A Pollution Prevention and Economically Viable Technology for Separation of Rare Earth Elements (REEs) from Powder River Basin Coal Ashes (DE-FE0027069)

PI and Co-PIs: Maohong Fan1[1,*] , Hanjing Tian[2], Eric Williams[3], Gabrielle Gaustad[3], Hertanto Adidharma[1], Maciej Radosz[1]

Other team members: Zaixing Huang[1], Kai Li[1], Kaiying Wang[1], ChooiKim Lau[1], Yan Luo[2], Saptarshi Das[3]

1- University of Wyoming; 2-West Virginia University, and 3-Rochester Institute of Technology

*** Corresponding PI: mfan@uwyo.edu, (307) 766 5633**

UNIVERSITY OF WYOMING

Main goals

- Identify and sample developable amount of coal ashes that have at least 300 ppm REEs as well as characterize the coal ashes
- Successfully develop robust processes to produce "green" solid containing at least 2.0 weight % total REE content on an elemental basis and measured on a dry basis from PRB coal ashes with high overall recovery efficiency of RREs in coal ashes and low pollutant emission
- Reduce REEs recovery energy consumption compared to current commercialized REE recovery technologies
- Decrease the overall coal ash based REEs recovery cost compared to current commercialized REE recovery technologies

Experiments

Raw Materials – Safe and inexpensive as well as widely available

- Raw materials containing REEs
  - Solids (which can contain low than 300 ppm REEs)
    - **Coal ashes – targets**
    - Overburdens or other solids containing REEs
    - Sludge from various processes
    - Ores
  - Liquids
    - Waste water from coal mining and coal-based energy industries
    - Any other produced and waste waters containing REEs
- Extracting agents
  - Wastes or low-cost materials

Extraction Operation - *Green and Short as well as Simple*

- Low **or** zero **<u>net</u>** addition of cations and anions to the close REEs extraction system
- Water from REEs extraction
  - Containing almost zero external species
    - Reused internally for multicycle REEs extraction
- Zero air pollutant emission
- Zero addition of anions and cations to the after-REEs-extraction coal ashes

Extraction Operation – *Green and Simple as well as Multifunctional*

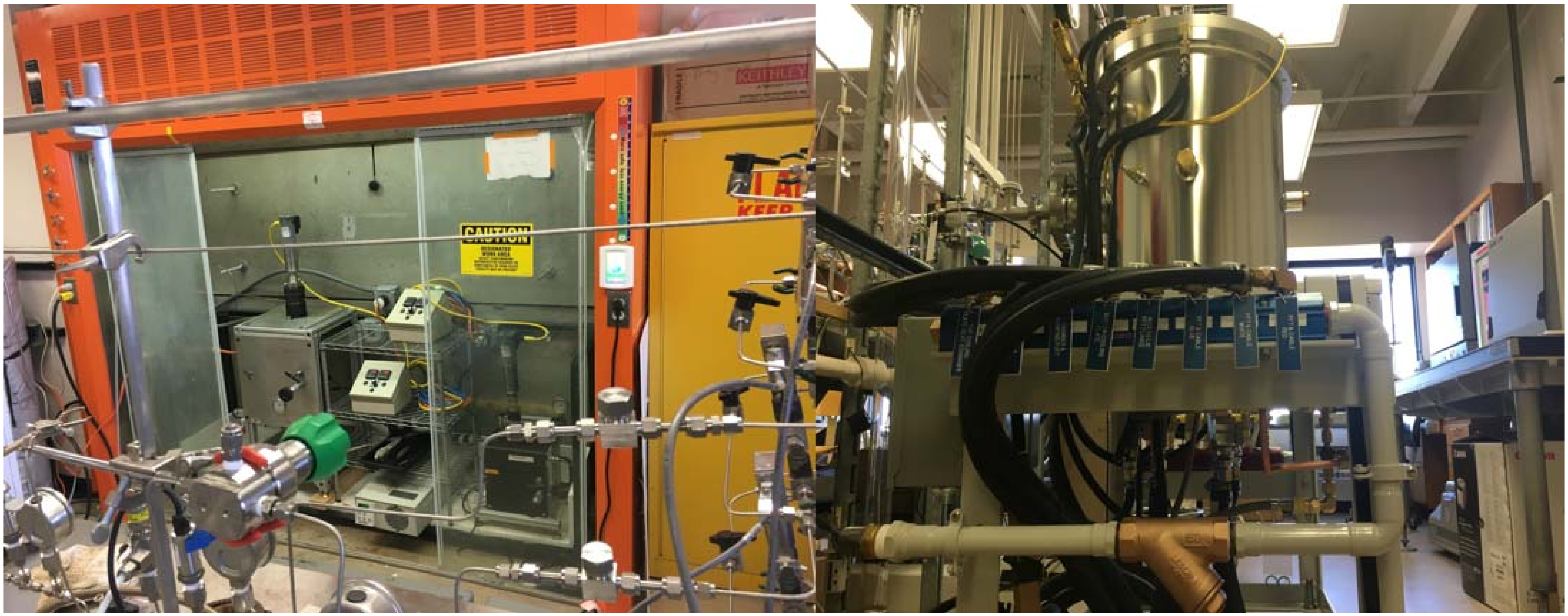
- Operation steps are designed to
  - Be short
  - Be multifunctional
  - Have high selectivity for collecting desired species
  - Achieve maximum atom economy
    - Based on the integration of
      - REEs chemistry
      - Theories for separations of homogeneous and heterogeneous mixtures
      - Aqueous chemistry
      - Solid-state chemistry
      - Environmental chemistry
- Inexpensive and safe materials are used
- Generation of at least two value-added products in addition to the major desired product, REEs-containing solid.

