



Extraction of rare earth elements from acid mine drainage precipitates

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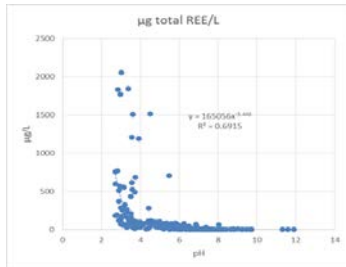


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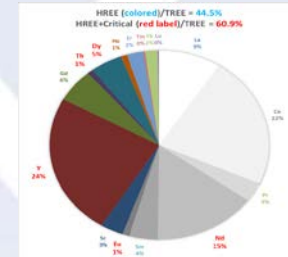
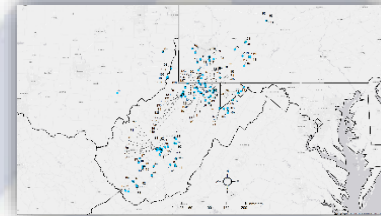


Presentation Outline

1 REEs in AMD



2 Resource Characterization



3 Process Design/Test



4 Summary and Questions



Classification

Rare Earth Elements

		Light		Critical																	
		Heavy		*Unstable																	
H																	He				
Li	Be															B	C	N	O	F	Ne
Na	Mg															Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac																			
			Ce	Pr	Nd	Pm*	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu					
			Th	Pa	U	Np	Pt	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr					



Our REE Projects

DE-FE0026927

- Phase 1 **ETD30 Completed**
 - Development of a cost-effective & environmentally benign process to treat and recover REEs from AMD
 - Perform a preliminary process system Design and Techno-Economic Analysis
- Phase 2 **ETD50**
 - Build and operate a bench-scale pilot plant
 - Update cost and performance metrics
 - Supply chain/commercialization plan
 - Target product grade = 2% REE

DE-FE0026444 **ETD39 Completed**

- Conduct a broad sampling campaign (> 150 sites).
- Perform a detailed assessment at promising sites
- Report REE concentrations and elemental distributions

DE-FE0031524 **ETD53**

- Develop a novel process for capturing REEs upstream of AMD treatment
- Synthesize with a downstream process to produce high-grade REE products, >90% REO



Definitions:

- **Basket Price**
 - Weighted value
 - market price of each REE oxide x concentration/total REE concentration
 - Assumed market price of a kilogram of mixed rare earth oxide
- **Contained Value**
 - Basket price x mass of dry sludge = \$/ton of dry sludge



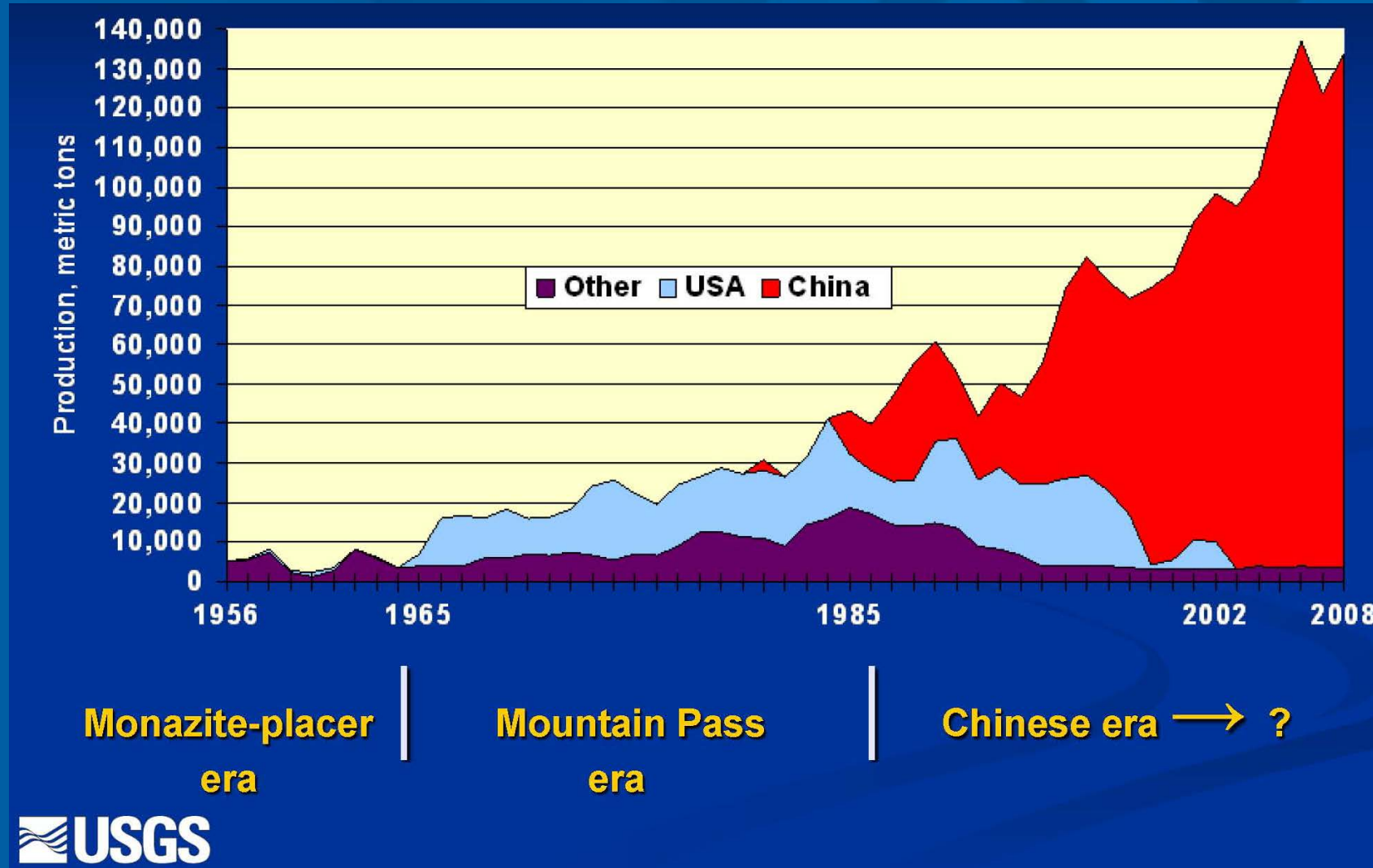
MOLYCORP REE MINE, MOUNTAIN PASS CA

Drivers:

- The U.S. imports nearly all of its REEs
- Mostly from China
- One operating US mine (maybe)
- USDOE seeks additional domestic sources from fossil energy sources
- Minimal environmental footprint
- Move quickly to market



Our strategic disadvantage: China controls exports ~ 35kt/yr



Monazite-placer
era

Mountain Pass
era

Chinese era → ?



Projected TREE demand through 2025 (tons/year)

	Global demand @ 7% ann. Growth	USA demand	
		total*	defense**
2017	158,403	15,840	792
2018	169,845	16,984	849
2019	182,176	18,218	911
2020	195,469	19,547	977
2021	209,804	20,980	1,049
2022	225,265	22,527	1,126
2023	241,947	24,195	1,210
2024	259,951	25,995	1,300
2025	279,387	27,939	1,397



This assumes that USA manufacturing demand does not increase beyond current rates

* 10% global

** 5% USA demand



RARE EARTH ELEMENTS IN AMD SLUDGE



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Global demand/supply

REE as oxide	2015 demand tons/year	2015 supply tons/year
total REE	180,000	208,500
cerium	65,500	82,500
neodymium	37,500	32,500
europium	750	600
terbium	475	400
dysprosium	2,750	1,800

Many deposits have high concentrations but low recoverability: The granite counter top argument

Current and Proposed REE Developments

Conc.	mg/kg	basis	location
0.0300%	300	total REE	south China
0.0160%	160	Dysprosium	Kipwa, Canada
0.5800%	5,800	total REE (low)	Dotson Dike, Alaska
1.0540%	10,540	total REE (high)	Dotson Dike, Alaska



USDOE/NETL Project objectives

- Feedstock TREE > 300 mg/kg
 - Characterize and quantify
- Concentrate TREE > 2%
 - Small scale demonstration
- Prove significant supply to the domestic market



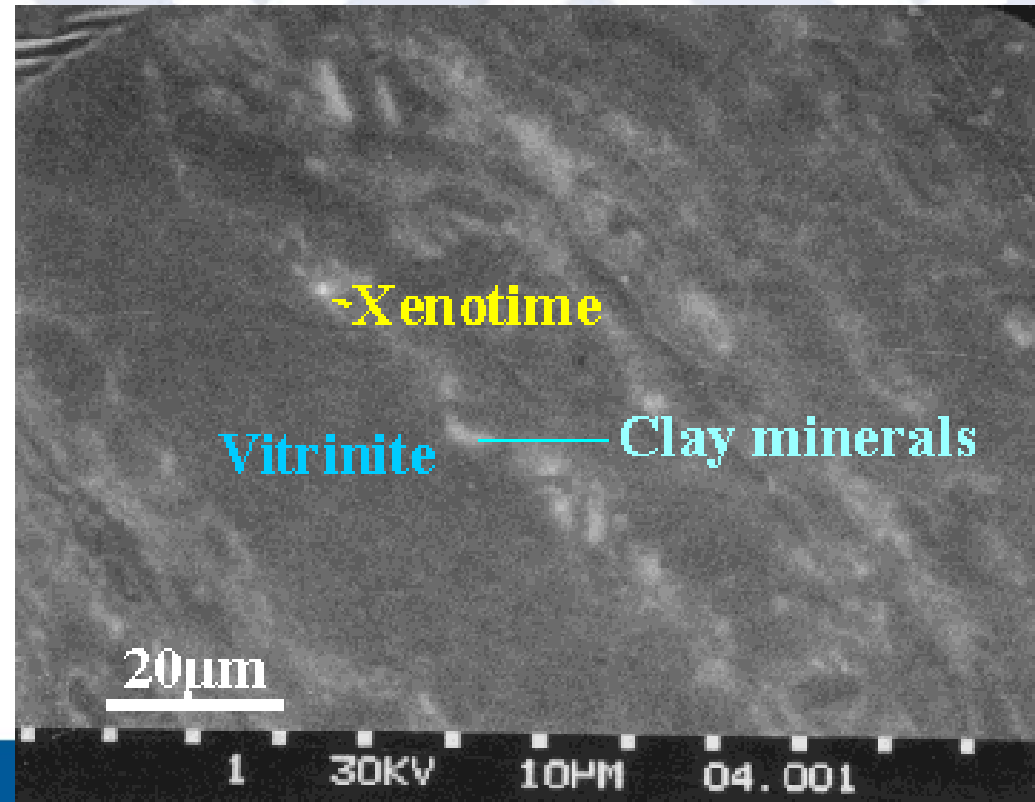
Conventional REE Ores

- Bastnasite (carbonate) or monzonite (phosphate)
 - both generally in igneous complexes
- Extraction requires severe comminution, acid dissolution to liberate REE from Al-Si matrix
- Refining via solvent extraction/electro-winning
- Contains uranium and thorium....So the tailings are acidic and radioactive
- Chinese deposits include iron ore and laterites



