the 27 slides scanned using DE radiography, 11 slides had no potential RE particles after thresholding. The number of sections removed from each slide and which slides contained potential RE particles can be seen in Table 32.

Table 32

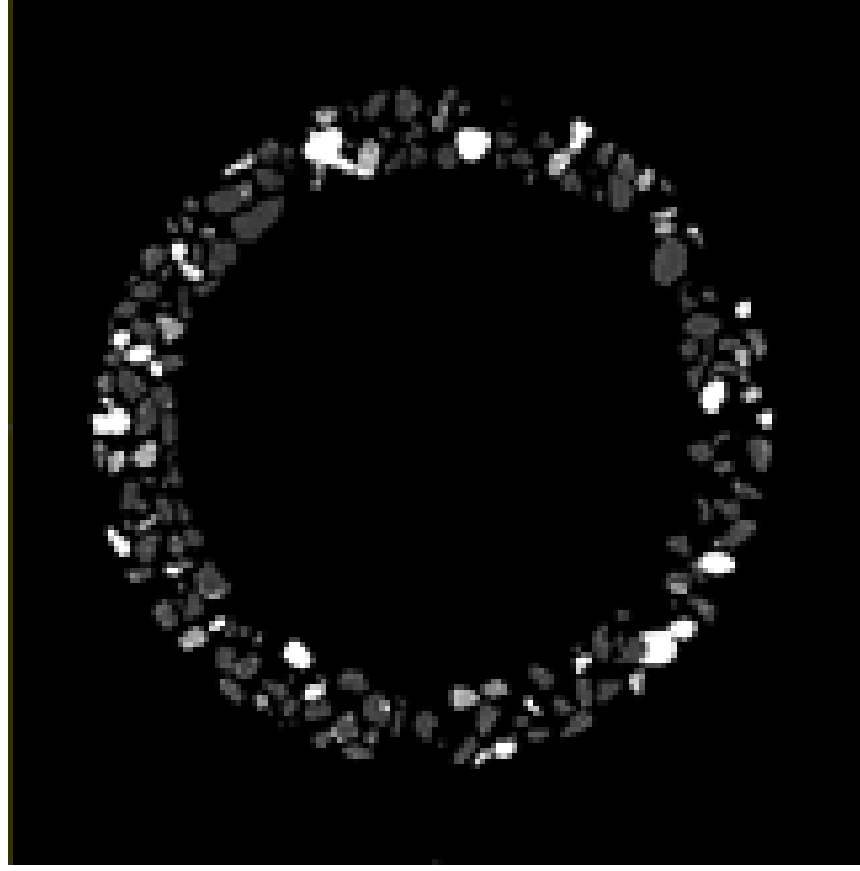
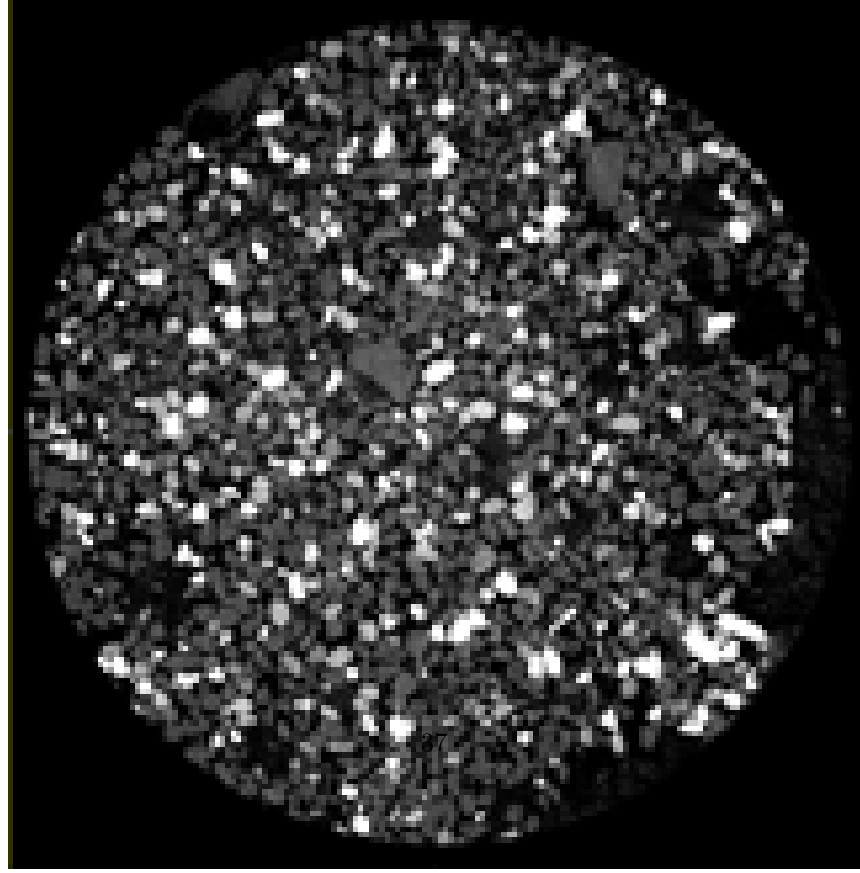
Number of Sections with Potential RE Particles on Each Slide

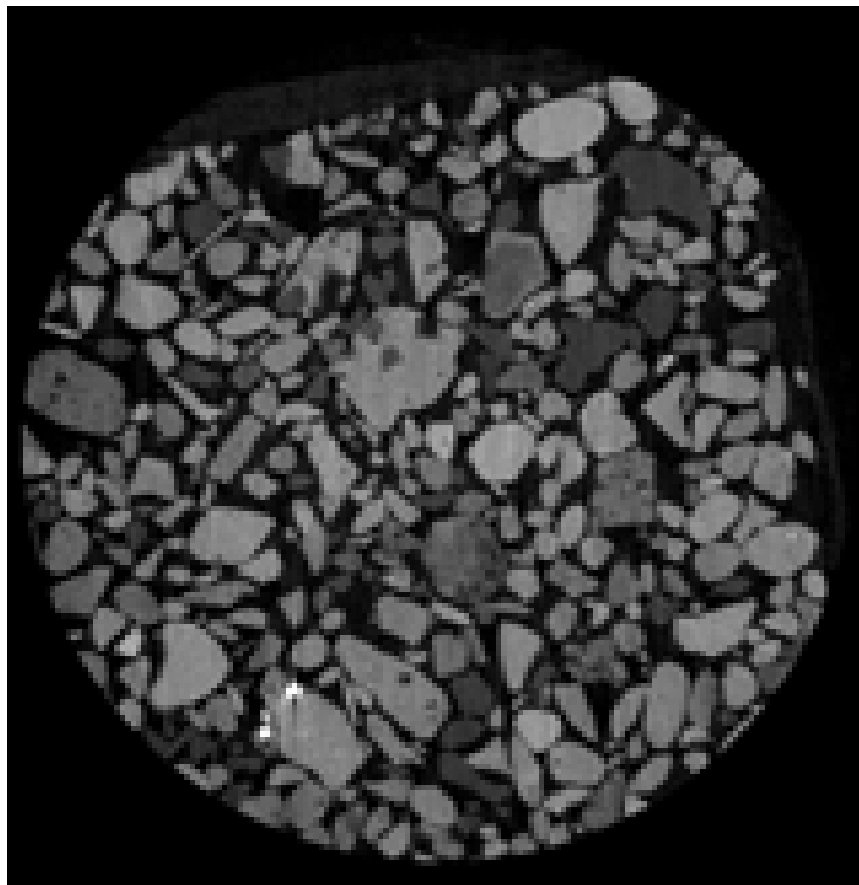
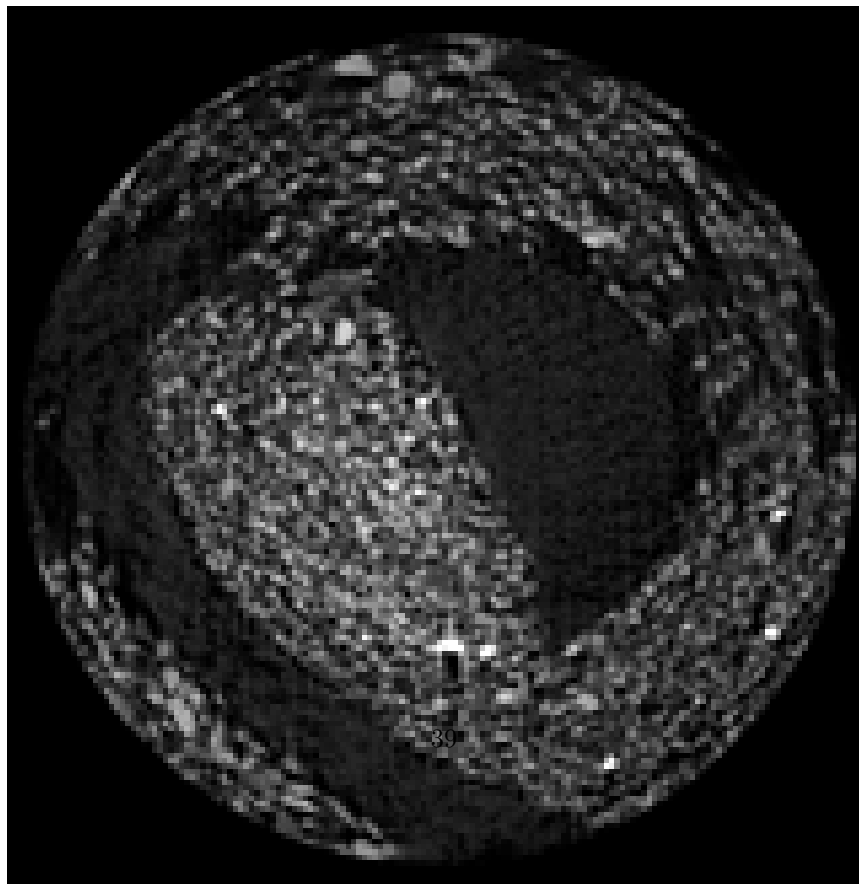
Sample Stream	Size Range	Slide Number	Number of Sections with Potential RE Particles
Shaking Table Concentrate	>106 μm	2	3
Shaking Table Concentrate	>106 μm	3	3
Shaking Table Concentrate	75-106 μm	11	8
Shaking Table Concentrate	75-106 μm	13	5
Shaking Table Concentrate	53-75 μm	22	1
Acid Plant Feed	>106 μm	32	2
Acid Plant Feed	>106 μm	33	8
Acid Plant Feed	75-106 μm	41	8
Acid Plant Feed	75-106 μm	42	6
Acid Plant Feed	75-106 μm	43	3
Acid Plant Feed	53-75 μm	53	10
Phosphogypsum	>106 μm	61	11
Phosphogypsum	>106 μm	62	14
Phosphogypsum	75-106 μm	71	1
Phosphogypsum	75-106 μm	72	7
Phosphogypsum	53-75 μm	82	12