Major Results Achieved for the Project

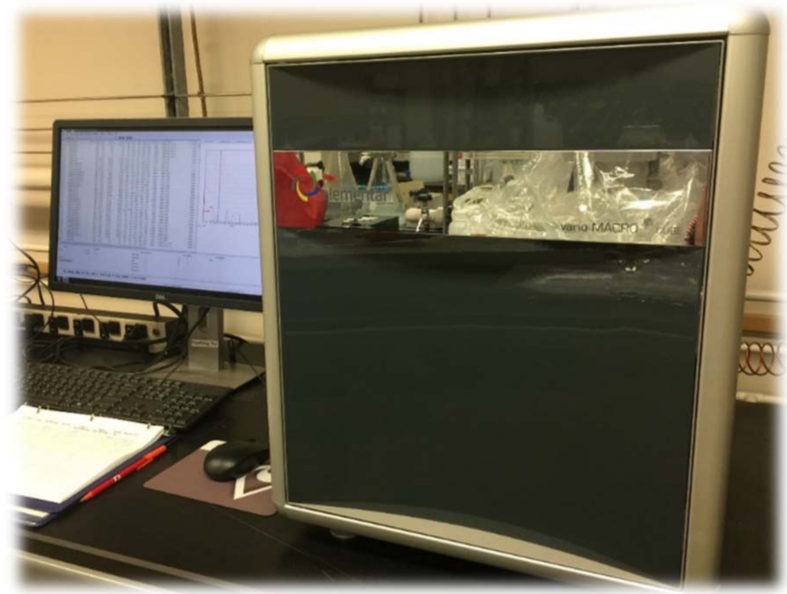
- **Extraction process – Green**
  - Operation steps are designed to
    - Be short
    - Be multifunctional
    - Have high selectivity for collecting desired species
    - Achieve maximum atom economy
      - Based on the integration of
        - REEs chemistry
        - Theories for separations of homogeneous and heterogeneous mixtures
        - Aqueous chemistry
        - Solid-state chemistry
        - Environmental chemistry
  - Less expensive materials are used
  - Safer materials are used
  - Generation of at least two value-added products in addition to the major desired product, REEs-containing solid.