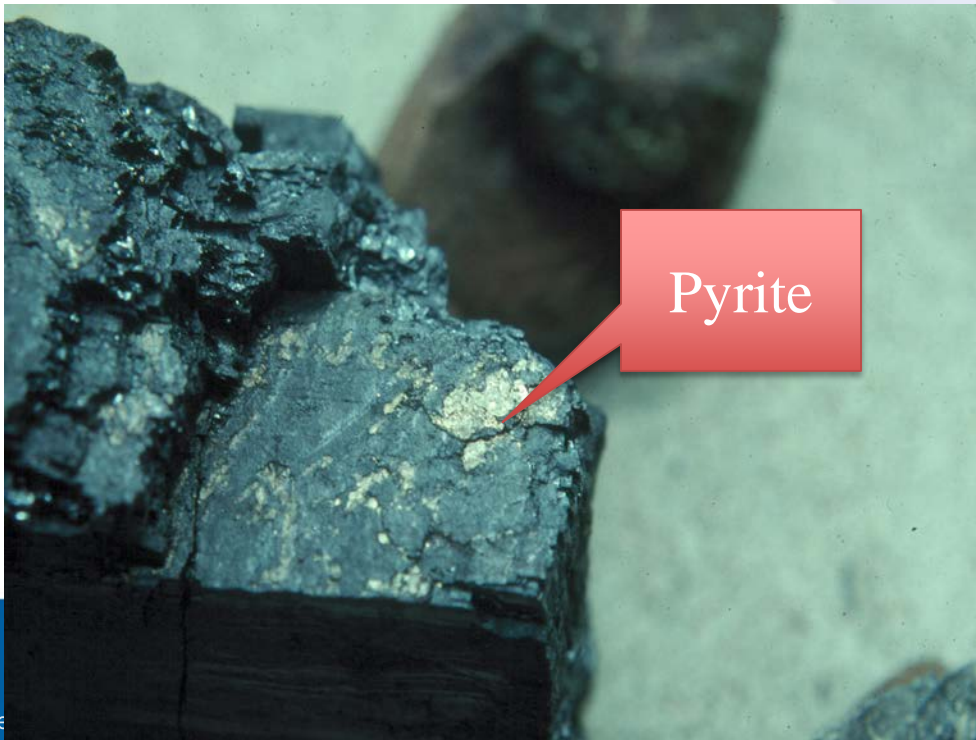
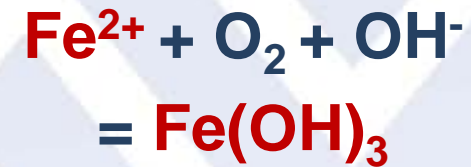
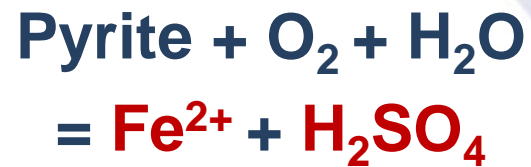
Mineral associations in WV coals from WVGES

- Monazite (less commonly xenotime): REE (PO₄ SiO₄) weathered from granite as **micron-sized particles**
- Does not dissolve in weak acid, requires concentrated acid to liberate REEs
- When burned in a PC boiler nearly all of the inert minerals fuse into alumino-silicate glass
- Which is even more resistant to acid attack