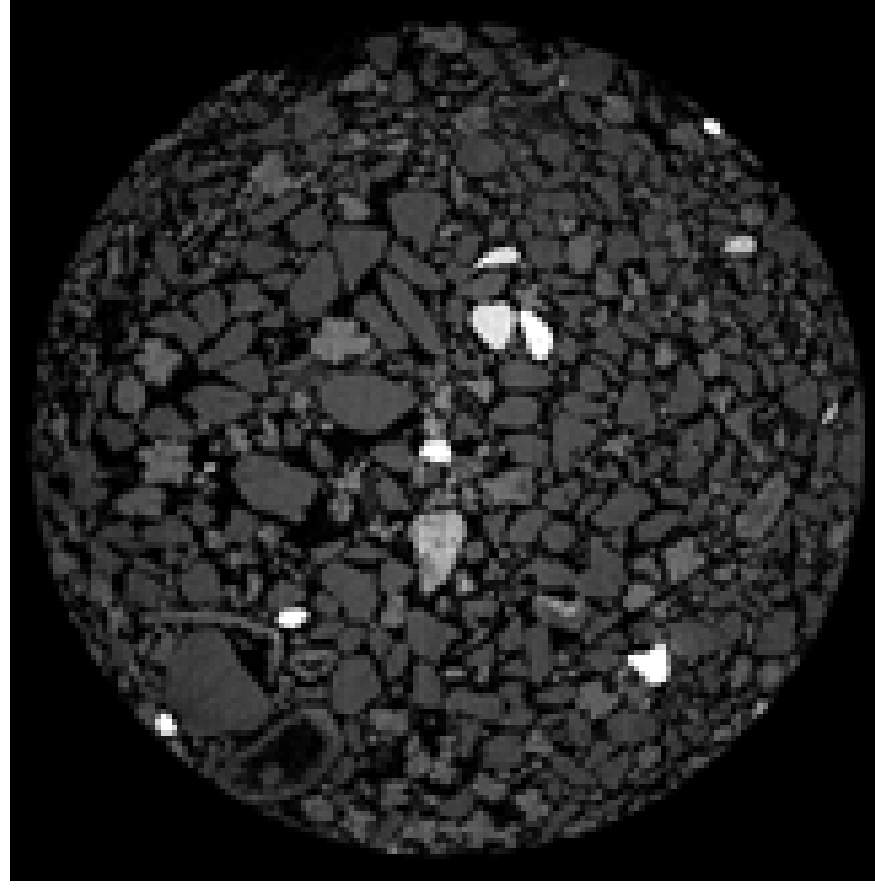
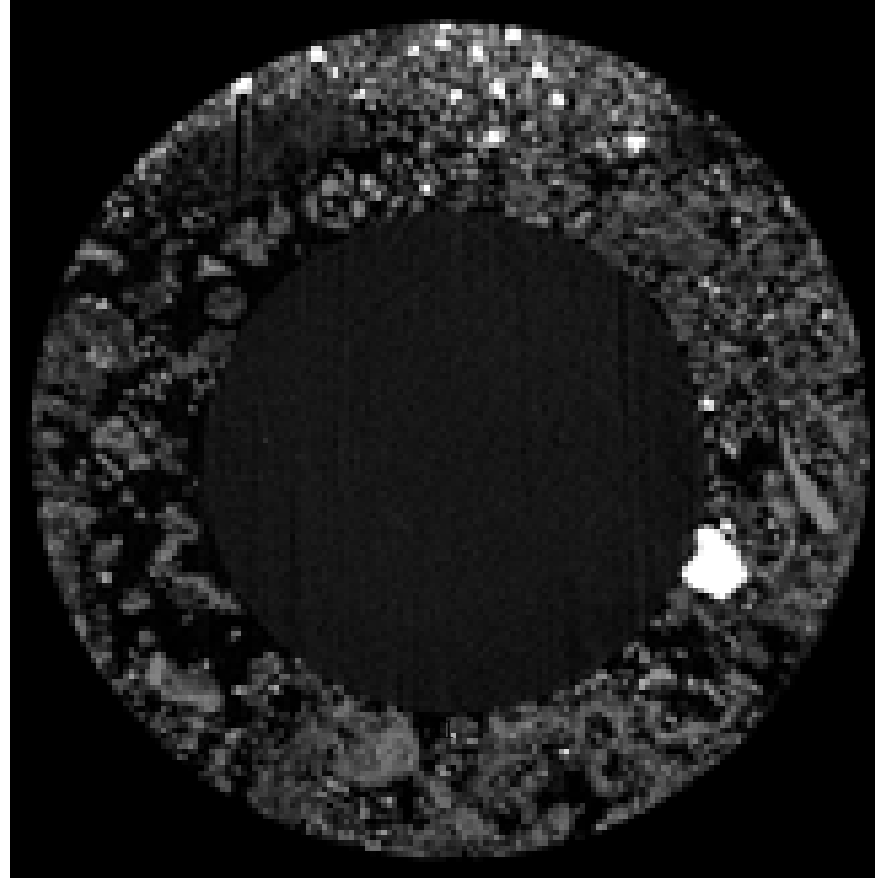
Notice that for Shaking Table Concentrate and Acid Plant Feed, the majority of the sections contain particles in the size range 75-106 μm and only a small amount of particles are in the size class 53-75 μm , and that the Phosphogypsum had the most particles come from the size range >106 μm and the least amount from the 75-106 μm range. This is important for the possible size range and liberation analysis for RE particles in those sample streams.

4.9. HRXMT Scan Results

The 3D digital samples can be viewed as 2D slices, as seen in Figure 24, or as full 3D renderings, as in Figure 25. Using a digital viewing program, Drishti, the 3D images can be thresholded to view their individual mineral breakdown, shown in Figures 26, 27, and 28. When imported to ImageJ, the number of particles past a certain threshold can be counted to get an accurate concentration.

