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Separation of Rare Earth Elements From Coal and Coal Products

Final Report

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Technical report detailing separation, characterization and enrichment of rare earth elements from various field and preparation plant solid samples.

DISCLAIMER

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Contents

Nomenclature

Abbreviation	Description
$AmmSO_4$	Ammonium Sulfate
BmimCl or IL	Ionic liquid: 1-butyl-3-methylmimidazolium chloride. Explained in Appendix I
Ch.U or DES	Deep Eutectic Solvent. Explained in Appendix I
ICP-AES	Inductive Coupled Plasma-Atomic Emissions Spectroscopy (also ICP-OES)
PSU#8	Refuse, coal preparation plant refuse material – source 8
PSU#10	Refuse, coal preparation plant refuse material – source 10
PSU#16	C' Pit cleanings, samples obtained from screen rejects in an open pit mine in central Pennsylvania
PSU#17	Roof clay, overburden rock from open pit mine.
REE	Rare Earth Elements
SEM-EDS	Scanning Electron Microscopy-Energy Dispersive Spectroscopy
TREE	Total Rare Earth Element (Concentration, typically provided as ppm or mg/kg)

Executive Summary

Separation of Rare Earth Elements from Coal, Coal-Products, and Overburden

Introduction: Rare earth elements (REEs) are of strategic importance to the defense interests of the United States and of economic importance to several segments of the domestic electronics industry. Since a large portion of the rare earth market is still concentrated with few producers and subject to trade fluctuations, it is pertinent to explore domestic sources. In order to investigate the potential for rare earth extraction from domestic resources, a series of separation and enrichments experiments were conducted on locally available materials/minerals.

Technical Procedures: Samples were collected from surface mines in Pennsylvania as well as from various coal preparation plants and coal-burning power plants. The four main samples were shortlisted out of a list of more than 20 samples and include an overburden material (roof rock), pit cleanings from a coal surface mine, and two refuse materials from coal preparation plant refuse streams. The collected samples were prepared using standard mineral processing procedures and subjected to various separations procedures and characterization analyses.

The separation/enrichments procedures deployed were:

- Gravity separation (float-sink/washability tests).
- Magnetic separation methods.
- Electrostatic separation methods.
- Ion exchange-based leaching methods.

The collected samples and their derivatives from various separation/enrichment methods were analyzed for REE concentrations by multiple analytical techniques. In addition, the samples were also subject to proximate analysis.

Key Findings: The roof rock sample contained the largest concentration of total REEs on a whole material basis and responded best to gravity separation and ion exchange leaching techniques. The pit cleaning sample exhibited low potential to ion exchange treatment methods. The pit cleanings sample did show a marked response to magnetic enrichment, but it is to be noted that this was a sample with lower bulk REE content. However, it is a coal product with a fair amount of combustible material and the combustion of carbonaceous material typically results in the REEs remaining in the combustion ash, and at a higher concentration in the ash. Among the two refuse materials, one of the samples (PSU#8) showed a very clear separation and enrichment behavior under electrostatic separation, while the other refuse sample (PSU#10) showed no significant discriminatory behavior under any tests.

Recommendations: It is recommended to continue with leaching tests on the ashed material of pit cleanings and one of the refuse materials for further enrichment. The roof rock material has a higher REE content to begin with, so further leachability tests are recommended and process optimization for leachability with ammonium sulfate should be further investigated.

Introduction

Rare earth elements (REEs) comprise of 17 elements made up of the Lanthanide series of elements and the elements scandium and yttrium, which are routinely found alongside Lanthanide ores and exhibit similar properties. While not necessarily rare, their extraction is a time-consuming and economically challenging process. In order to investigate the scope of rare earth extraction from domestic resources, a series of separation and enrichments tests were performed on locally available materials/minerals. For this purpose, various rock and mineral samples were collected from a few selected sites in Pennsylvania. These included weathered material from the overburden (roof rock) in an open pit coal mine in central Pennsylvania, screen rejects from a coal blending yard, and ash from an operating fluidized bed power plant (clinkers, bottom ash, fly ash, etc.) [1]. Additionally, preparation plant refuse material (15 samples) was also collected. Some of the clinkers from a circulating fluidized bed power plant, certain refuse piles (PSU#16), the roof rock material (PSU#17), and some coal preparation plant refuse material (PSU #1, PSU #3, PSU#8, PSU#10) showed relatively higher "spot" values of Lanthanum when analyzed by a hand-held X-ray fluorescence (XRF) analyzer. Washability analyses (float-sink) and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) analysis were conducted on samples PSU #17, PSU #16, PSU#10, and PSU#8. An overall schematic of the methodology employed is outlined in Figure 1.

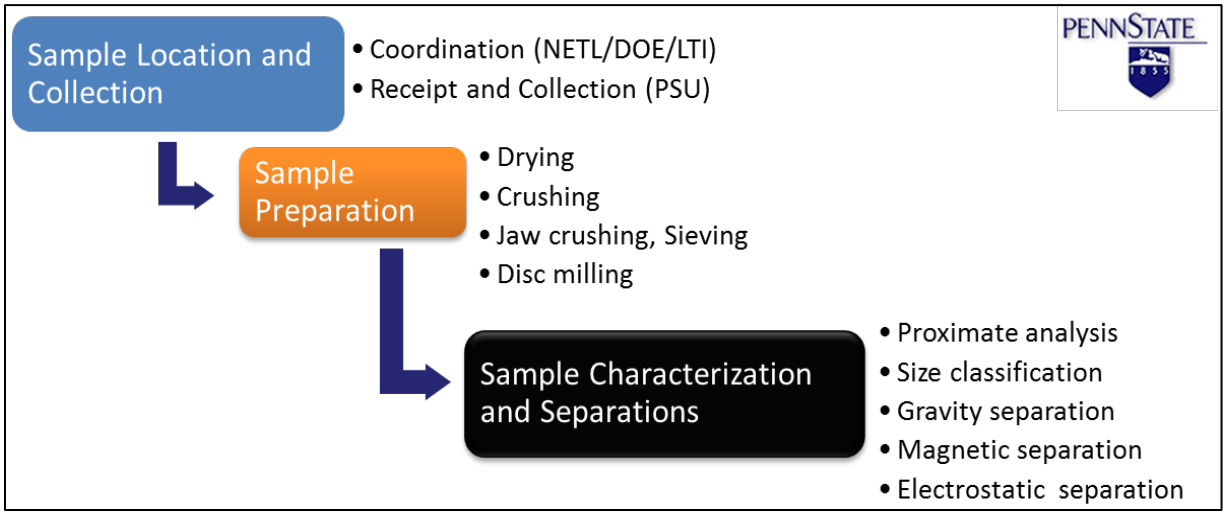


Figure 1: Schematic view of project progression.

Sample Collection

Materials from refuse piles (screen refuse) were hand-picked from a central Pennsylvania coal-blending yard. From a nearby open pit coal mine in central Pennsylvania, "roof rock" material from the overburden and large-sized material rejected by the mine by screening (referred to as "pit cleanings") were also collected. Sample sizes are run-of-mine/large lumps. Clinkers, bottom ash (fluidized bed plant ash cooler), and flyash samples were collected from another central Pennsylvania circulating fluidized bed power plant burning waste coals. Fuel samples were also collected from the two fuel trains at this plant. A map showing approximate locations of the collection sites is provided in **Error! Reference source not found.**.

Figure 2: Approximate location of sample collection sites.

Additionally, about 15 samples of material from coal preparation plant refuse streams were also collected for REE investigation and two samples were chosen for detailed analysis from this set. Two of these preparation plant refuse samples (PSU#8 and PSU#10) were about two pounds each; these were riffled down to one pound and then size classified. The field samples from the open pit mine (PSU#16 and PSU#17) were a drum load each; these were crushed and then riffled down to about a few pounds each. These four samples were characterized as whole samples before the separation and enrichments protocols.

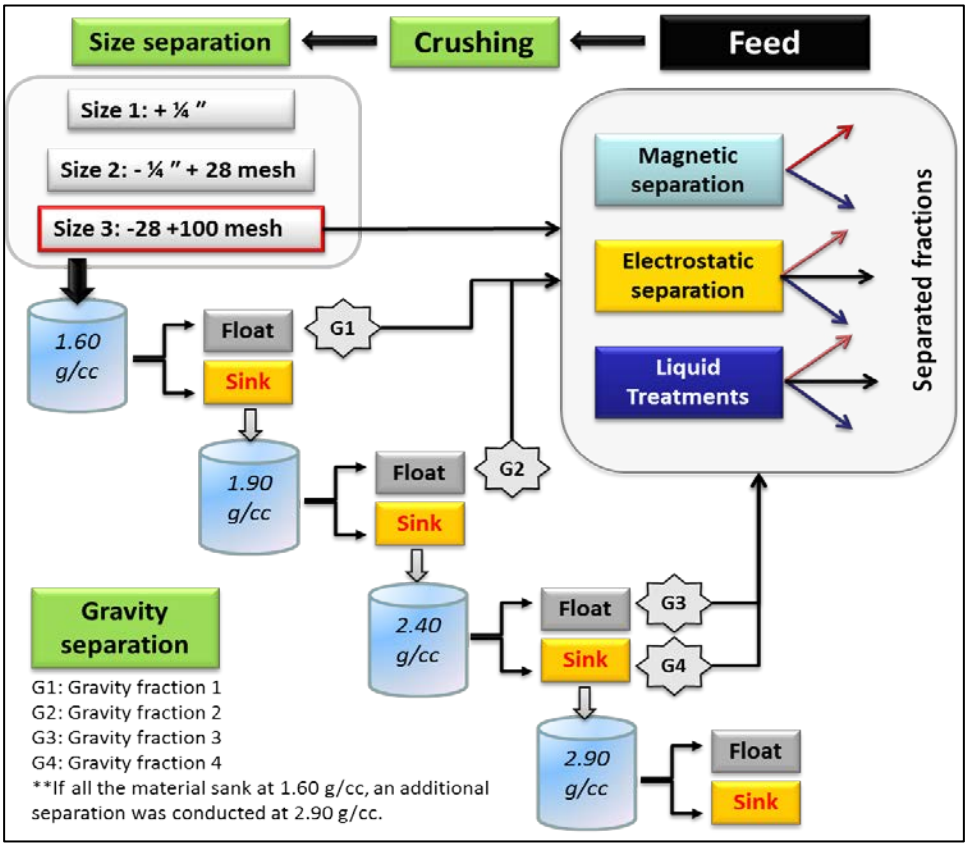


Figure 3: Schematic depiction of sample preparation, enrichment, and characterization procedures.

Proximate Analysis

Preliminary characterization was carried out on a series of samples (roof rock clay from a pit mine, screen rejects from a pit mine – Upper Kittanning seam, and refuse samples from several preparation plants). Proximate analysis was conducted in accordance with ASTM D5142 [3]. The mean values and visual observations are presented in Table 1.

Table 1: Proximate analysis data of first round samples (VM: volatile matter).

Sample ID	Sample	Moisture Wt. %	VM Dry Wt. %	Ash Dry Wt. %	Fixed Carbon Dry Wt. %.%	Visual Observation of Ash
PSU#8	Prep plant refuse 8	2.01	10.16	65.84	24.00	Orange brown, very friable, low adherence, slight caking
PSU#10	Prep plant refuse 10	0.30	9.88	81.69	8.44	Brown, friable, slightly caking, some adherence to walls
PSU#16	Pit cleanings	0.68	17.14	50.02	32.85	Friable, lightly caking, cream color with darkened surface
PSU#17	Roof rock overburden	0.51	14.31	86.66	0.00	Substantial caking, adheres to crucible wall, deep red, not easily friable

Sample Preparation Protocol

Sample preparation was performed according to the following procedure:

a. Samples were riffled to obtain representative working samples from bulk sample.

b. Samples were crushed with a jaw crusher if necessary to pass ¼-inch screen.

c. Samples were then crushed further using a roll crusher or disc mill and screened with 8 mesh, 28 mesh, and 100 mesh screens (Tyler mesh).

d. Separated samples were grouped into three major particle classes: (d_1: +¼-inch mesh), and size 2 above was spilt into two fractions (d_2: -28 mesh +100 mesh), (d_3: -100 mesh).

e. Based on certain experimental constraints associated with separation procedures, the particle class -28+100 mesh was chosen for further experiments.

f. The sample matrix was projected to be between 40 to 60 separated fractions based on the multiple separation methods envisaged (12 per collected head sample). The matrix size was variable because not all starting samples would have provided detectable yields in the selected gravity, magnetic, and electrostatic separation splits.

Separation and Characterization Protocols

1) Multiple physical separation methods have been employed on roof clay material (-28 +100 mesh size fraction) and the following physical separations were completed.

    a) Float-sink separation: Initial washability analyses were conducted [2] for size fraction d_2 at 1.6, 1.9, and 2.4 specific gravity values. The various gravity

fractions (separated using various specific gravity liquids) denoted by the letter "G" are:

i. G_1: 1.6 g/cc (1.6 float).

ii. G_2: 1.6 – 1.9 g/cc (1.6 sink to 1.9 float).

iii. G_3: 1.9 – 2.4 g/cc (1.9 sink to 2.4 float).

iv. G_4: 2.4 g/cc (2.4 sink). For certain samples, depending on the yield of this fraction, an additional separation was performed at G_5: 2.9 g/cc (2.9 sink).

b) Magnetic separation at multiple field strengths starting from the higher field strength.

c) High tension electrostatic separation, conducted at multiple field strengths.

2) Enrichment Treatments (Wet Methods): Samples were treated with liquids to promote ion exchange or leaching of REEs out of the matrix.

a) Ammonium Sulfate Leaching.

b) Ionic Liquid Application (BmimCl).

c) Eutectic Liquid Treatment (Ch.U).

3) Proximate analysis or ash yield tests were conducted on the original and separated samples wherever an adequate amount of separated sample was available [3].

4) Characterization of samples with SEM-EDS was carried out and semi-quantitative mineral count analyses were performed on polished cross section samples or powder ash samples embedded in suitable mounts [4].

5) Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) analyses were also performed on samples to obtain REE concentrations (per procedure ASTM 6387).

Table 2: Inventory of various separations.

Sample	PSU#8 (Plant Refuse)	PSU#10 (Plant Refuse)	PSU#16 (Pit Cleanings)	PSU#17 (Roof Rock)
Size Classification (+28, -28+100, -100 mesh)	Over 100 g	Over 100 g	Over 100 g	Over 100 g
Gravity Separation Cut at 1.6, 1.9, 2.4, 2.9 g/cc	1.6, 1.9, 2.4 approx. 20 g	1.6, 1.9, 2.4 approx. 20 g	1.6, 1.9, 2.4 approx. 20 g	1.9, 2.4, 2.6 approx. 40 g
Magnetic Separation (Ferro, Electromagnetic and Non-magnetic)	~ 2 g	~ 2 g	Trace	~ 5-10 g
Electrostatic Separation (Conducting, Neutral, Insulating)	~3-4 g	~3-4 g	~4-5g	~4-5 g

Results of the physical separations of the selected samples and characterizations are presented in the following pages.

Roof Rock

One 55-gallon drum of sample, including several rocks larger than 10 inches, was collected from the overburden of the coal seam. After crushing and size separation, several hundred grams of sample in the (-28+100 mesh) size was used for most of the subsequent separation tests. Some amount of this sample, separated at +8 mesh by size, was sent out to a commercial testing laboratory for ICP-AES analysis of REEs. A bar chart of the total REE data is presented in Figure 4.

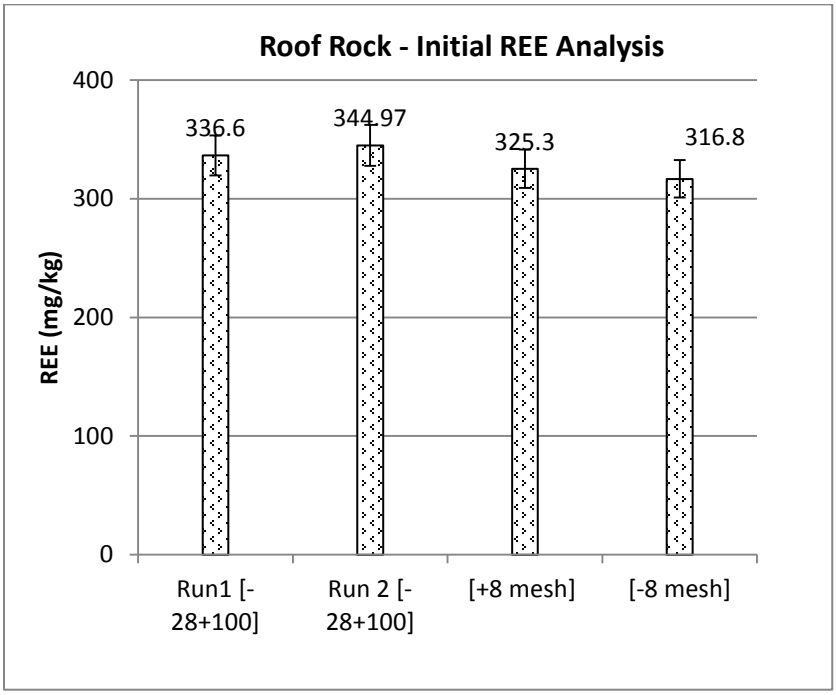


Figure 4: Total rare earth content of the untreated original roof rock samples (PSU#17) evaluated by ICP-AES analysis. The average of the Run1 and Run2 (340.8 mg/kg) is taken as the representative REE value in roof rock samples used in various tests prior to separation.

Float-Sink Separation

Gravity separations were conducted at 1.6 g/cc, 1.9 g/cc, 2.4 g/cc, and 2.9 g/cc for the roof clay samples and at 1.6, 1.9, and 2.4 for the pit cleanings and the preparation plant refuse samples. A bulk of the sample is in the density range of 2.4 to 2.9 g/cm^3. The separation yields and ash yields are shown in Table 3. The ash yield for the heaviest fraction was slightly less than the middle fraction, a possible indicator of higher proportion of gaseous reaction products.

Table 3: Gravity separation yields. Float-sink analyses were performed at all progressively increasing densities for PSU#17 (Roof rock). Most of material sank at 1.9 g/cc and only traces floated.

Roof Rock (PSU#17)	1.9 Float	1.9-2.4	2.4-2.9	2.9 Sink
Yield (Wt. %)	Trace	2.41	87.88	9.71
Ash (dry) (Wt. %)	N/A	68.44	89.46	78.75

The heaviest fraction did not show appreciable REE components under microscopic analysis. Representative images from microscopy are shown below in Figure 5. These images show the

concentration of various elements. For example, Figure 5 indicates the location of Yttrium atoms in the field of view. A comparison of the semi-quantitative data from the SEM-EDS is shown in Table 4.

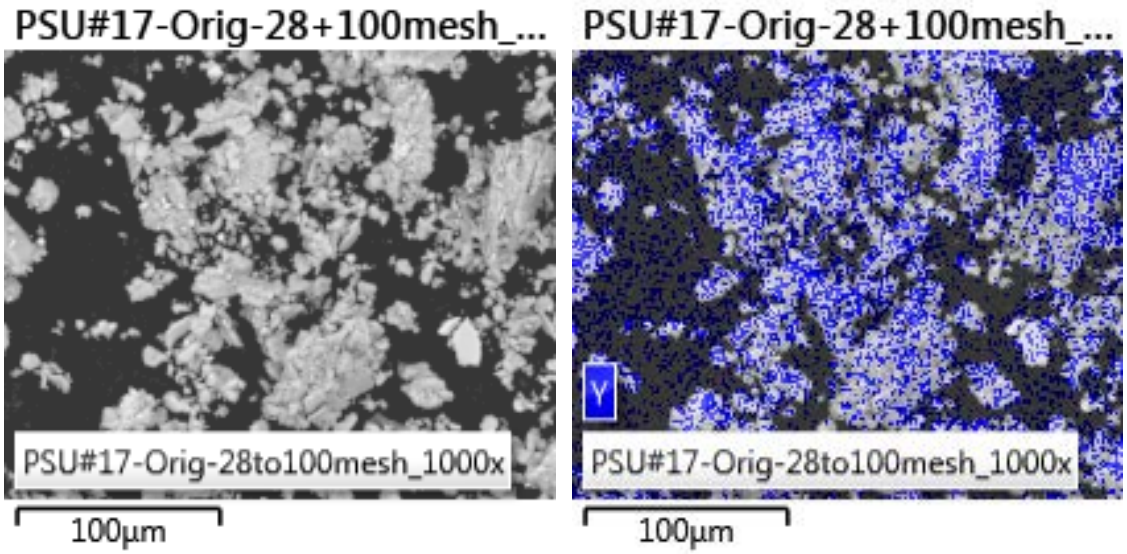


Figure 5: Electron Micrograph of Roof Rock sample and Yttrium elemental map from EDS. Surface concentrations of rare earth element Yttrium (symbol Y) are visible prominently in this section of the sample.

Table 4: Key REE components detected* in gravity fractions of the Roof Rock (Semi-quantitative data from SEM-EDS). (*in microscopic zones and not indicative of bulk sample). TREE is the total REE concentration.

PSU#17 Roof Rock (Original)	Wt. % (%)	PSU#17 Roof Rock (1.9-2.4 g/cc)	Wt. % (%)	PSU#17 Roof Rock (2.4-2.9 g/cc)	Wt. % (%)
Y	0.04	Y	0	Y	0
La	0.06	La	0	La	0.05
Ce	0.06	Ce	0	Ce	0.08
Nd	0	Nd	0.05	Nd	0
Ho	0.02	Ho	0	Ho	0
Yb	0.01	Yb	0.22	Yb	0
TREE (mg/kg)	1900	TREE	2700	TREE	1300

Visually, as well as by surface intensity measurements, there seemed to be no major differences between samples from different gravity fractions. However, it may be possible that the lighter fractions could contain a slightly higher proportion of REEs. The roof rock is a type of clay with the bulk composition dominated by Si, Al, O, and Fe. The rare earths appear to be distributed finely in the clay matrix at sub-1000 ppm levels, which is the detection limit of the EDS sensor.

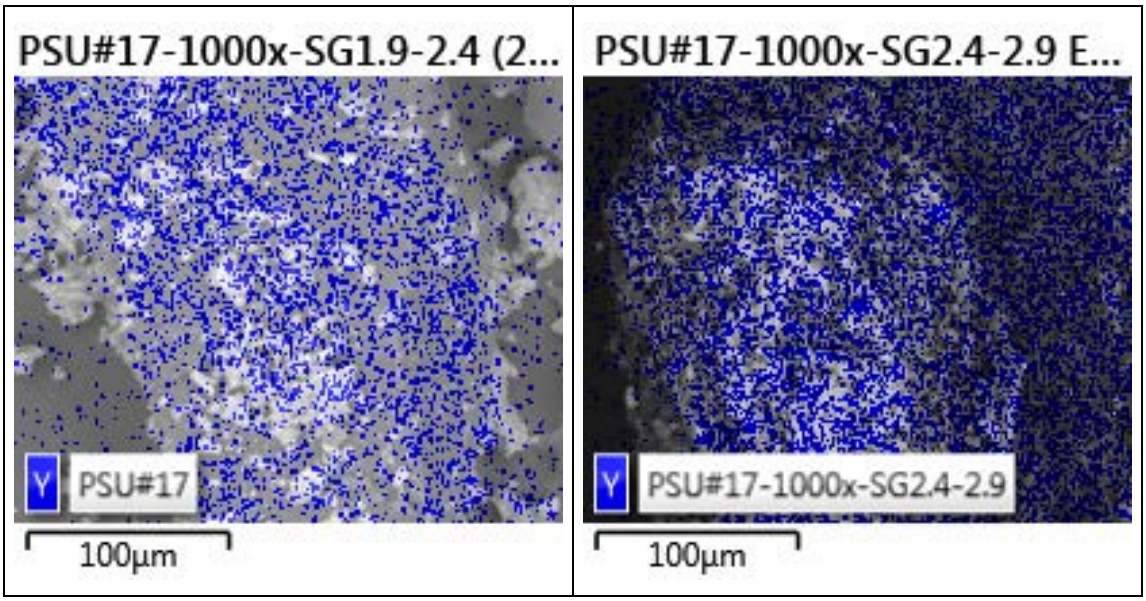


Figure 6: EDS maps of Yttrium in gravity fractions of Roof clay. Surface concentrations of Yttrium are similar between the two heavier gravity fractions of the roof rock sample. This observation is qualitative however, as quantitative data was not possible during preliminary SEM analysis of unpolished samples.

Samples were also shipped out for ICP-AES analysis of REEs. Samples were shipped without any additional treatment or ashing in most cases, and ash yields along with REE values are reported on original sample basis. A graphical summary of the total REE content is presented in Figure 7 and detailed elemental values are presented in Table 5.

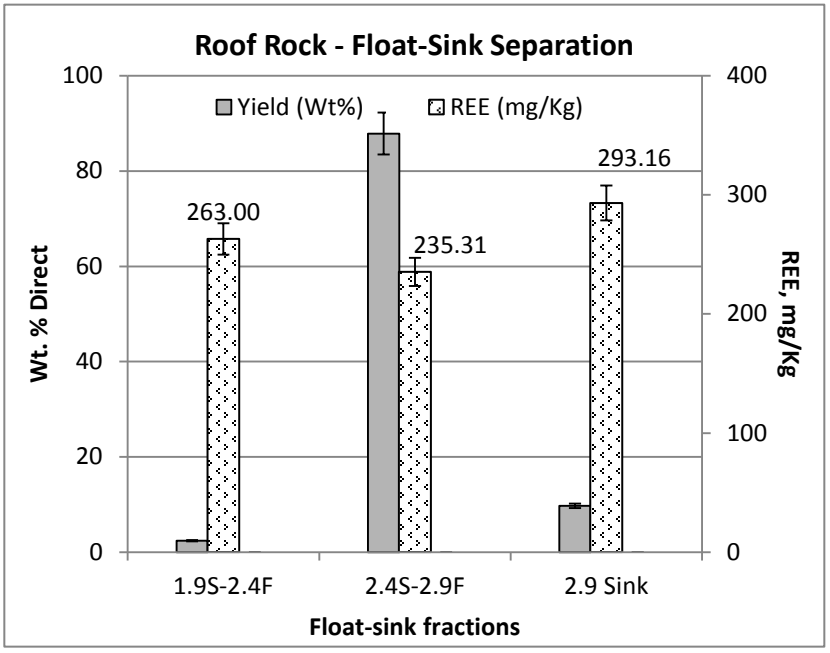


Figure 7: Separation yield from gravity separation (left Y axis) and REE concentration of separated fractions (right Y axis, measured by ICP-AES) is shown above. Bulk of the roof rock is in the 2.4-2.6 g/cc gravity fraction (over 87 Wt. %). The heaviest fraction (2.9g/cc sink) accounts for ~10 Wt. %% and was expected to yield a higher REE content.

It was seen that the total rare earth content of the heaviest gravity fraction is slightly higher than the lighter density fractions. However, the REE content of the heaviest gravity fraction was expected to be much higher (closer to 1200 mg/kg) than the detected quantity. The distribution as seen currently indicates that a closer inspection of the 2.4 to 2.9 fraction would be needed going forward. The full set of elemental values obtained by ICP-AES is provided in Table 5. For some samples Lithium values were also measured; however, this analysis was not conducted for all samples, so Lithium values are reported only where measured.

Table 5: Rare earth element concentration in gravity fractions reported on whole mineral basis of Roof Rock (ICP-AES data by ASTM 6387). Ash values are reported by vendor, measured as part of the digestion procedure prior to ICP-AES.