REEs Extraction Lab

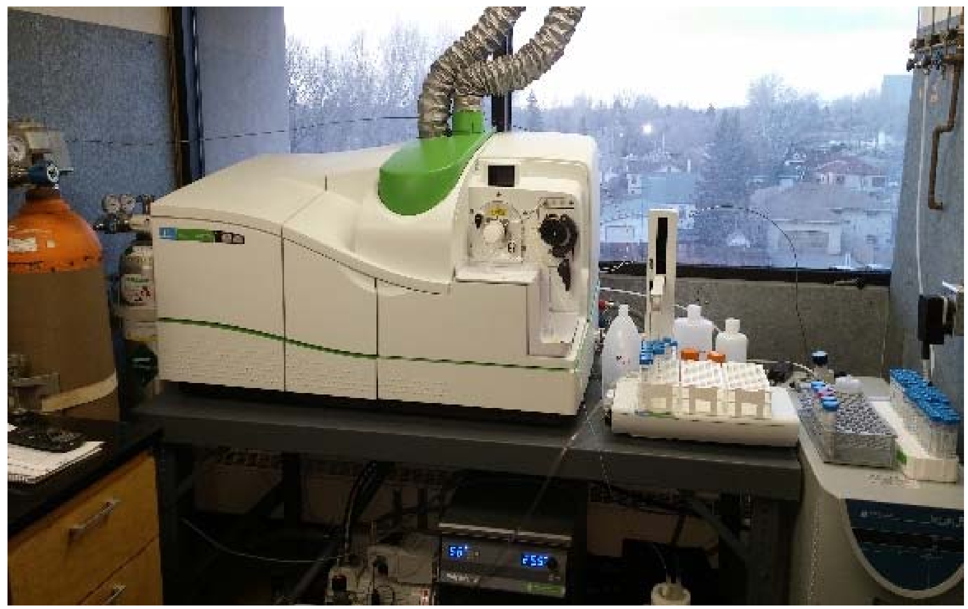
Extraction Apparatus



Grinding and C-H-N-S Analysis Equipment



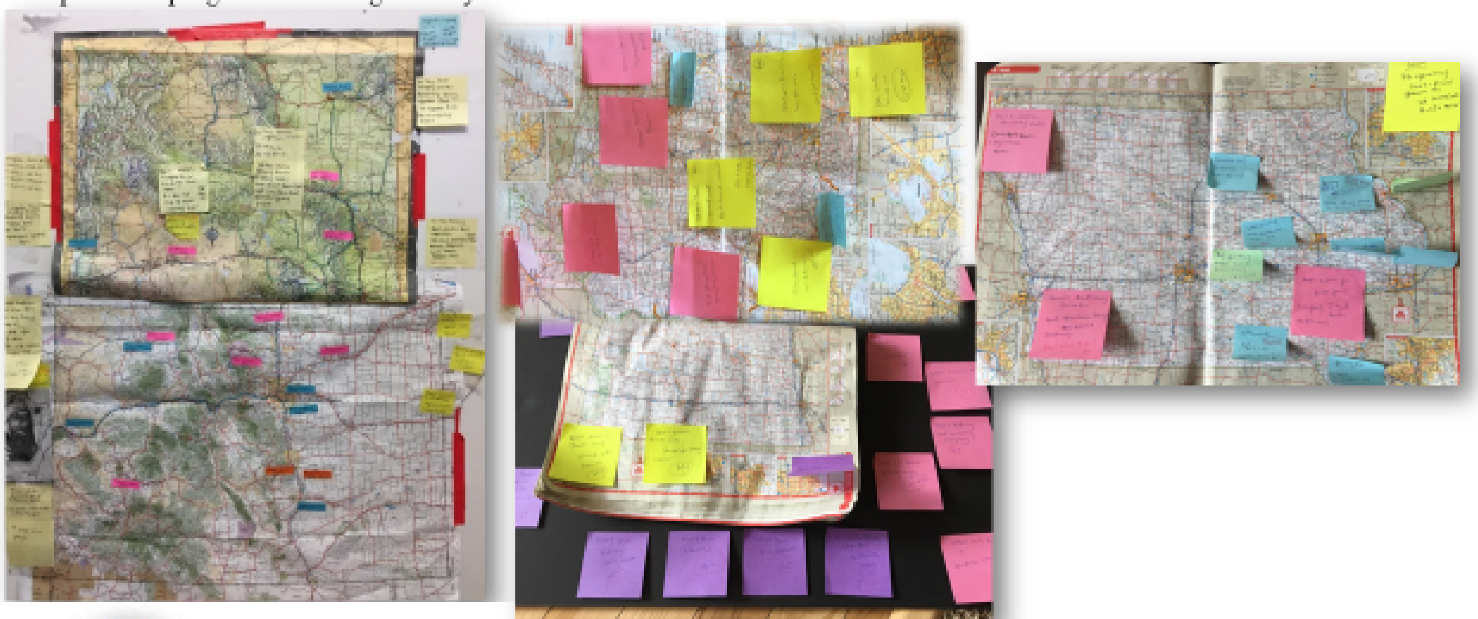
BET and REEs Analysis Equipment



Results

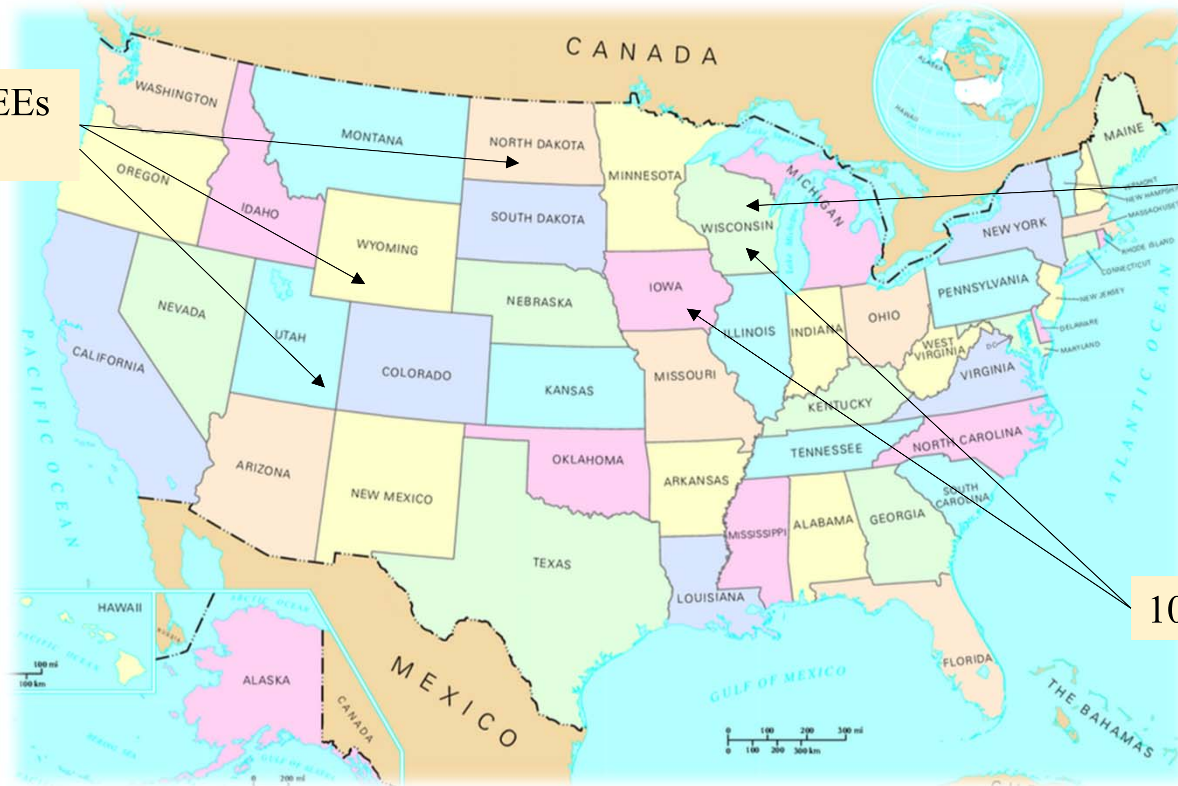
>300 ppm REEs Containing Fly Ashes

Pinpoint the progress of finding coal fly ashes



UNIVERSITY of WYOMING

>300 ppm REEs Containing Fly Ashes



33 M tons with REEs > 300 ppm

15 M tons with REEs > 300 ppm

100 M tons to be tested

Some Fly Ashes Collected from Power Plants

>300 ppm REEs Containing Fly Ashes

- Number of power plants contacted: 43
- Tons of fly ashes available: ~150 M tons
- Tons of fly ashes containing > 300 ppm REEs
  - Known: ~ 48 M tons in collected ~58 M tons
  - Unknown: ~ 100 M tons to be tested

Characteristics of Several Targeted Samples

Sample ID	C (%)	H (%)	N (%)	S (%)
CH	0.88	0.21	0.03	4.19
DJ	0.89	0.82	0.06	5.58
FS	1.8	0.31	0.03	3.41
JE	0.52	0.01	0.02	1.28
LR	0.26	0.25	0.02	0.91
WD	0.56	0.24	0.04	3.5