Acid Mine Drainage Chemistry

1. H_2SO_4 leaches REEs from shale
2. REE's precipitate with $\text{Fe}(\text{OH})_3$



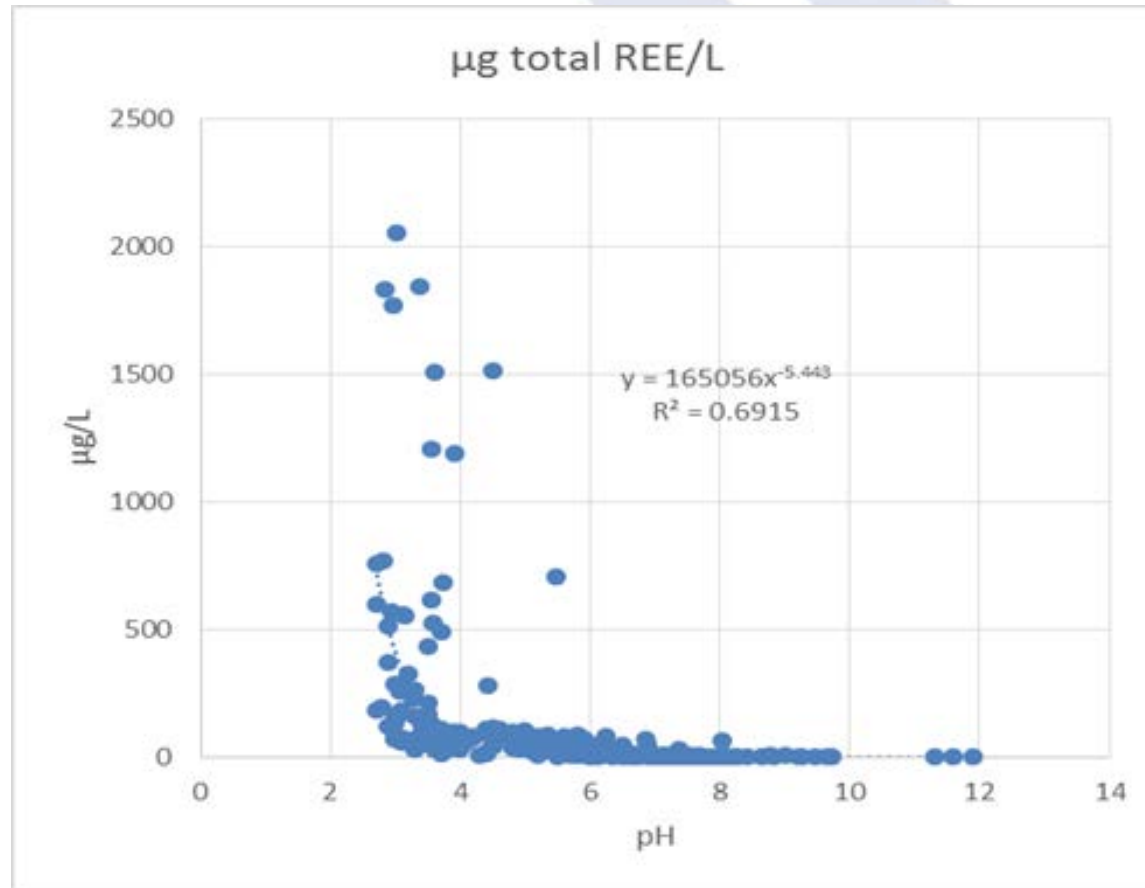
Typical, large AMD treatment plant

Lime tower left, clarifier center

Mixers, aerators



REE concentration in AMD is a function of raw water pH



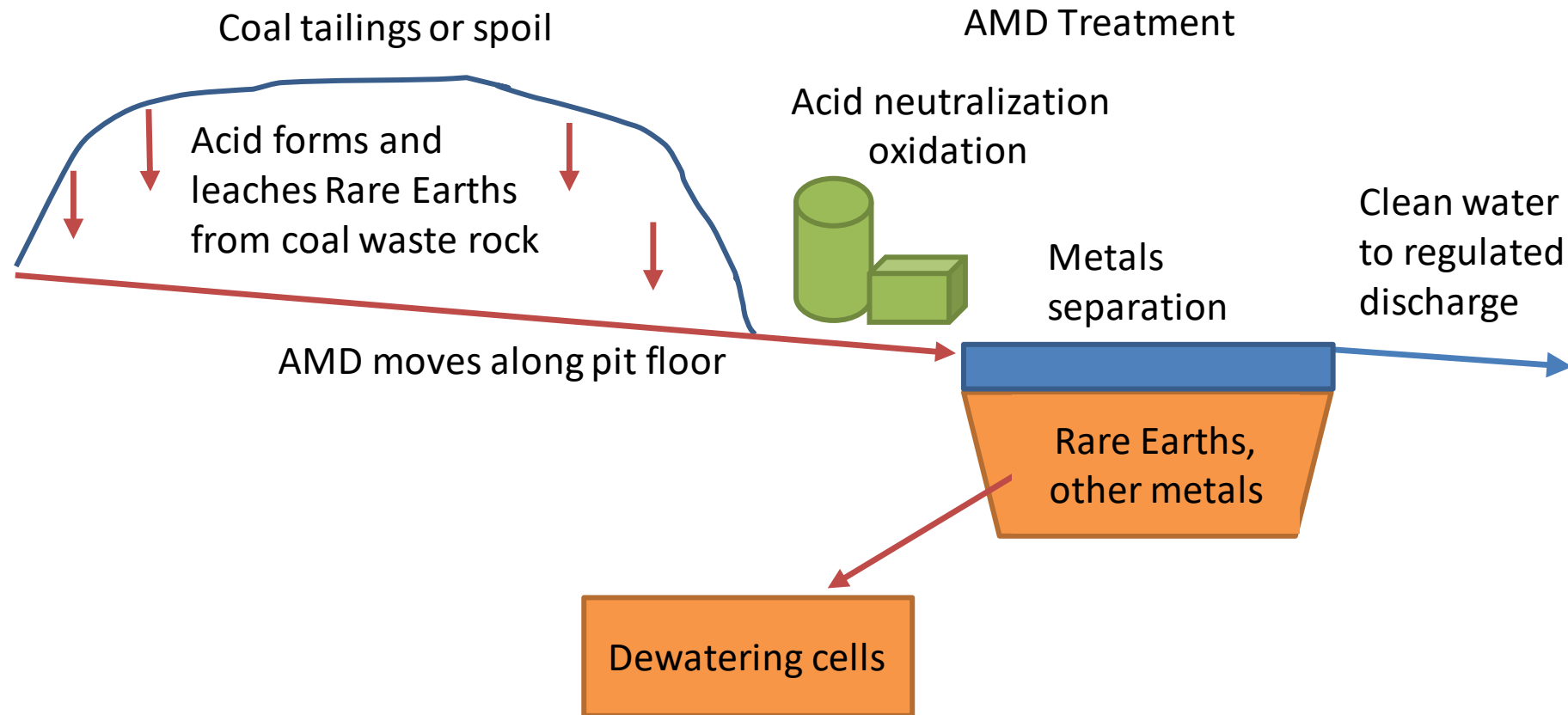
Solubility perfectly mirrors Fe^{3+}



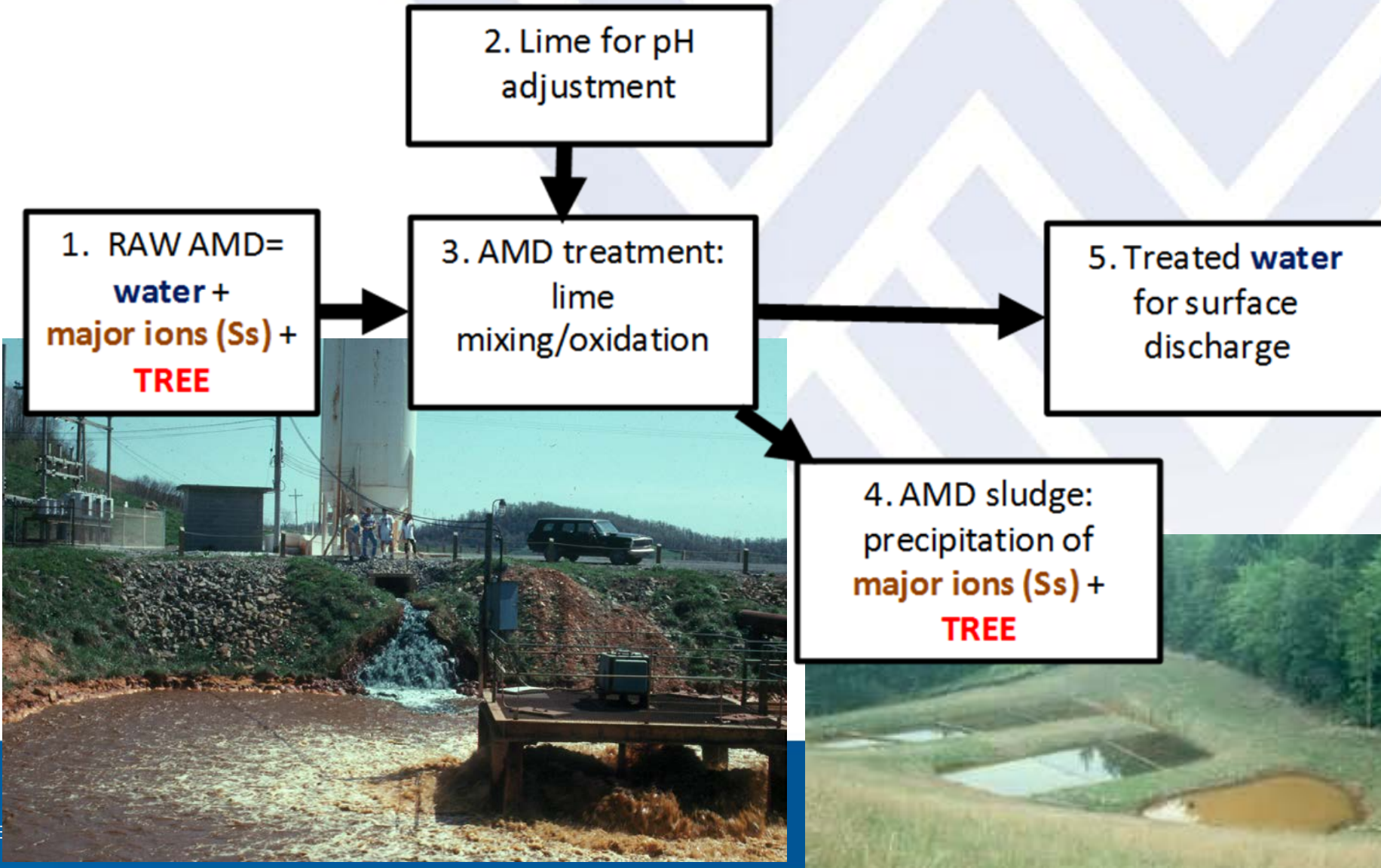
AMD Sludge: $\text{Fe}(\text{OH})_3$ and anything else that precipitates as a hydroxide



Acid Mine Drainage (AMD) Treatment Typical layout



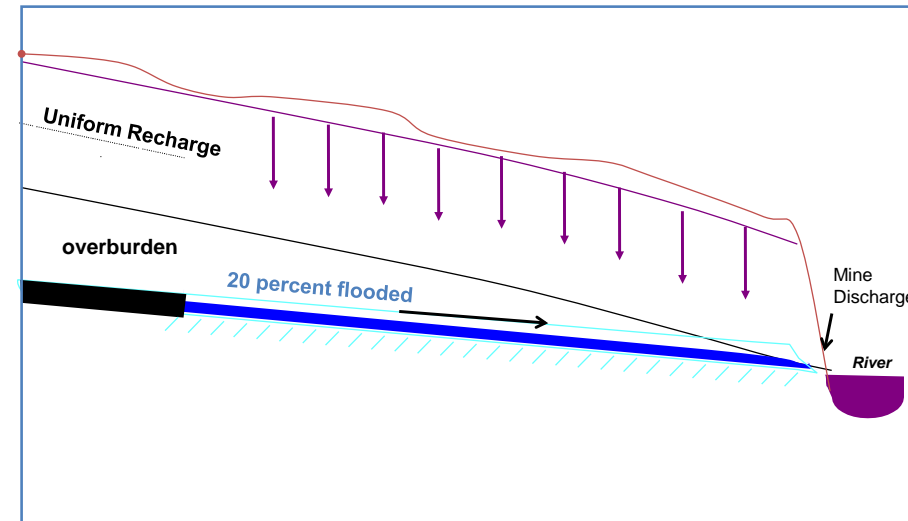
Conventional AMD Treatment



In deep mines the extraction point will control REE concentration

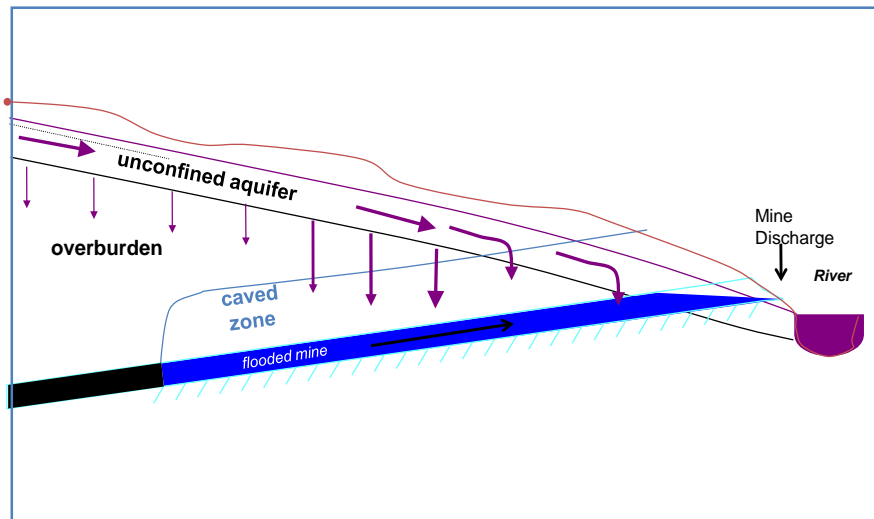
Low pH/high REE

Unflooded, Free Draining

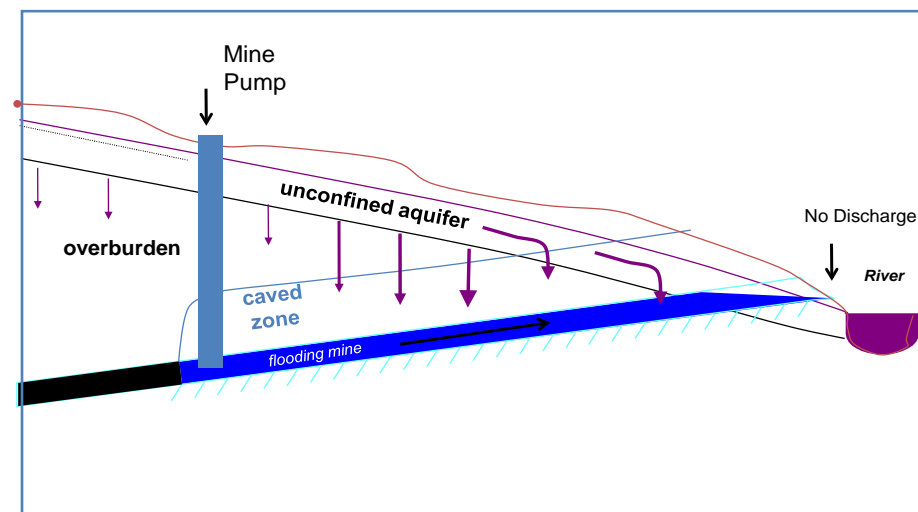


High pH, low REE

Flooded High Dilution



Flooded Mine Low Dilution



Resource characterization, Valuation

Metal value: \$555/kg each REE Processed to pure metal

Oxide value:

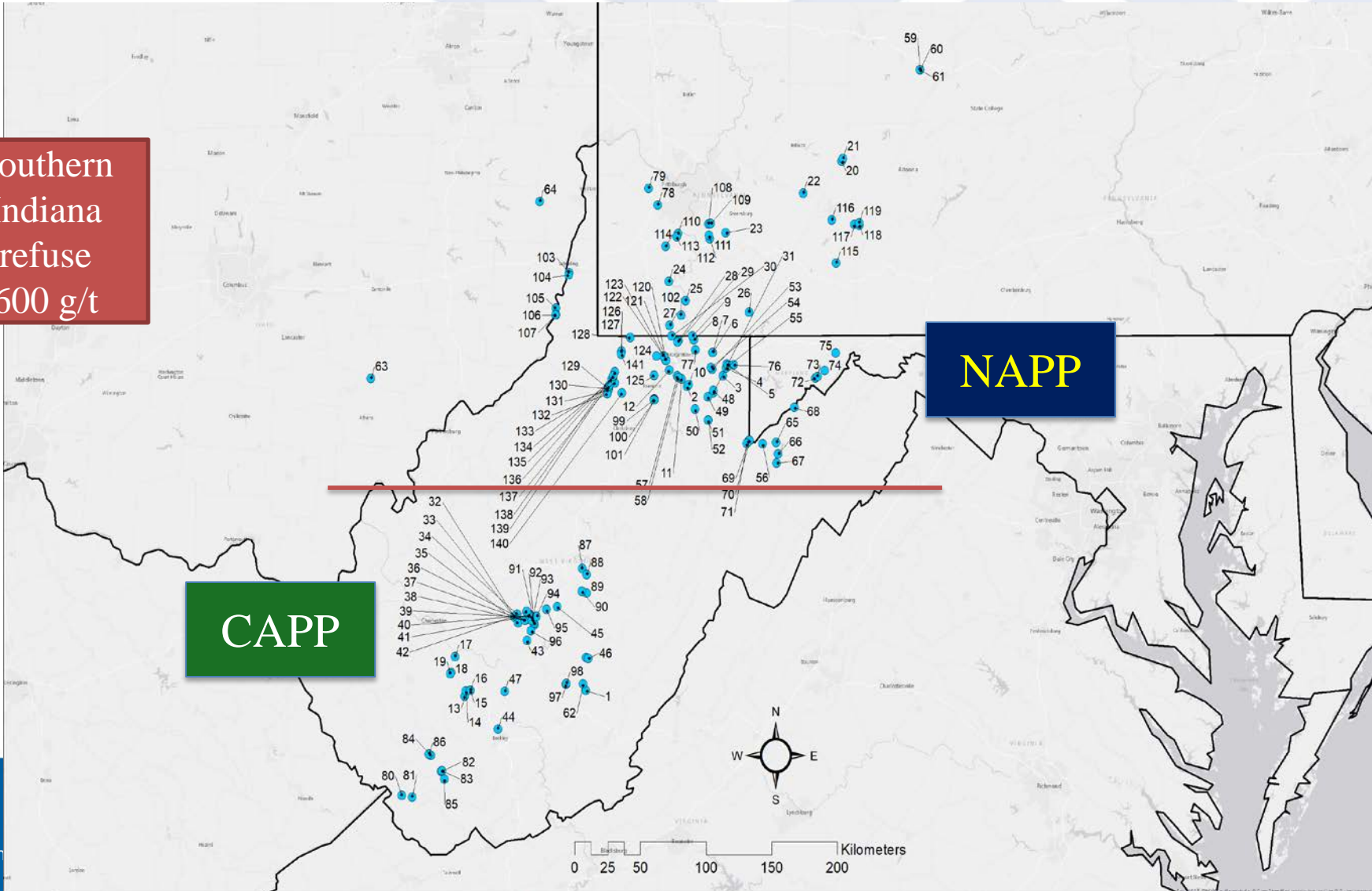
Basket price: \$237.23/kg TREE
weighted value

Contained value: \$129.16/t dry sludge
accounts for handling and processing



140 Sampled locations: MD, OH, PA, WV

Southern Indiana refuse
600 g/t



CAPP

NAPP

Central vs. Northern Appalachian coal basins

Little difference between REE distribution or total concentration (g/t)

A sample from the **Illinois Basin** was similar to typical, low pH Appalachian AMD

Sites sampled:

CAPP 42

NAPP 110

	CAPP	NAPP	All
La	41.4	38.4	39.9
Ce	97.1	95.0	96.0
Pr	14.4	14.0	14.2
Nd	66.5	64.5	65.5
Sm	18.2	17.6	17.9
Eu	4.4	4.5	4.4
Sc	12.8	14.9	13.8
Y	88.6	108.7	98.7
Gd	23.9	24.3	24.1
Tb	3.4	3.7	3.6
Dy	18.8	20.7	19.8
Ho	3.5	4.0	3.8
Er	9.1	10.7	9.9
Tm	1.0	1.4	1.2
Yb	6.7	8.1	7.4
Lu	0.9	1.2	1.0
TREE	410.6	431.6	421.1

LREE

Critical

HREE



AMD treatment concentrates REE in sludge to about 700 g/t

REE in NAPP vs. CAPP whole coal.
Physical separation can increase REE concentrations to about 500-600 g/t

Pittsburgh Seam

mg TREE/kg

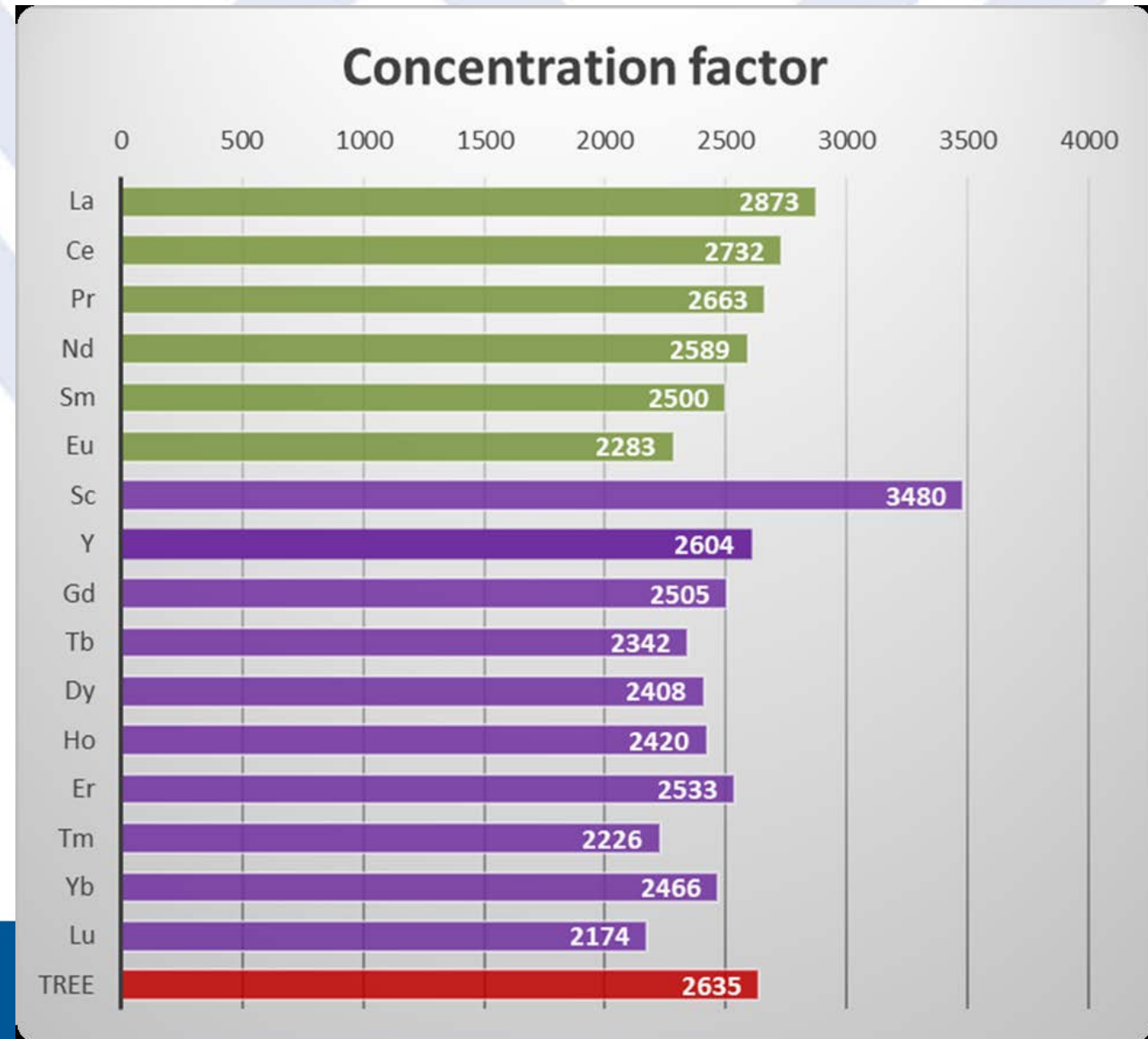
max	146.3
mean	34.6
min	7.3
st. dev.	22.0