Sample & Method Description	Roof Rock 1.9S-2.4F	Roof Rock 2.4S-2.9F	Roof Rock 2.9S
Ash, Wt. % Dry	*55.49*	*89.75*	*81.15*
Elements on Dry Sample Basis	mg/kg	mg/kg	mg/kg
Ce	108	89.7	101
Dy	2.66	2.24	2.03
Er	5.31	5.61	6.49
Eu	2.77	4.49	4.06
Gd	10.2	4.71	9.13
Ho	2.77	4.49	4.06
La	34.1	28.3	31.4
Lu	2.77	4.49	5.88
Nd	25.7	21.8	42.2
Pr	17.7	17.9	14.6
Sm	7.08	6.51	4.06
Sc	16.8	18.6	18.7
Tb	2.77	4.49	5.48
Tm	1.39	2.24	2.03
Yb	2.88	3.14	5.48
Y	20.1	16.6	36.5
Th	9.74	9.65	10.1
U	2.77	4.49	4.06
Ir	24.3	4.49	4.06
Co	31.4	23.8	90.5
Al	73,130	99,550	60,840
Ca	4,720	1,490	9,390
Li	Not Analyzed	Not Analyzed	51.9
Total Rare Earth (TREE) mg/kg	**263.0**	**235.3**	**293.16**

Magnetic Separation

A low-intensity ferro-magnet was run over thinly spread sample layers to remove any loose ferromagnetic material that may have been present in the sample. This is usually done as a safety measure prior to electromagnetic separation. Except for the PSU#8 refuse sample, all other samples showed negligible response to the ferro-magnet. Subsequent to this procedure, a cross-belt electromagnetic separator was used to separate samples that are attracted by an electromagnetic field. Figure 8 depicts a schematic of the magnetic separation apparatus. Feed particles are fed along a belt and pass under a magnetic field applied over a belt moving perpendicular to original belt. Magnetic particles are picked up by the perpendicular (upper) belt and fall into a collection bin when the particles leave the magnetic field. Magnetic separation was performed on the roof rock sample at a field strength corresponding to a 4A current. The roof rock sample showed appreciable separation yielding around 37% of material that was susceptible to magnetization under a field.

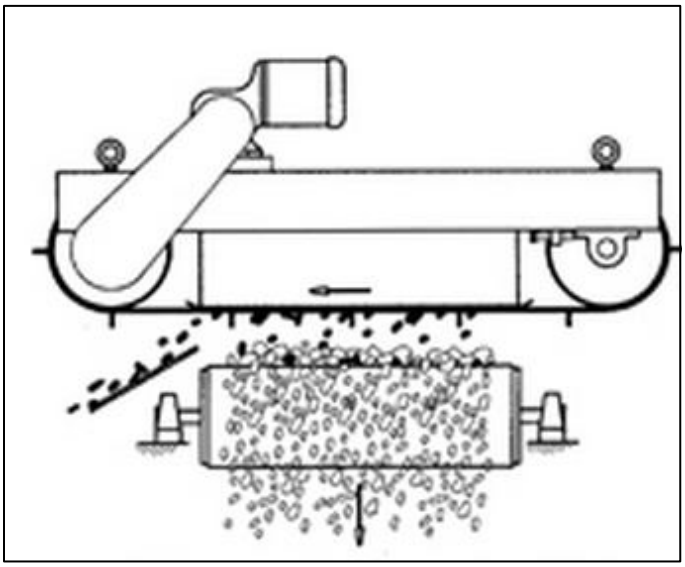


Figure 8: Schematic of a cross-belt magnetic separator. (Source: http://www.pmlindia.com/products/magnetic-cross-belt-separator **retrieved 11/18/2014)**

Proximate analysis of the fractions is presented in Table 6 and no major differences are observed between the magnetically separated fractions. A bar plot of the total REE in the separated fractions (Figure 9) shows the non-magnetic fraction to be slightly enriched in rare earths compared to the magnetic separated fraction. Detailed data on the rare earths is reported in Table 7.

Table 6: Proximate analysis of magnetically separated samples.

Sample Fraction	Volatile Dry (Wt. %)	Ash Dry (Wt. %)	Fixed Carbon Dry* (Wt. %)
PSU#17 Non-magnetic	10.71	89.31	0.00
PSU#17 Magnetic	15.16	85.59	0.00

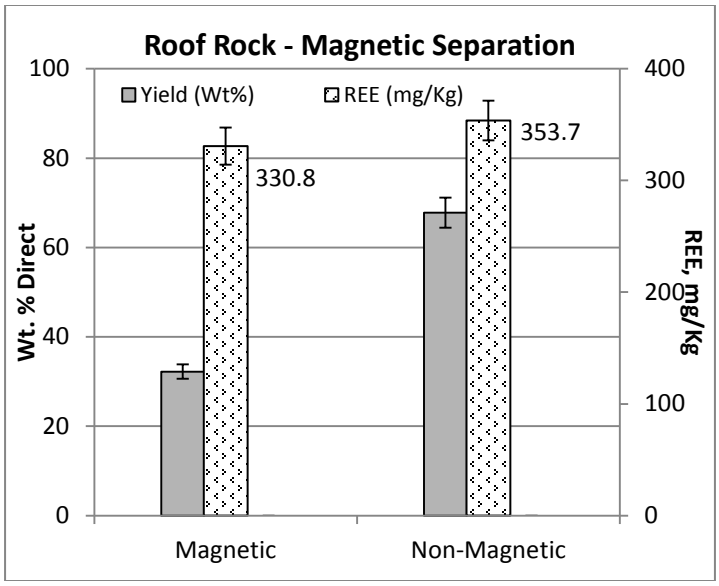


Figure 9: About 37% of the roof rock separated into the magnetic fraction while the non-magnetic fraction shows a slight enrichment (at 353.7 mg/kg) compared to parent material at 340.8 mg/kg. The separation yield from the magnetic technique is depicted on the left Y axis.

The ICP analysis results for the magnetically separated fractions of the roof rock indicate no significant enrichment differences for the roof rock material by means of the magnetic separation process. The fractions are also very similar in ash yield and other properties so the magnetic separation method may not be a useful method for this sample material.

Table 7: ICP-AES analysis data of magnetically separated fractions of Roof Rock (PSU#17).

Sample & Method Description	Roof Rock MAGNETIC	Roof Rock NON-MAGNETIC
Ash, Wt. % Dry	85.77	89.91
Elements on Dry Sample Basis	mg/kg	mg/kg
Ce	106	119
Dy	2.14	4.05
Er	6.65	7.42
Eu	4.29	4.5
Gd	7.72	8.32
Ho	4.29	4.5
La	52.0	55.1
Lu	4.29	4.5
Nd	55.8	42.7
Pr	19.7	26.5
Sm	4.29	10.8
Sc	20.6	21.6
Tb	4.29	4.5
Tm	2.14	2.25
Yb	4.72	4.5
Y	31.7	33.5

Th	12.9	13.3
U	4.29	4.5
Ir	4.29	4.5
Co	33.2	26.3
Al	86,670	105,150
Ca	3,920	1,400
Li	80.0	Not Analyzed
Total Rare Earth (TREE) mg/kg	**330.8**	**353.7**

Figure 10 shows some elemental maps of Neodymium in the magnetically separated fractions of the roof rock. The SEM-EDS images contains only trace amount of red colored Nd specks, but almost equal distribution in both fractions. Both images have been artificially contrast enhanced to suppress the gray from the carbon.

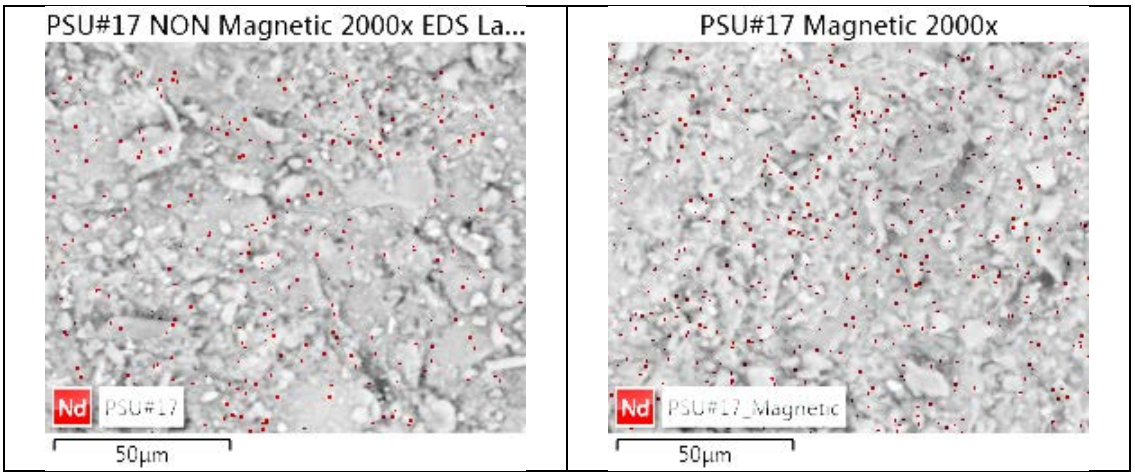


Figure 10: SEM-EDS images showing (Neodymium) Nd element maps on magnetically separated fractions of roof rock.

Electrostatic Separation

High-tension electrodes are used to create a corona discharge that helps in sorting conducting particles from insulating particles. The particles are passed over a rotating drum which helps in applying different trajectories to insulating and conducting particles based on their charges. The falling objects are collected in different pans and weighed. A schematic of the separation process is shown in Figure 11.

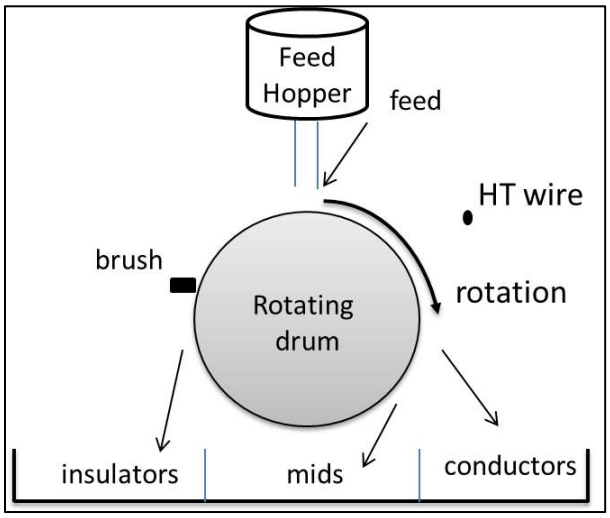


Figure 11: **Schematic of a high-tension electrostatic separator.**

Table 8: Yields from electrostatic separation of roof rock sample at 14kV high-tension application.

Sample	Conductors Wt. %	Middlings Wt. %	Insulators Wt. %	Voltage (kV)
PSU#17	**44.28**	**17.09**	**38.64**	**14**

Proximate analysis of electrostatic separated fractions of roof rock is given in Table 9 and no major differences are observed among the fractions.

Table 9: Proximate analysis of electrostatically separated samples showing highly similar volatile and ash yield components.

Sample Fraction	Volatile Dry (Wt. %)	Ash Dry (Wt. %)	Fixed Carbon Dry* (Wt. %)
PSU#17_Conductors	12.05	88.64	0.00
PSU#17_Middlings	12.25	88.33	0.00
PSU#17_Insulators	12.3	88.31	0.00

A plot of the total rare earth concentrations (based on ICP-AES analyses) in the electrostatic fractions is summarized in Figure 12.

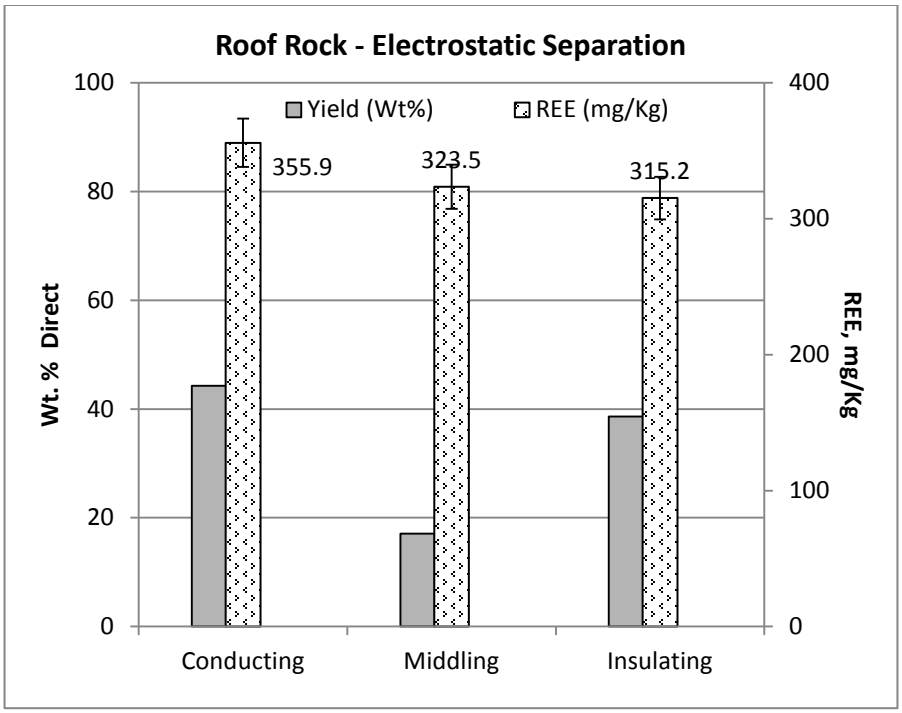


Figure 12: High-tension electrostatic separation of the roof rock split the fraction into nearly equal fractions (~40%) of conducting and insulating material with the remaining being non-responsive "middlings." The REE concentration is slightly enriched into the conducting material (at 356 mg/kg) compared to the other two fractions.

Elemental maps showing differences in the REE distribution are shown in the following montages using Yttrium as an example. Detailed maps are provided in

Appendix III: Magnetic Separations – SEM-EDS . On the surface, it appears that the insulators from the roof rock (PSU#17) could be more enriched in certain rare earths such as Yttrium, but a bulk analysis showed no major differences between the insulators and the conductors.

Yttrium

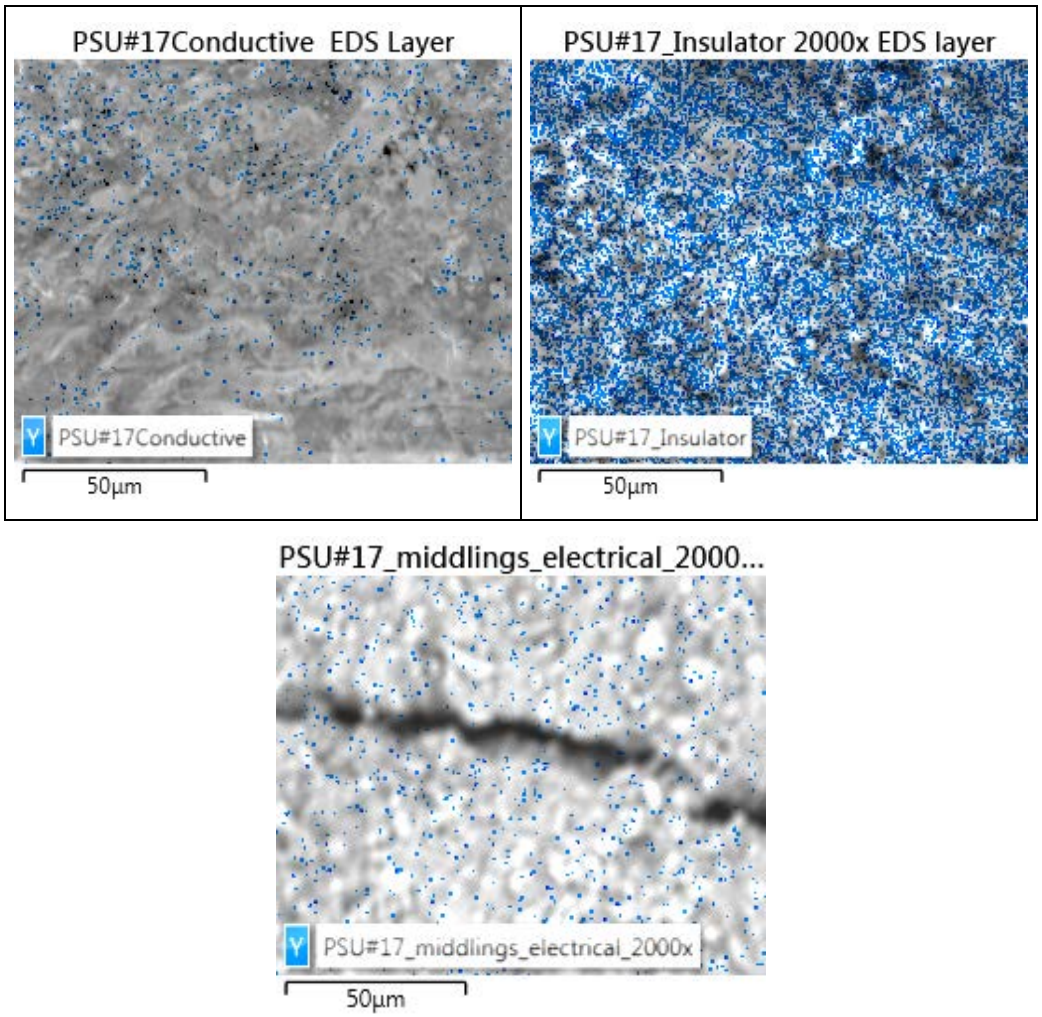


Figure 13: Yttrium distribution on the surface of electrostatically separated samples of roof rock material, obtained by SEM-EDS technique. On the surface, the "insulating" fraction shows a high concentration of Yttrium compared to the other two electrostatically separated fractions.

Detailed REE data obtained by ICP-AES of the electrostatically separated fractions is given in Table 10. Candidate samples showing preliminary positive concentrations for REEs from field analysis (by a portable XRF unit) were studied further by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) for mapping of elements [4]. SEM-EDS mapping was performed on a FEI Quanta instrument using the X-Act detector of Oxford Instruments and subsequent data processing was performed on Aztec software supplied by Oxford Instruments. Results are also presented in Appendix II-V. The roof rock material

(labeled PSU#17) showed fine dispersions of REEs among aluminosilicate clays outside of the carbon matrix.

Table 10: Results of ICP analysis data from electrostatically separated samples. For brevity, REE values of only the conducting and insulating fractions are provided here. The REE values for the middling fraction are similar to that of the original roof rock fraction.

	PSU 17 Roof Rock (-28+100 mesh) Original	**PSU 17 Roof Rock Conducting (-28+100 mesh)**	**PSU 17 Roof Rock Insulating (-28+100 mesh)**
Ash, Wt. % Dry	**88.95**	88.85	88.79
Elements on Dry Sample Basis	**mg/kg**	**mg/kg**	**mg/kg**
Ce	**137**	137	125
Dy	**<2.22**	<2.22	<2.22
Er	**6.67**	7.55	6.44
Eu	**<4.45**	<4.44	<4.44
Gd	**7.12**	8.44	6.44
Ho	**<4.45**	<4.44	<4.44
La	**41.4**	46	39.7
Lu	**<4.45**	<4.44	<4.44
Nd	**37.6**	38.9	33.7
Pr	**23.1**	24.7	21.5
Sm	**9.78**	10.7	9.32
Sc	**21.3**	21.1	19.8
Tb	**<4.45**	<4.44	<4.44
Th	**13.1**	11.1	11.3
Tm	**<2.22**	<2.22	<2.22
U	**<4.45**	<4.44	<4.44
Yb	**4.22**	4.89	4

Y	**26.2**	34.4	27.1
Ir	**<4.45**	<4.44	<4.44
Co	**27.4**	25.3	30.2
Al	**105,600**	102,510	97,290
Ca	**2,080**	1,870	2,130
Total Rare Earth (TREE):	**314.4**	**333.7**	**293.0**

Leaching Treatments (Ammonium Sulfate and Ionic Liquids)

Ammonium sulfate as leaching solvent

Based on literature studies on recovery of REEs, 1M ammonium sulfate was chosen as a lixiviant in the recovery of REEs from clay-carboneous materials [12, 13]. The detailed procedure is also reported in the end in Appendix I. Ammonium sulfate is used commercially in the industry and would likely serve as the choice of liquid for any larger-scale extraction method. Treatments employed in this study with ammonium sulfate were all at room temperature (particles were mixed with the liquid and stirred for about one hour at room temperature).

Ionic liquids as solvents for extraction

Ionic liquids (ILs) are currently being investigated as alternative reaction media to conventional solvents in organic synthesis, catalysis, separation, and electrochemistry [5-7]. Given their structure and diversity of functionality, ILs are capable of most types of interactions (e.g., dispersive, π−π, n−π, hydrogen bonding, dipolar, ionic/charge−charge) [5, 6].

Studies show that ILs can be efficient solvents for the extraction of cationic metal complexes from aqueous solution [8-11]. In the majority of studies on extraction of metal ions, mainly methylalkylimidazolium hexafluorophosphates, $[C_n mim][PF_6]$ and bis(trifluoromethanesulfonyl)imides, $[C_n mim][Tf_2N]$ have been used [8-10]. Combining with ILs, extractants such as octyl(phenyl)-N,N-dissobutylcarbamoylmethyl phosphine oxide, CMPO, 2-thenoyltrifluoroacetone, htta, bis(2-ethylhexyl)phosphoric acid, D2EHPA, etc. were used [8-11]. Metal extractions with ILs occur *via* ion-exchange process. A neutral extractant transfers the positively charged metal ion to the IL phase [9].

1-butyl-3-methylmimidazolium chloride (abbrev: IL: BmimCl) and a deep eutectic solvent (abbrev: ChU: DES), a cheaper and less toxic analogue of IL, was also used. One mol of choline chloride and 2 mol of urea were mixed and heated at 80°C until a uniform colorless liquid was obtained prior to use in the leaching experiment. The detailed procedures are attached in the end in Appendix I.

Results of Leaching Experiments

ICP-AES analysis was conducted on both solid residues and the liquid leachate. Possibly due to dilution and interference from certain elements, analysis of leachate did not yield detectable REE measurements. In order to account for this, REE values in the leachate have been estimated at the diluted state by mass balance calculations. In addition, the leachate REE values are reported as mg/kg with the reasonable assumption that leachate density is equal to that of water. Additional data is presented in Appendix V: Ionic Liquid Treated Samples – EDS Data

. It was seen that ammonium sulfate solution showed about 57% recovery of REEs and the IL 74% and deep eutectic solvent 88%.

The costs of IL and DES are prohibitively expensive, so it is likely that ammonium sulfate would be used for commercial processes. Further research would be needed on leaching conditions, sample particle preparation and the diffusion kinetics of the ion exchange process.

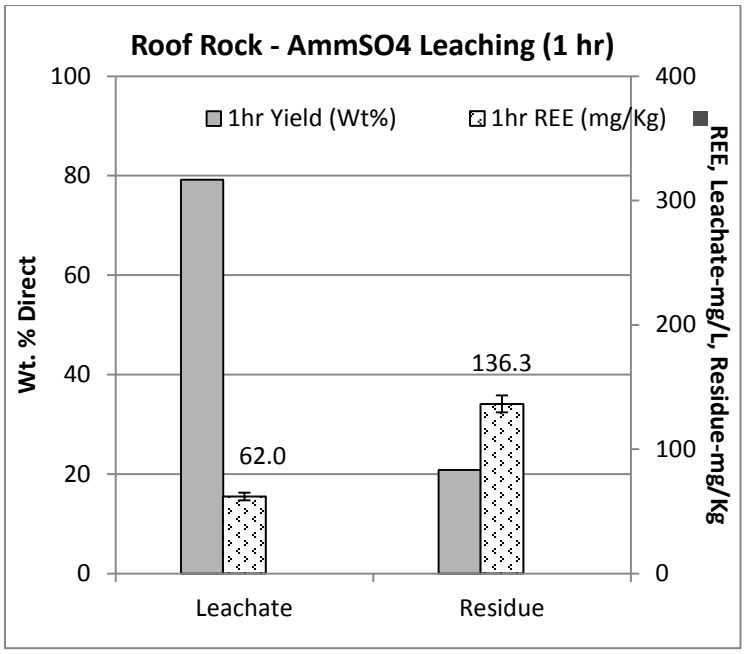


Figure 14: REE concentration in sample after ammonium sulfate treatment of roof rock. Leachate density is considered equivalent to 1 g/cc, which makes concentrations of mg/L comparable to mg/kg. The concentration in the untreated roof rock REE is 340.8 mg/kg.

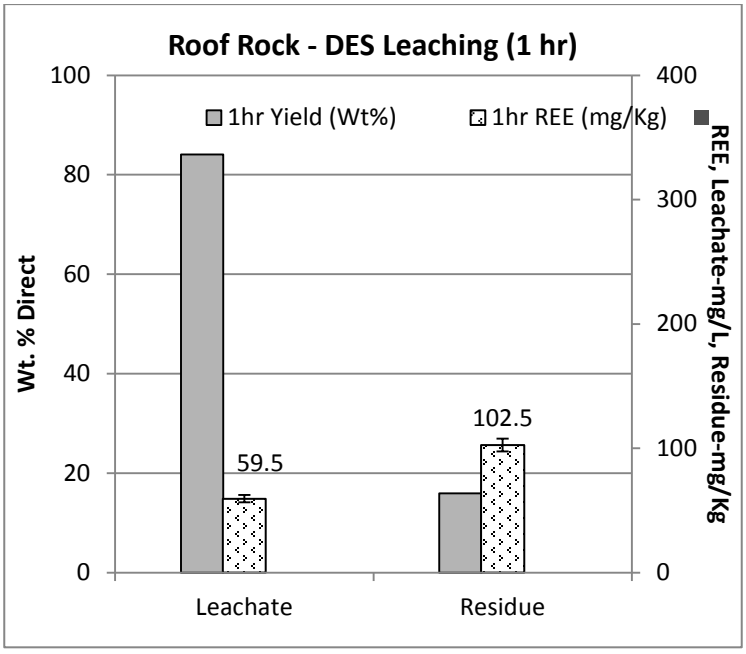


Figure 15: REE concentration after deep eutectic solvent (DES) treatment. DES is expensive compared to ammonium sulfate but this treatment shows the lowest concentrations of TREE in the residue.

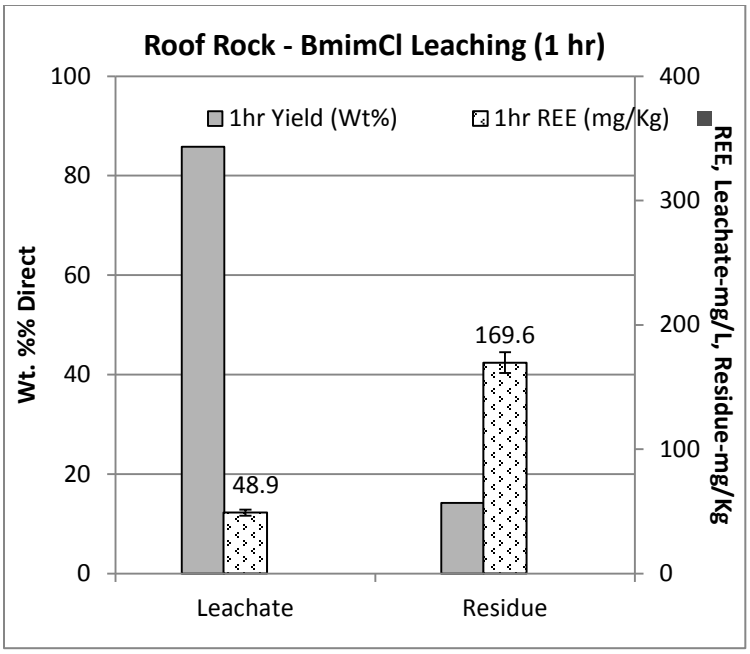


Figure 16: REE concentration after treatment with ionic liquid BmimCl. This solvent is also prohibitively expensive compared to ammonium sulfate but did not show enough leaching activity.

A comparison of the REE concentrations in the residues and the leachates from all three methods is provided in Figure 17. Based on the one- hour leaching tests, there appear to be some differences among the solvents. A lengthier leaching period of four hours was also deployed with each of the solvents to see the effect of time on the leaching process, and the results are shown in Figure 18.