Characteristics of Several Targeted Samples

BET surface area

Sample ID	Surface area/$m^2 \cdot g^{-1}$
CH	1.734
DJ	13.743
FS	5.990
JE	0.076
LR	0.905
WD	19.320

Moisture and organic carbon

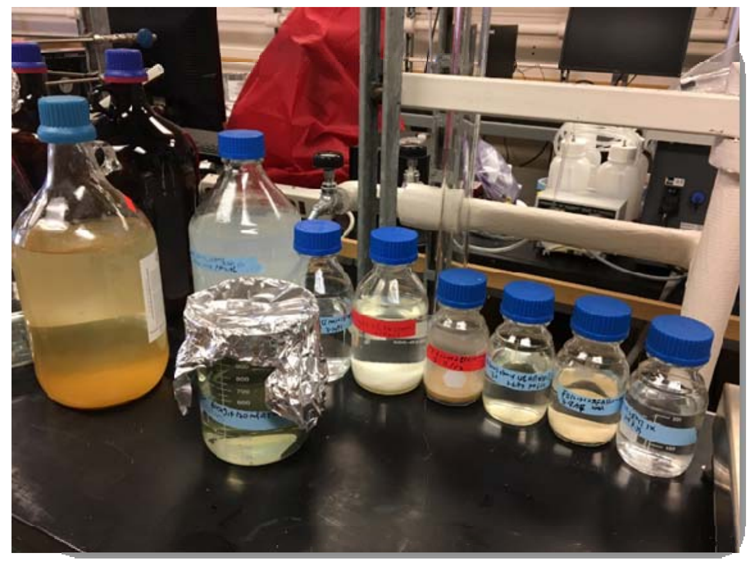
Sample ID	Moisture (%)	Organic carbon (%)
CH	0.41	1.91
DJ	6.54	4.26
FS	0.84	2.91
LR-1	0.37	0.61
LR-2	0.08	0.43
WD	1.23	3.08

REEs Concentrations in Several Fly Ashes (Dry Ash Basis)

DAB (dry ash basis)	CH (ppm)	DJ (ppm)	FS (ppm)	LR-1 (ppm)	LR-2 (ppm)	WD (ppm)
Ce	170.1	148.9	153.5	159.7	171.1	167.5
Dy	11.0	12.8	14.2	11.9	14.9	15.6
Er	7.0	7.4	8.3	7.4	9.0	8.9
Eu	3.6	4.7	5.3	3.8	5.8	5.4
Gd	14.4	16.5	22.4	15.2	22.4	23.6
Ho	2.2	2.5	2.8	2.4	2.9	3.0
La	90.7	79.5	77.6	86.9	89.0	87.0
Lu	1.2	1.1	1.2	1.2	1.3	1.2
Nd	101.9	96.0	102.6	98.5	109.3	111.1
Pr	23.5	18.1	23.7	22.6	24.8	25.4
Sm	15.1	16.9	23.1	15.4	23.8	24.0
Tb	1.9	2.2	2.5	2.0	2.5	2.7
Tm	1.1	1.1	1.2	1.1	1.3	1.2
Y	61.8	65.5	72.2	68.6	76.8	76.4
Yb	6.9	6.8	7.4	7.1	8.2	7.8
Total REEs (ppm)	512.4	480.2	517.8	503.6	563.1	561.0