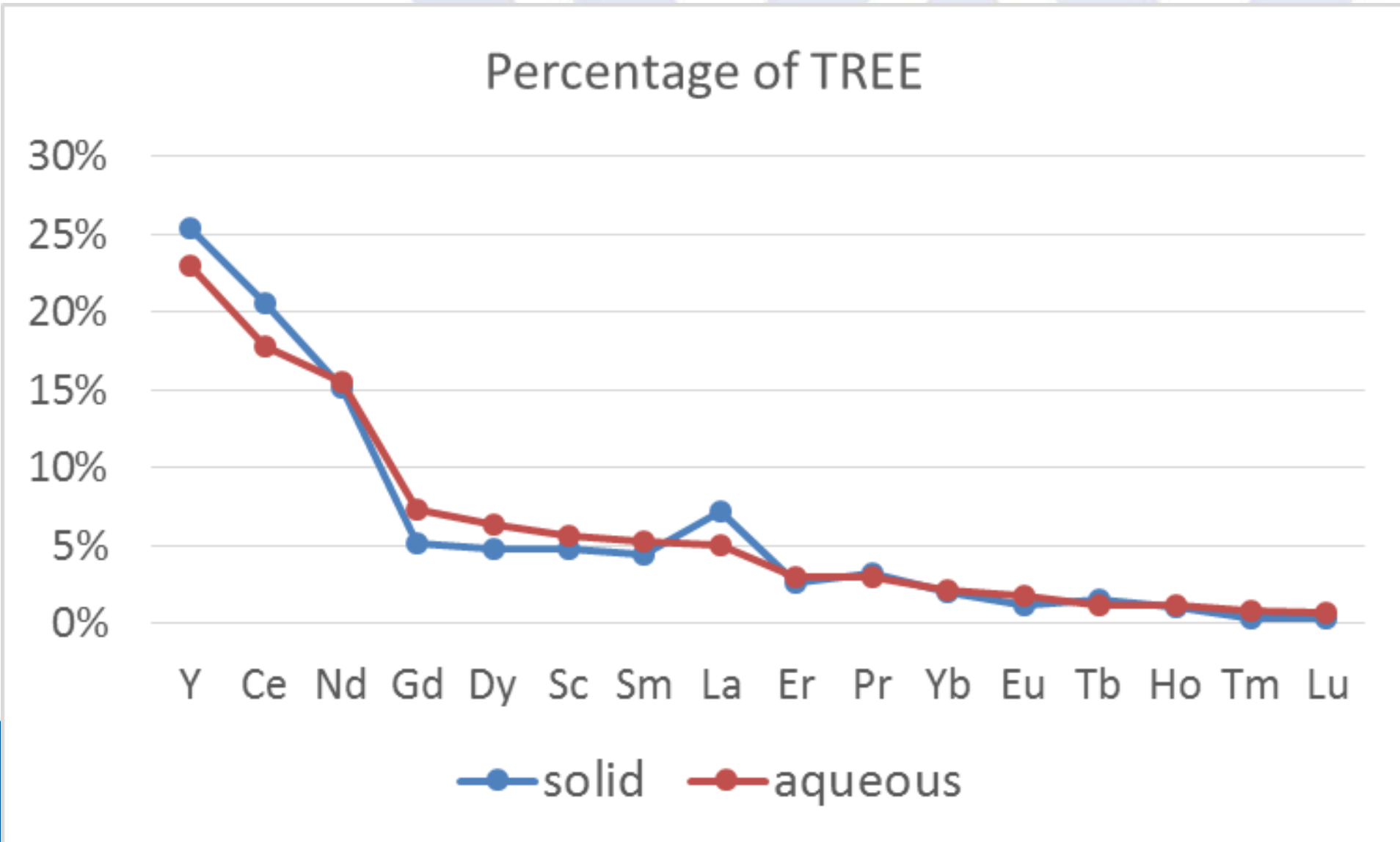
Eagle Seam

mg TREE/kg

max	225.7
mean	49.5
min	9.3
st. dev.	42.2

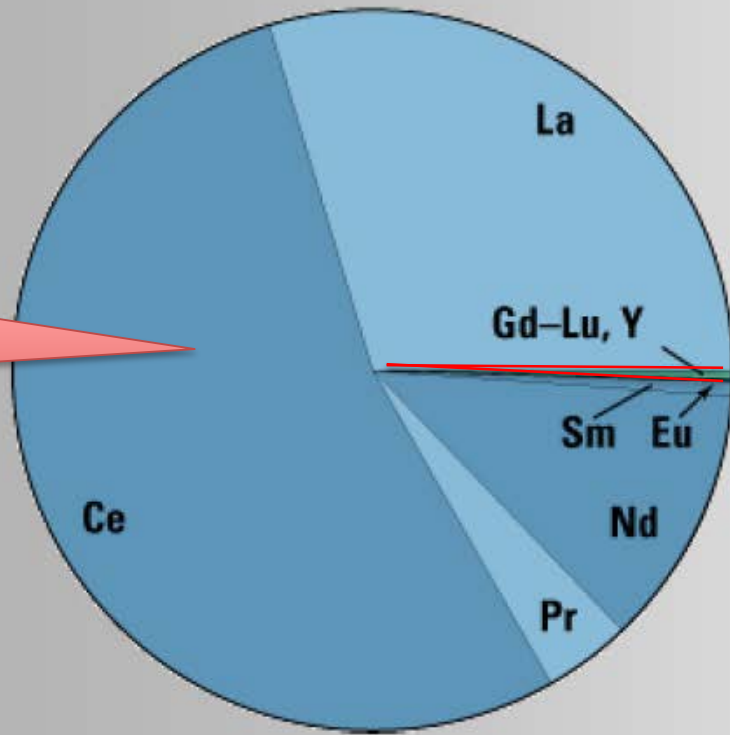


All REEs precipitate to AMDp with nearly equal enthusiasm

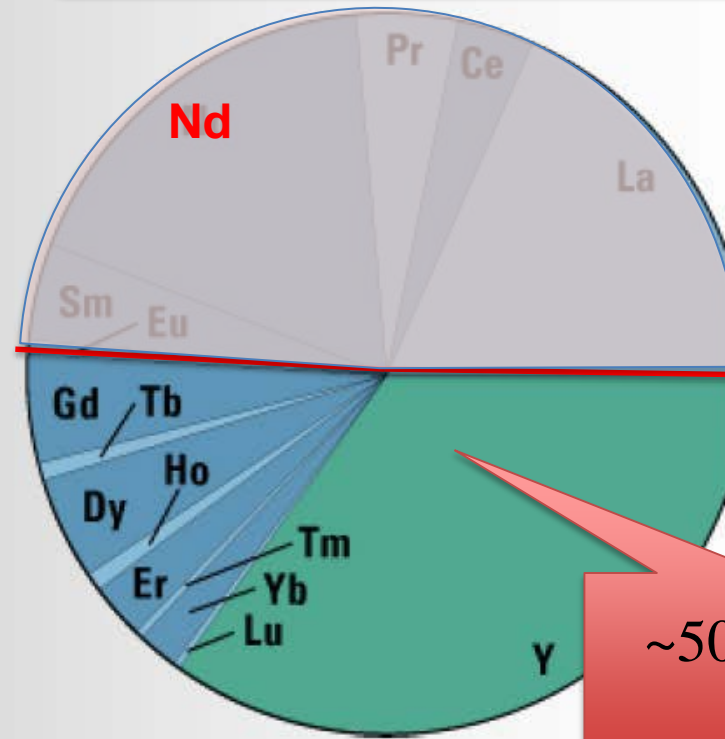


Distribution of HREE in AMD sludge is similar to south China clays

Bayan Obo, Mountain Pass



South China Clay



31	Ga	Ga
		Gallium
32	Ge	Ge
		Germanium
37	Rb	Rb
		Rubidium
39	Y	Y
		Yttrium
64	Gd	Gd
		Gadolinium
49	In	In
		Indium
55	Cs	Cs
		Cesium
73		

USGS facts sheets

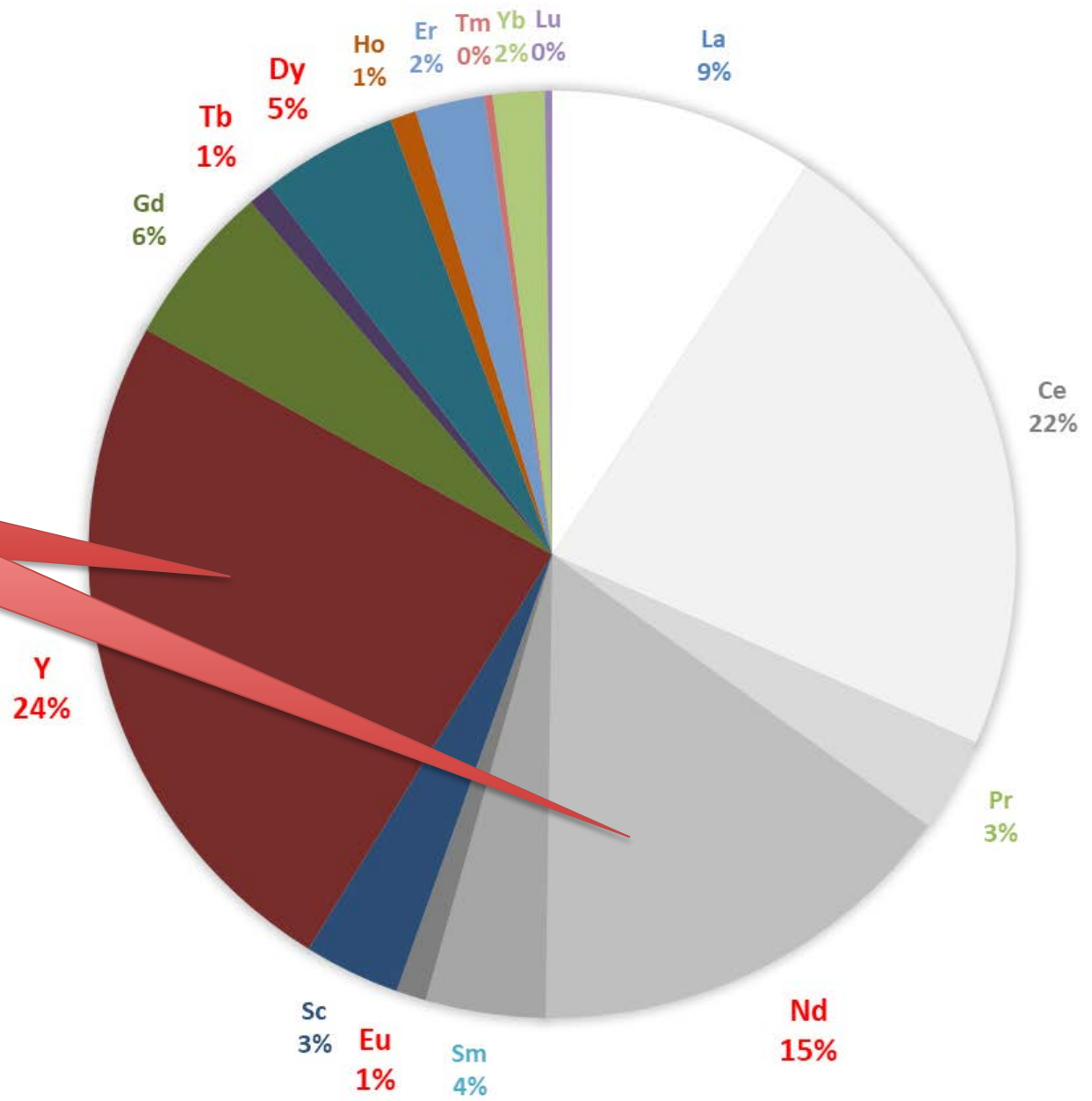
Heavy and Critical REEs in Acid Mine Drainage

n=155

High Y, Nd, both used in Nd: YAG lasers

Cobalt is present in all samples.
 $TREE \times 0.75 = Co$

HREE (colored)/TREE = 44.5%
HREE+Critical (red label)/TREE = 60.9%



REE concentrations and weighted in situ value

Scandium represents 82% of contained value.