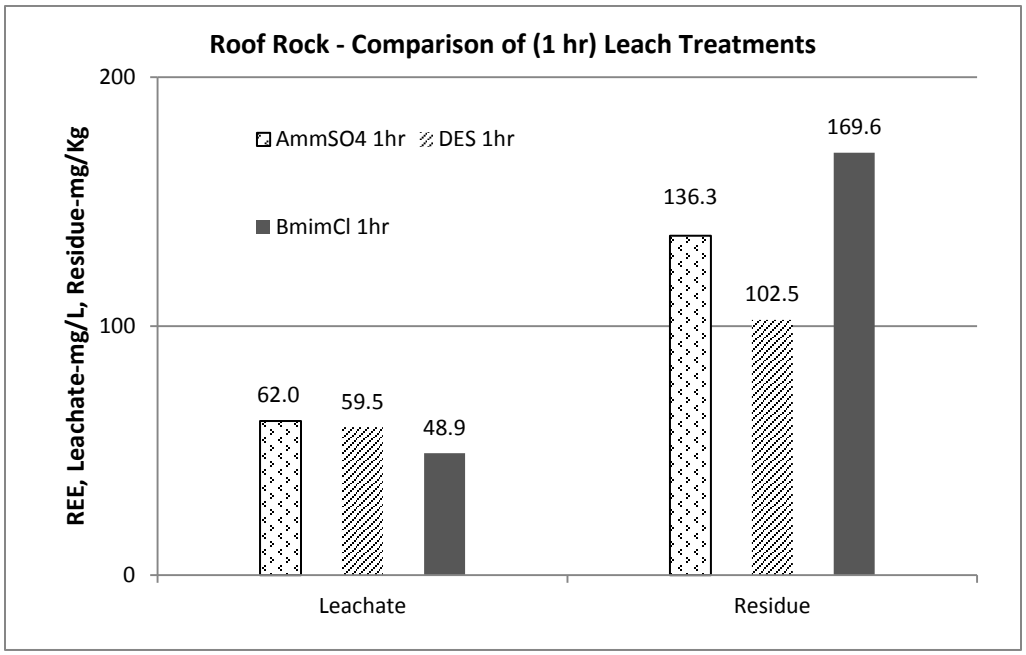


Figure 17: Comparison of the three solvents on residue and leachate REE concentrations. Since the leachate values are estimated by mass balance the lower REE for the ionic liquid DES may not be conclusive.

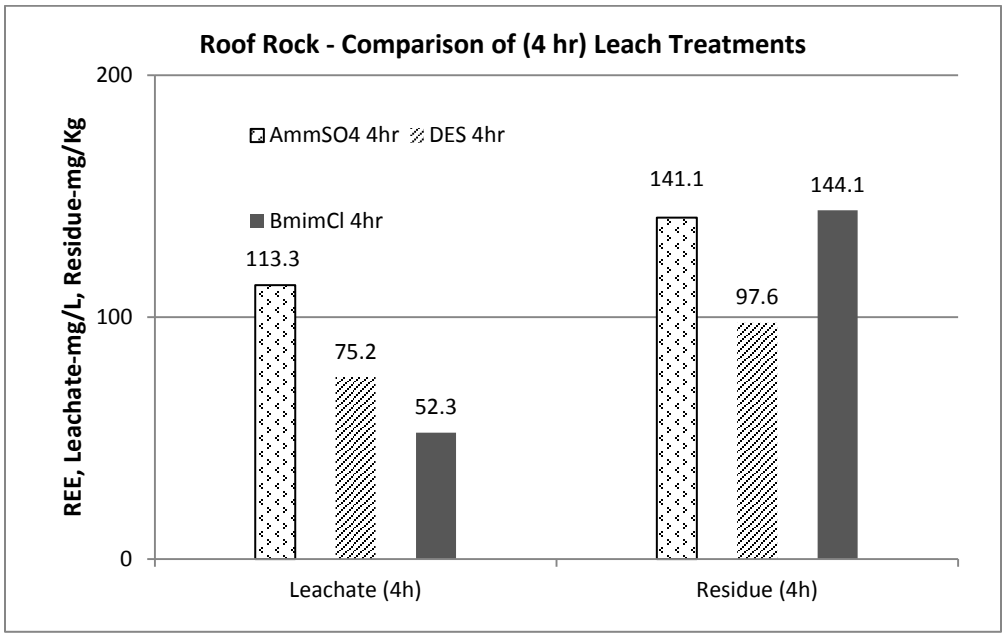


Figure 18: REE concentrations after 4 hour long treatments of roof rock samples. It is seen that the effect of time is most pronounced with the ammonium sulfate treated samples, with an almost 100% increase in the REE in the leachate.

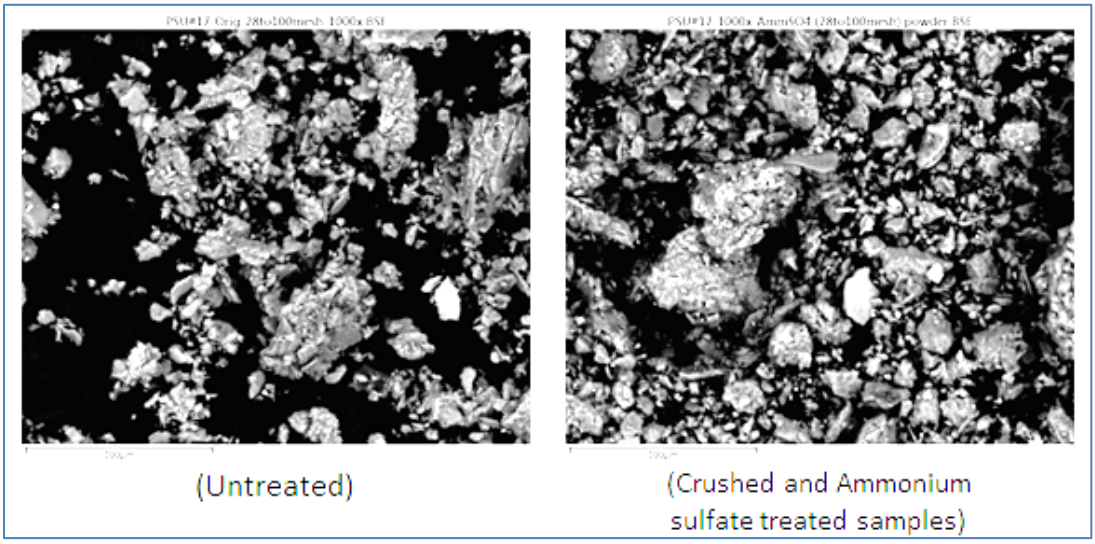
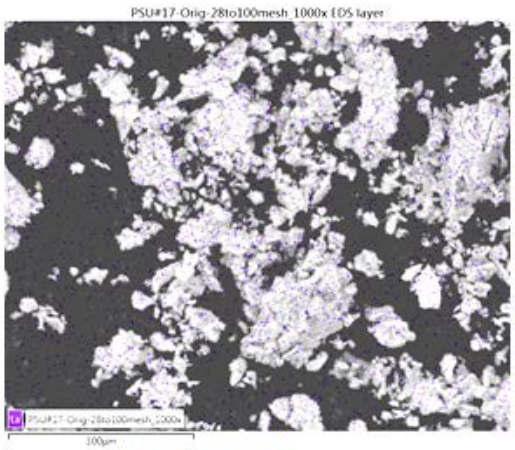
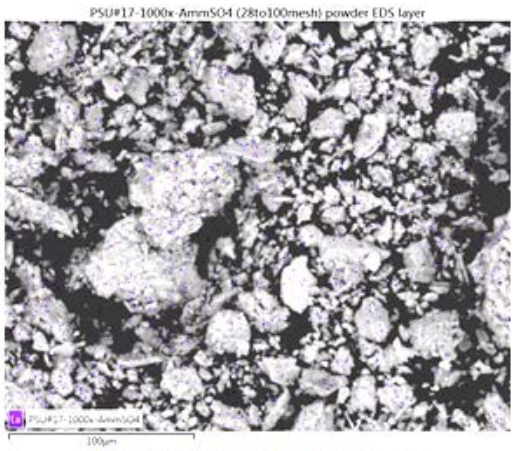


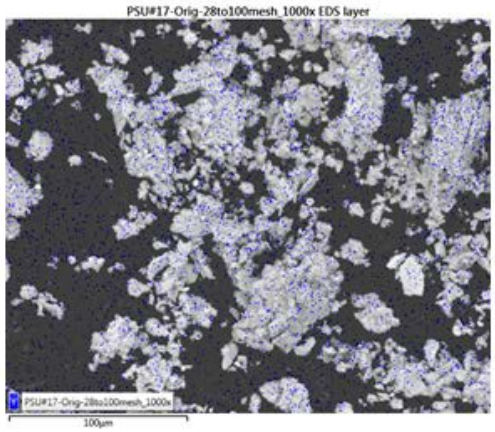
Figure 19: SEM images of Roof Rock (PSU#17) before and after treatment.



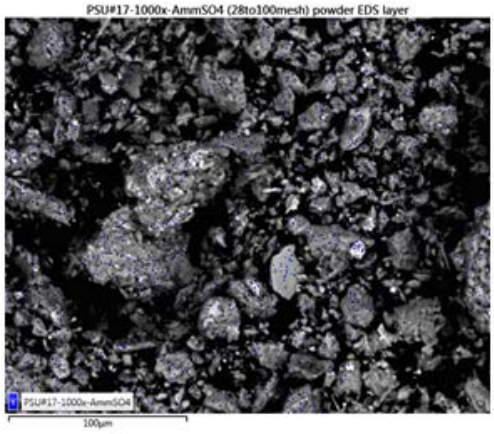
La (untreated)



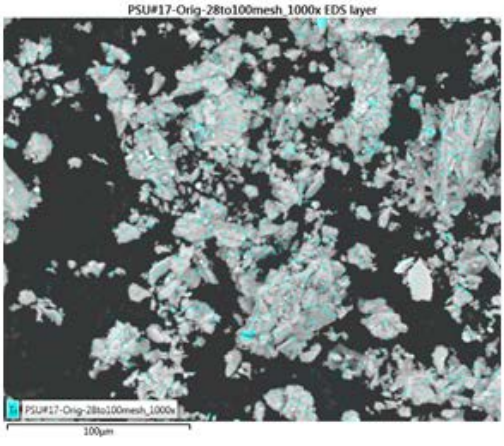
La (Crushed and Ammonium sulfate treated samples)



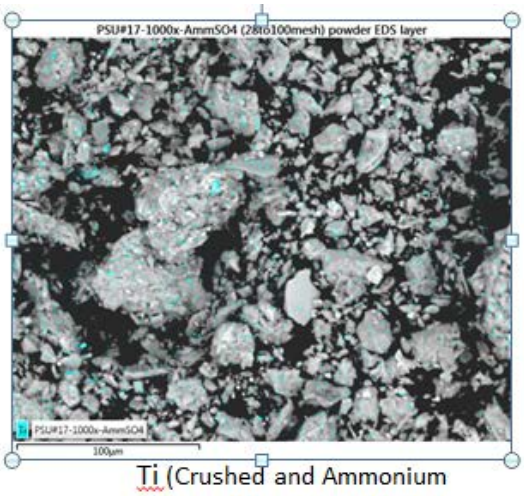
Yttrium (untreated)



Yttrium (Crushed and Ammonium sulfate treated samples)



Ti (untreated)



Ti (Crushed and Ammonium sulfate treated samples)

Electron Microscopy of Roof Rock – Flint Clay Sample (PSU#17)

The following section shows preliminary SEM-EDS analysis of a small region of a roof rock (Flint clay) from an open pit mine.

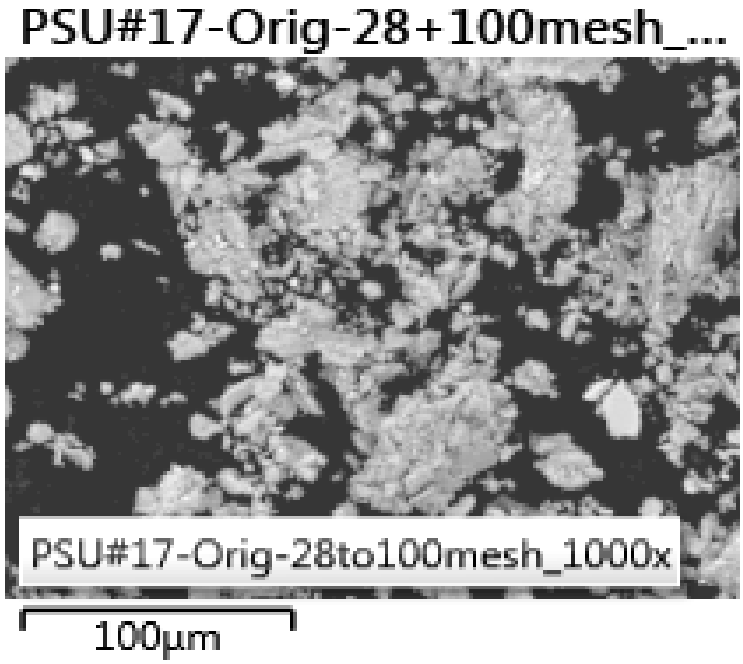


Figure 20: High degree of charging of sampling during electron microscopy imaging at high vacuum.

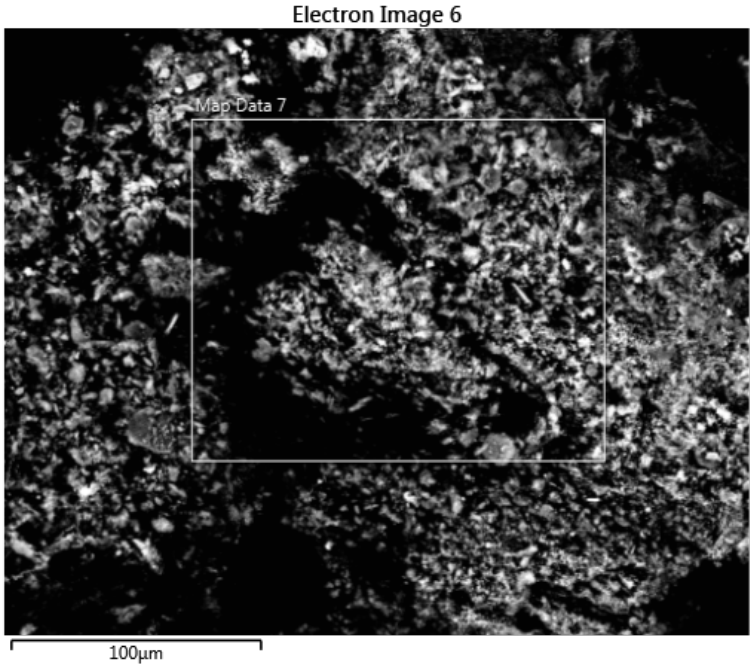


Figure 21: Roof rock PSU#17 elemental Map zone in EDS.

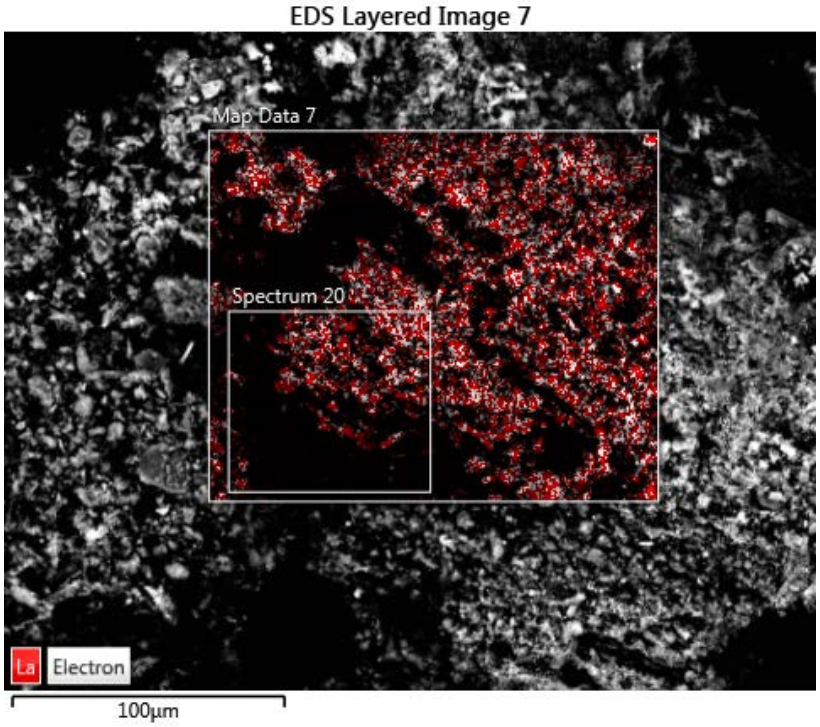


Figure 22: EDS map of elements with high intensity in mapped spectra. La was ranked third behind C, Al, and O and above Fe and Si in this sample's small region analysis.

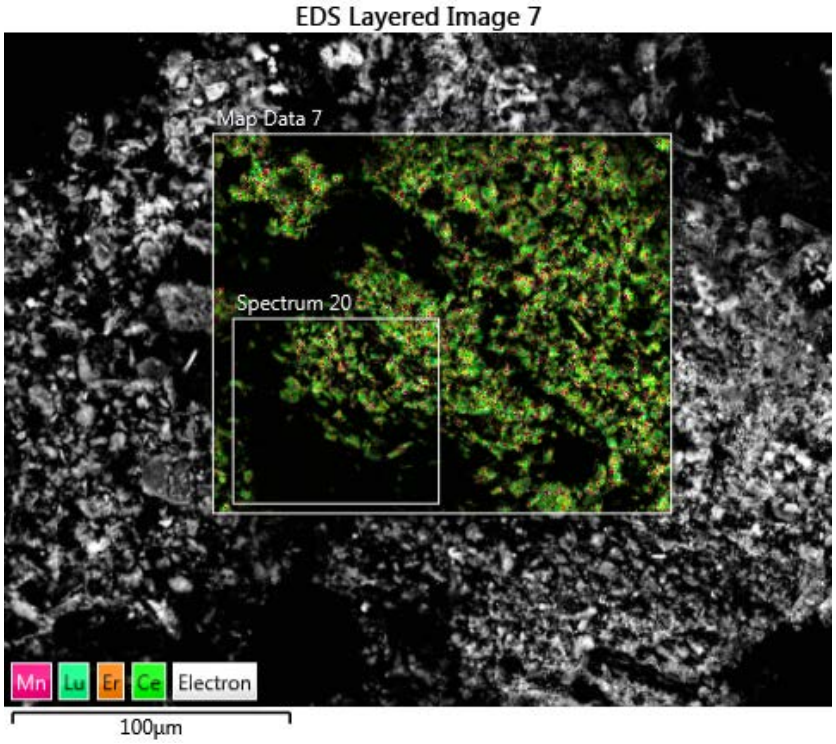


Figure 23: EDS compositional mapping (Mn, Lu, Er, Ce – present in trace quantities) of narrow rectangular region Spectrum 20 in Flint clay roof rock. The sigma (accuracy) of detection for Ce, Er, and Lu are within detection limits so the level of those two elements cannot be confirmed.

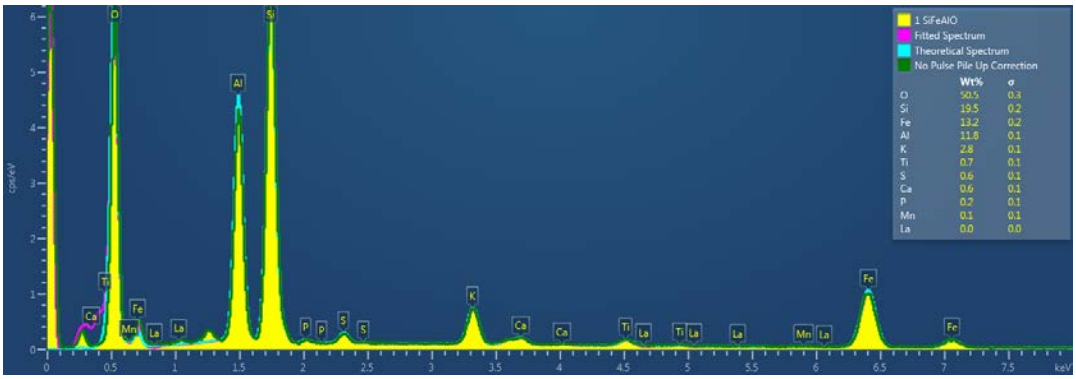


Figure 24: Composition analysis of marked zone Spectrum 20 in Figure 3.

Table 11: Semi-quantitative elemental concentration in SEM-EDS field of view.

Element	Wt. %%
O	50.49
Al	11.82
Si	19.50
P	0.25
S	0.64
K	2.79
Ca	0.57
Ti	0.68
Mn	0.08*
Fe	13.18
La	0.00*
Total	100.00

*Below detectable limit of 0.1 Wt. %%. Values may not be reproducible on other representative samples. Note also that at this stage of rock analysis, the process is similar to “prospecting” in the mineral industry.

Based on above data, it can be seen that the roof rock is a type of clay with the bulk composition dominated by Si, Al, O, and Fe. The rare earths could be distributed finely in the clay matrix at sub-1000 ppm levels in SEM micrographs, which is the detection limit of the EDS sensor.

Pit Cleanings and Refuse Samples

This group of samples comprised of C' pit cleanings (coded as PSU#16) and two refuse samples (PSU#10 and PSU#8) obtained from coal preparation circuits of power plants. The C' pit cleanings are samples that were collected from screen rejects on site from a central Pennsylvania open pit mine and affiliated coal blending yards in proximity to the mine. All samples were mineral rich samples of coals.

Float-Sink Separation

Gravity separation at 1.6, 1.9, and 2.4 specific gravities was performed on the samples. The pit cleanings mostly separated into extreme ends of the density spectrum. The preparation plant refuse material separated more into the heavier density segments evenly but the ash yields between the two heavier fractions were vastly different. Table 12 depicts the data of float-sink separation yields and the associated dry-ash values of each fraction.

Table 12: Yields from Gravity Separation of the coal based samples. These samples were subjected to 2-3 density separations based on their separation characteristics. Pit cleanings had a minor error in separation due to loss of finer material along with the liquid. ND: not determined.

Sample	Descriptor	1.6 Float	1.6-1.9	1.9-2.4	2.4 Sink
PSU#16 (yield Wt. %%)	Pit Cleanings	34.29	1.30	6.86	57.55
Ash (dry), Wt. %%		3.30	23.26	68.25	88.69
PSU#10 (yield Wt. %%)	Refuse	5.83	43.54	6.06	44.58
Ash (dry), Wt. %%		3.73	8.99	48.40	94.47
PSU#8 (yield Wt. %%)	Refuse	9.68	44.50	20.09	25.73
	Ash (dry), Wt. %%	5.15	13.19	54.77	90.21-

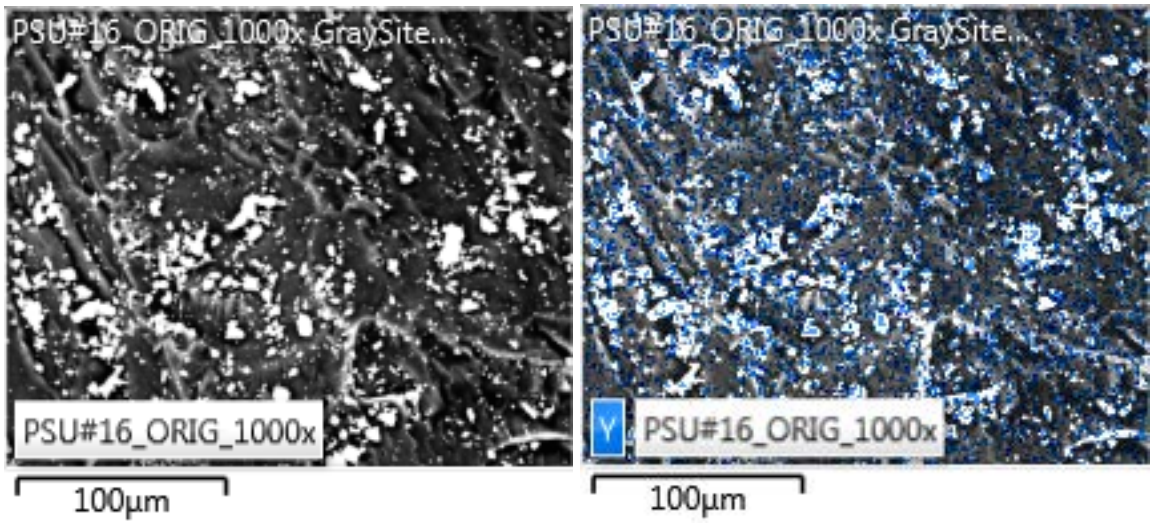


Figure 25: Electron micrograph of C' pit cleanings and Yttrium overlay elemental map over the same.

Distribution of Yttrium is shown in Figure 25 and the spot concentration of key REEs in the micrograph are given in Table 13.

Table 13: Semi-quantitative elemental concentration in PSU#16 pit cleanings within SEM-EDS field of view.

Pit Cleanings PSU#16_ORIG 1000x GraySite	Wt. %
Y	0
La	0.02
Ce	0.02
Nd	0
Ho	0.01
Yb	0.01
Total	100
TREE (mg/Kg)	600

ICP-AES analysis of 1.6 float and 1.6-2.4 and 1.9 sink fractions was conducted for the C' pit cleanings (PSU#16) sample. The pit cleanings sample appears to be composed of light organic material (1.6 float) or heavier mineral-rich material 1.9 sink (Figure 26).

The yield of the 1.6S-1.9F fraction and the 1.9S-2.4F fraction were both relatively small (together accounting for only 7% by weight) was negligible during the gravity separation. Since the pit cleanings show an appreciable increase in the REE content with density, gravity separation would be considered a suitable method of enrichment. Further, since the higher gravity fractions still contain 12 to 30% volatile or combustible material, working with ash generated from this sample could also be considered advisable for rare earth extraction.

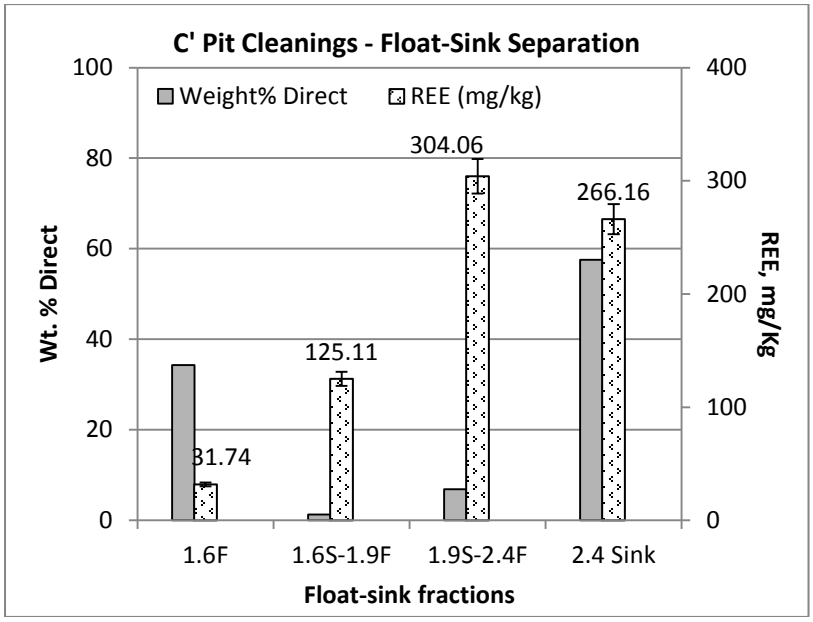


Figure 26: Float-sink separation yields and REE concentrations of separated fractions in the C' pit cleanings (PSU#16) sample. Most of the rare earths are enriched in the heavier fractions and at a substantially higher amount than in the untreated material (114 mg/kg).