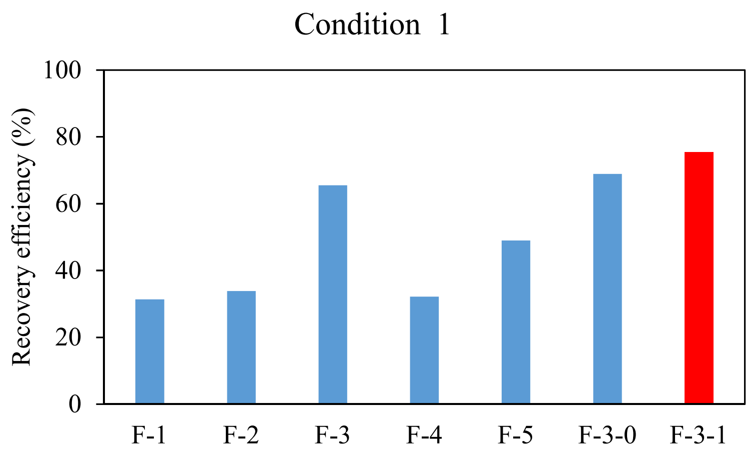
Piles of REEs Containing Samples from Leaching and Separation Processes for ICP-MS Analysis

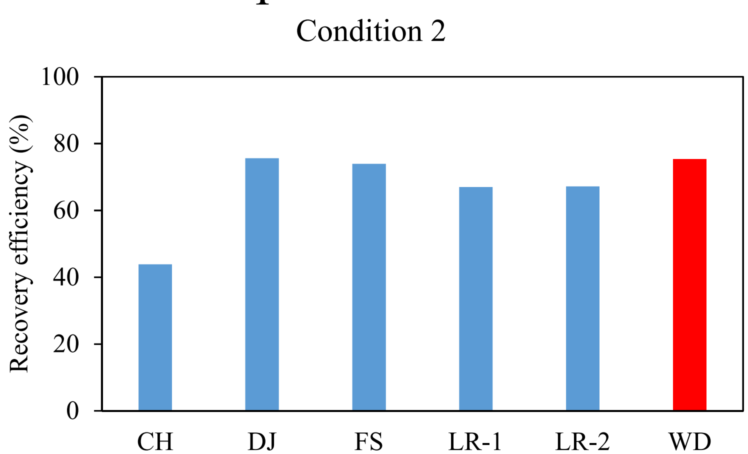
Piles of REEs Containing Samples from Leaching and Separation Processes for ICP-MS Analysis

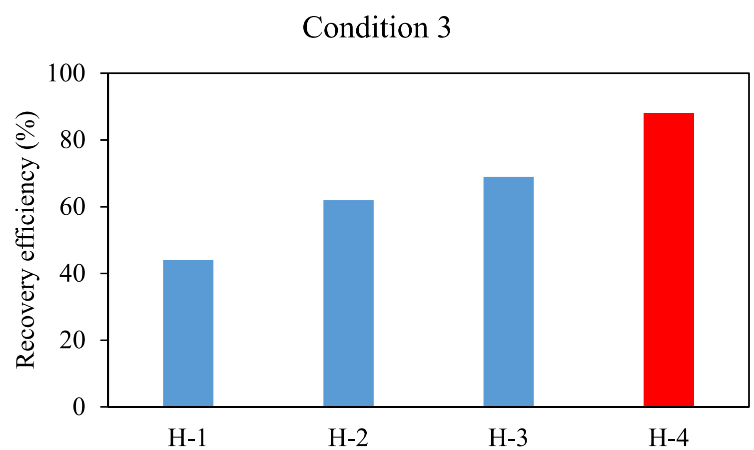


Recovery Efficiencies of REEs in Fly Ashes

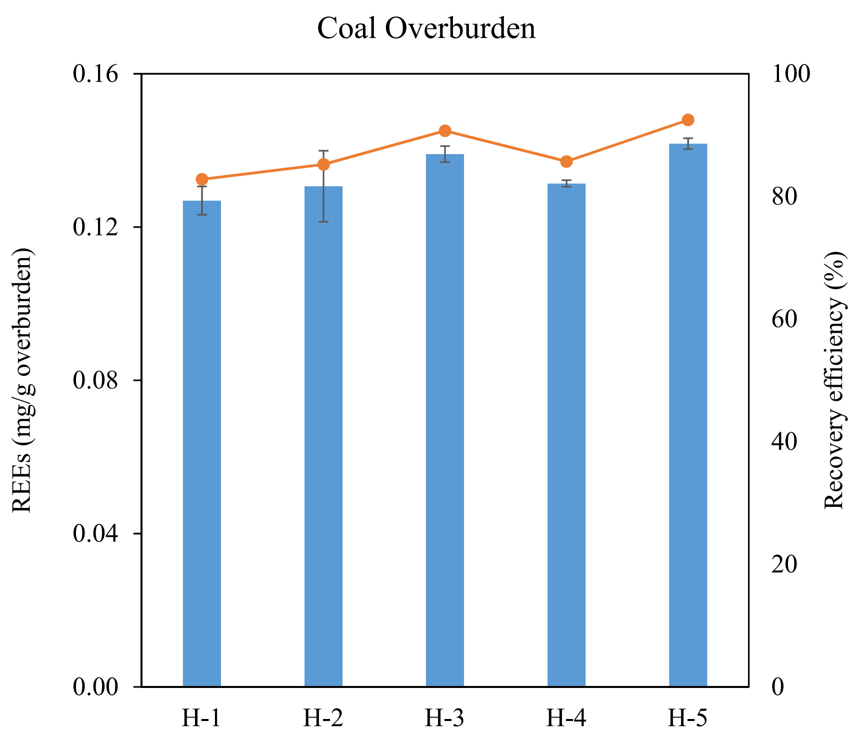
- High REEs recovery efficiencies are achievable with the new method which is
  - Environmentally friendly
  - Highly selective
  - Inexpensive