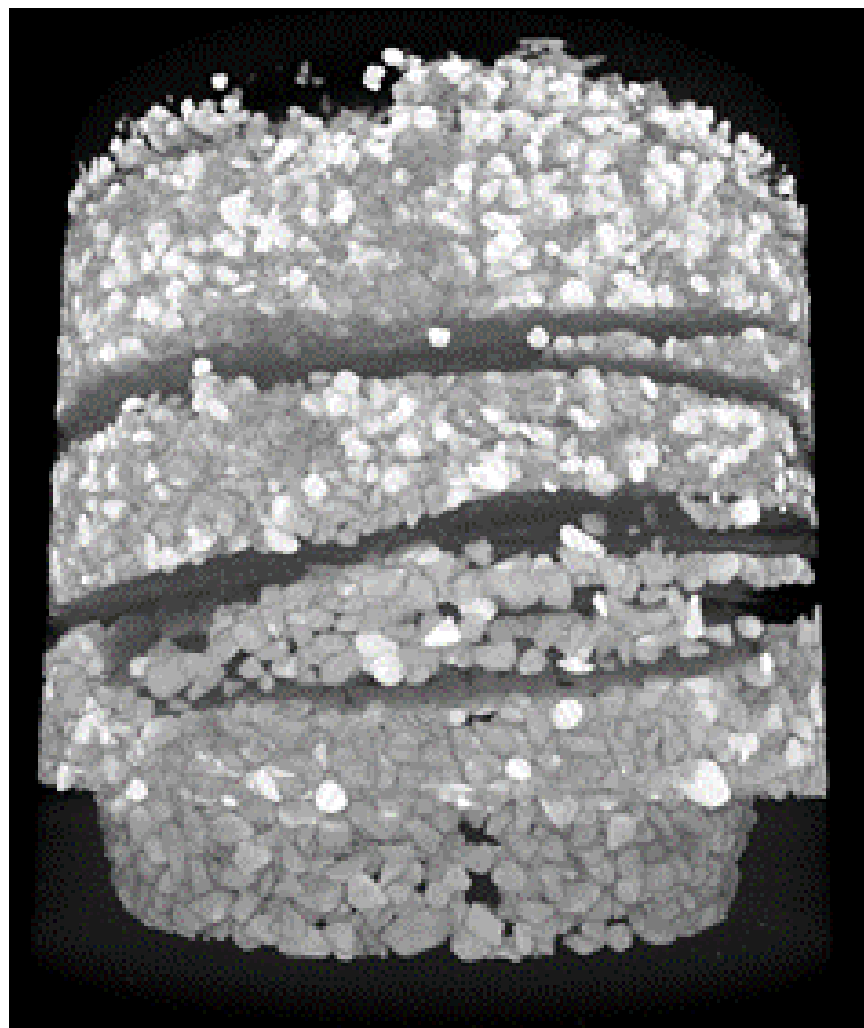




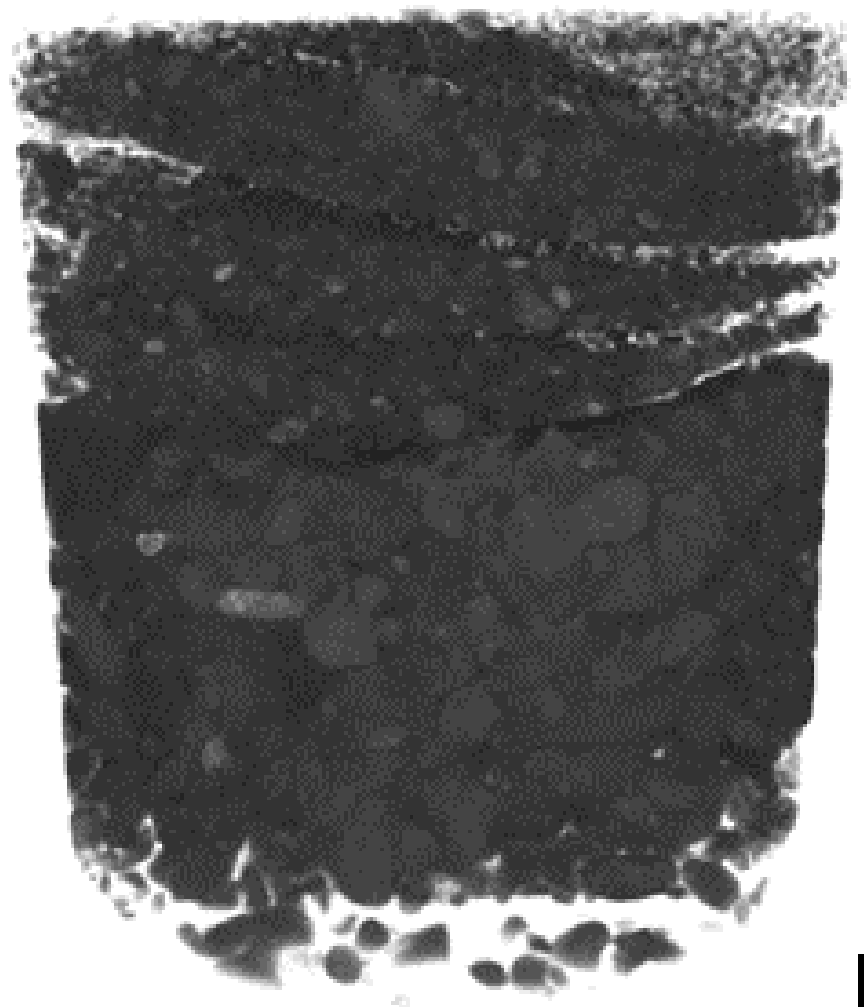


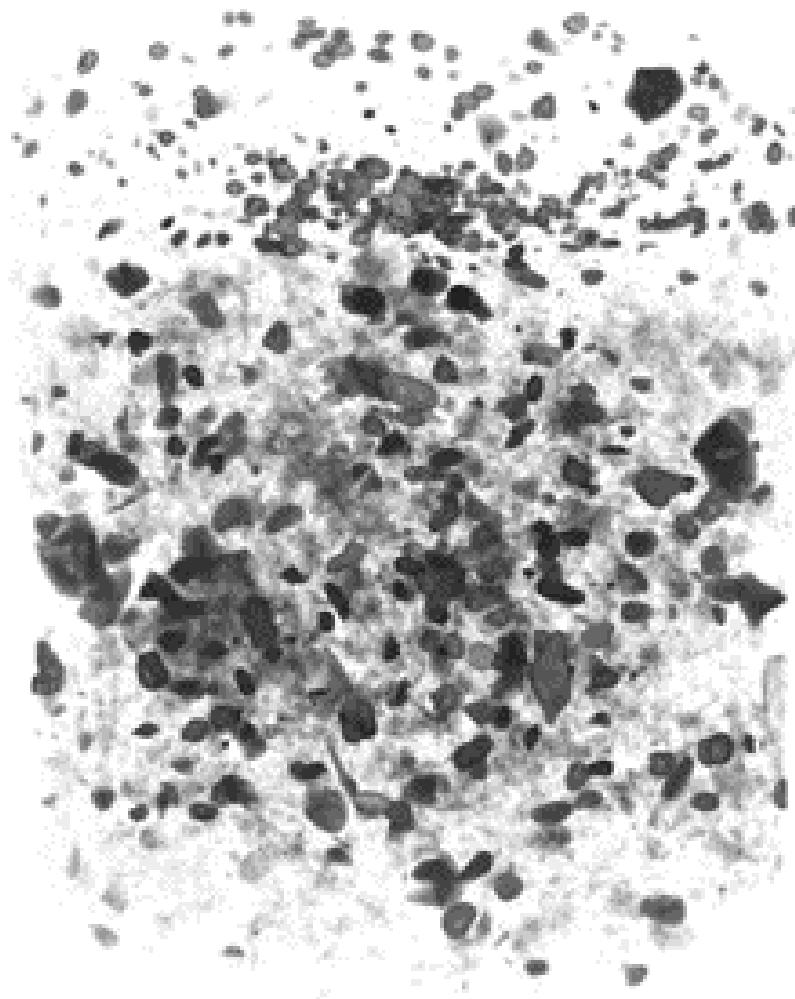
(a) (b) (c)

Figure 24. 2D Slice from (a) Shaking Table Concentrate, (b) Acid Plant Feed, and (c) Phosphogypsum after Reconstruction.



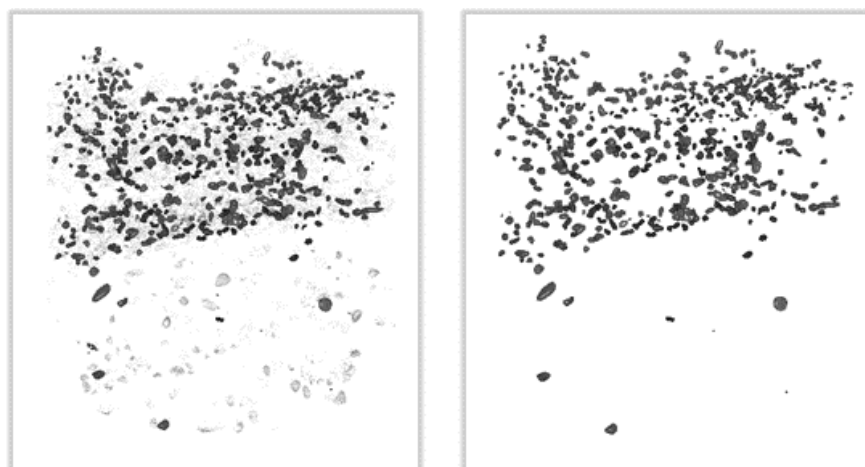
(a) (b)



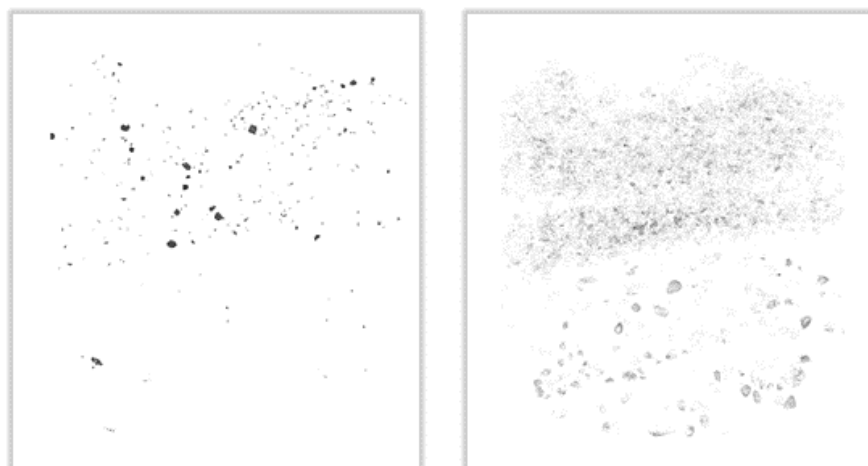


(c)

Figure 25. 3D Reconstruction of (a) Shaking Table Concentrate, (b) Acid Plant Feed, and (c) Phosphogypsum.