For the refuse samples of PSU#8 and PSU#10, ICP-AES could be conducted only on the 1.6 float and 1.6 sink fractions at this time. The results do again indicate that the lightest fraction (1.6

float) contains negligible amount of REEs and is also the fraction with very little ash content. For both of materials, it is reasonable to assume that the rare earths are then contained in the heavier fractions predominantly but additional investigation into intermediate densities is required.

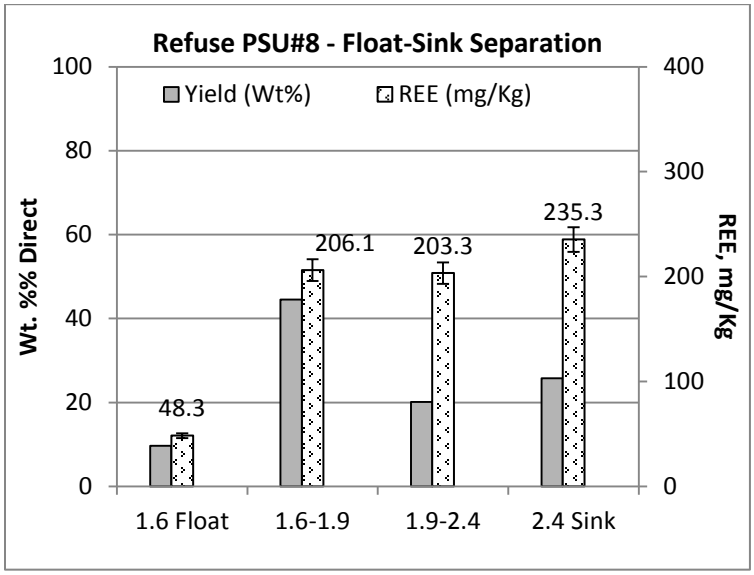


Figure 27: Total REE concentrations in PSU#8 gravity separated fractions.

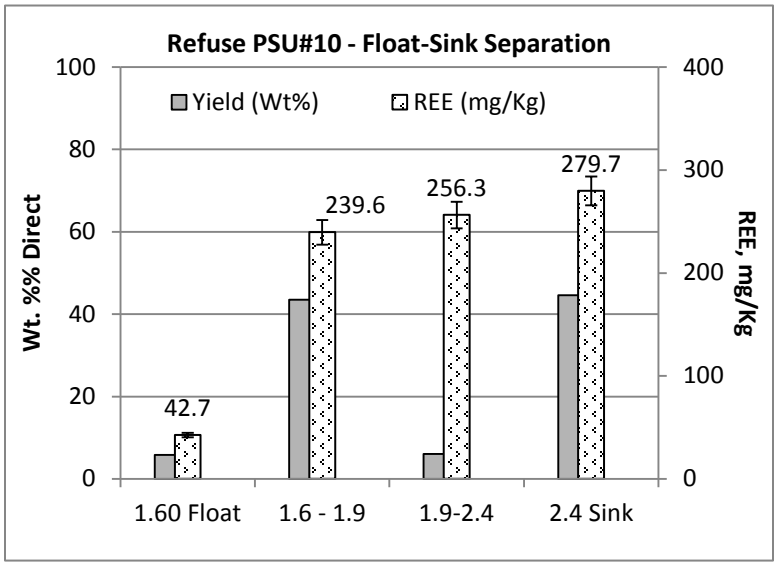


Figure 28: Total REE concentrations in PSU#10 gravity separated fractions.

Magnetic Separation –Pit Cleanings and Refuse samples

Magnetic separations were performed in the same apparatus as the roof rock samples under similar conditions (4A current). The yields of the fractions are shown in Table 14. Proximate analysis results on these samples are provided in the Appendix in Table 19. The pit

cleanings sample (PSU#16) showed appreciable difference in ash yield between the conducting and insulating materials. The magnetic fraction yield due to an electromagnetic field application is low for these three samples, with only PSU#10 showing some (10%) amount of magnetic material yield during the test.

Table 14: Yields from magnetic separation of coal samples. (Samples separated at 100% field as PSU#17).

Sample	Non-mag. Wt. %.%	Mag. Wt. % (4A)	Ferro Mag. Wt. %
PSU#16	99.00	0.29	0.00
PSU#10	90.27	9.52	0.00
PSU#8	96.86	2.75	0.01

The ICP-AES analysis of the pit cleanings samples are shown in

Table 15. The non-magnetic material, which comprises more than 99% of the total materials, contains less than 1% total REEs. The magnetic material appears to show enrichment (~400 ppm) of total rare earths, but the overall weighted yield could be extremely low to justify this method as the primary separation technique for this sample.

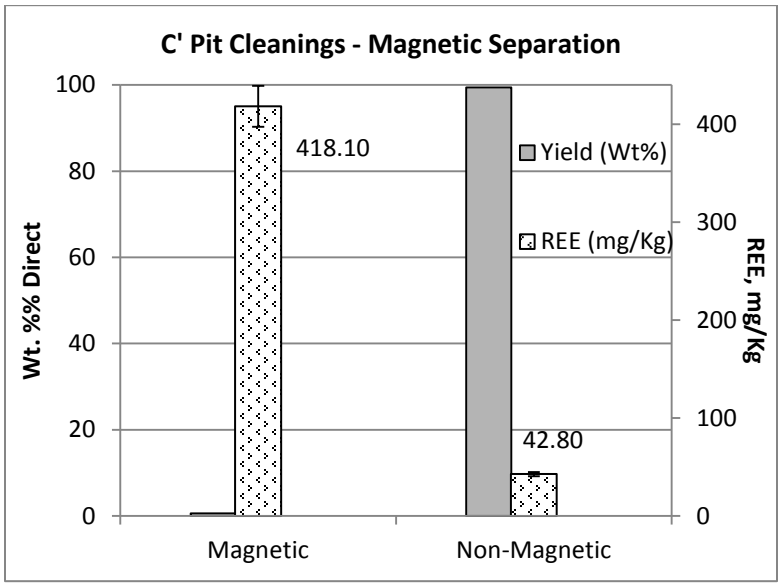


Figure 29: ICP-AES analysis of magnetically separated pit cleanings fractions. Although the overall yield from the separation is low for the magnetic fraction, the REE enrichments improved significantly.

Table 15: ICP Data from magnetic separated pit cleanings (PSU#16).

	PSU 16 Pit cleanings (-28+100 mesh)	PSU 16 Magnetic (-28+100 mesh)	PSU 16 Non-Magnetic (-28+100 mesh)
Ash, Wt. % Dry	56.87	77.96	73.87
Elements on Dry Sample Basis	mg/kg	mg/kg	mg/kg
Ce	68.5	223	0.05
Dy	1.42	3.1	<1.85
Er	3.41	5.82	<3.69
Eu	<2.84	<3.90	<3.69
Gd	<2.84	6.98	<3.69
Ho	<2.84	<3.90	<3.69
La	18.5	22.1	0.15
Lu	<2.84	6.21	<3.69
Nd	14.6	56.2	0.11
Pr	10.8	14.7	<3.69
Sm	3.7	11.6	<3.69
Sc	12.9	16.7	<3.69
Tb	<2.84	6.21	<3.69
Th	6.68	8.92	<3.69
Tm	<1.42	<1.95	<1.85
U	<2.84	<3.90	<3.69
Yb	1.71	5.82	<1.85
Y	9.38	29.9	<3.69
Ir	<2.84	70.2	<3.69
Co	13.9	55.5	<3.69
Al	66,150	60,740	490
Ca	656	1,250	<9.23
Total Rare Earth (TREE):	144.9	408.3	0.3

Magnetic separation of the refuse samples PSU#8 and PSU#10 and the associated REE analysis is given in Figure 31.

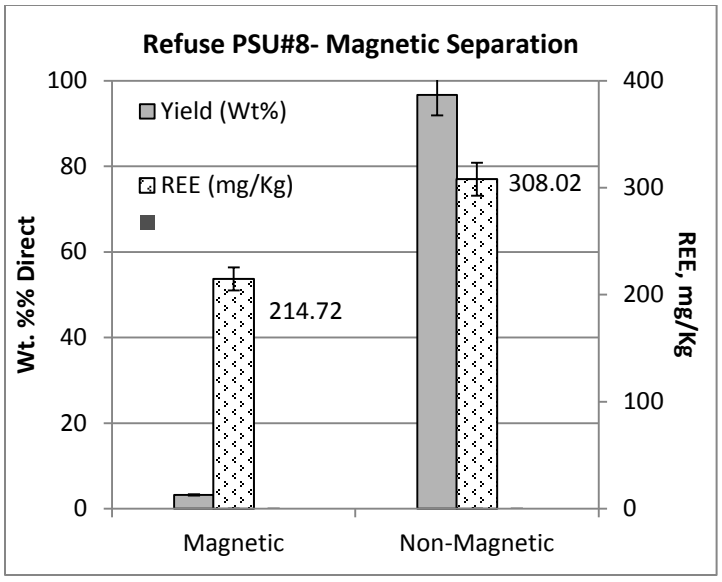


Figure 30: REE concentrations of magnetically separated fractions in PSU#8 showing a marked REE enrichment in the non-magnetic fraction.

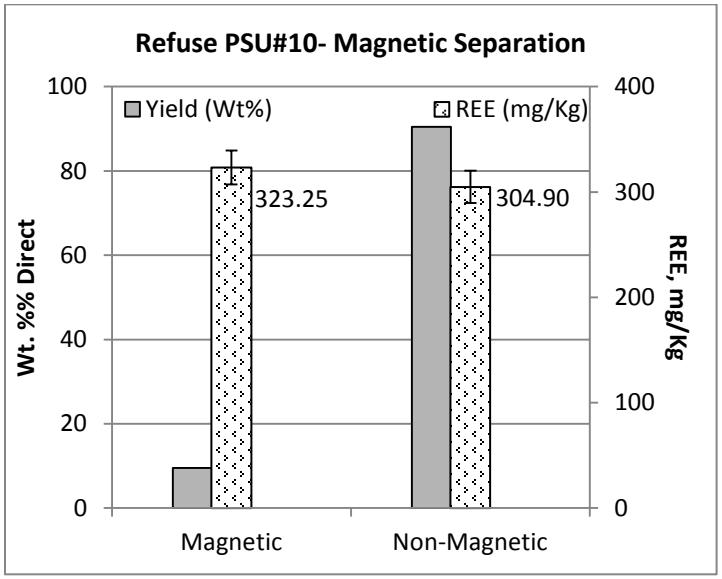


Figure 31: REE concentrations of magnetically separated fractions in PSU#10 refuse samples.

Electrostatic Separation

Electrostatic separations carried out on this set of samples yielded diverse results (

Table 16). The pit cleanings sample (PSU#16) showed appreciable amount of material going into insulating fractions. Among the refuse samples, the separation was fairly even for PSU#10 between the insulators and the conductors. For sample PSU#8, *most* of the material was conducting and the rest was evenly distributed between insulating and neutral groups.

Table 16: Yields from electrostatic separation of coal-based samples.

Sample	Conductors Wt. % . %	Middlings Wt. %. %	Insulators Wt. %	Voltage Applied (kV)
PSU#16	17.56	6.31	76.13	14.5
PSU#10	47.90	11.17	40.93	14
PSU#8	81.54	10.44	8.02	13

REE concentrations by ICP-AES analyses of the electrostatically separated fractions from the pit cleanings sample are shown in Figure 32. The REE content was low in the highest yielding insulating fraction while the low yielding (less than 20%) conducting fraction showed a relatively high REE content (~340mg/kg) for this sample. However, since the pit cleanings bulk sample is not inherently a high REE sample (maximum content measured was ~220 mg/kg), it is hard to draw solid conclusions from this data alone. The REE analyses of the separated refuse samples PSU#8 and PSU#10 is presented in Figure 33 and Figure 34. Sample PSU#8 shows a marked enrichment in conductors over the rest with high yields also being present in the conducting fraction. Hence, refuse sample PSU#8 can be considered a likely candidate for electrostatic separation methods. Additionally, since it has about 35% combustible material, the enrichment procedures could be tested on the ash from PSU#8 to possibly improve REE enrichment.

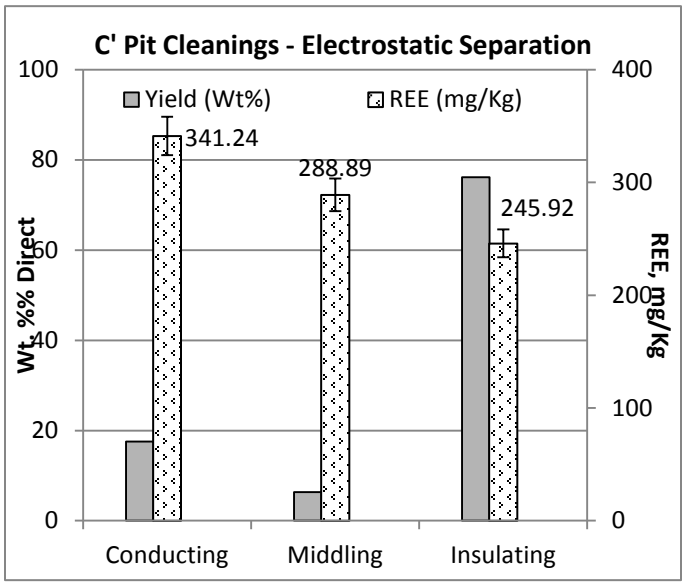


Figure 32: REE concentrations in the electrostatically separated fractions of pit cleanings. There is some amount of enrichment in the conducting material. The results of these fractions need to be viewed with caution as the bulk pit cleanings material shows wide disparity for REE concentration under different tests.

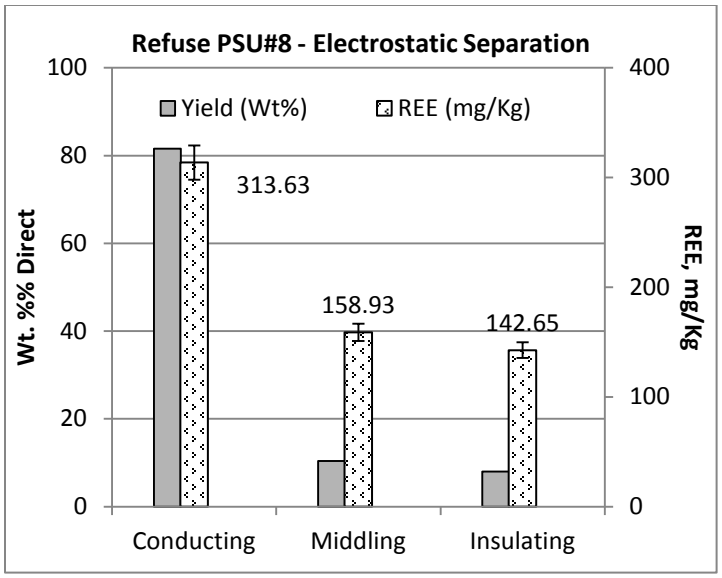


Figure 33: REE concentrations in electrostatically separated fractions of refuse sample PSU#8.

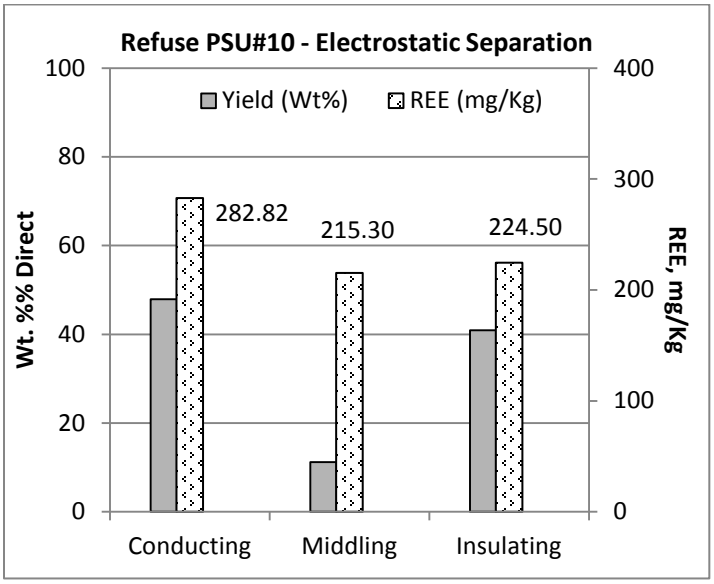


Figure 34: REE concentrations in electrostatically separated fractions of refuse sample PSU#10.

Leaching Treatments on Pit Cleanings Sample

Leaching studies were conducted with the three different solvents on the pit cleanings sample for one- and four-hour durations. Results from the separations are presented in Figure 35 through Figure 39. The residue in the pit cleanings after DES leaching treatment showed the largest enrichment compared to the respective leachate concentration. Ammonium sulfate treatments did not show any appreciable leaching of REEs from the source mineral.

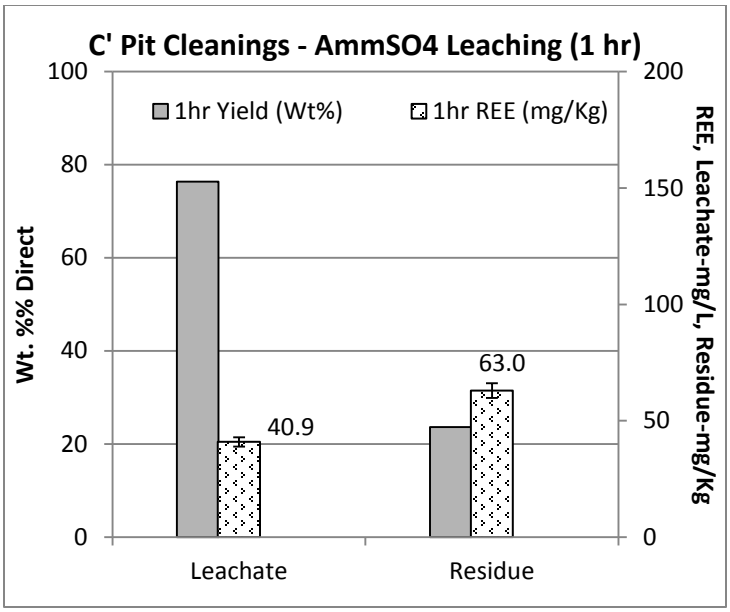


Figure 35: REE Leaching in pit cleanings with ammonium sulfate solution.

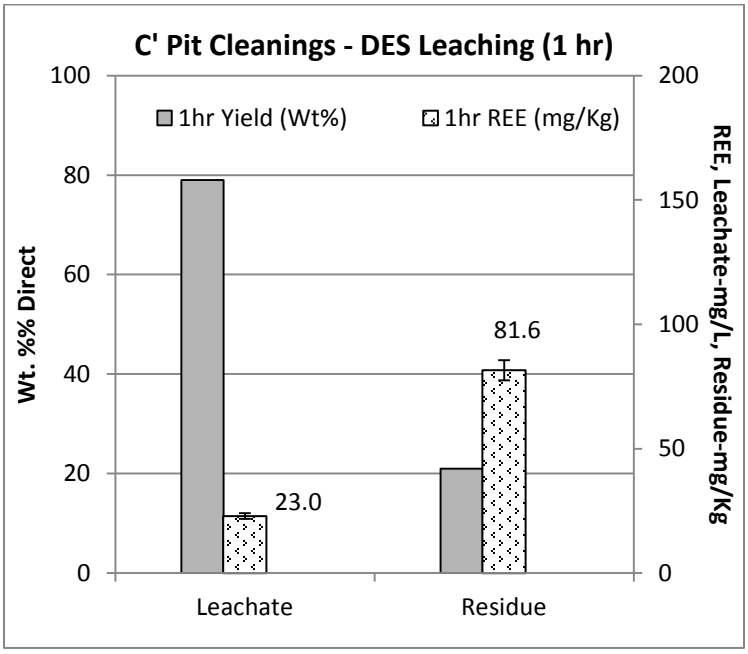


Figure 36: REE leaching from pit cleanings using Deep Eutectic Solvent (DES).

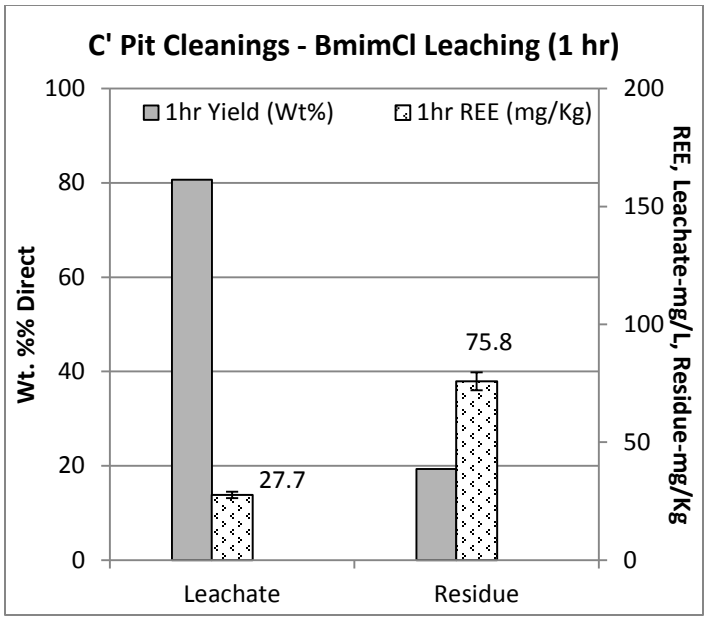


Figure 37: REE leaching of pit cleanings by Ionic Liquid BmimCl.

Comparing the different treatments, no appreciable difference was seen among the three solvent treatments used with the pit cleanings (Figure 38). In addition, the increased time of leaching (four-hour experiments) also yield no substantial differences between the one- and four-hour REE data in the residues or the leachates (Figure 39). This could indicate that the manner of interaction of the leaching materials with the pit cleanings may not be conducive to significant ion exchange activity. However, investigations on the ash of pit cleanings to see if they are conducive to ion exchange treatments are recommended as the treatments would be on partially enriched material after the removal of volatile and combustible substances from this sample.

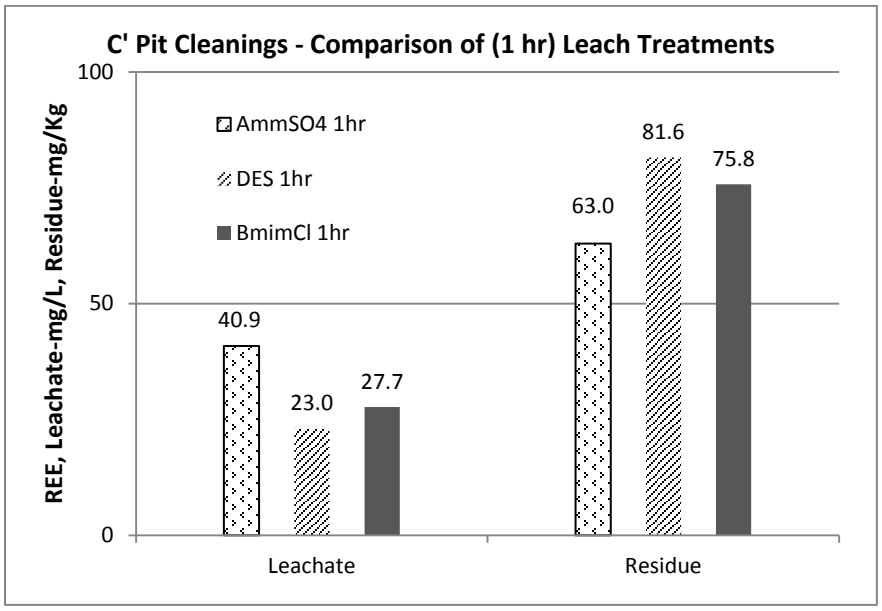


Figure 38: Solvent leaching comparison for Pit Cleanings.

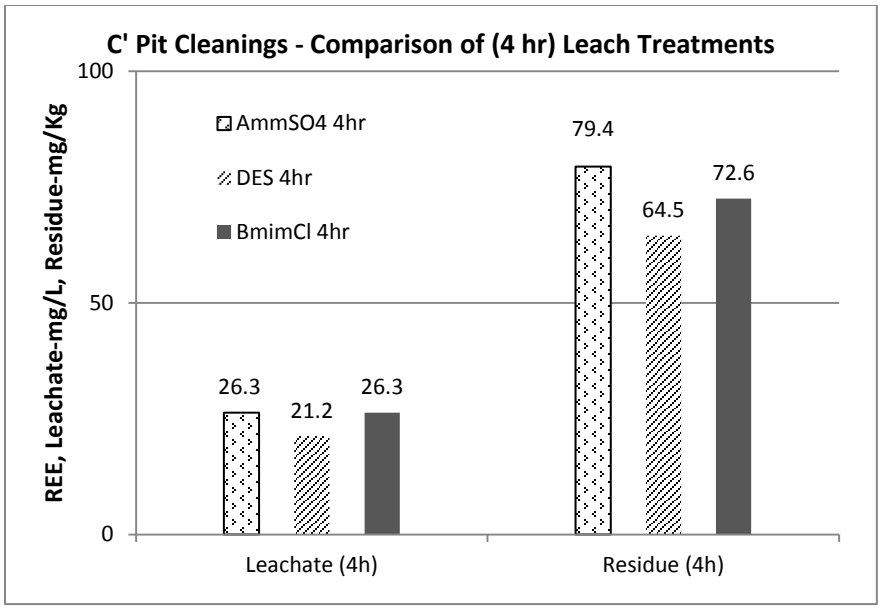


Figure 39: REE values from leached pit cleanings sample after four-hour treatment. There is no substantial difference upon increasing the time of leaching for this sample.

Conclusions

The results of the different samples from the various separation processes varied in degree, but it was seen that the roof rock sample contained the largest concentration of total REEs on a whole material basis. The roof rock material also responded best to gravity separation and ion exchange leaching treatments. Further experiments to optimize the leaching processes on roof rock material are highly recommended. The pit cleaning sample showed very little response to ammonium sulfate treatments but showed some response to the expensive IL treatments. As such, the pit cleaning sample showed low potential to ion exchange treatment methods. The pit cleaning sample however did show a marked response to magnetic enrichment. It is to be noted that the pit cleaning sample was a sample with lower bulk REE content. However, it is a coal product with a fair amount of combustible material and the combustion of carbonaceous material typically results in the REEs remaining in the combustion ash, and at a higher concentration in the ash. Hence, ion exchange treatments on the ash of pit cleanings are recommended. Among the two refuse materials, one of the samples (PSU#8) showed a very clear separation and enrichment behavior under electrostatic separation while the other refuse sample (PSU#10) showed no significant discriminatory behavior under any of the separation methods except gravity separation.

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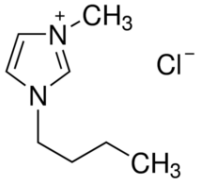
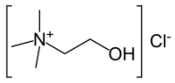
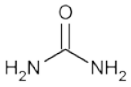
10. Jensen, M.P., et al., *Mechanisms of Metal Ion Transfer into Room-Temperature Ionic Liquids: The Role of Anion Exchange.* Journal of the American Chemical Society, 2003. **125**(50): p. 15466-15473.
11. Kubota, F., Y. Baba, and M. Goto, *Application of Ionic Liquids for the Separation of Rare Earth Metals.* SOLVENT EXTRACTION RESEARCH AND DEVELOPMENT-JAPAN, 2012. **19**: p. 17-28.

Acknowledgments

Assistance from the staff of Penn State Material Research Institute (Julie Anderson, Maria DiCola, Trevor Clark, John Cantolina and Dustin Hess), the EME Department (Tom Motel), and the EMS Energy Institute (Gareth Mitchell) is gratefully acknowledged. Assistance of PSU graduate student Aditi Khadilkar in the conduct of leaching experiments is also duly noted and appreciated.