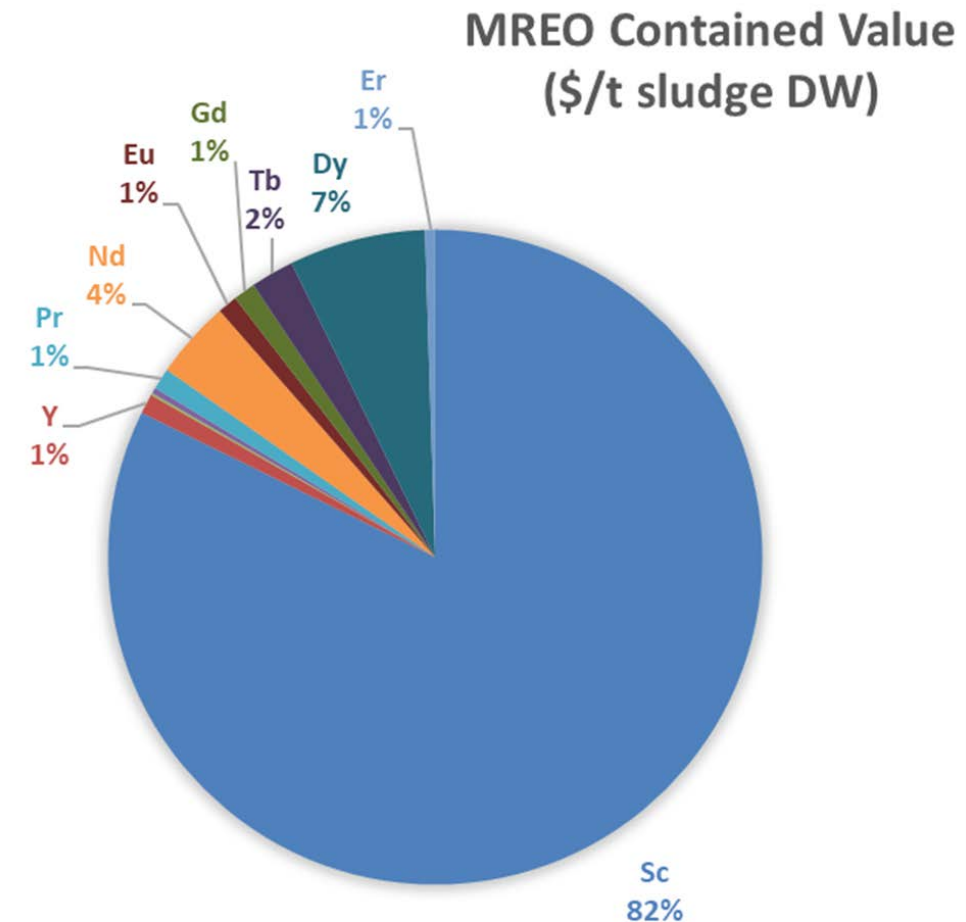
LREE

Critical

HREE

	TREE g/t DW	% TREE	\$/kg elemental	weighted value \$/kg TREE
La	39.2	9.2%	\$ 7.00	\$ 0.65
Ce	95.6	22.4%	\$ 7.00	\$ 1.57
Pr	14.1	3.3%	\$ 85.00	\$ 2.81
Nd	65.0	15.3%	\$ 60.00	\$ 9.16
Sm	17.8	4.2%	\$ 7.00	\$ 0.29
Eu	4.4	1.0%	\$ 150.00	\$ 1.57
Sc	14.3	3.4%	\$ 15,000.00	\$ 504.32
Y	103.3	24.2%	\$ 35.00	\$ 8.49
Gd	24.2	5.7%	\$ 55.00	\$ 3.12
Tb	3.6	0.9%	\$ 550.00	\$ 4.68
Dy	20.2	4.7%	\$ 350.00	\$ 16.62
Ho	3.9	0.9%		
Er	10.2	2.4%	\$ 95.00	\$ 2.28
Tm	1.3	0.3%		
Yb	7.7	1.8%		
Lu	1.1	0.3%		
sum	425.9			\$ 555.56

Scandium represents 82% of the metal value in AMD derived REEs. n=155



Contained sludge value=market value of REEs excluding transport and processing



Small AMD sludge drying cell

0.5 ac, 10 ft deep, 80% moisture

Sludge DW 2,712 t

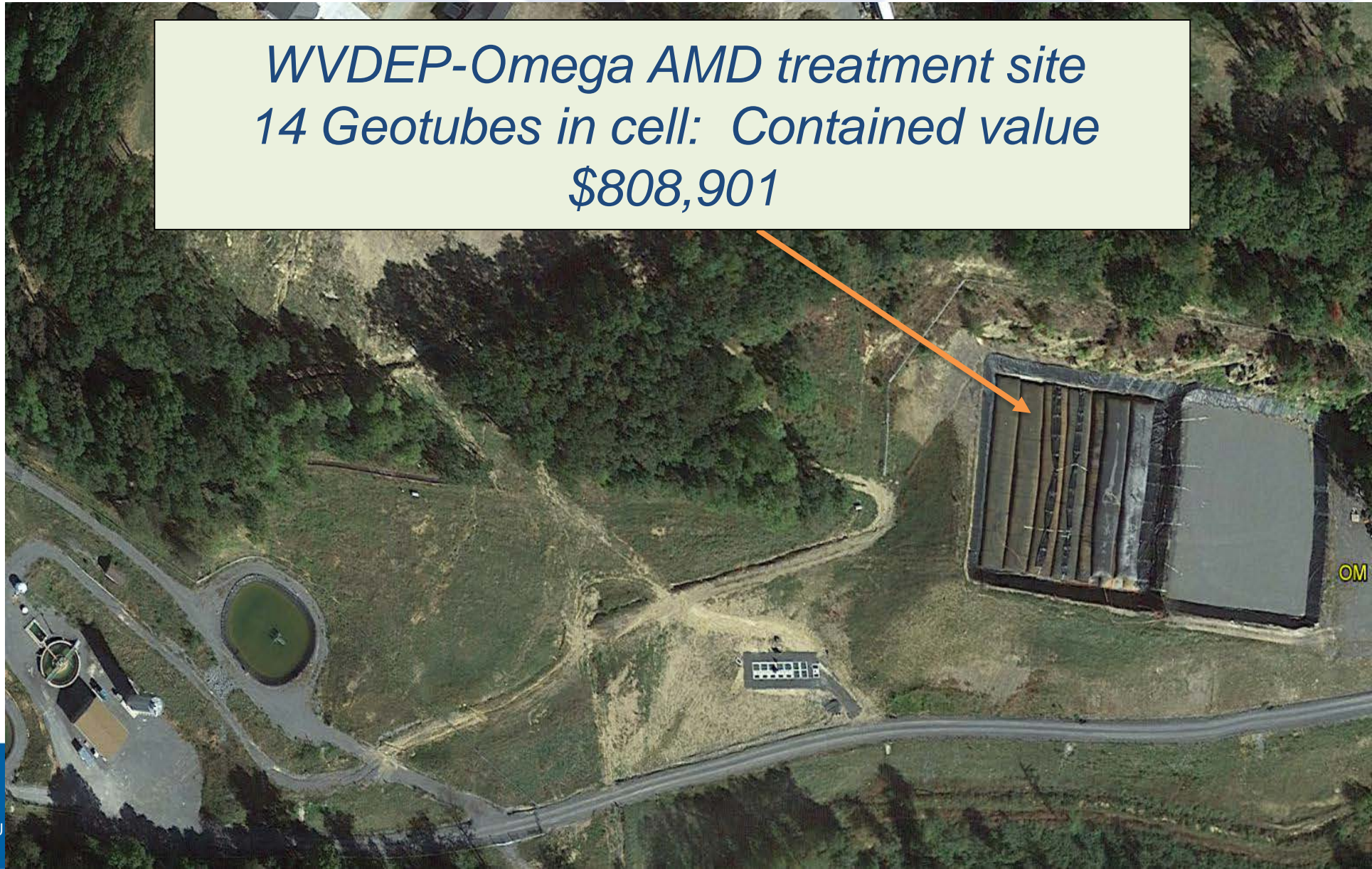
\$135/kg REE

Contained REE value = \$365,963



Accessibility/Extractability/Dewatering

*WVDEP-Omega AMD treatment site
14 Geotubes in cell: Contained value
\$808,901*



Estimated REE production CAPP/NAPP

Sludge cells sampled, this project		76
Sludge (Dry)	1,637,312	m ³
Sludge	3,602,086	tons DW
average TREE grade	708.5	g/t
TREE	1,421	tons DW
REE Basket Price (MREO)	\$ 237.23	/kg TREE
contained TREE value	\$ 337,103,830	