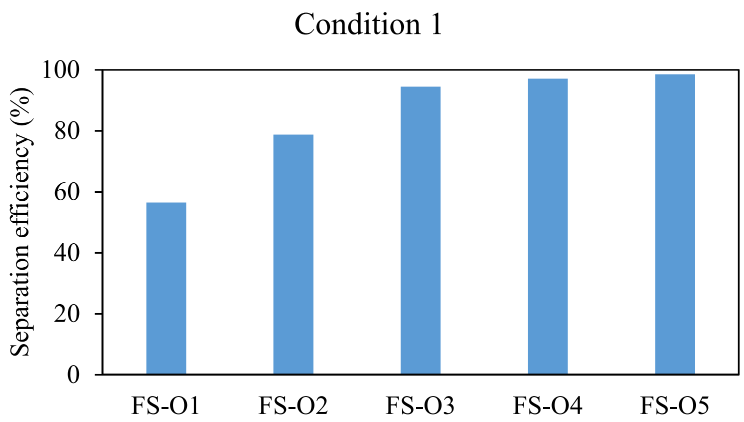


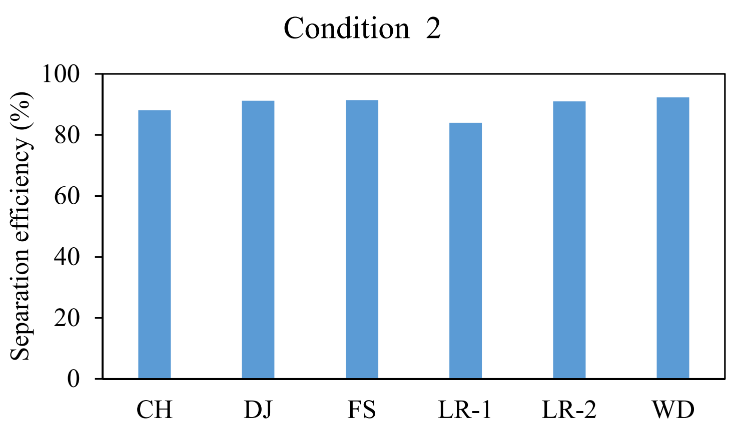
Recovery Efficiencies of REEs in Coal Overburden



- Coal overburden in Wyodak contains ~ 150 ppm REEs
- The new REEs extraction method works well for overburden
  - 83-93% REEs extraction efficiencies were achieved
  - The conditions for extracting the REEs from overburden are milder than those with fly ashes
  - It is anticipated that the concentrations of REEs in REEs-containing products are higher

REEs Separation





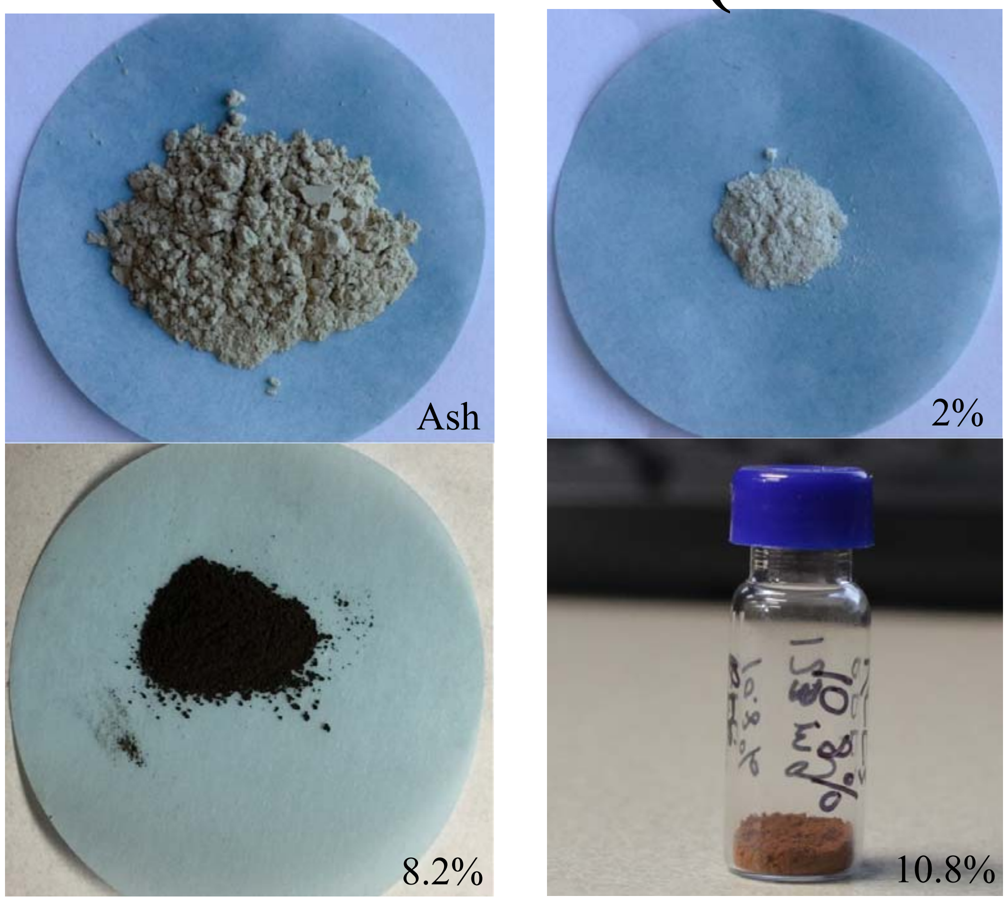
- High separation efficiency for the two approaches