Appendix I: Leaching Procedures

Samples	Leaching solvent	Procedure
PSU17 Roof Rock -28+100 mesh	**$AmmSO_4$** Ammonium sulfate 1M solution	a) 1:2 w/w solid to solvent prepared by mixing sample with Ammonium sulfate solution. b) The mixture was stirred at room temperature ~20°C for an hour. c) Whatman Ashless 5µm filter paper used for filtration. d) Rinse the solid part with deionized water three times. e) Kept the solution part with sealed container under room temperature. f) Dried the solid part under vacuum oven for 12 hours at 20°C.
PSU17, 1.9 Sink -1/4"+28 mesh	Ammonium sulfate 1M solution	Same above (20 °C)
PSU17, 2.9 Sink -28+100 mesh	Ammonium sulfate 1M solution	Same above (20 °C)
PSU17 Roof rock -28+100 mesh	**BmimCl** 1-butyl-3-methylimidazolium chloride 	Same procedure as above, except step b): The mixture were stirred and heated under 60°C for an hour
PSU17 -28+100 mesh	**Ch.U** Deep eutectic solvent (Choline Chloride Urea 1:2 mol mixture)  Choline Chloride  Urea	Same above

Appendix II: Float-Sink Separations – SEM-EDS Data

Gravity separations were performed at specific gravities 1.6, 1.9, 2.4 for all samples and additionally at 2.9 for the roof rock (see Figure 3).

Electron Micrograph

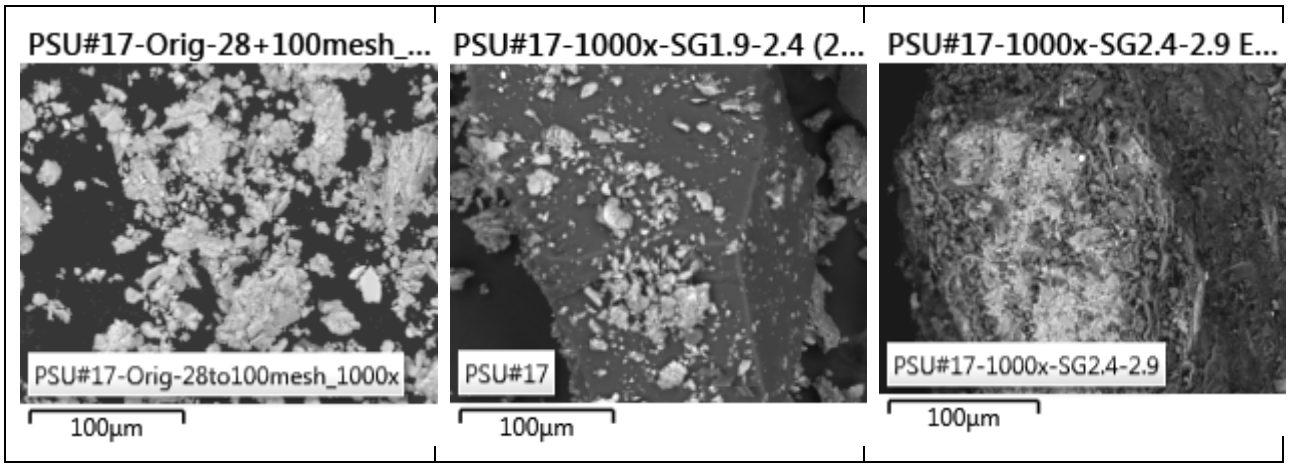
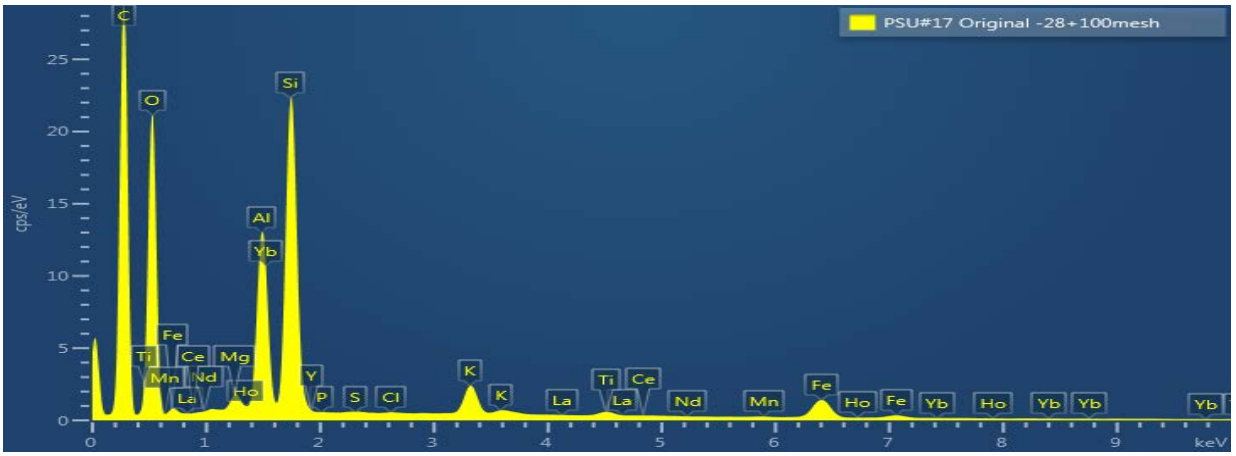
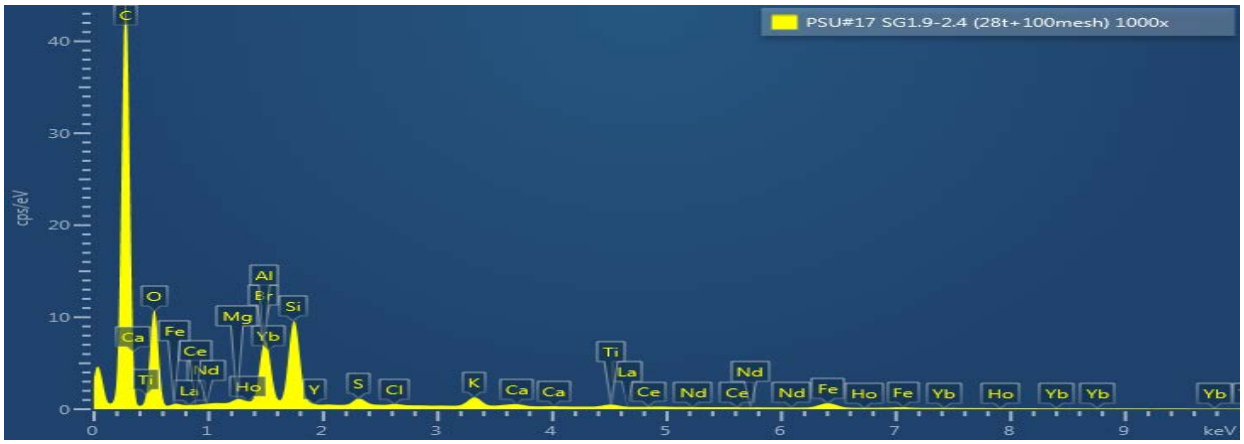


Figure 40: SEM images of gravity separated roof rock sample fractions.





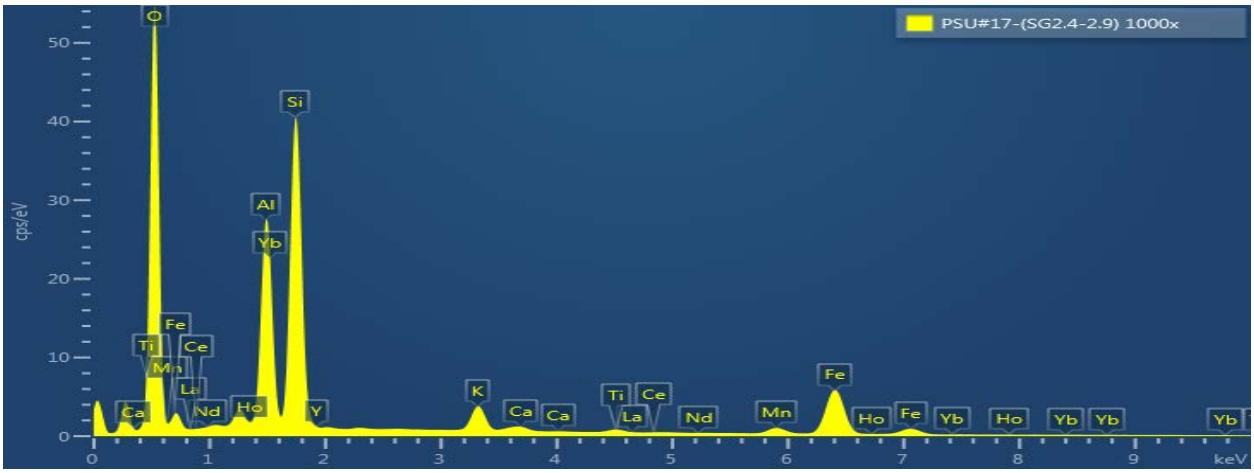
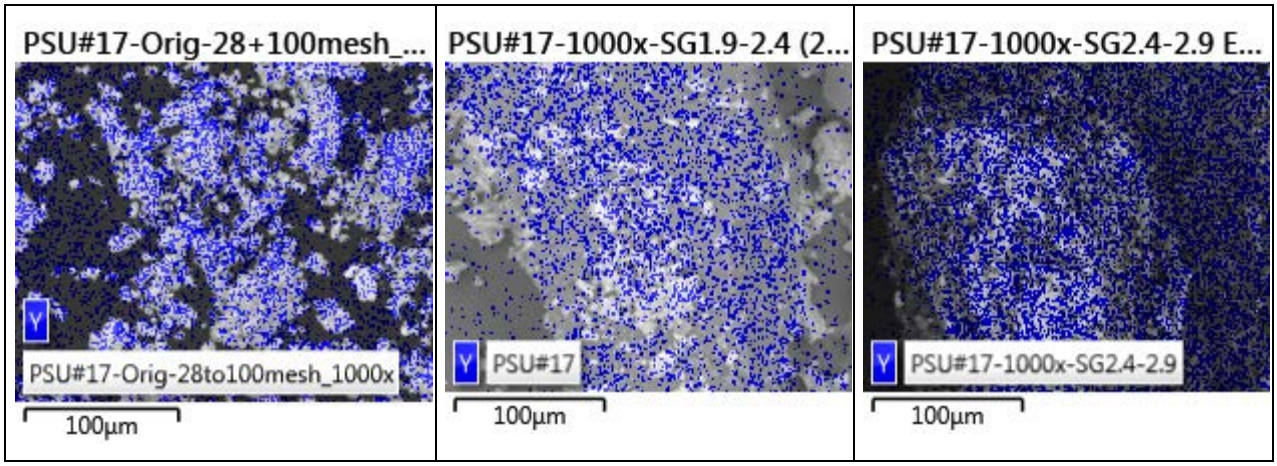


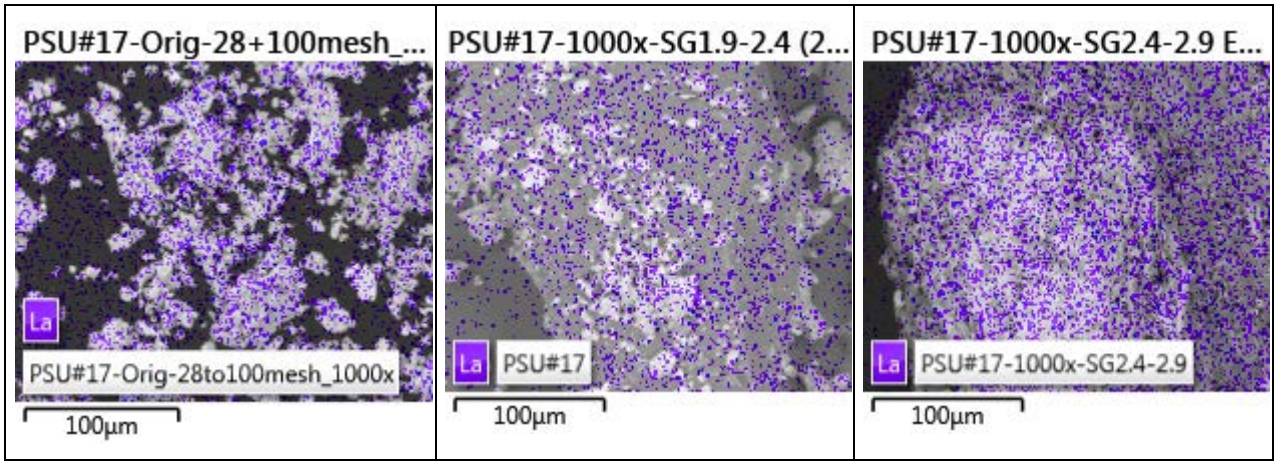
Figure 41: Representative spectra from EDS analysis of roof rock samples. The prominent peaks are from Al, O and Si. Rare earths are however detectable on semi-quantitative basis in several regions of SEM images.

The montage of EDS maps overlaid on SEM images of the original roof rock and separated gravity fractions in the following pages provide a quick visual overview of the scattered presence of major rare earth elements on the surfaces of mineral particles.

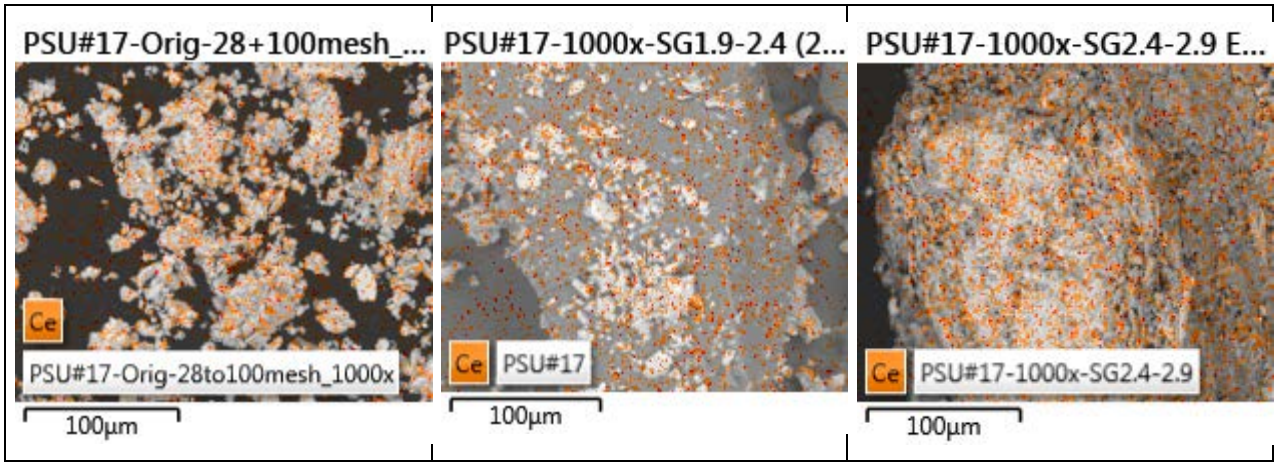
Yttrium



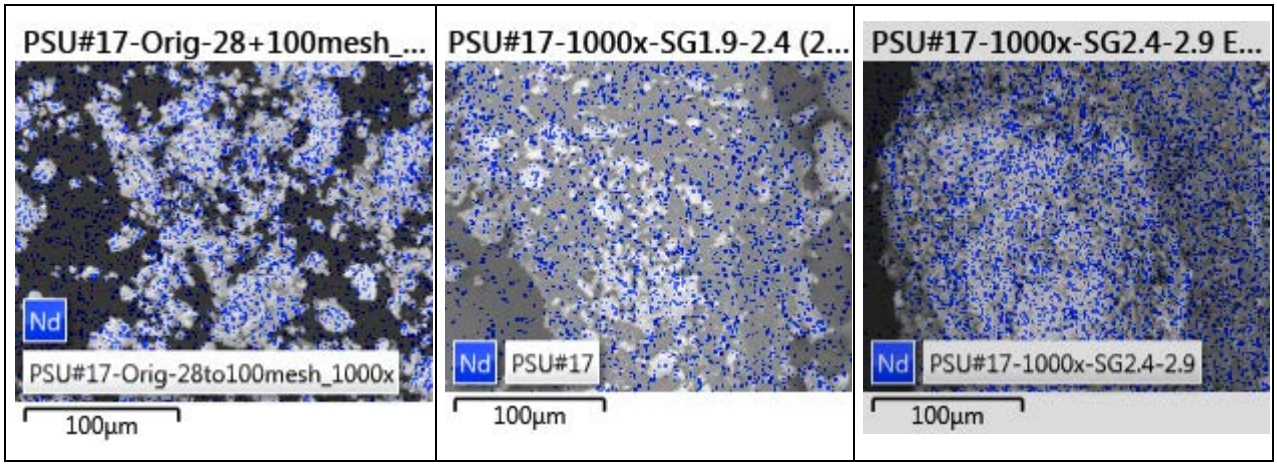
Lanthanum



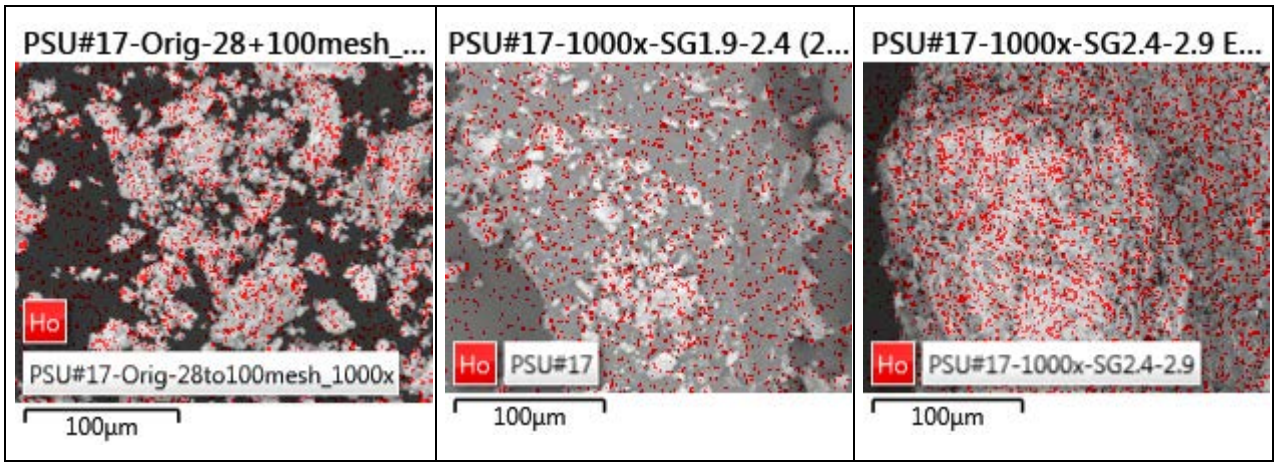
Cerium



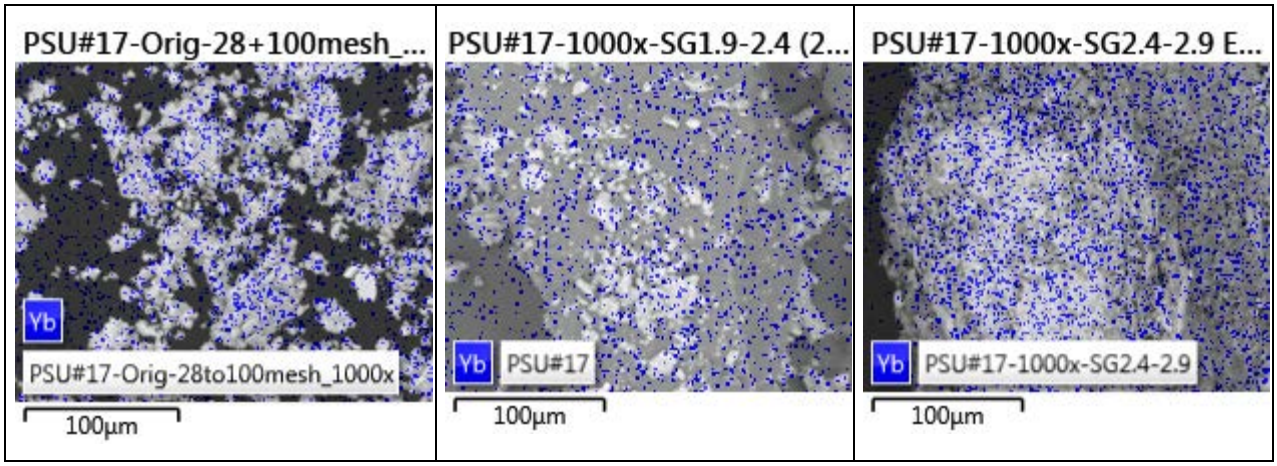
Neodymium



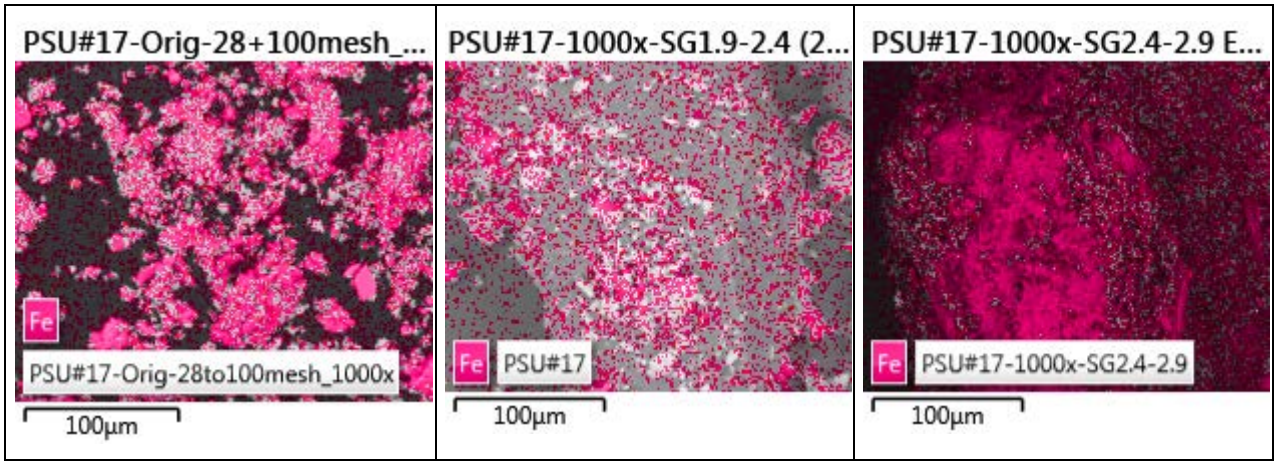
Holmium



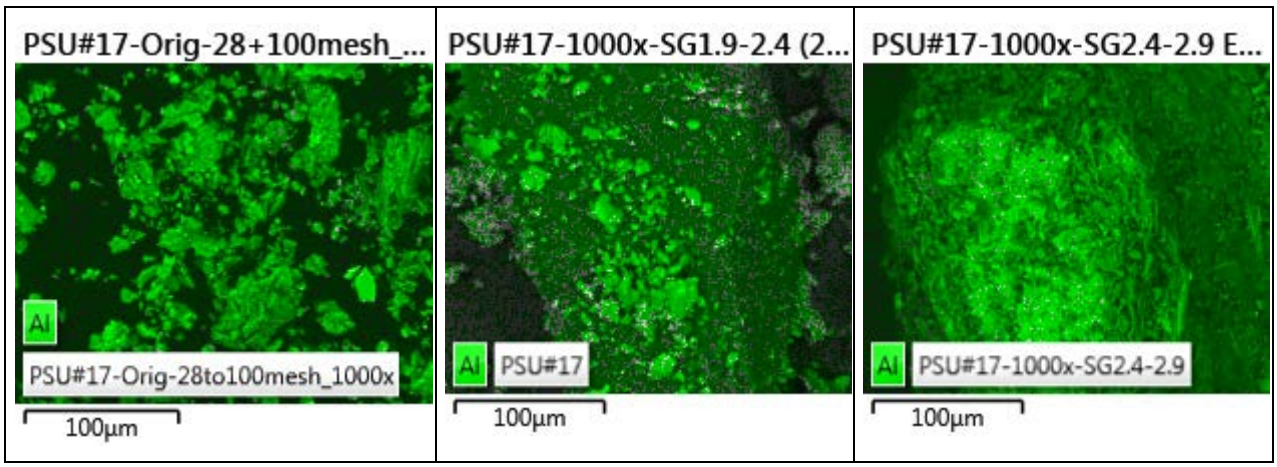
Ytterbium



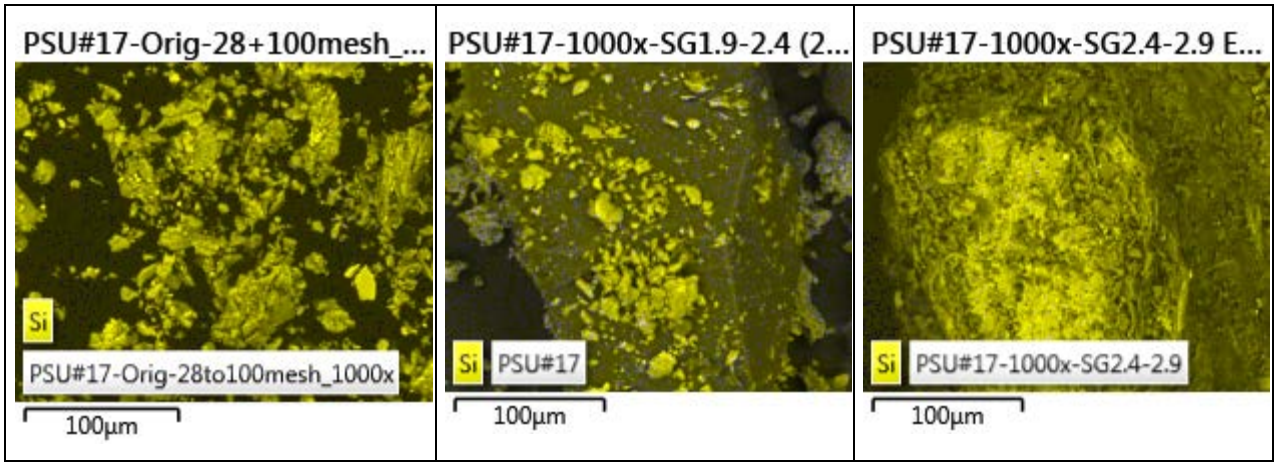
Iron



Aluminum



Silicon



Magnesium

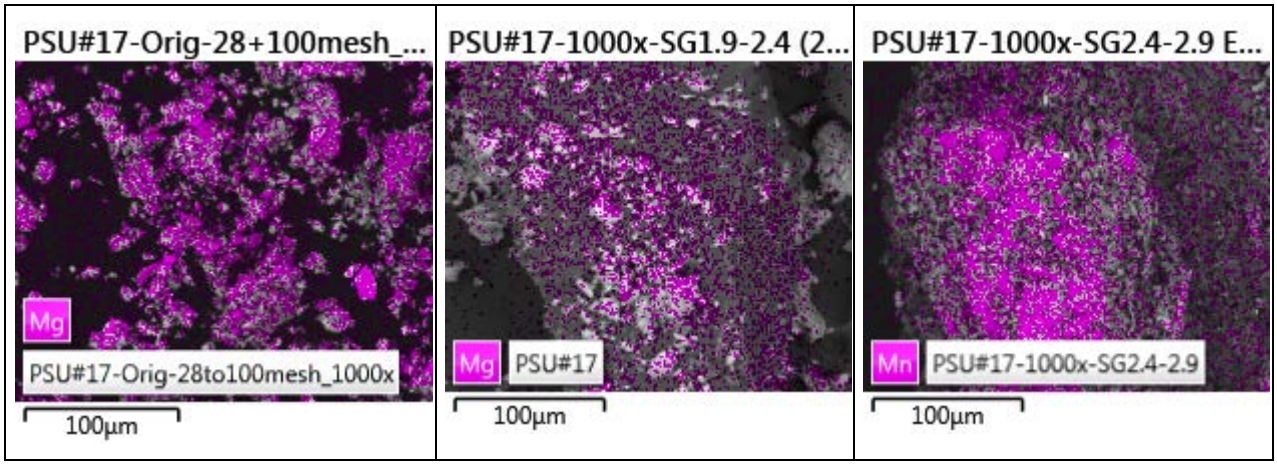


Table 17: Comparison of semi-quantitative elemental data of surface regions in the preceding SEM images of gravity separated roof rock fractions is provided here. The total REE concentrations are provided in wt% (on a whole mineral basis), to compare on a ppm scale, the REE values would need to be multiplied by 1000.