Estimated annual REE production: Appalachian Basin

	low	High
AMD production	1,503,371	6,626,156 gpm
avg. TREE concentration	0.269	0.269 mg/L
Annual TREE production	807	3,555 tons/year
REE Basket Price (MREO)	\$ 237.23	\$ 237.23 /kg
Contained TREE value	\$ 191,362,343	\$ 843,435,793 /yr



Summary: The AMD sludge resource

Key findings:

REE content, untreated coal mine AMD

CAPP	233.5	μg/L
NAPP	304.2	μg/L
all	286.9	μg/L

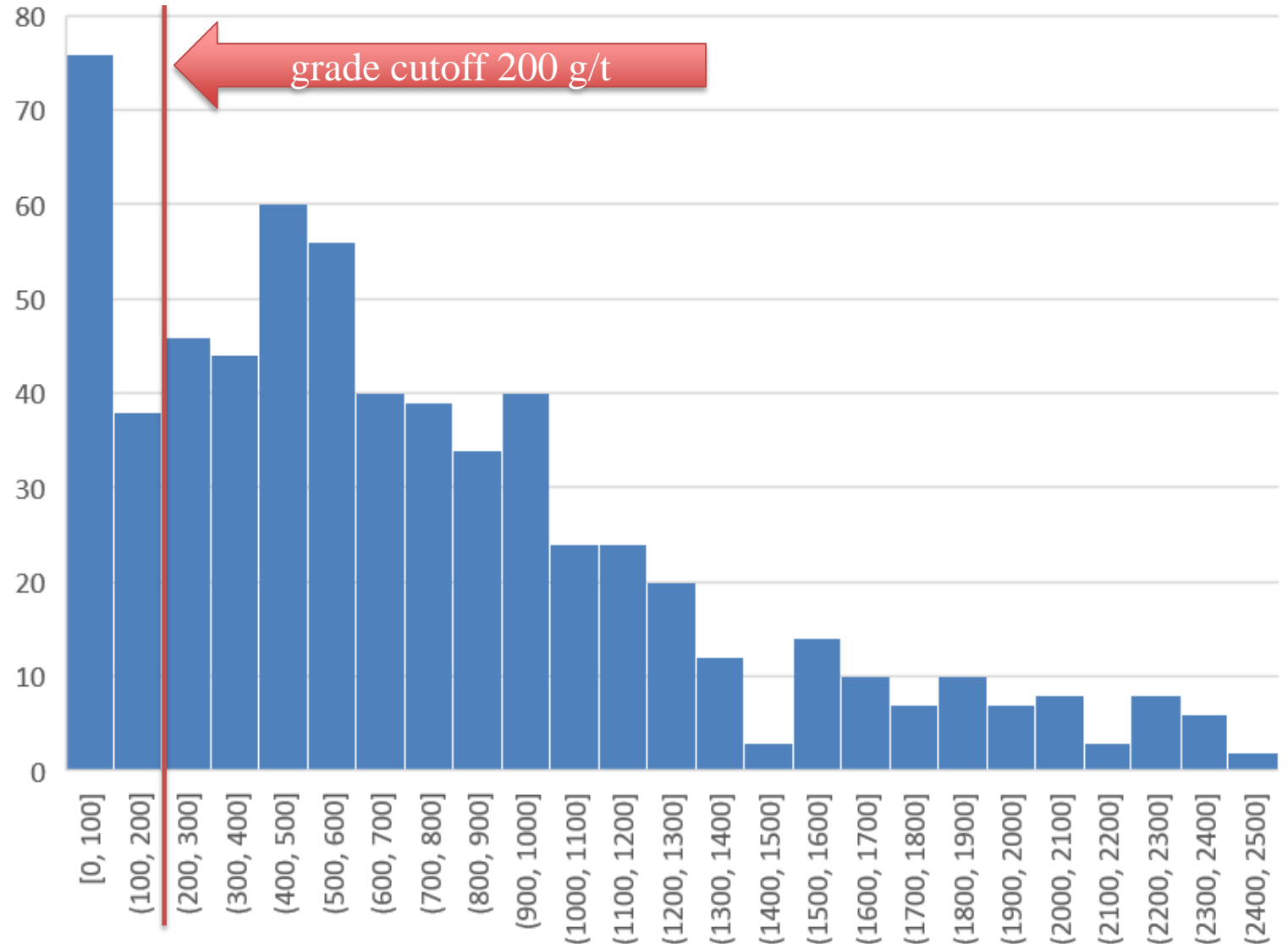
REE content AMD sludge:

CAPP	666.4	g/t
NAPP	750.6	g/t
all	708.5	g/t

Available REE stored at mines

1421 t
\$ 296 million

Frequency distribution: Sludge REE concentration (n=631)



1. High proportion of heavy and critical REE: 45%, 60%

2. Very low U, Th <2%

3. Nearly as much Co as REE

n =	Sludge (g/t)		
	CAPP 144	NAPP 485	All 629
La	79.2	58.3	68.7
Ce	160.7	162.5	161.6
Pr	23.7	24.3	24.0
Nd	104.3	113.8	109.0
Sm	26.4	32.0	29.2
Eu	6.4	8.4	7.4
Sc	12.6	20.9	16.7
Y	151.7	192.8	172.3
Gd	34.5	44.2	39.3
Tb	5.1	7.0	6.0
Dy	28.3	39.0	33.6
Ho	5.4	7.4	6.4
Er	14.2	19.9	17.0
Tm	1.9	2.8	2.3
Yb	10.4	15.1	12.8
Lu	1.6	2.3	2.0
TREE	666.4	750.6	708.5
LREE	400.8	399.2	400.0
HREE	265.6	351.4	308.5
HREE/TREE	39.9%	46.8%	43.5%
HREE+critical/TREE	56.5%	63.1%	60.0%
U	4.8	7.0	5.9
Th	6.6	7.5	7.0
U+Th/TREE	1.7%	1.9%	1.8%
Co	666.0	737.8	701.9



Valuation based on Mixed Rare Earth Oxides

Basket Price (\$/kg TREE DW)		
CAPP	\$	157.83
NAPP	\$	258.40
Avg. all	\$	237.23

Contained REE Value (\$/ton sludge DW)		
CAPP	\$	107.50
NAPP	\$	134.94
Avg. all	\$	129.16



PROCESS DESIGN



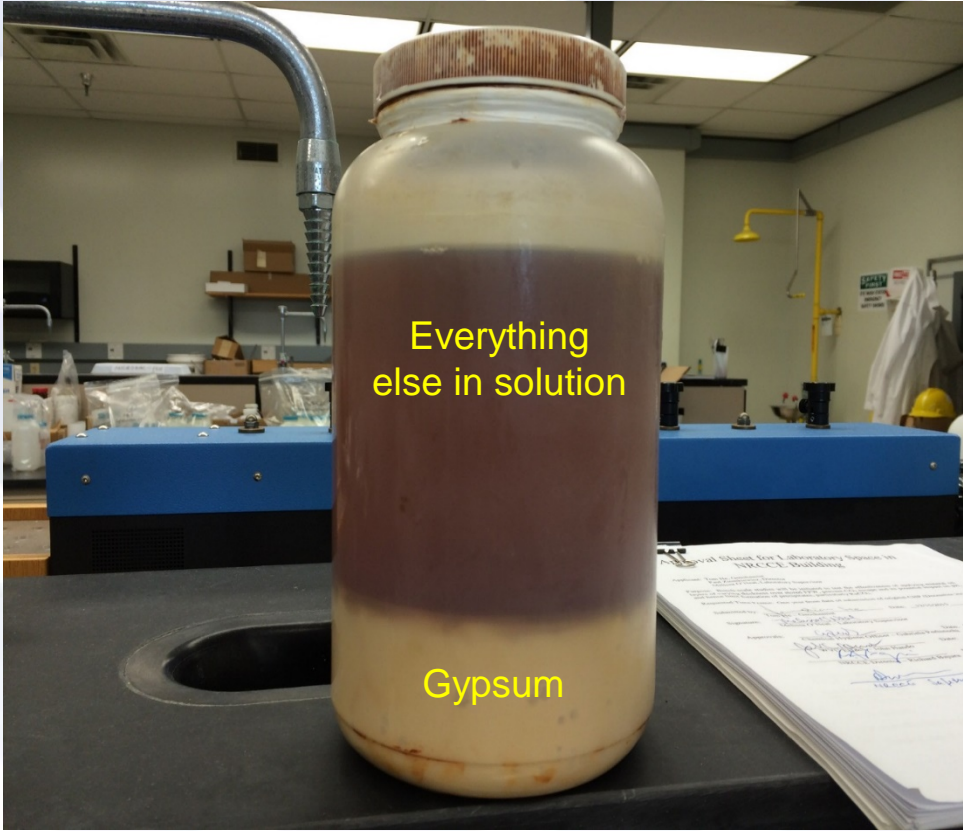
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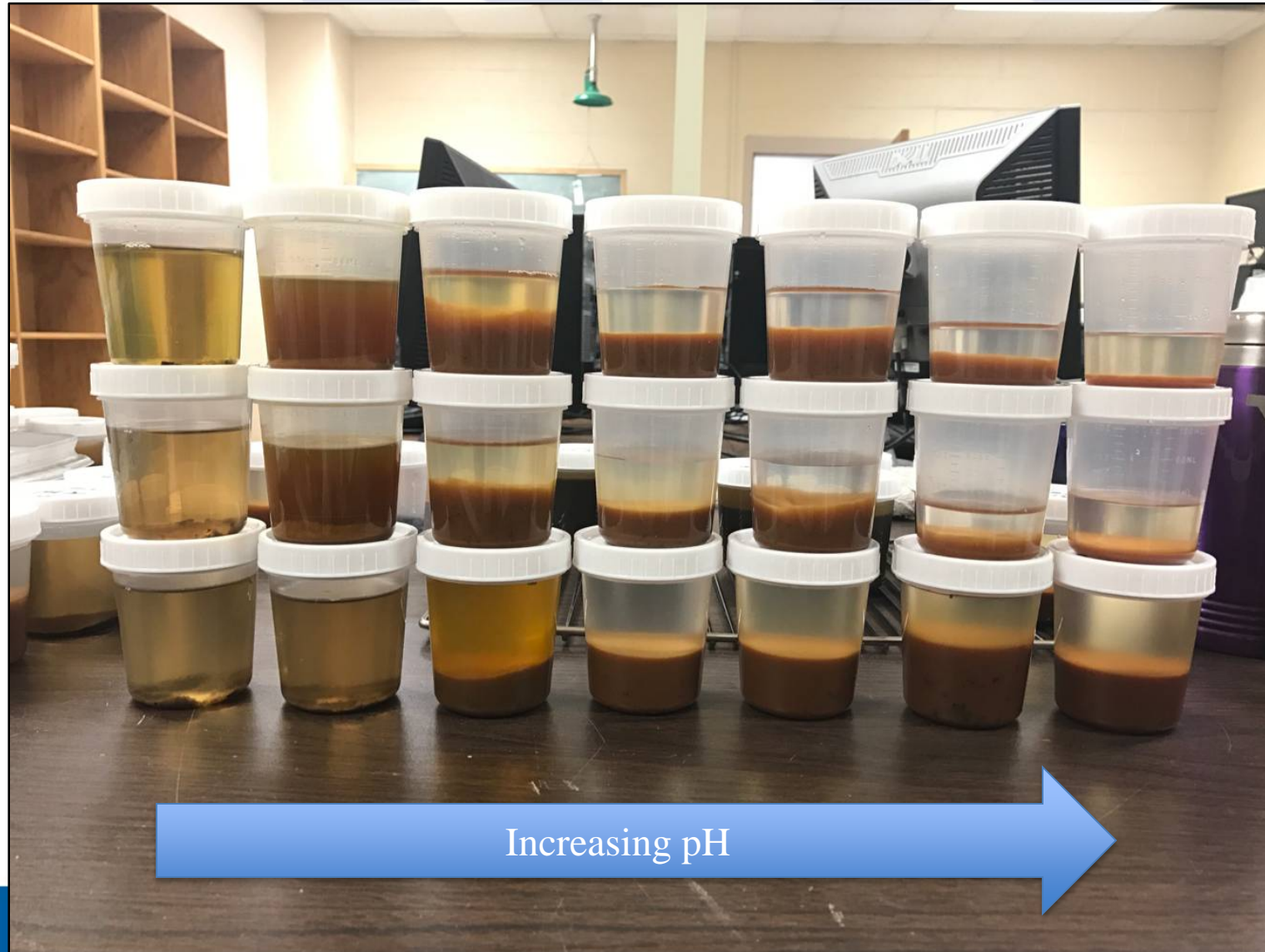
AMD sludge cells, Mine 42 Windber PA