Conditions	% REEs in product (REEs-containing solids)
1	2.1
2	3.5
3	2.7
4	3.7
5	6.0
6	7.6
7	8.2
8	10.8

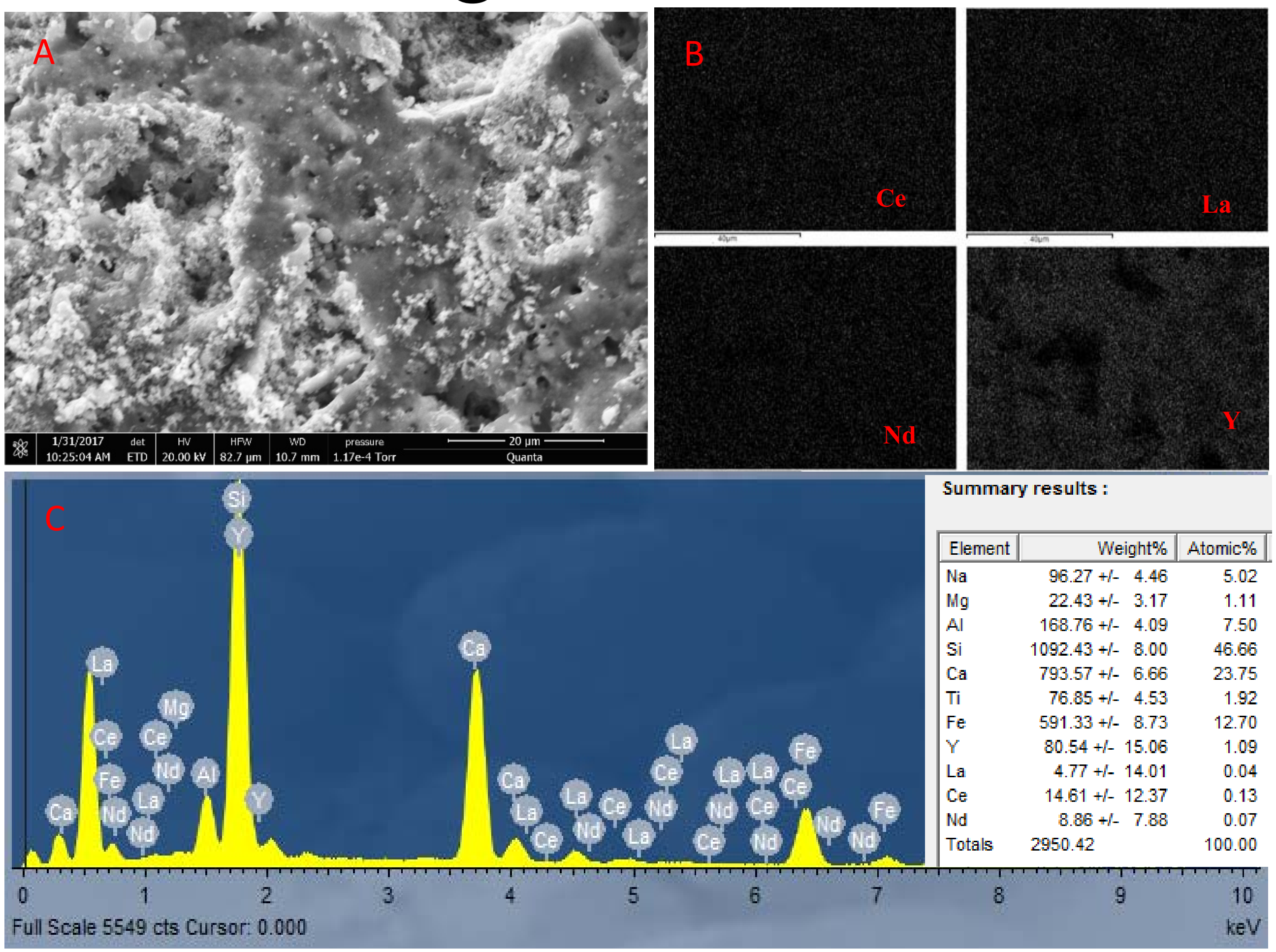
By-products

- The process generates highly valuable by-products along with REEs oxides
  - Al/Fe (coagulants)
  - Sc ($4,200,000/ton)
- The green nature of the recovery method makes ashes re-usable after REEs recovery