PSU#17 Original - 28+100 mesh Wt. %%		PSU#17 (SG 1.9-2.4) - 28+100 mesh Wt. %%		PSU#17 (SG2.4-2.9) Wt. %%	
O	58.67	O	58.17	O	57.4
Mg	1.09	Mg	0.96	Mg	0
Al	11.29	Al	10.67	Al	11.07
Si	19.94	Si	16.99	Si	17.02
P	0.05	P	0	P	0
S	0.04	S	1.67	S	0
Cl	0	Cl	0.39	Cl	0
K	2.78	K	2.55	K	1.9
Ca	0.18	Ca	0.58	Ca	0.32
Ti	0.55	Ti	1.07	Ti	0.35
Mn	0.12	Mn	2.55	Mn	1.11
Fe	5.09	Fe	4.12	Fe	10.69
Y	0.04	Y	0	Y	0
La	0.06	La	0	La	0.05
Ce	0.06	Ce	0	Ce	0.08
Nd	0	Nd	0.05	Nd	0
Ho	0.02	Ho	0	Ho	0
Yb	0.01	Yb	0.22	Yb	0
Total	100	Total	100	Total	100
TREE	0.19	TREE	0.27	TREE	0.13

Appendix III: Magnetic Separations – SEM-EDS Data

A cross-belt magnetic separator was used at an operating current of 4A (corresponding to a standard field strength for the apparatus) to separate particles susceptible to magnetization under an electromagnetic field.

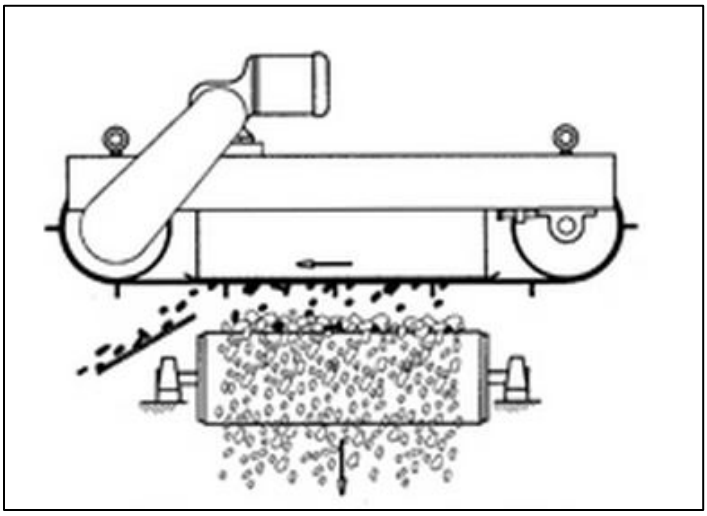


Figure 42: Schematic of a cross-belt magnetic separator. Feed particles are fed along a belt and pass under magnetic field applied over a belt moving perpendicular to original belt. (Source: http://www.pmlindia.com/products/magnetic-cross-belt-separator retrieved 11/18/2014).

Since the roof rock sample showed an appreciable separation at 4A (~37 Wt. %), lower field strengths were also investigated for the roof rock material. The yields at 3A and 2A values along with the original 4A test are presented in Table 18. It is seen that even at half the field strength, about 20% of the material is magnetized and separates from the bulk. Ferro magnetic material is removed prior to the induced magnetic separation as a safety precaution. The roof rock sample contained no ferroelectric material.

Table 18: Yields from magnetic separation for Roof Rock (PSU#17) at various field strength settings.

Field Strength	Non-magnetic Wt. %%	Magnetic Wt. %	Ferro Magnetics Wt. %
Field: 100 units	61.95	37.22	0.00
Field: 75 units	71.41	28.59	0.00
Field: 50 units	79.74	20.26	0.00

Proximate Analysis of magnetic and electrostatic separated fractions

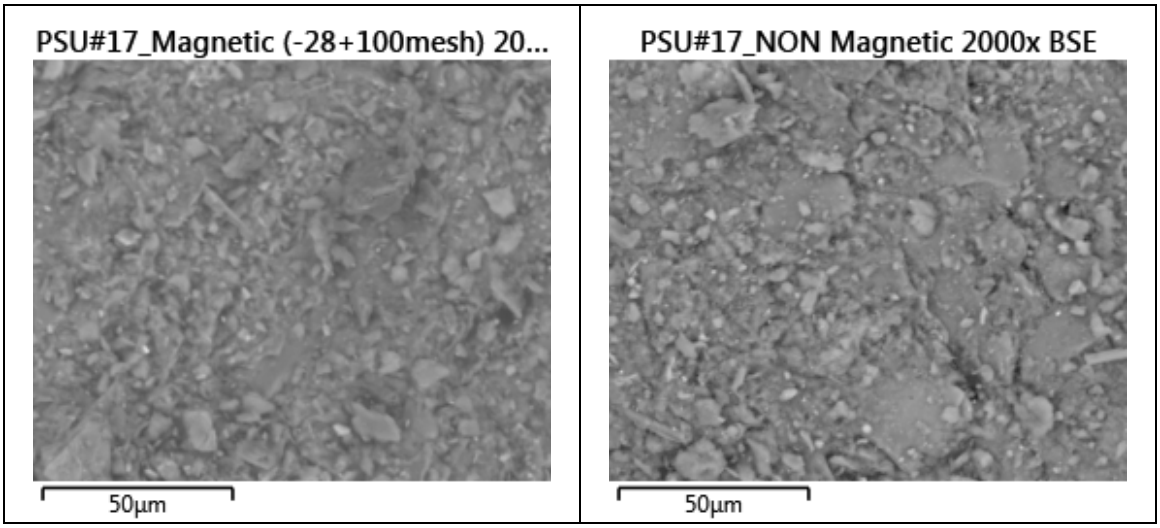
Proximate analysis of the magnetic and electrostatically separated samples was also conducted whenever a *reasonable* amount of sample was collected to be used in the analyzer. The results are shown in Table 19**Error! Reference source not found.**. PSU#16 (pit cleanings) showed appreciable difference in ash yield between the conducting and insulating materials and PSU#10 showed some amount of difference between the neutral (middling) group of sample and

the other two charging groups. PSU#8 showed significant difference in the ash yield between magnetic and non-magnetic materials.

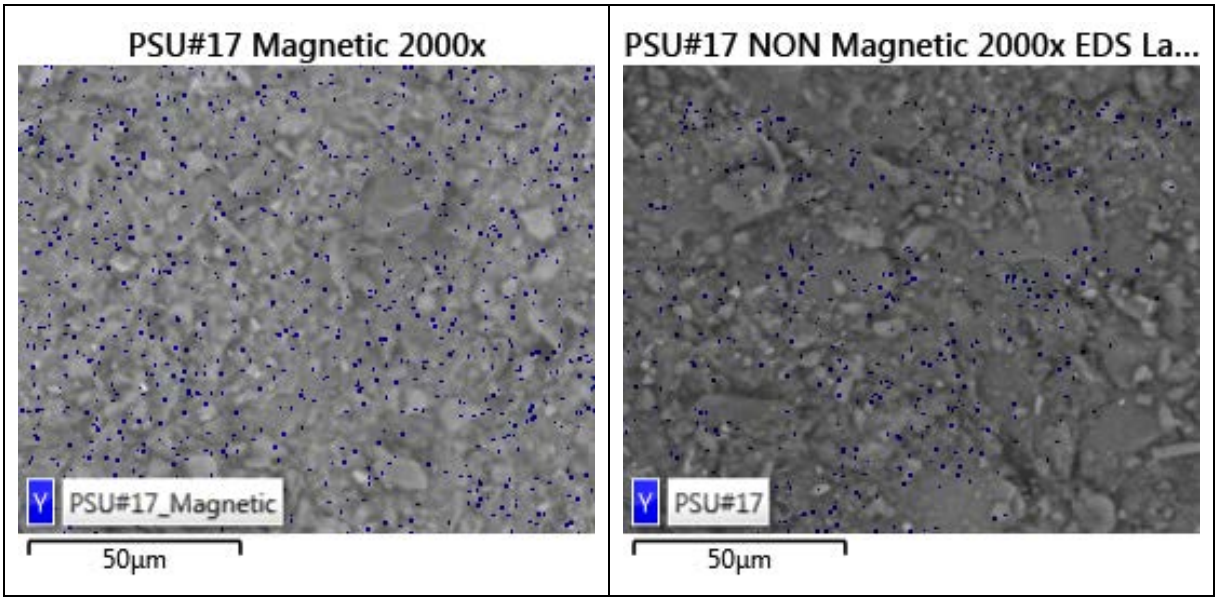
Table 19: Proximate analysis of magnetic and electrostatically separated samples. PSU#16 yielded very little magnetic sample so proximate analysis could not be conducted. (ND: Not determined.)

Name	Volatile Dry Wt.%	Ash Dry Wt. %	Fixed Carbon Dry Wt. %
PSU#16_Middlings	23.23	52	24.77
PSU#16_Insulating	17.25	55.16	27.59
PSU#16_Conducting	14.8	79.43	5.77
PSU#16 Non-mag	11.83	74.65	13.52
PSU#16 Magnetic (low sample)	ND	ND	ND
PSU#10_Middlings	17.28	76.14	6.58
PSU#10_Insulating	13.05	83.92	3.03
PSU#10_Conducting	12.91	79.91	7.17
PSU#10 Non-magnetic	8.68	81.18	10.14
PSU#10 Magnetic	14.65	85.78	0.00
PSU#8_Middlings	15.8	65.62	18.58
PSU#8_Insulating	18	74.12	7.88
PSU#8_Conducting	13.37	61.97	24.66
PSU#8 Non-magnetic	11.2	67.16	21.64
PSU#8 Magnetic	23.84	71.86	4.3

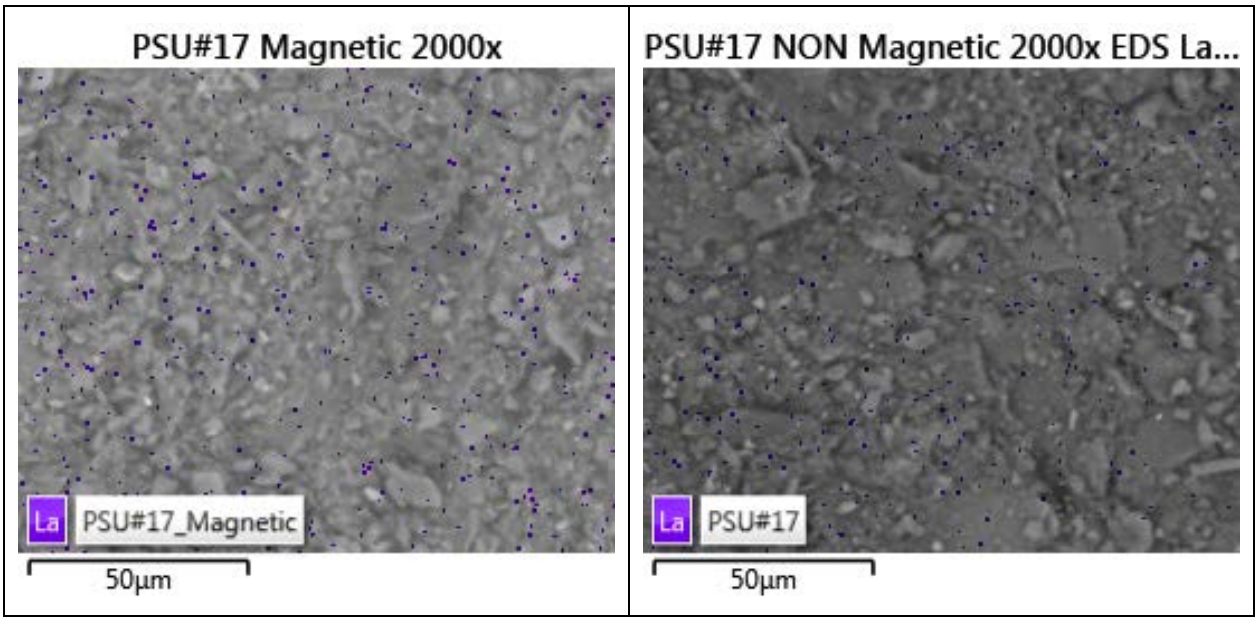
Electron Micrograph



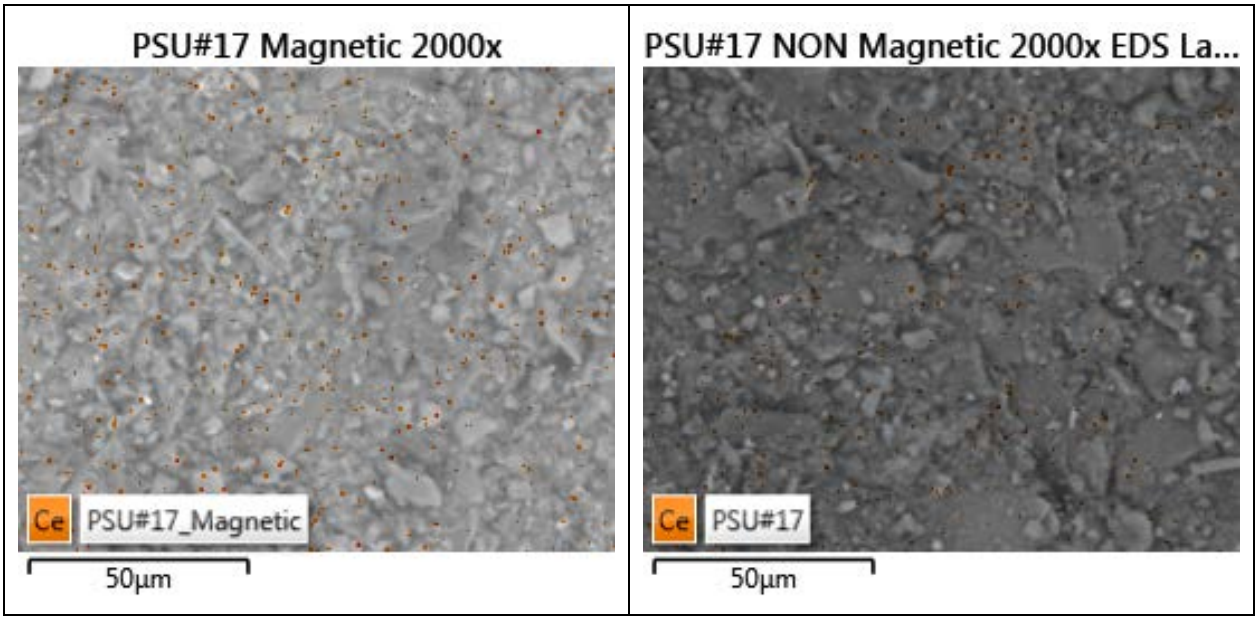
Yttrium



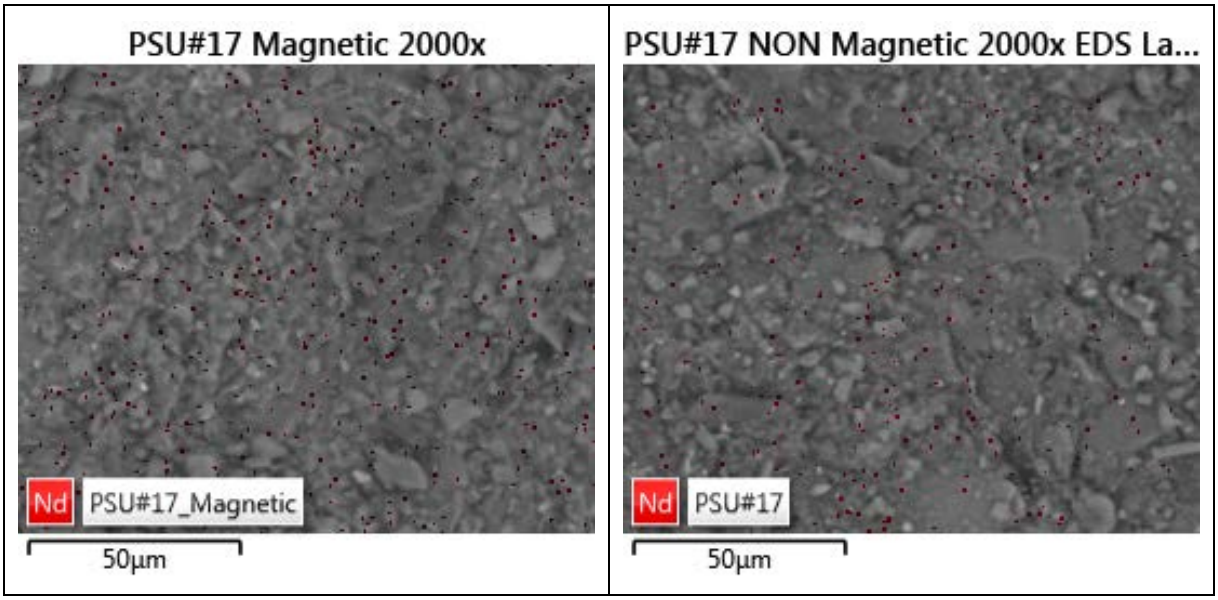
Lanthanum



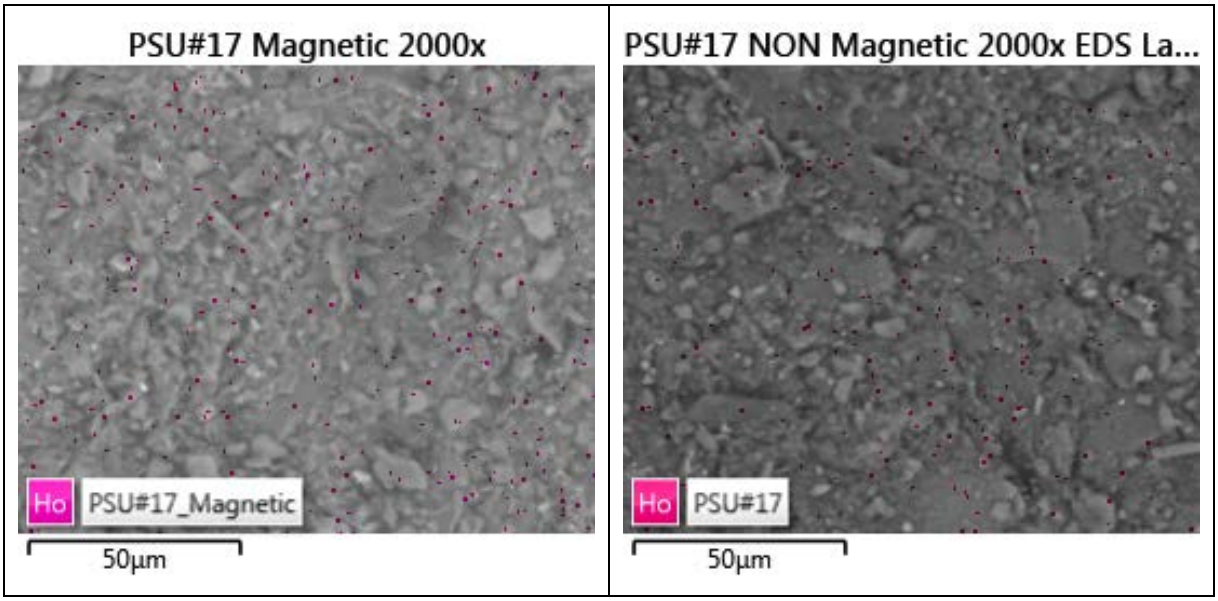
Cerium



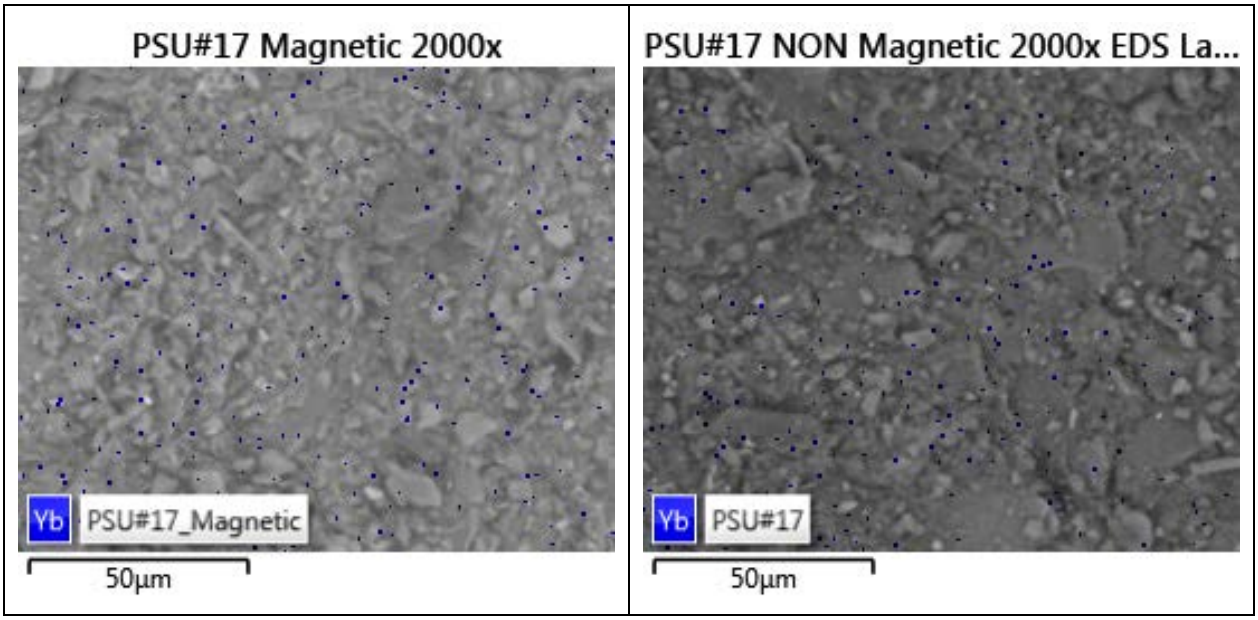
Neodymium



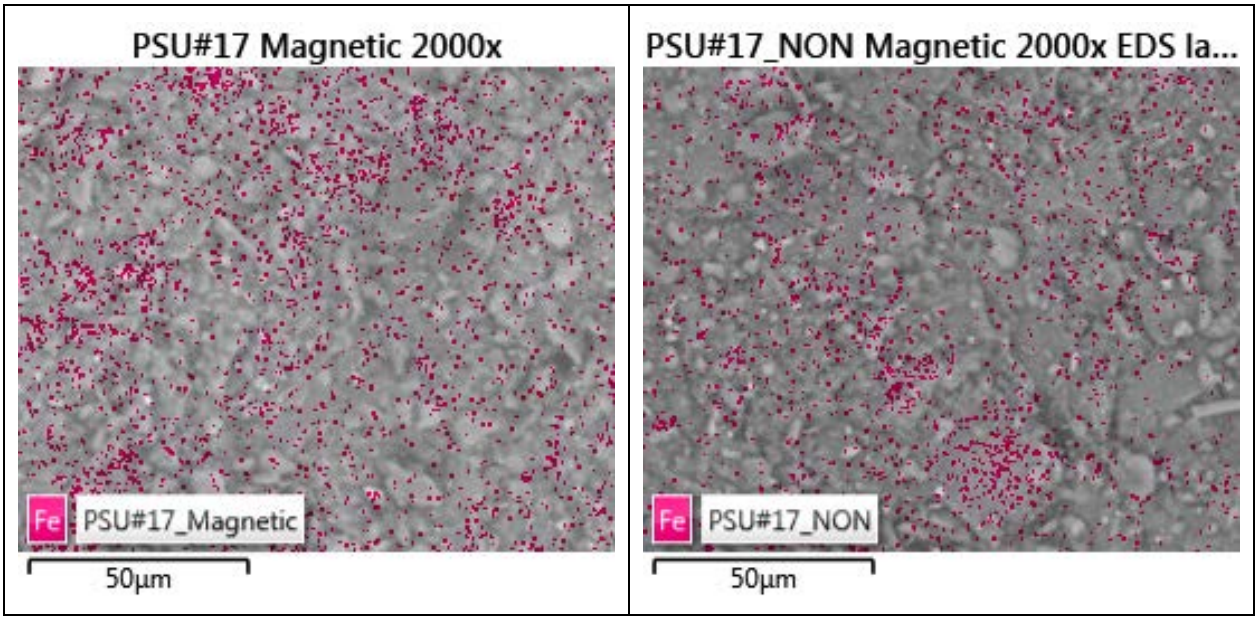
Holmium



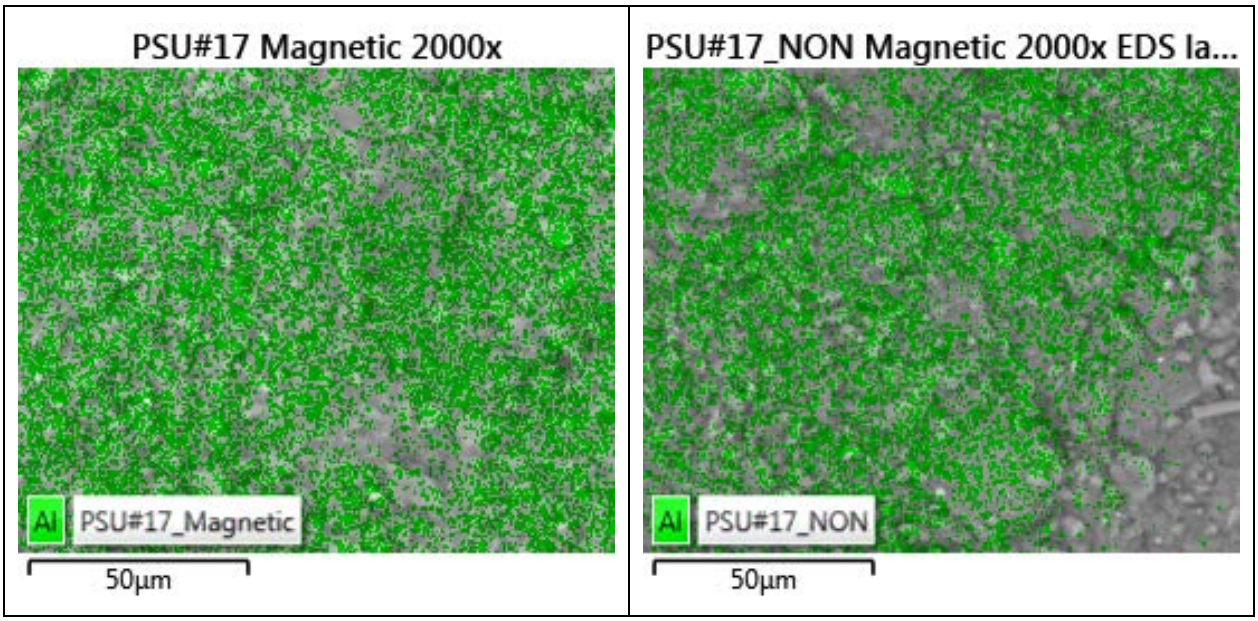
Ytterbium



Iron



Aluminum



Silicon

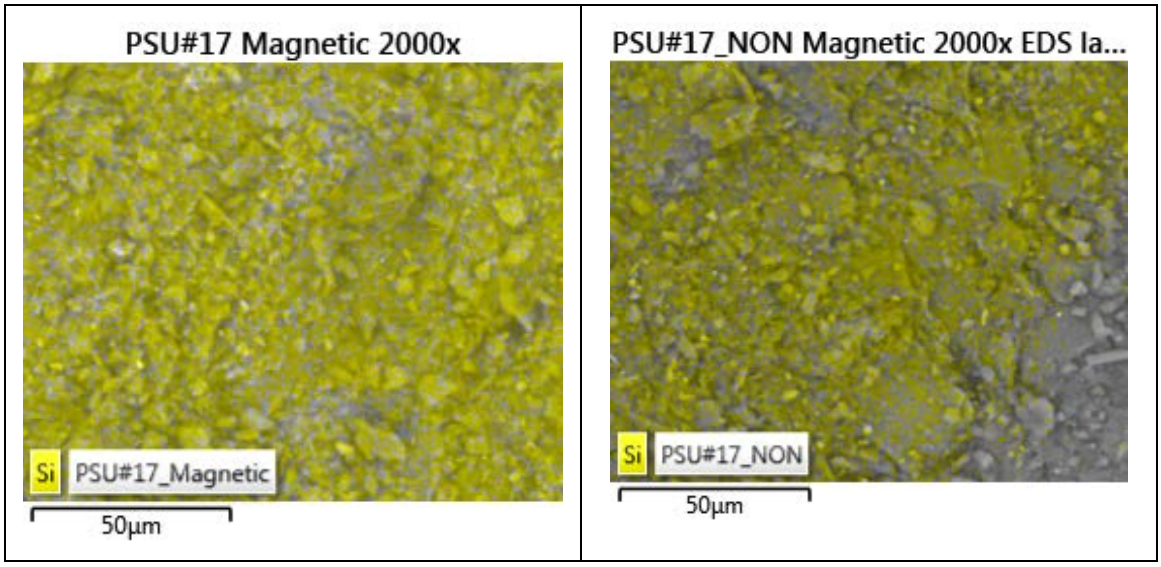


Table 20: Semi-quantitative elemental concentration data from SEM-EDS (Magnetic vs non-magnetic samples). At the surface level, there appears to be no major difference in REE concentrations between the magnetically separated fractions.