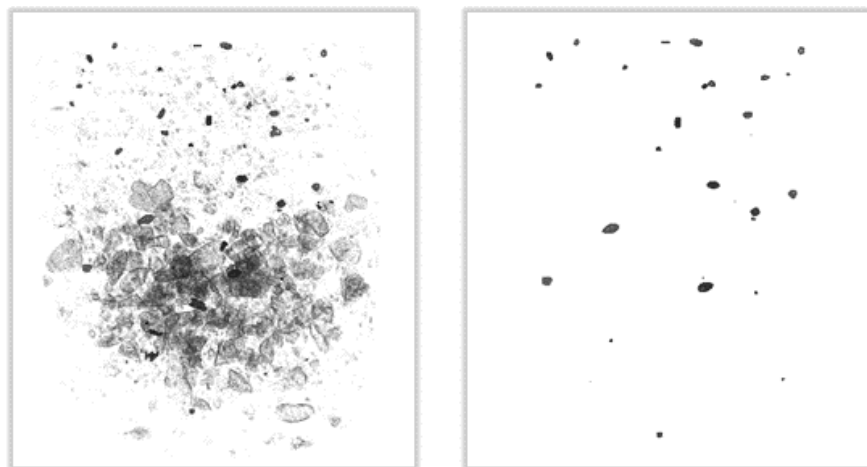


(a) all minerals (b) monazite

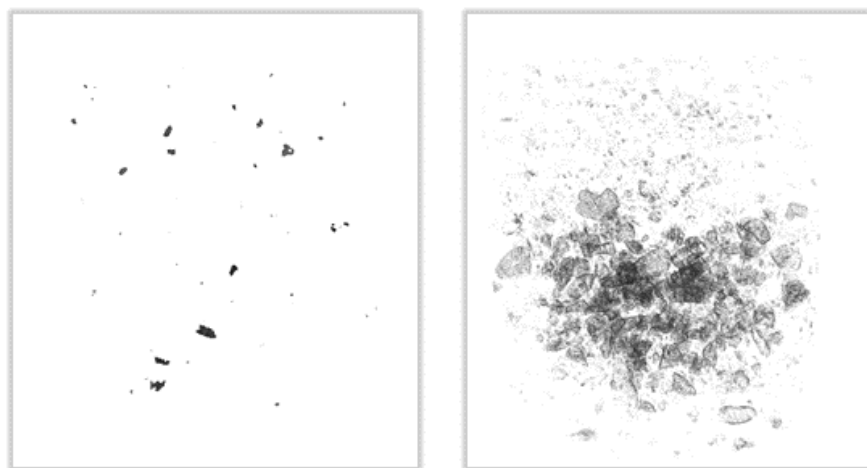


(c) zircon (d) apatite

Figure 26. Shaking Table Concentrate 3D Reconstruction by Mineral Composition.

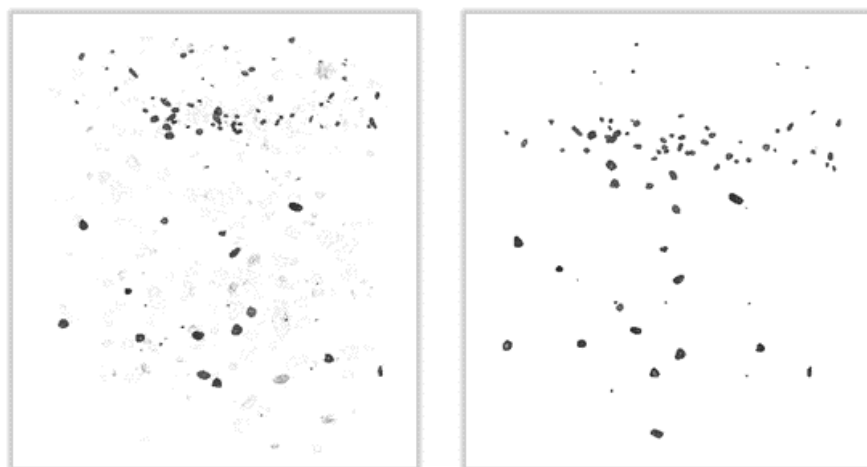


(a) all minerals (b) monazite

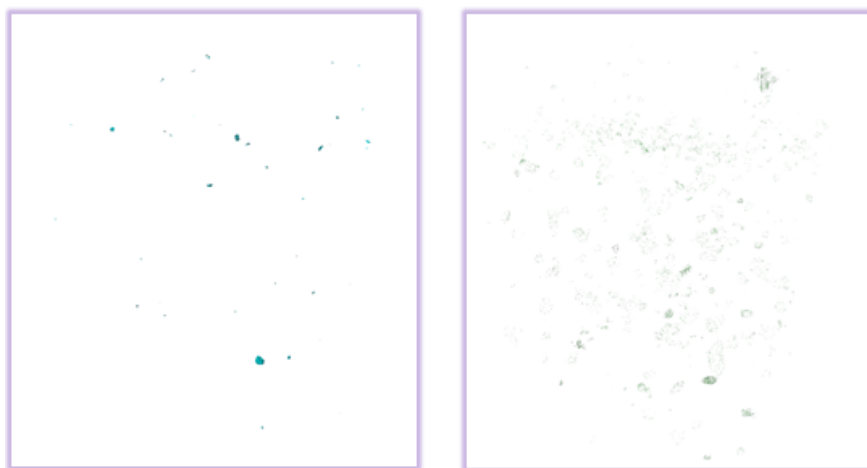


(c) zircon (d) apatite

Figure 27. Acid Plant Feed 3D Reconstruction by Mineral Composition.



(a) all minerals (b) monazite



(c) zircon (d) apatite

Figure 28. Phosphogypsum 3D Reconstruction by Mineral Composition.

4.10. Particle Analysis from HRXMT

The final mineral count per sample after reconstruction was found using the 3D Object Counter plugin through ImageJ and using the thresholding values per mineral found in Figure 18. The final mineral count can be found in Table 33.

Table 33

Final Monazite Count per Sample

	Number of RE Particles	RE Particle Concentration (ppm)
Shaking Table Concentrate	660	2157
Acid Plant Feed	32	104
Phosphogypsum	87	284

During the final thresholding of the particles, there was some inevitable overlap between the monazite CT numbers and the zircon CT numbers, as shown in Figure 18. There could be some error in the particles identified as monazite. Per sample, 18 particles from the Shaking Table Concentrate, 5 particles from the Acid Plant Feed, and 7 particles from Phosphogypsum belong to this somewhat nebulous zone. However, as these are at the very edge of the zircon identification zone, where the CT number is between 9000 and 10000, it was ultimately decided that these particles are most likely monazite and so they were counted in the RE particle category. Of those identified as zircon, 164 particles from the Shaking Table Concentrate, 26 particles from the Acid Plant Feed, and 28 particles from Phosphogypsum also belong to the region belonging to both monazite and zircon. However, as the CT numbers in this range, between 8000 and 9000, are closer to the peak of zircon and only belong to the edge of monazite, the particles can be reasonably identified as zircon and not monazite. Therefore, the ppm count shown in Table 32 can be reasonably concluded as accurate.

Using ImageJ, a visual examination of each sample can determine the degree of liberation of the monazite particles. Because the DE slides were separated in the HRXMT samples by paper, it is possible to look at each size class individually to examine the degree of liberation for each size class of each sample. For the Shaking Table Concentrate, the monazite particles in all three size classes are fully liberated. Additionally, reexamining the mineral breakdown by approximate size classes, found in Figures 29, 30, and 31, notice that in the Shaking Table Concentrate the majority of the monazite is found at the top of the sample. All three HRXMT samples were prepared so that the largest particles were found at the bottom and the smallest at the top. However, because the Shaking Table Concentrate only contained one section of one slide in the size range 53-75 μm , most of these particles near the top of the sample were located on the slides with particle size 75-106 μm . This means that the majority of the monazite particles can be found in this size range and fully liberated, making it the optimum size for grinding and processing.

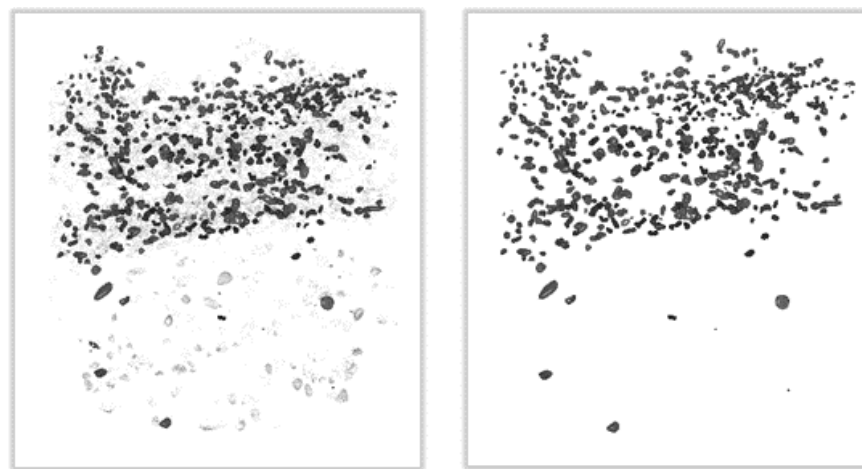


Figure 29. Monazite in 3D Reconstruction of Shaking Table Concentrate Separated Approximately by Size Class.

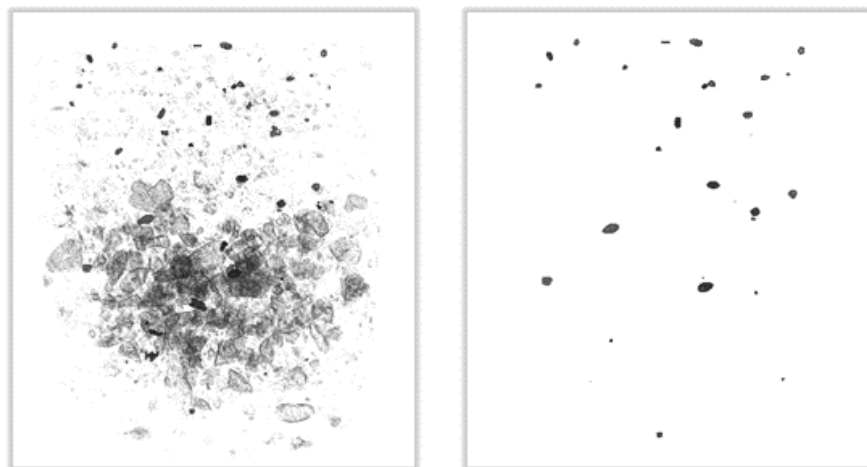


Figure 30. Monazite in 3D reconstruction of Acid Plant Feed Separated Approximately by Size Class.