Photos of the Products Containing Different % of REEs (elements based)



SEM-EDS Images of REEs-Containing Solid



Summary results :

Element	Weight%	Atomic%
Na	96.27 +/- 4.46	5.02
Mg	22.43 +/- 3.17	1.11
Al	168.76 +/- 4.09	7.50
Si	1092.43 +/- 8.00	46.66
Ca	793.57 +/- 6.66	23.75
Ti	76.85 +/- 4.53	1.92
Fe	591.33 +/- 8.73	12.70
Y	80.54 +/- 15.06	1.09
La	4.77 +/- 14.01	0.04
Ce	14.61 +/- 12.37	0.13
Nd	8.86 +/- 7.88	0.07
Totals	2950.42	100.00

SEM-EDS Images of REEs-containing Solid

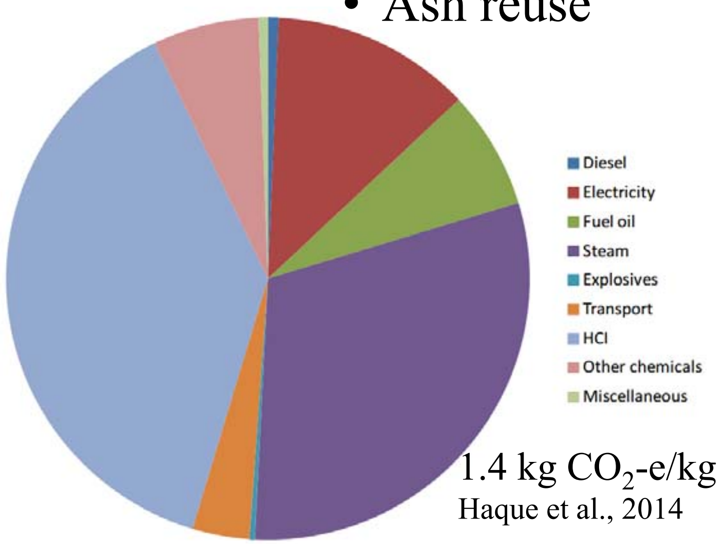
- A- The morphology image indicate the presences of various undesired material in the REEs-containing solid or product
- B- Dispersion image clearly show the existence of the four major REEs in the product
- C- The semi-quantitative analyses of REEs in the REEs-containing solid with SEM-EDS
  - Major REEs in the solid are Ce, La, Nd and Y
  - Major inorganic impurities are Ca, Fe, Mg, Al and Si
  - The concentrations in the table are close to with those detected with ICP-MS

Environmental Impact

- Conventional method
  - Heavy metals/radioactive/ water/gas emission
  - Waste gas (9,600-60,000 m^3/ton REEs)
    - Flue gas concentrate
    - HF
    - SO_2
    - H_2SO_4
  - Acid water (200 m^3/ton REEs)
  - Radioactive waste (1.4 tons/ton REEs)

Navarro and Zhao, 2014

- New method
  - No heavy metals/ radioactive waste discharge
  - No air pollution
  - Water reuse
  - Ash reuse



1.4 kg CO_2-e/kg REO

Haque et al., 2014

Cost-Effectiveness

- > 50% energy consumption reduction – why?
  - Equipment – Simple
  - Operation – Safe and easy
  - Process – Short
  - Extraction condition - Mild

- > 30% cost reduction – Why?
  - Materials – Inexpensive
    - Waste materials from other industries can be used for recovering REEs
  - Capital investment – Low
  - Labor requirement – Low
  - Emission and discharge control or secondary pollution prevention – Almost zero

REOs	**Primary Energy MJ/kg**	**GHG kg $CO_{2\text{-}e}$/kg**
La	177	9.3
Ce	157	8.3
Pr	798	41.4
Nd	743	38.5
Sm, Eu, Gd (mixed oxide)	1,074	55.6

Haque et al., 2014

Conclusions

- All the goals set for the project are achieved, especially
  - The actual REEs concentrations (the highest one to date: 10%) in products >> the set goal (2%); and >10% or >> 10% is achievable.
  - The tons of qualified coal ashes we found >> the set goal (10 M tons)
- A new pathway for producing critical materials – REEs is opened by integrating the knowledge from multi fields
  - With various desired characteristics
  - Without the limitation of location and time
- The new pathway makes impossible possible in REEs production field - huge amounts of conventionally considered unrecoverable REEs can be recovered with the transformational technology
- The new pathway could inspire the significant advancement of new theories in chemistry and technologies in mineral processing industries