Element	PSU#17_Magnetic 2000x Wt. %.%	PSU#17_Non-Magnetic 2000x Wt. %.%
O	55.59	52.8
Mg	1.37	1.29
Al	12.73	13.5
Si	21.72	23.14
K	2.93	3.45
Ti	0.52	0.66
Fe	4.86	4.8
Co	0.01	0
Y	0	0.1
La	0	0
Ce	0	0
Nd	0.09	0
Ho	0.18	0
Yb	0	0.27
Total	100	100
Total REE (on a carbon free basis)	0.27	0.37

Appendix IV: Electrostatic Separations – SEM-EDS Data

High tension electrostatic separations were performed on four different samples.

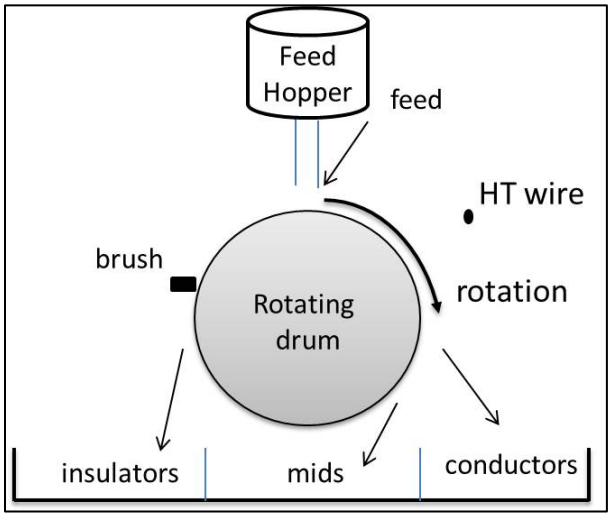
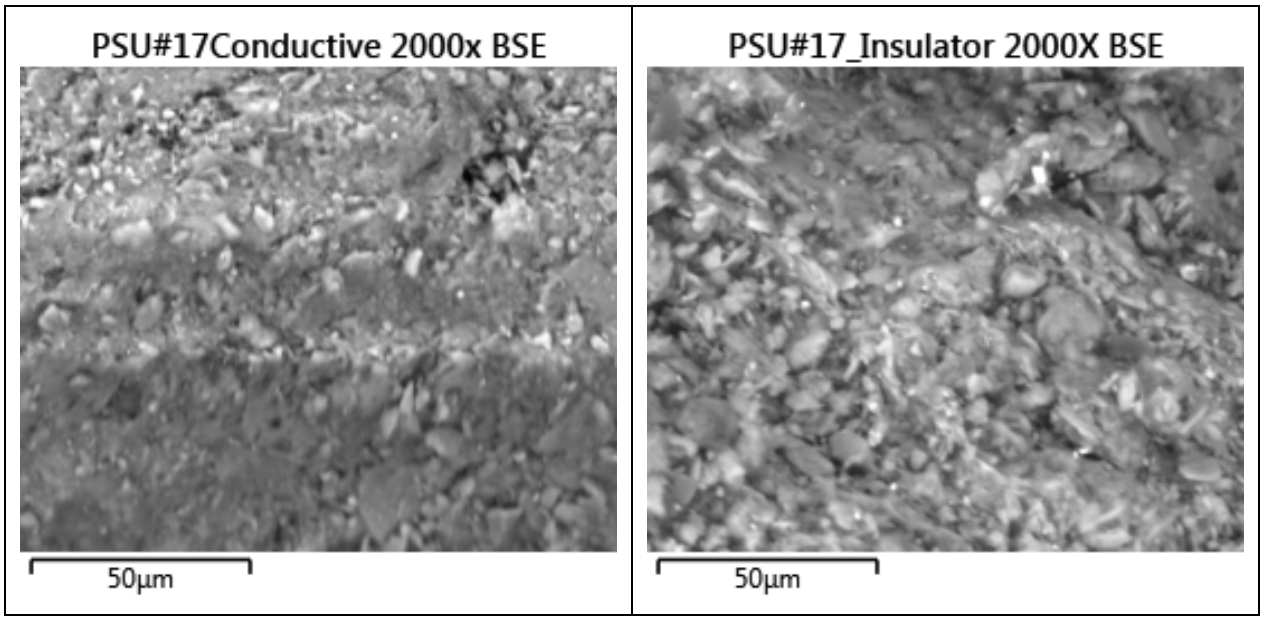
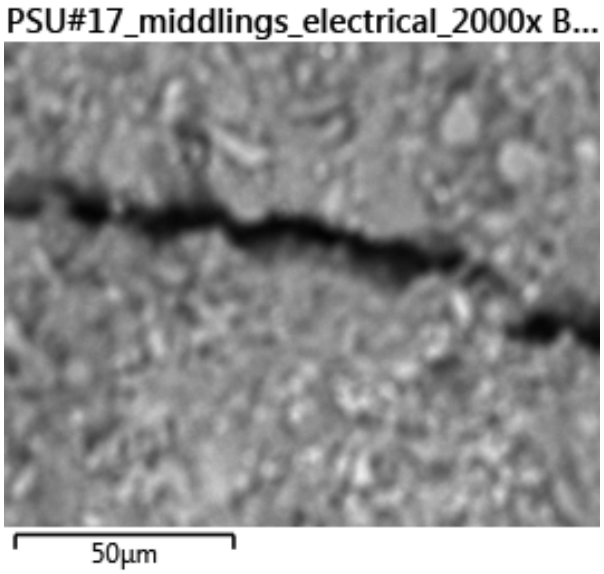


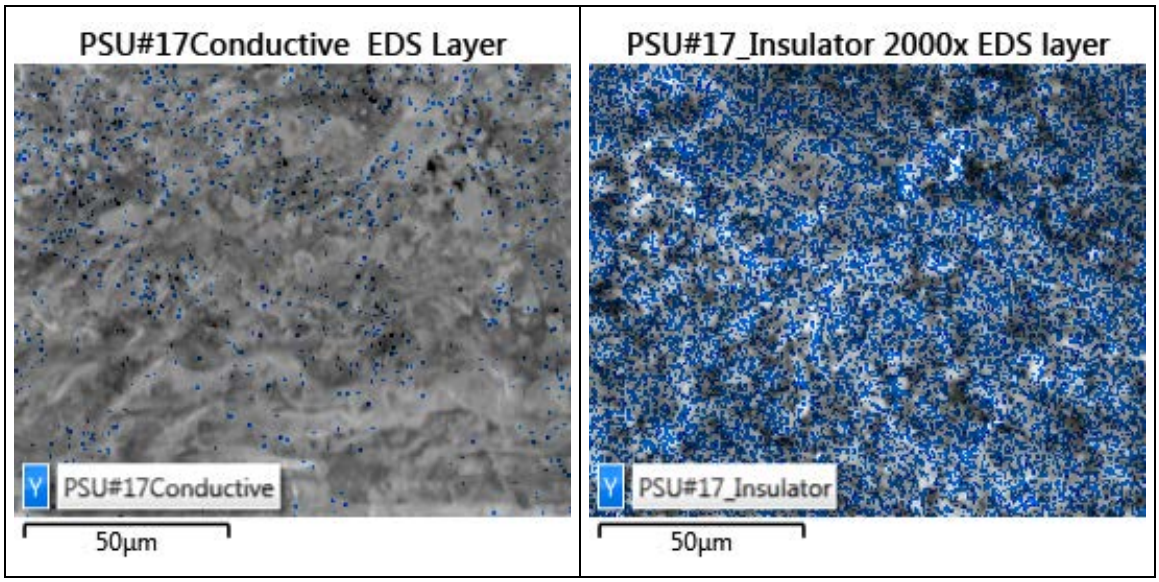
Figure 43: Schematic of an Electrostatic separator. Feed particles are fed on to a rotating drum and a large DC voltage is applied at the point of takeoff from the drum. Conducting particles follow the momentum while insulating particles are held closer to the drum due to the charge they acquire.

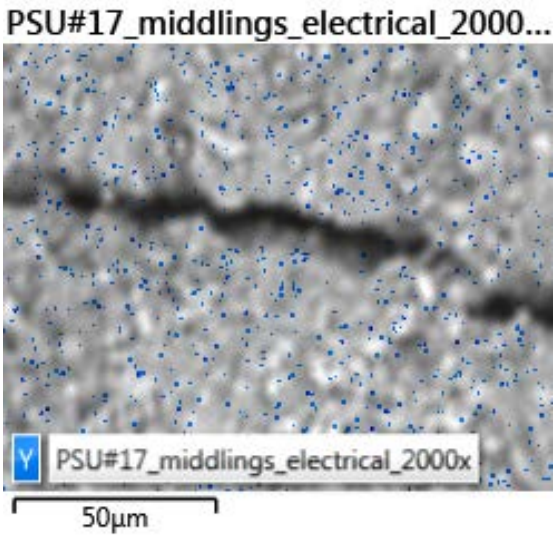
Electron Micrograph



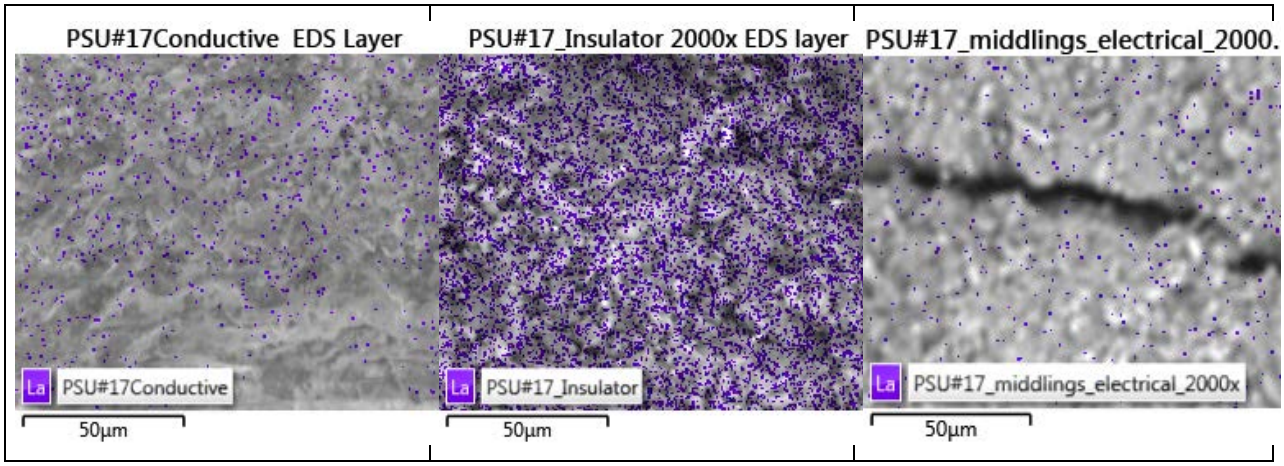

PSU#17_middlings_electrical_2000x B...
50µm

Yttrium

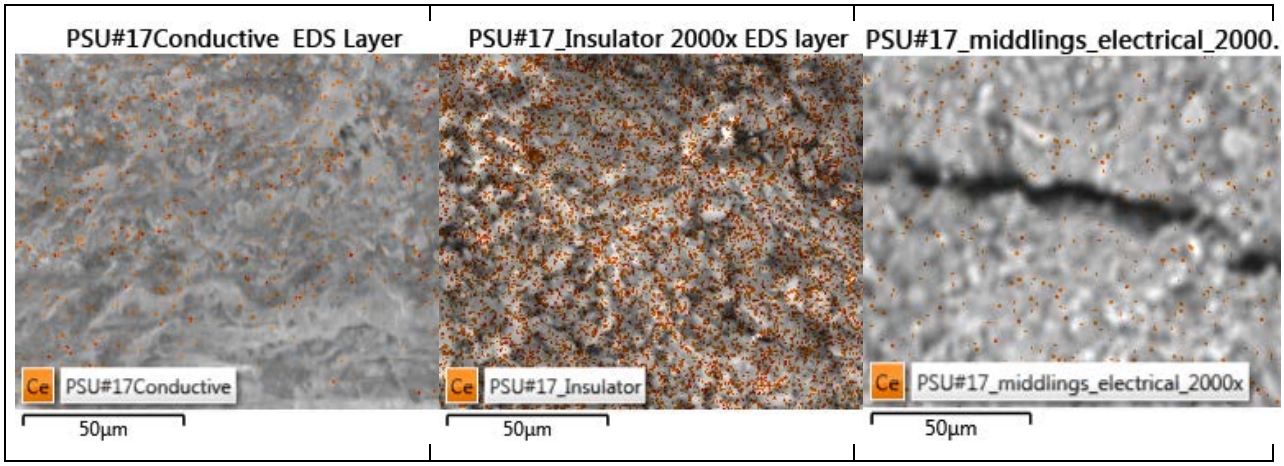

PSU#17Conductive EDS Layer
Y
PSU#17Conductive
50µm
PSU#17_Insulator 2000x EDS layer
Y
PSU#17_Insulator
50µm



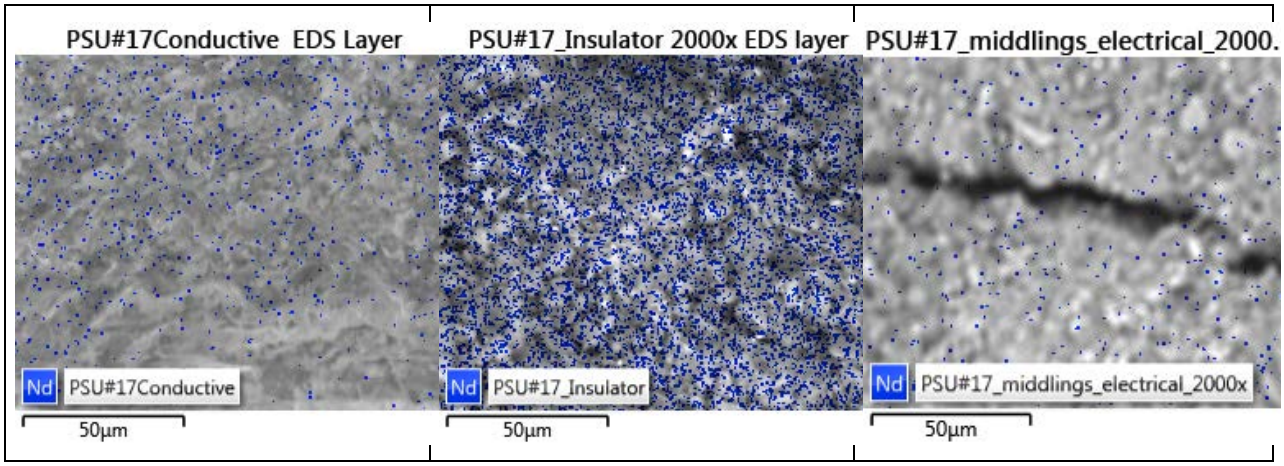
Lanthanum



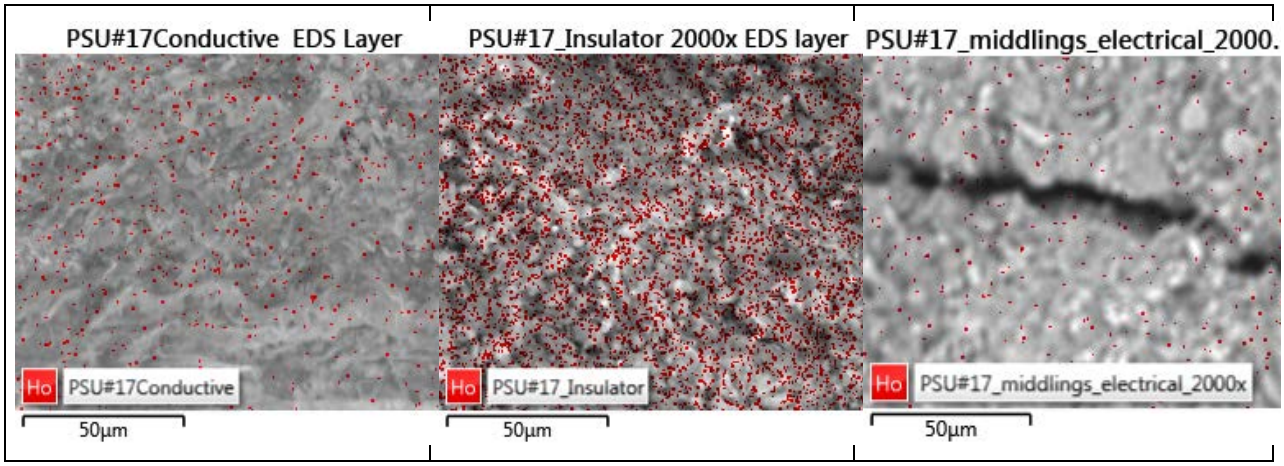
Cerium



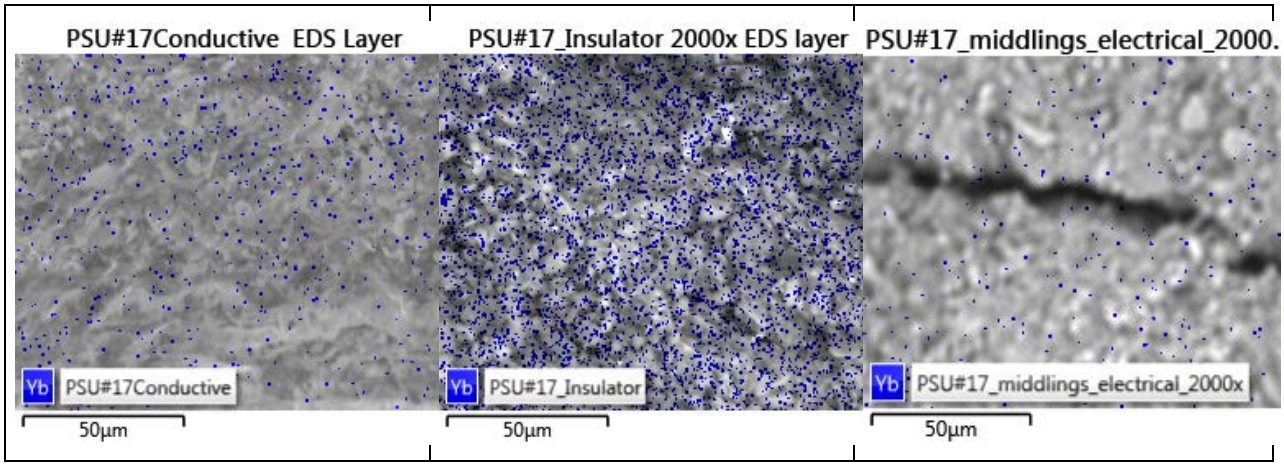
Neodymium



Holmium

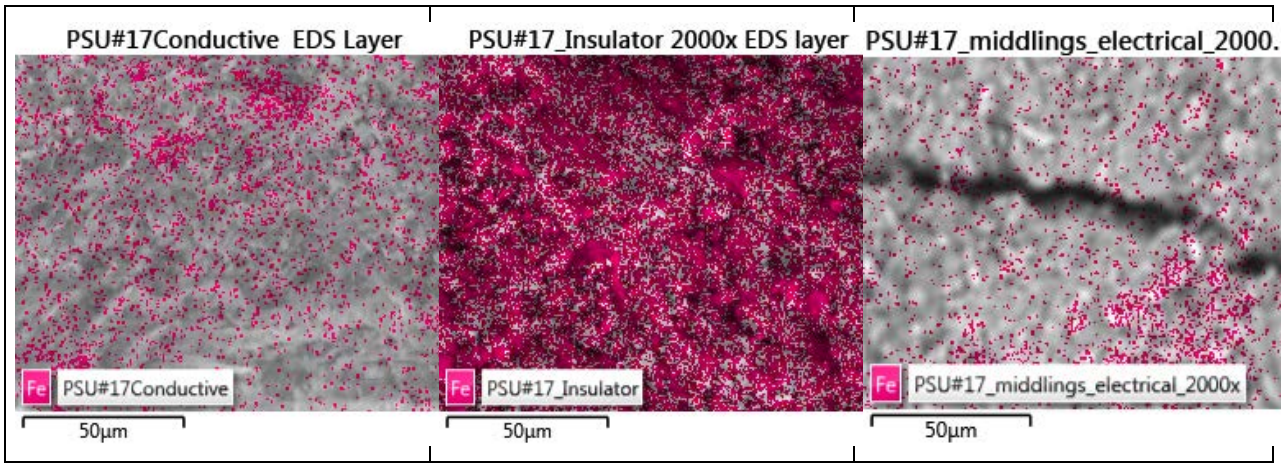


Ytterbium

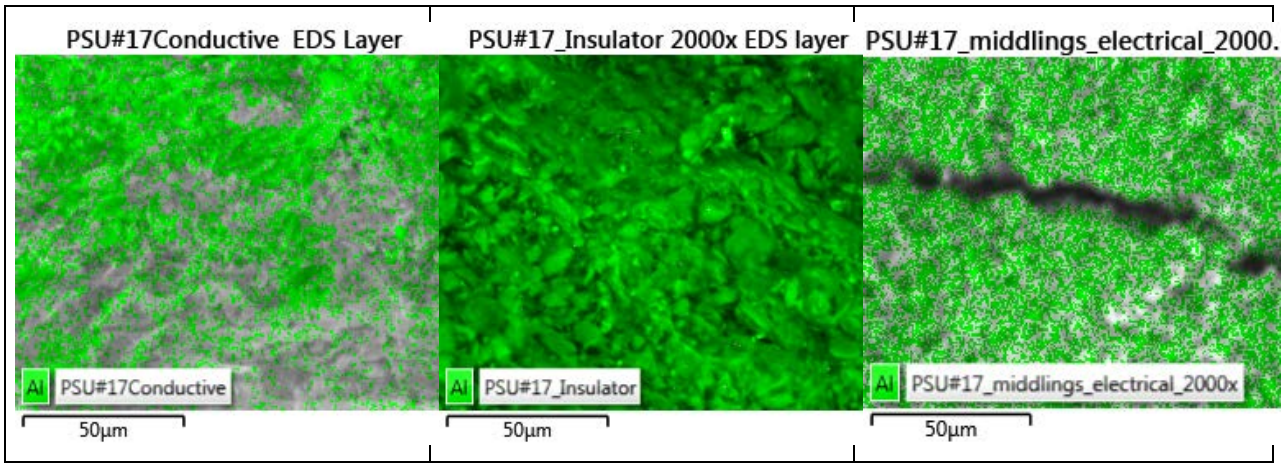


Iron

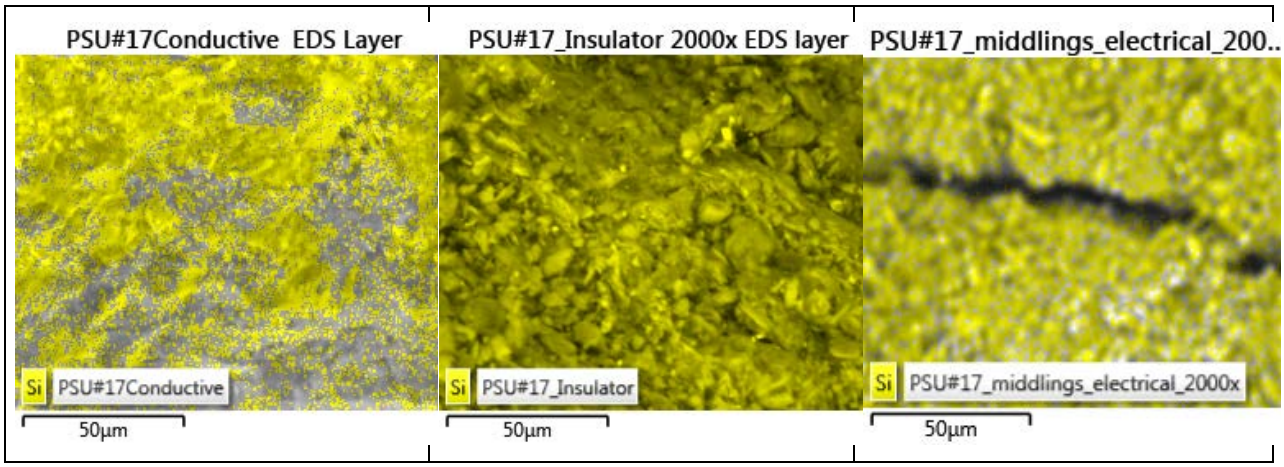
(Iron in the insulators is present as oxidized form as part of the clay)



Aluminum



Silicon



Magnesium

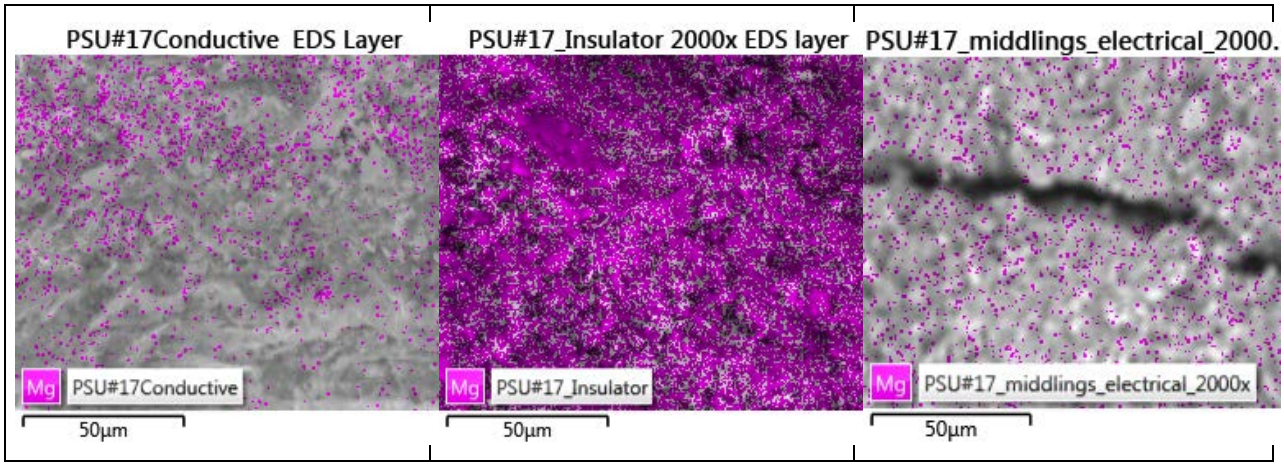
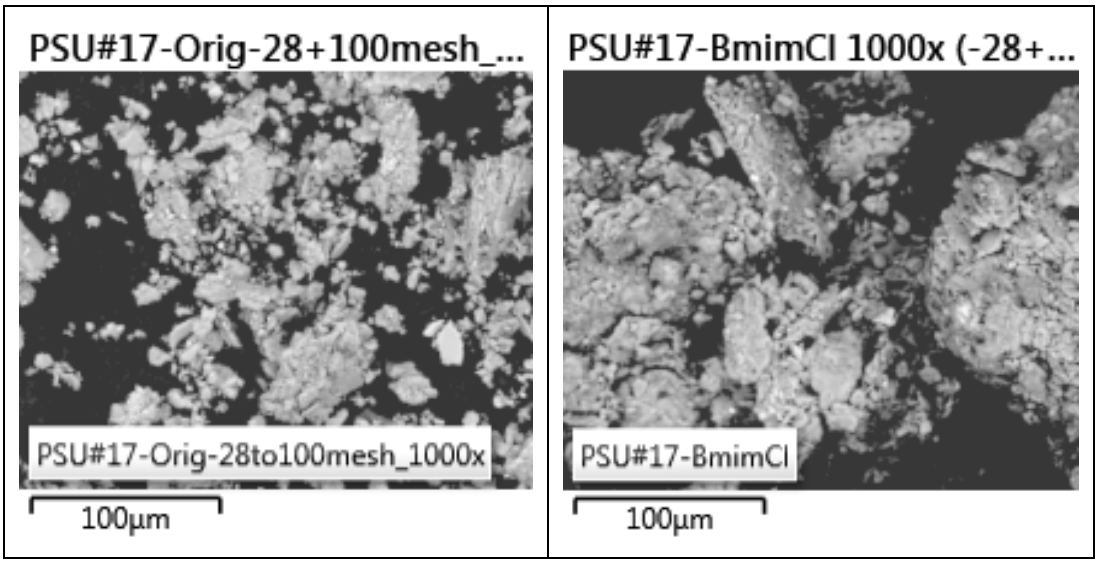


Table 21: Semi-quantitative data from Elemental analysis of certain particles from electrostatic separation.