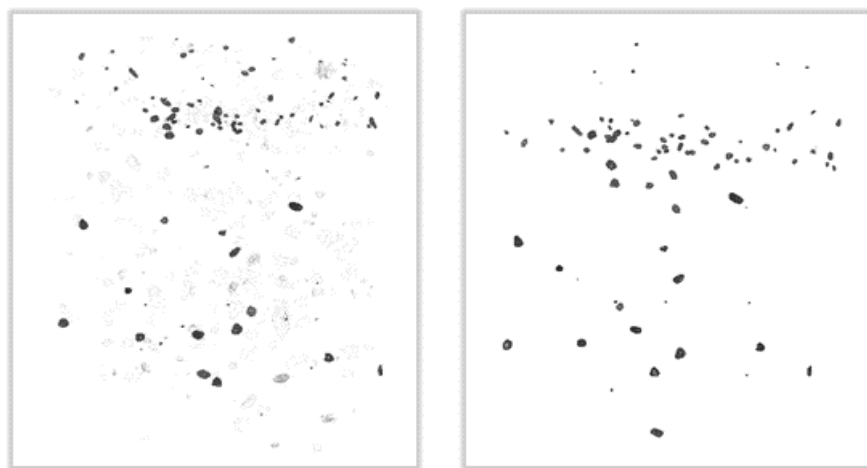


Figure 31. Monazite in 3D Reconstruction of Phosphogypsum Separated Approximately by Size Class.

The Phosphogypsum is liberated to a similar degree. In the size range $>106\ \mu\text{m}$, the majority of the monazite particles are fully liberated, though with a few particles that are partially locked, making about a 95% degree of liberation. For the size classes $75\text{-}106\ \mu\text{m}$ and $53\text{-}75\ \mu\text{m}$, all the monazite particles are fully liberated. The Phosphogypsum sample (Figure 31) has a similar grouping as the Shaking Table Concentrate further from the top of the sample, where particles from the $75\text{-}106\ \mu\text{m}$ were located, as well. However, there are many particles grouped together throughout the rest of this sample as well, especially in the $>106\ \mu\text{m}$ range. Because the majority of the RE particles are liberated as well, the optimum size range cannot be stated as clearly as the Shaking Table Concentrate, but should be in the approximate range of $75\text{-}106\ \mu\text{m}$, although a larger size could reasonably be considered.

The Acid Plant Feed had a bit different liberation analysis than the other two samples. For the size class $>106\ \mu\text{m}$, the majority of the monazite particles are not liberated at all. In fact, the RE particles are about 95% fully locked. An example of this can be seen in the 2D slice of the sample shown in Figure 32. However, in the smaller size ranges, the monazite is nearly fully liberated. As with the other two samples, only a small amount of the HRXMT sample came from the size range $53\text{-}75\ \mu\text{m}$, therefore making this size range not ideal for grinding, even though monazite particles in this size range are fully liberated. The Acid Plant Feed

(Figure 30) has a much lower concentration of monazite than the other two samples and it is concentrated relatively uniformly throughout the sample and throughout the size groups. Because the particles $>106\ \mu\text{m}$ are not liberated, but not many particles from $53\text{--}75\ \mu\text{m}$ were potential RE minerals, the size class $75\text{--}106\ \mu\text{m}$ should be considered as a good size range for monazite retrieval.

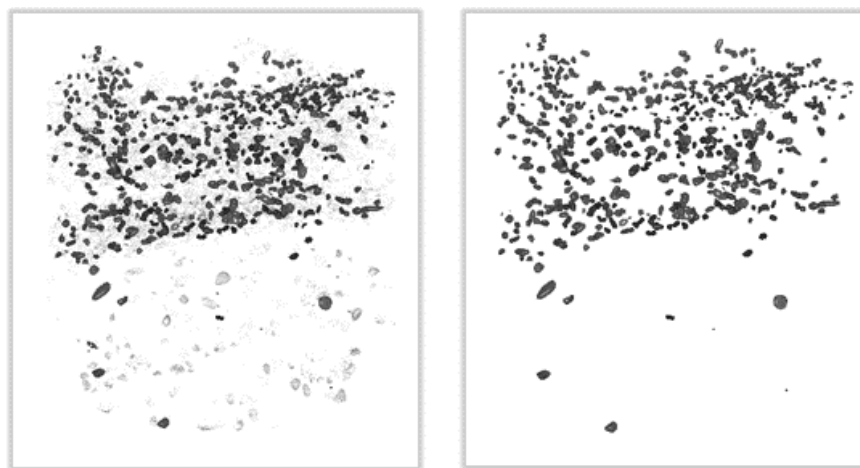


Figure 32. A Locked Particle of Acid Plant Feed Found in the Size Class $>106\ \mu\text{m}$.

4.11. Conclusions and Recommendations

Using DE radiography and HRXMT, the concentration of RE minerals in the samples provided were as follows: 2157 ppm in the Shaking Table Concentrate, 104 ppm in the Acid Plant Feed, and 284 ppm in Phosphogypsum. Judging from the degree of liberation for each sample and size range, the best particle size to find fully liberated monazite particles is $75\text{--}106\ \mu\text{m}$, although other sizes can be reasonably considered for the Acid Plant Feed and Phosphogypsum.

While the concentrations follow the trend from the chemical analysis, meaning that the Shaking Table Concentrate has a higher concentration than the Acid Plant Feed, the concentration for the Acid Plant Feed is much lower than anticipated. Part of this error can be explained due to a portion of all the samples, the particles that were $<53\ \mu\text{m}$, were not being included in the analysis. However, some error could be caused by RE particles not being identified on the DE slides and so were not transferred to the HRXMT sample. For this to happen, there could have been a manual error in the physical process of removing the particles or an error due to an incorrect thresholding value. The lower than expected concentration could be caused by any of the three described scenarios or all three possibilities compounded.

From these results, it can be concluded that DE radiography followed by HRXMT scanning is an effective and efficient method for resource identification, particularly for RE mineral identification. Based on the accuracy of DE radiography correctly identifying potential RE particles, DE radiography could even be used solely to identify RE particles given a machine that can produce X-rays at a sufficiently high energy level. Because of the amount of information this method of resource identification can provide about the individual particles in each sample, in addition to the level of accuracy HRXMT has due to its three dimensional nature, it is recommended that DE radiography be used to semi-quantitatively identify minerals of interest followed by a thorough particle analysis from HRXMT scanning and reconstruction in order to isolate and characterize RE particles.

The main limitation of this method is the amount of time required for HRXMT scanning. This is reduced by using DE radiography to “pre-concentrate” the HRXMT samples with particles more likely to be RE minerals, but the time still required to scan enough particles to gain a reliable accuracy is not insignificant. However, if an X-ray source could produce X-rays of high enough energy level, identification confirmation by

HRXMT would not be a necessary follow up to DE radiography. RE particle identification could be done in a matter of minutes instead of hours or days. In this sense, the project is further limited by the maximum energy level the X-ray machine can produce. As demonstrated in previous literature, the maximum effective atomic number that can be accurately identified using solely DE radiography with the machine used in this project is an atomic number of 40 and so HRXMT verification is necessary.

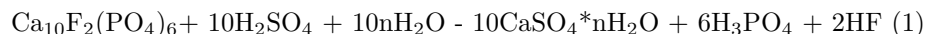
Despite these limitations, this project has demonstrated that DE radiography followed by HRXMT is still a more effective method for particle identification and liberation analysis than other methods available. Using DE radiography first reduces the time necessary for just HRXMT scanning and using HRXMT for particle verification compensates for insufficient energy levels during DE radiography. It is recommended that this method be used in the future for RE identification and analysis.

REE UPGRADING AND EXTRACTION FROM PHOSPHATE

5.1. Extraction of Rare Earths from PG

5.1.1. REE in Phosphogypsum from Wet Phosphoric Acid Process Production

The “wet acid” process usually refers to the manufacturing of phosphoric acid by reacting phosphate rock with sulfuric acid. The first phosphoric acid plant was built in Germany in about 1870 and in the U.S. in 1890 (Beaton, 2010). The past decade has seen many new phosphoric acid plants constructed in major phosphate producing countries such as Morocco, China and the Middle East. The primary chemical reaction in the “wet acid” process may be expressed in the following equation using fluorapatite to represent phosphate rock:



Depending on the value of n, the process is defined as the di-hydrate (n=2) process, hemi-hydrate (n=1/2) process, or anhydrate process. The term $\text{CaSO}_4 \cdot \text{nH}_2\text{O}$ in the equation is simply referred to as Phosphogypsum (PG).

The dihydrate (DH) process is used most widely in the world, and is the main wet acid process practiced in the United States. It was reported that the DH process required a low capital cost, with a very low production cost and great flexibility in using various qualities of phosphate rock. One distinguishable advantage of the process is its capability of producing an acid from which uranium can be extracted easily. This process is generally designed for a 24-28% P_2O_5 acid.

Under the CMI project, FIPR collected and characterized numerous phosphogypsum and phosphoric acid samples. Results show that during the wet process, approximately 70% of the REE in the phosphate rock feed reports to phosphogypsum, with the remaining 30% mainly ending up in the filter acid.

5.1.2. Leaching of Phosphogypsum and Acid Sludge

Considering the easy integration of the sulfuric acid system with the existing phosphoric acid manufacturing process, phosphogypsum leaching focused on leaching with sulfuric acid solutions. Experimental results indicated that the REE leaching efficiency increased rapidly, reached a maximum, and then began to decrease with sulfuric acid concentrations ranging from 0 to 10 % and at temperatures ranging from 20 to 70 °C. At a sulfuric acid concentration of 5 % and leaching temperature of 50 °C, the REE leaching efficiency obtained a maximum value of approximately 43 %. Increasing the leaching time or liquid/solid ratio further increased the leaching efficiency. Leaching recovery of over 80% was achieved by countercurrent leaching of the phosphogypsum. An intensive leaching study also showed a 2.5% sulfuric acid solution was as effective as a 5% solution.

Three sets of leaching tests were conducted. The first set of tests was designed to study the effect of acid concentration using sulfuric acid solutions of 0%, 1%, 2.5%, 5%, and 10% sulfuric acid by weight. These tests were conducted in the above glass reactor, each with 500 grams of phosphogypsum at two temperature levels (room temperature and 75° C), respectively. Five samples of the leachate were taken at leaching time

intervals of 5, 10, 30, 60, and 120 minutes, with each sample analyzed for REE content to calculate recovery and plot leaching kinetics curves.

Another set of tests was stage wise washing and leaching to maximize REE recovery by the following sequence:

5% (or 2.5% depending on results from the first set of tests) sulfuric acid solution; room temperature, washing for 10-20 minutes

5% sulfuric acid solution; room temperature, leaching for about 60 minutes

23% sulfuric acid solution; room temperature, leaching for about 60 minutes

93% sulfuric acid solution; 230°C, leaching for about 60 minutes

The third set of tests was the development of a countercurrent leaching flowchart, as shown in Figure 33. The numbers in this flowchart represent phosphoric acid sludge, which will be discussed later, but the concept is the same for PG.

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image60.emf available at <https://authorea.com/users/622355/articles/645744-rare-earths-in-phosphate-characterization-extraction>

Figure 33. Conceptual Countercurrent Leaching Flowchart.

5.1.3. Solvent Extraction Experiments on the Phosphogypsum Leachate

The optimal leachate from the above three sets of leaching tests were selected for solvent extraction experiments using the reagents system recommended by ORNL. These tests were conducted using laboratory shakers with each test consuming 250 ml of leachate. Most of the solvent extraction parameters were evaluated, including the O/A ratio, contacting time, temperature, solvent concentration, and acid strength. Extraction isothermals and kinetics curves were established.

5.2. Recovery of REE from Phosphoric Acid Sludge

5.2.1. Pre-treatment of Phosphoric Acid Sludge

Over 80% of the world's phosphate rock is used for the production of wet process phosphoric acid. In many operations, the filter acid (about 28-30% P_2O_5) is evaporated in two stages, first to 40% P_2O_5 and then to 54% P_2O_5 . Each evaporation stage produces a sludge, but the majority of the REE in the filter acid eventually ends up in the final sludge. Results show that REE concentration in the 54% P_2O_5 sludge is ten (10) times higher than that in the 40% P_2O_5 sludge.

The goal of the sludge pre-treatment research is to generate a solid material high in heavy REE content as a feed for downstream processing and recovery of the REE. Since the phosphoric acid value in the sludge is many orders of magnitude higher than the REE, maximizing recovery of the phosphoric acid value is critical to the overall economics. Settling test results indicate that the as-received sludge settles too slowly to use thickener or any other mechanical means for solid-liquid separation. When the sludge is diluted to 30% P_2O_5 , it becomes readily treatable with mechanical solid-liquid separation techniques. Leaching characteristics of the sludge using dilute sulfuric acid solution is similar to those of phosphogypsum, but REE leaching is more challenging due to the presence of Fe and Al precipitates. However, 80% REE recovery is still possible by countercurrent leaching of alcohol-washed sludge.

The phosphoric acid sludge containing about 54% P_2O_5 is extremely viscous with a viscosity of 12 centistokes at room temperature. Traditional solid-liquid separation devices are not suitable for this material without some kind of pre-treatment. As shown in Figure 34, the as-received sludge settles extremely slowly.

[CHART]

Figure 34. Settling Rate of As-Received Phosphoric Acid Sludge in A Graduated Cylinder.

Under the CMI project, numerous approaches were tested as pre-treatment to enhance S-L separation, including flocculation, addition of sawdust, and acid dilution (Allaadini and Zhang, 2018, 2019a, 2019b). Figure 35 indicates that dilution of the sludge to 30% P_2O_5 increased the settling rate by nearly two orders of magnitude. Therefore, this method was selected as the main pre-treatment approach for phosphoric acid sludge. After dilution, S-L separation was achieved using a filter press.

[CHART]

Figure 35. Settling Rate of Diluted Phosphoric Acid Sludge (30% P_2O_5) in A Graduated Cylinder.

Standard settling testing were conducted on diluted sludge (to 30, 35 and 40% P_2O_5 , respectively) in a graduated cylinder for 6 hours. Parallel settling tests on the same samples were conducted to evaluate the effect of flocculation and sonication, respectively.

Based on the settling tests, a large volume of the treated sludge that renders the fastest settling rate will be prepared and tested using a laboratory filter press.

5.2.2. Leaching of Sludge Solids

Although a majority of the sludge is gypsum, the leaching characteristics of sludge are different from those of phosphogypsum. Therefore, some leaching tests on the sludge solids will be similar to leaching of phosphogypsum, and the others are quite different.

Again, three sets of leaching tests were conducted on the sludge. The first set of tests was designed to study the effect of acid concentration using sulfuric acid solutions of 0%, 1%, 2.5%, 5%, and 10% sulfuric acid by weight. The second set of tests was conducted mainly to study the effect of temperature and phosphorus content in the sludge. The third set of tests again examined countercurrent leaching, using the same procedure as for phosphogypsum.

Figure 36 shows the effect of sulfuric acid concentration on REE leaching recovery, while Figure 37 demonstrates the effect of leaching time. The best leaching results, again, were obtained by countercurrent leaching. Total REE concentration in the leachate reached about 290 ppm at a recovery of over 80%, under the following conditions: 1) sulfuric concentration, 2.5% (wt.); 2) leaching temperature, 25°C; 3) liquid to solid ratio (wt./wt.), 3.5:1; and 4) leaching time, 2 hours for each stage.

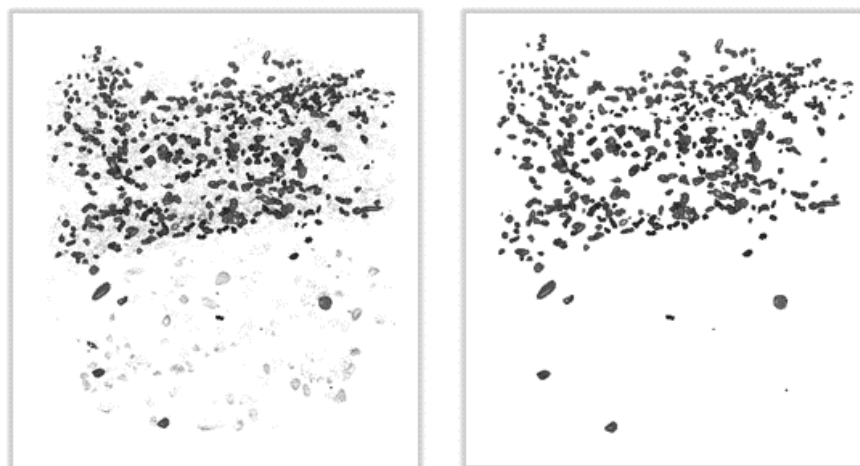


Figure 36. Effect of Sulfuric Acid Concentration on Leaching Recovery.

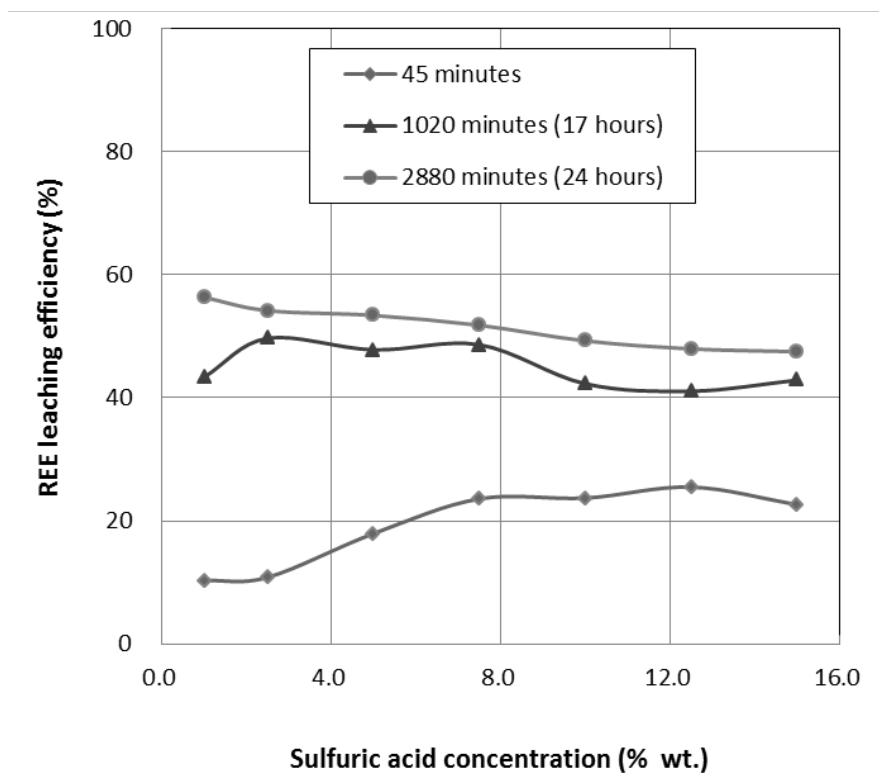


Figure 37. Effect of Leaching Time on Leaching Recovery.