PSU#17 Conducting 2000x	Wt. %%		PSU#17 Insulating 2000x	Wt. %%		PSU#17 Middling 2000x	Wt. %%
O	52.13		O	58.42		O	56.46
Mg	1.11		Mg	1.27		Mg	1.11
Al	12.9		Al	11.68		Al	12.11
Si	22.98		Si	21.16		Si	21.27
K	3.44		K	2.86		K	2.74
Ca	0		Ca	0.18		Ca	0.22
Ti	0.9		Ti	0.47		Ti	0.42
Mn	0		Mn	0.07		Mn	0
Fe	5.9		Fe	3.79		Fe	5.42
Y	0		Y	0.09		Y	0.25
La	0.25		La	0		La	0
Ce	0.35		Ce	0		Ce	0
Nd	0		Nd	0		Nd	0
Ho	0		Ho	0		Ho	0
Yb	0.04		Yb	0.01		Yb	0
Total	100		Total	100		Total	100
Total REE*	0.64		Total REE	0.01		Total REE (on a no carbon basis)	0

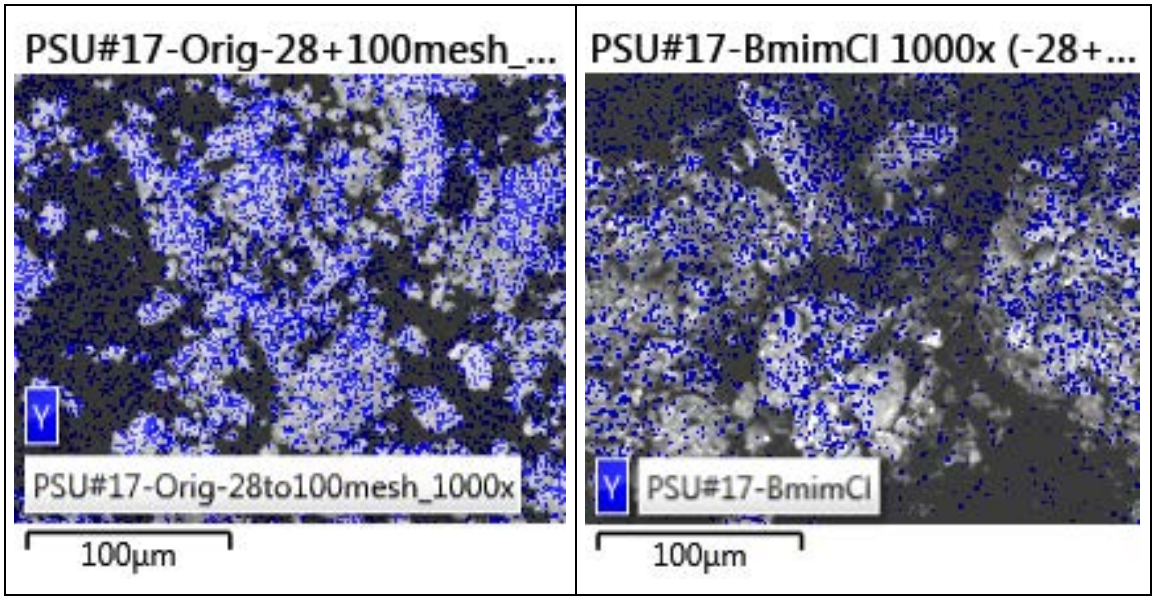
Appendix V: Ionic Liquid Treated Samples – EDS Data

Electron Micrograph

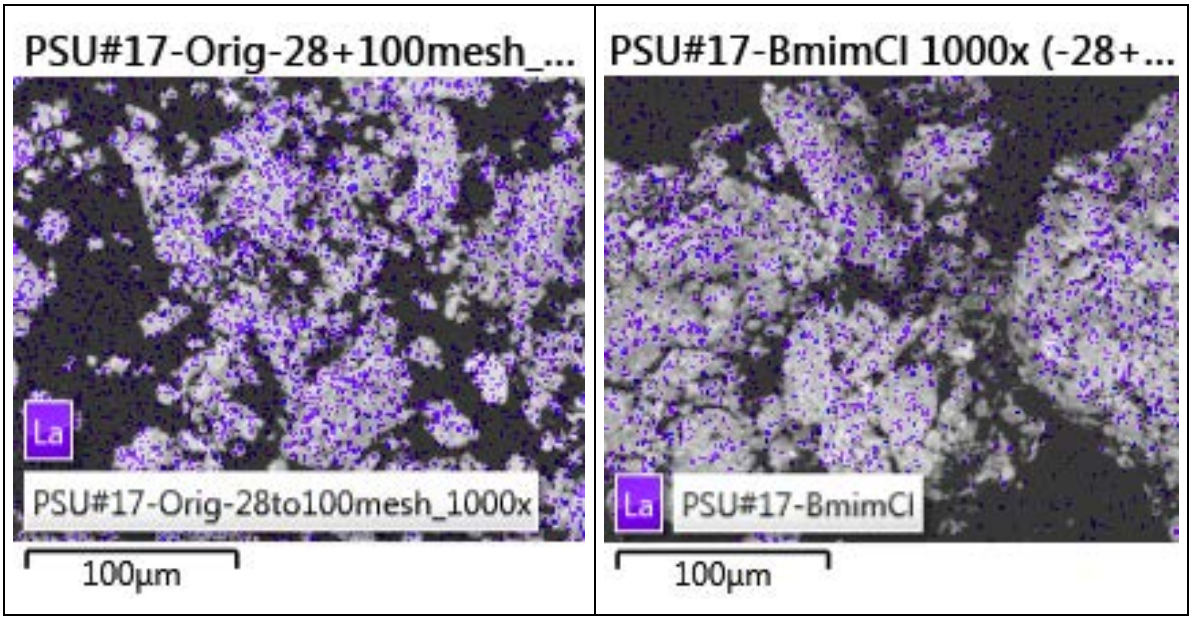


PSU#17 Roof Rock and BmimCl Treated Sample

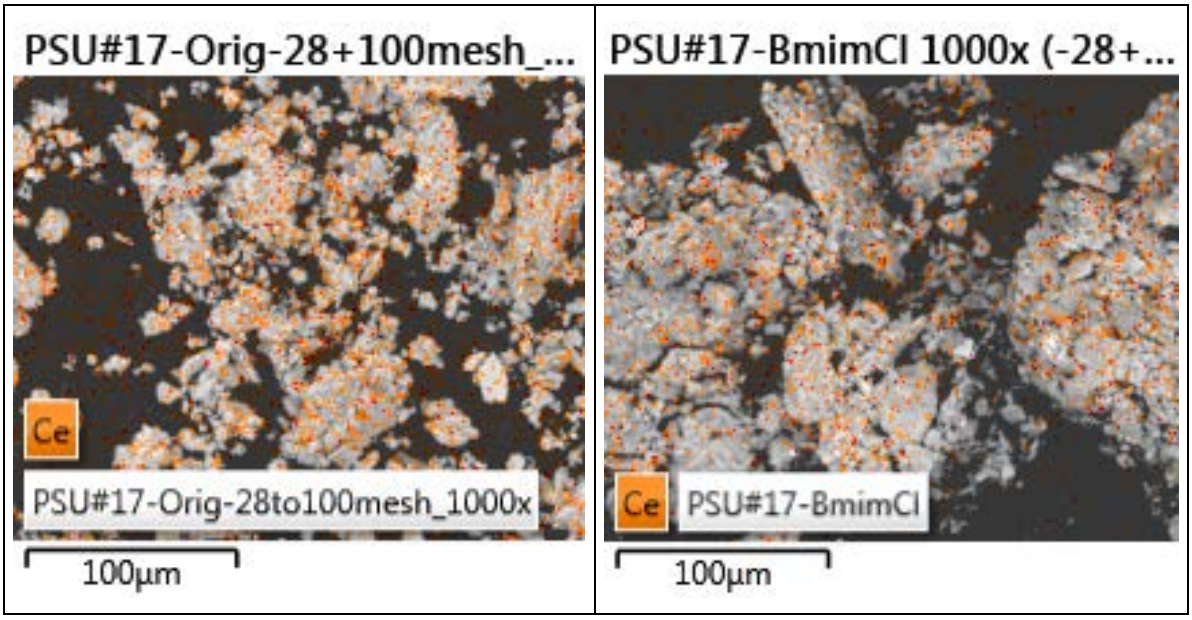
Yttrium



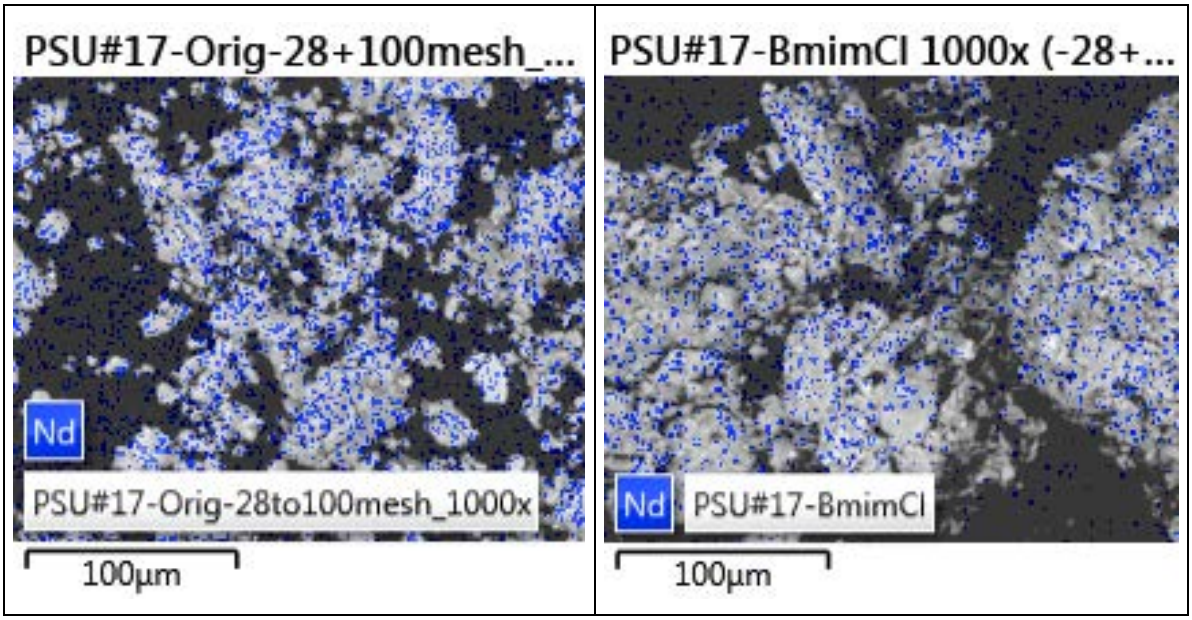
Lanthanum



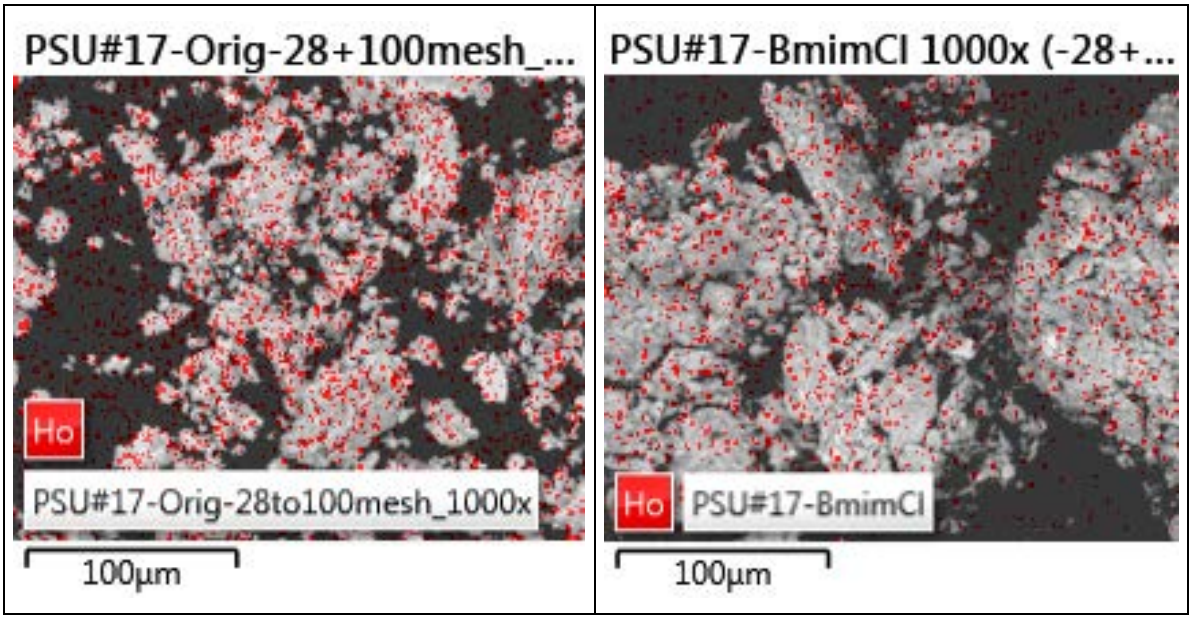
Cerium



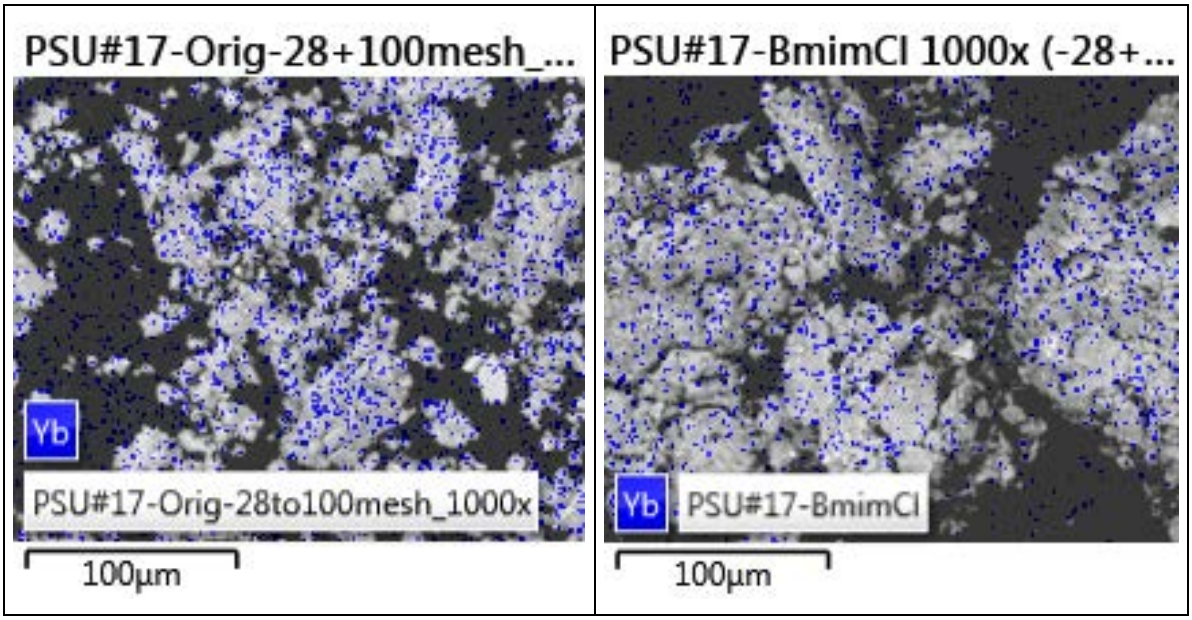
Neodymium



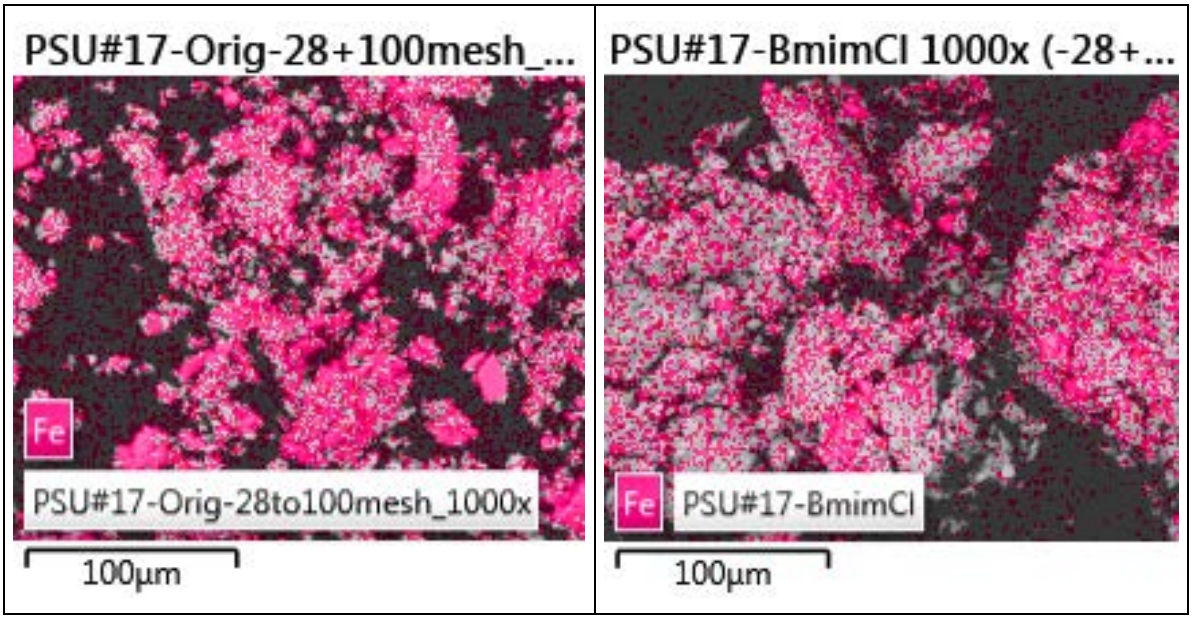
Holmium



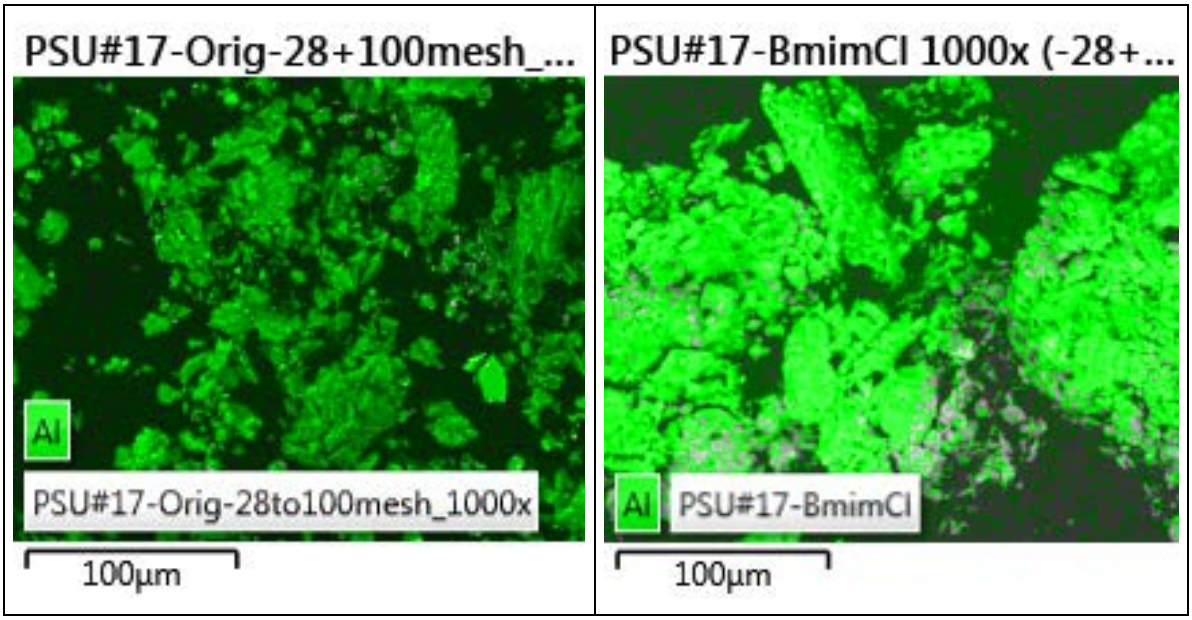
Ytterbium



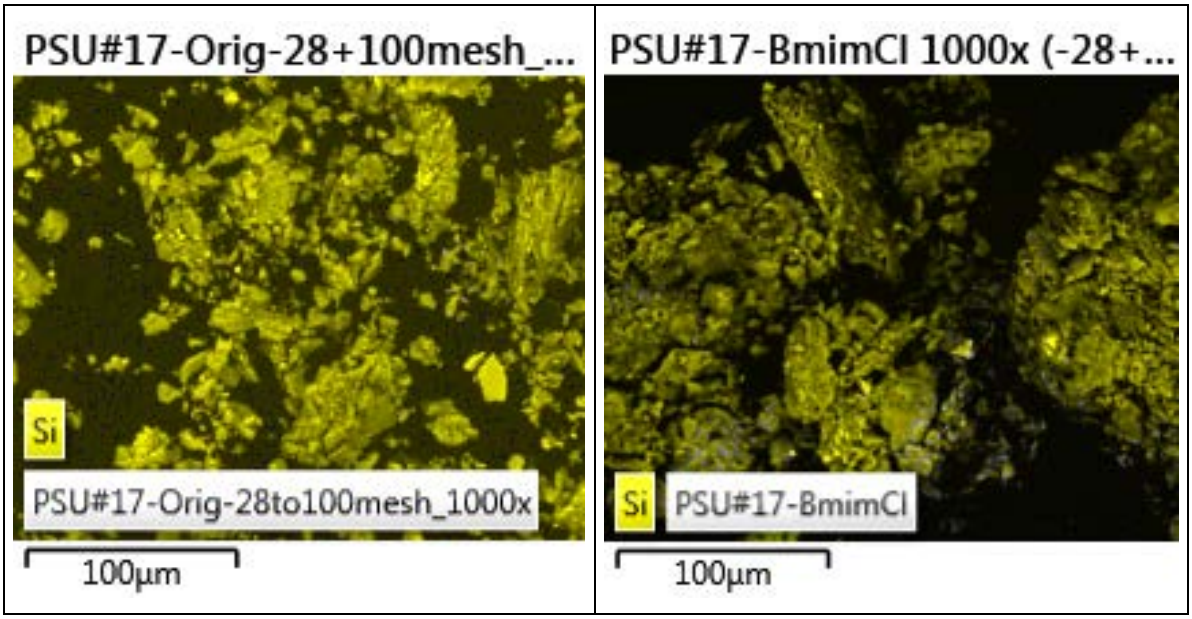
Iron



Aluminum



Silicon



Magnesium

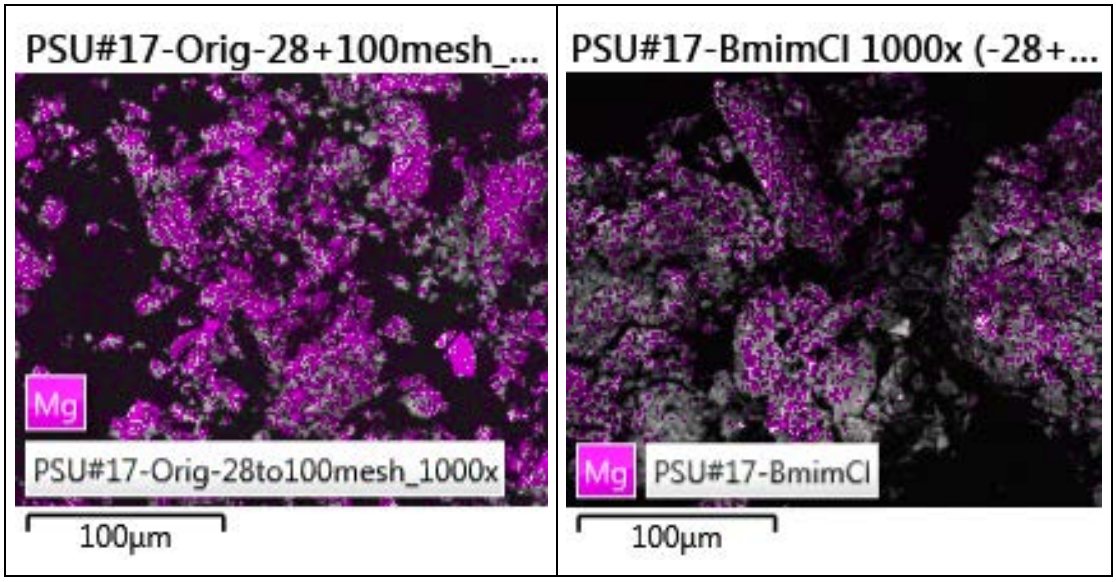


Table 22: Comparison of elements from the EDS spectrum between untreated and BmimCl treated samples. The surface concentration of REEs is observed to be an order of magnitude higher on the treated samples.

PSU#17-Untreated (-28+100 mesh)	Wt. %%	PSU#17 BmimCl	Wt. %%
O	54.07	O	54.45
Mg	2.29	Mg	1.12
Al	11.9	Al	0.84
Si	17.61	Si	1.49
P	0.06	P	8.38
S	0.04	S	0.00
Cl	0.02	Cl	0.41
K	2.08	K	0.08
Ca	0.13	Ca	17.36
Ti	0.39	Ti	0.39
Mn	0.44	Mn	0.46
Fe	10.7	Fe	13.61
Y	0.01	Y	0
La	0	La	0.37
Ce	0	Ce	0.03
Nd	0.08	Nd	0
Eu	0.19	Eu	0.49
Ho	0.01	Ho	0
Yb	0	Yb	0.52
TREE (mg/Kg)	290	TREE	1410

* * *