5.3. Recovery of REE from Amine Flotation Tails

As is shown in Figure 2 above, a majority of phosphate rock product in Florida is produced by a two-stage flotation process. The first stage is direct (rougher) flotation of phosphate using fatty acid, and the second stage is reverse flotation of the rougher concentrate using amine. Analysis of numerous samples showed that the fatty acid flotation tails contain very low content of REE, but the amine flotation tails contain over 200 ppm REE. Mineralogical analyses discussed in above indicated that REE occur in amine tails mainly as monazite and xenotime. The specific gravity of these rare earth minerals is significantly higher than that of silica (the main component of amine tails), making it possible to pre-concentrate the REE-containing minerals by gravity separation. In this case, a shaking table was used to separate rare earth and phosphate minerals from silica.

Table 34 shows what one stage of shaking table separation could achieve (Liang et al., 2018). The concentrate analysis was as follows: 187.38 ppm Y, 131.86 ppm La, 251.23 ppm Ce, 164.23 ppm Nd, and 29.96 ppm Pr.

Table 34

Results of One-stage Shaking Table Separation of Amine Tails

Product	Yield (wt%)	Total REE (ppm)	Total REE recovery (%)
Feed	100	201.90	100
Concentrate	12.51	657.39	40.73
tailings	87.49	136.77	59.27

The gravity separation concentrate was leached for REE and P recovery based on the dihydrate process of

phosphoric acid production simulated in a 2.5L water-bath batch reactor. The effects of four main factors on REE and phosphorus leaching efficiencies were investigated, including phosphoric acid addition in the initial leaching pulp, leaching temperature, stoichiometric ratio of H_2SO_4 to calcium oxide (CaO), and weight ratio of liquid to solid (Liang et al., 2018). In each leaching test, 400g of the shaking table concentrate were used and the solution was sampled every 15 minutes to monitor the leaching development through chemical analysis. After leaching, the pulp was filtered and the residue was washed three times for chemical analysis.

Phosphoric acid can react with phosphate rock resulting in soluble monocalcium phosphate and releasing REE. Indeed, studies showed that adding phosphoric acid to pulp is beneficial for both P_2O_5 and REE leaching (Wang et al., 2010; Liang et al., 2017). Therefore, in this research phosphoric acid was added into the initial leaching acid mixture with sulfuric acid, with the P_2O_5 concentration ranging from 0 to 20% in the initial pulps. Figure 38 indicates a significant impact of the phosphoric acid ratio on REE leaching efficiency and REE content in the solution. In this figure, L.E. stands for Leaching Efficiency (recovery).

[CHART]

Figure 38. Effect of Phosphoric Acid Concentration in Initial Pulp on Leaching Efficiency (leaching temperature = 75°C ; stoichiometric ratio of H_2SO_4 to CaO = 1.2; Ratio of liquid to solid = 3.5) (Liang et al., 2018).

The shaking table concentrate was upgraded further by flotation. In the flotation process, sodium carbonate was used as the pH adjustor, sodium silicate as the silica depressant, and fatty acid/fuel oil (at a ratio of 1:0.5) as the collector. Flotation results are shown in Table 35.

Table 35

Results from Flotation of Shaking Table Separation Concentrate

Product	Yield (wt%)	Total REE (ppm)	Total REE recovery (%)	$\text{P}_2\text{O}_5\%$	% P_2O_5 recovery
Feed	100	621.75	100	8.12	100
Concentrate	25.28	1809.50	73.18	26.37	82.07
tailings	74.72	219.88	26.82	1.95	17.93

5.4. Recovery of REE from Phosphate Clay (slime)

As mentioned earlier, phosphate beneficiation in Florida generates over one ton of phosphate clay (slime) per ton of phosphate rock produced. On that basis, the industry has been producing 20-40 million tons of waste clay annually depending on the rate of phosphate mining over the years. Since the beginning of large scale washing and desliming practices for phosphate beneficiation, over two billion tons of such slime have been accumulated, which contain approximately 600 million tons of phosphate rock, 600,000 tons of rare earth elements (REE) including 200,000 tons of yttrium, and 80 million kilograms of uranium.

The tremendous potential for recovering P, REE and U in phosphate clay has drawn numerous industrial partners to the CMI phosphate project led by the FIPR Institute.

Figure 39 summarizes the proposed processing steps by the FIPR Institute. Success of this ambitious research effort depends on three key elements: 1) successful removal of clay minerals, 2) upgrading of phosphate as well as REE-containing materials, and 3) removal of magnesium from the phosphate concentrate, thus making it suitable for producing high value phosphoric acid. To accomplish these goals, we propose multistage cyclone separation to remove the clay minerals, innovative gravity separation and flotation to concentrate the phosphate, and smart chemistry to selectively leach magnesium from phosphate.

Figure 39. Proposed Approach for REE, U and P Recovery from Phosphate Clay.

Selective leaching of Mg is usually conducted at pH 2.8-3.5, temperature $65\text{-}75^\circ\text{C}$, and 30% solids. Several cyclone separation campaigns were conducted to separate clay minerals from non-clay minerals, both in the

lab and on the plant site. Two hydrocyclone testing systems were used in those tests, with one using a 4-inch cyclone, and another with a 2-inch and a 1-inch cyclone.

5.4.1. One-Stage Separation of Using a 4-inch Cyclone & Downstream Processing

The 4-inch cyclone cuts relatively coarse and one-pass separation could recover roughly 20% of the mass with less than 20% of the REE in the head sample. Table 36 shows results from one of the tests.

Table 36

REE Distribution in Cyclone Classification Products Using A 4-Inch Cyclone

Product	Yield (wt%)	Total REE (ppm)	Total REE recovery (%)
Feed	100	314.37	100
Underflow	20.68	266.46	17.53
Overflow	79.32	326.86	82.47

Fatty acid flotation of the underflow product produced a concentrate with 455 ppm REE at a total REE recovery of 81.85%. Over 90% REE recovery was achieved by leaching the flotation concentrate at 230°C with concentrated sulfuric acid at a stoichiometric ratio of $\text{H}_2\text{SO}_4/\text{CaO}$: 1.5 7.0 for 240 min.

5.4.2. Two-Stage Separation Using a 2-inch Cyclone

Since the product yield using a 4-inch cyclone was low (about 20%), a 2-inch cyclone was designed and tested for two-stage separation of the phosphate clay. In this scheme, the overflow from stage 1 was used as the feed for the second stage separation. Table 37 shows the first stage separation results, while Table 38 shows the second stage separation results.

Table 37

First Stage Separation of Phosphate Clay - Two Duplicate Tests

Sample	Wt% yield	REE Concentration (ppm)	REE Concentration (ppm)	REE Concentration (ppm)
		Y	Nd	La
UF 1	61.5	49.3	29.5	32.1
OF 1	38.5	71.3	49.0	51.1
UF 2	62.2	51.7	30.9	33.6
OF 2	37.8	74.9	52.1	54.0

Table 38

Second Stage Separation of Phosphate Clay - Two Duplicate Tests

Sample	Wt% yield	REE Concentration (ppm)	REE Concentration (ppm)	REE Concentration (ppm)
		Y	Nd	La
UF 3	14.4	61.96	40.05	43.90
OF 3	85.6	63.02	40.72	44.98
UF 4	13.9	61.13	39.98	42.79
OF 4	86.1	65.32	42.67	45.67

The above two tables show that a much higher weight yield was produced from phosphate clay using the

2-inch cyclone. The first stage recovered about 62% of the total mass, and the second stage scavenged 14% from the stage one tails, giving an overall weight yield of approximately 67%. Particle size distribution analysis using a laser analyzer shows that much of the fine clay particles were removed, Figures 40 and 41.

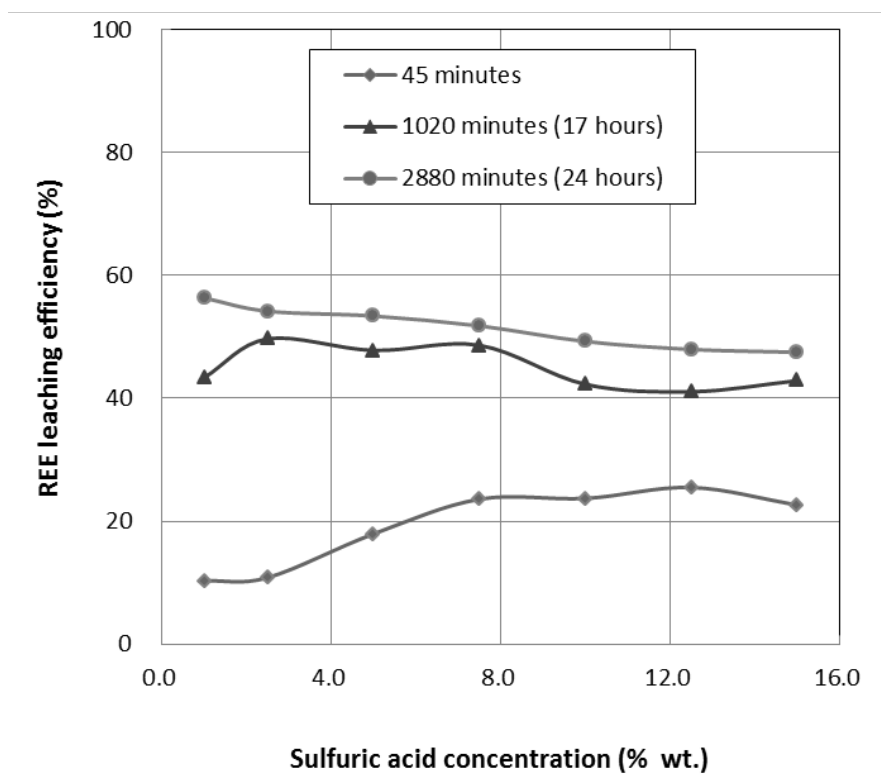


Figure 40. Size Distribution of Overflow from 2-inch Cyclone Testing - Mean size 4.294 μm ; Cumulative 10%: 0.206 μm ;
Cumulative 50%: 4.294 μm .

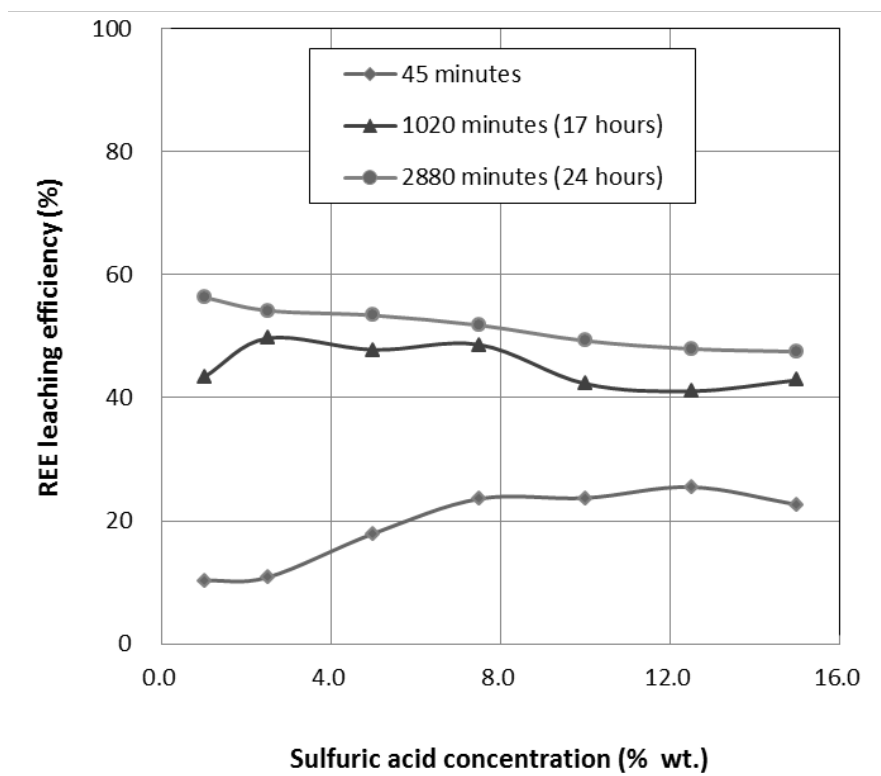


Figure 41. Size Distribution of Underflow from 2-inch Cyalone Testing - Mean size 213.298 μm ; Cumulative 10%: 4.469 μm ; Cumulative 50%: 232.947.

Mineralogical analysis using X-ray diffraction also indicates efficient removal of clay minerals using a cyclone. As shown in Table 39, after using a cyclone, the underflow product is free of three of the clay minerals, kaolinite, montmorillonite and illite.

Table 39

XRD Analysis of Cyclone Products Using the 2-inch Cyalone

Phase	Chemical Formula	Weight %	Weight %
		Overflow	Underflow
Quartz	SiO_2	3.7	54.8
Apatite	$\text{Ca}_5\text{P}_3\text{O}_{12}(\text{OH}, \text{F})$	15.0	13.7
Wavellite	$\text{Al}_3\text{P}_2\text{O}_{16}\text{H}_{13}$	0.6	0.0
Dolomite	CaMgC_2O_6	2.7	5.8
Kaolinite	$\text{Si}_2\text{Al}_2\text{O}_9\text{H}_4$	10.6	0.0
Montmorillonite	$\text{Al}_4\text{Si}_8\text{CaO}_{24}\text{H}_2$	2.7	0.0
Illite	$\text{Al}_4\text{Si}_2\text{KO}_{12}\text{H}_3$	0.7	0.0
Amorphous Content	Amorphous Content	64.1	25.8

5.5. Recovery of REE from Phosphate Rock

The wet process phosphoric acid manufacturing process can be represented by the following simplified reaction (Zhang, 2014):



Depending on the n value in equation (1), the process is defined as the dihydrate ($n=2$) process, hemihydrate ($n=1/2$) process, or anhydrate process. The dihydrate process is most widely used worldwide because it is more tolerant to rock feed variations and easy to operate (Becker, 1983). The process uses phosphoric acid to react with ground phosphate rock containing 28-32% P_2O_5 . The reaction results in a slurry of phosphoric acid and calcium sulfate dihydrate (phosphogypsum or PG). This slurry is filtered commonly using pan filters to produce a filter phosphoric acid containing about 28-30 P_2O_5 and the by-product PG. The filter cake (PG) undergoes a three-stage countercurrent washing prior to being pumped to the disposal stack. The PG washing solution containing around 17% P_2O_5 is sent back to the reactor. In some operations, the filter acid is concentrated to about 54% phosphoric acid by two-stage evaporation. The concentrated acid is processed using a centrifuge to recover the solid precipitates.

Several investigations including the CMI study found that in the phosphoric acid manufacturing process, about 30% of the REE in phosphate rock reports to phosphoric acid and 70% ends up in phosphogypsum (Al-Thyabat and Zhang, 2015a, 2015b, 2016; Wang et al, 2010; Liang et al., 2017).

The most recent study by Liang is perhaps the most comprehensive one on this topic (Liang et al., 2017). In this research, the effect on REE leaching efficiency of five major parameters during the dihydrate wet process was investigated, including leaching time, temperature, initial phosphoric acid concentration in the reactor, H_2SO_4 to CaO ratio, and liquid to solid ratio. It was found that the initial phosphoric acid concentration in the pulp had the highest impact on REE leaching efficiency from phosphate rock, as is shown in Figure 42.

[CHART]

Figure 42. Effect of Phosphoric Acid Concentration in Initial Pulp on Leaching Efficiency (leaching temperature 70, stoichiometric ratio of H_2SO_4 to CaO 1:10, ratio of liquid to solid 3:5).

Liang's investigation indicated that up to 70% of the REE in phosphate rock could be dissolved into the acid solution by adjusting the processing parameters during the dihydrate acidulation process.

SUMMARY

REEs in Florida phosphate has much higher proportions than traditional rare earth ores of heavy rare earths and some of the more critical elements such as yttrium and neodymium. REEs occur in phosphate ore in three major forms, xenotime, monazite, and calcium substitution in the phosphate crystals. These critical elements in phosphate ore got distributed into five major streams during mining and processing, including phosphate clay, flotation tails, phosphoric acid/phosphoric acid sludge, and PG. Depending on ore properties and mining operations, about 30-40% of the REEs in phosphate ore reports to phosphate clay, 10% to flotation tails (mainly the amine tails), 15-20% to phosphoric acid/phosphoric acid sludge, and 35-40% to PG

Considering the easy integration of sulfuric acid system with the existing phosphoric acid manufacturing process, recovery of REEs from PG focused on leaching with sulfuric acid solutions. Experimental results indicated that REE leaching efficiency increased rapidly, reached a maximum and then began to decrease with sulfuric acid concentrations ranging from 0 to 10 percent and at temperatures ranging from 20 to 70 degC. At a sulfuric acid concentration of 5 percent and leaching temperature of 50 degC, REE leaching efficiency obtained a maximum value of approximately 43 percent. Increasing the leaching time or liquid/solid ratio further increased the leaching efficiency. Leaching recovery of over 80% was achieved by countercurrent leaching of PG. Leaching study also showed that a 2.5% sulfuric acid solution was as effective as a 5% solution.

Phosphoric acid sludge offers the best opportunity for REE recovery from phosphate processing for three reasons: 1) it contains highest REE concentration (over 2000 ppm) among the processing streams, 2) processing of this stream would not trigger current environmental regulations, and 3) processing of this stream would not interfere with the phosphoric acid manufacturing process, the main business of the phosphate

industry. Pre-treatment and recovery of phosphoric acid are critical to economic recovery of REEs from the sludge.

No matter what further processing approach is selected, gravity separation ought to be the first step to pre-concentrate REE-containing minerals, mainly xenotime and monazite in amine tails, because these minerals are much heavier than silica that is the major gangue mineral in this stream. Flotation may well be the best option for further processing the gravity separation concentrate to upgrade both phosphate and REE minerals. One stage shaking table separation could concentrate 41% of the REE in a 12.5% mass, increasing REE concentration from 202 ppm to 657 ppm. The shaking table concentrate was further upgraded by flotation achieving 73% REE recovery and 82% phosphate recovery and enriching REE concentration to 1809 ppm.

Due to its ultra-fine particle size and complex mineral composition, the phosphate clay is extremely difficult to process. Based on this multi-year research funded by CMI, an ambitious processing flowsheet was devised (Fig. 42) for comprehensive recovery of both REEs and other valuable elements from the clay. The flowsheet involves four major approaches: 1) removal of clay minerals using small hydrocyclones, 2) upgrading of phosphate as well as REE-containing materials from the cyclone underflow product by innovative gravity separation or flotation, 3) selective leaching of the concentrate from step 2 to remove and recover magnesium, and 4) stage wise leaching of the Mg-free product for REE recovery and phosphoric acid production.

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