Steel Shaft sludge dissolved
in H_2SO_4 , pH 1



Separations Tests



HCl

HNO₃

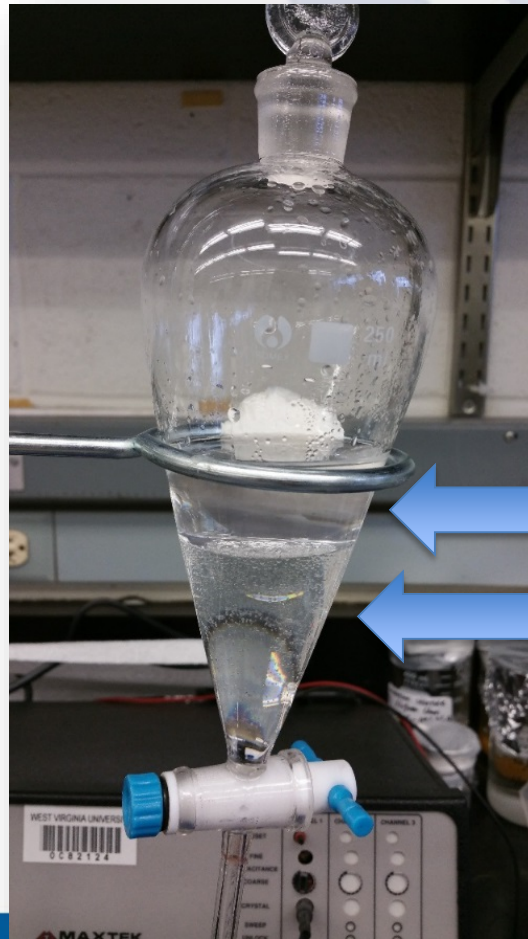
H₂SO₄

Increasing pH



Separations Test

Solvent Extraction in D2EHPA



Organic Phase

Aqueous Phase



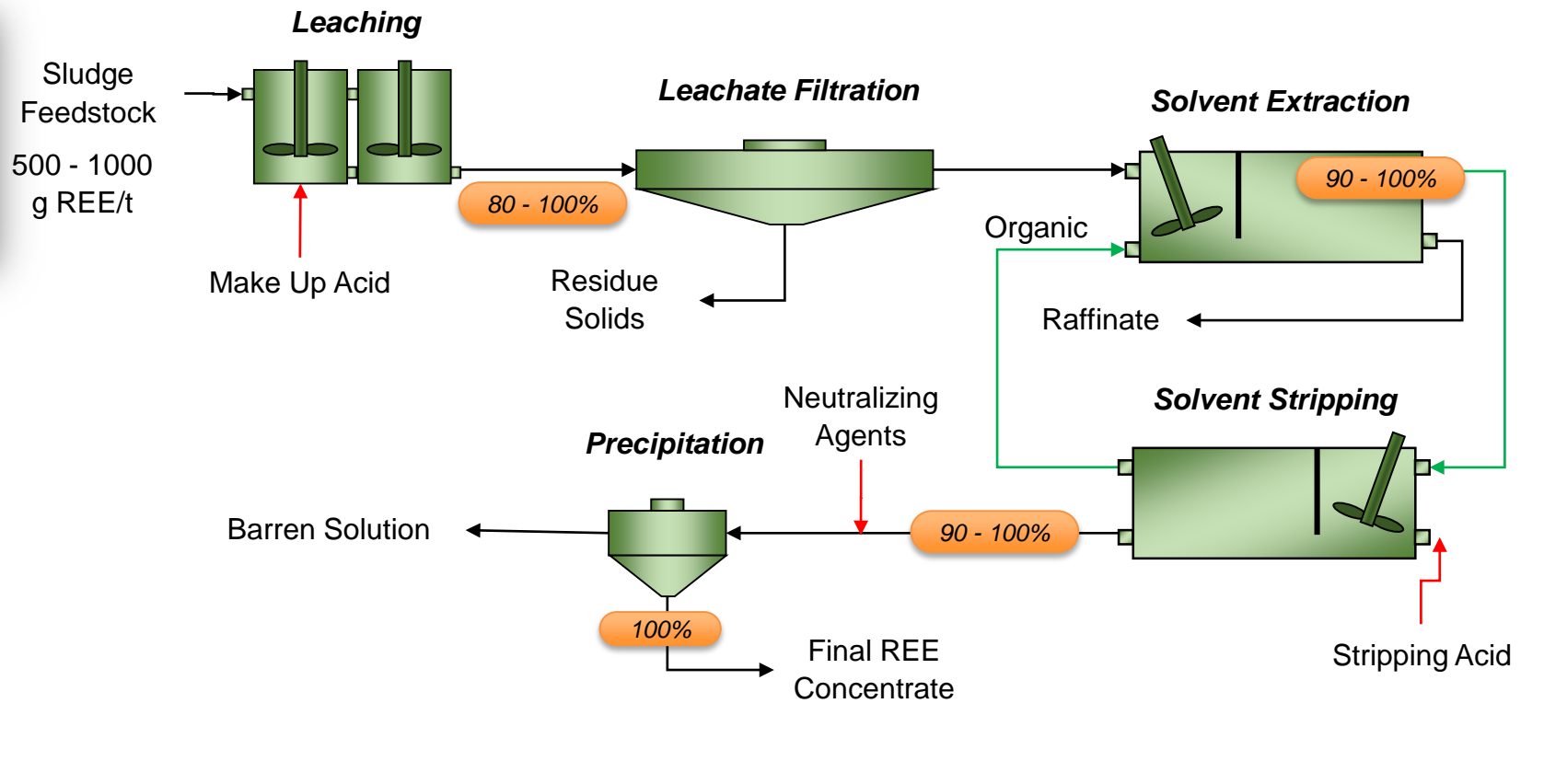
Conceptual Process Flowsheet

All processes at ambient pressure and temperature



Sludge Feedstock
500 - 1000 g REE/t

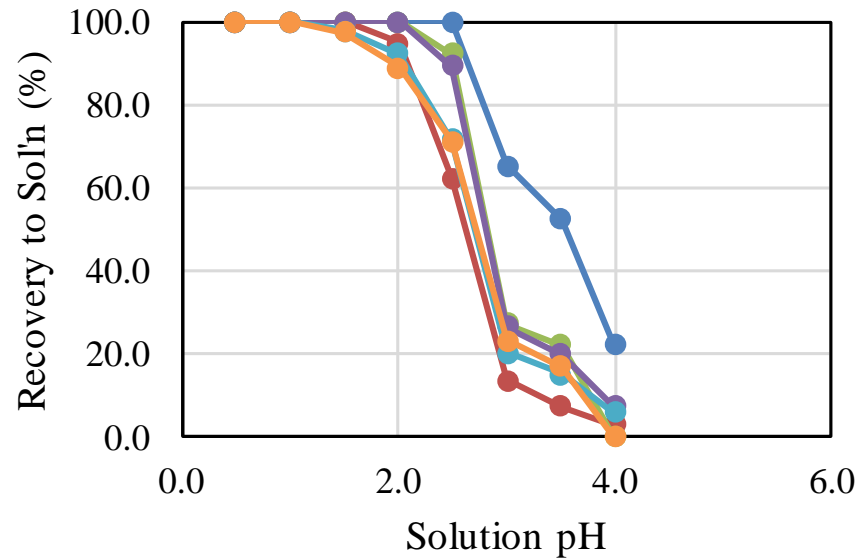
REE recovery



Acid Leaching at Ambient Temperature and Pressure

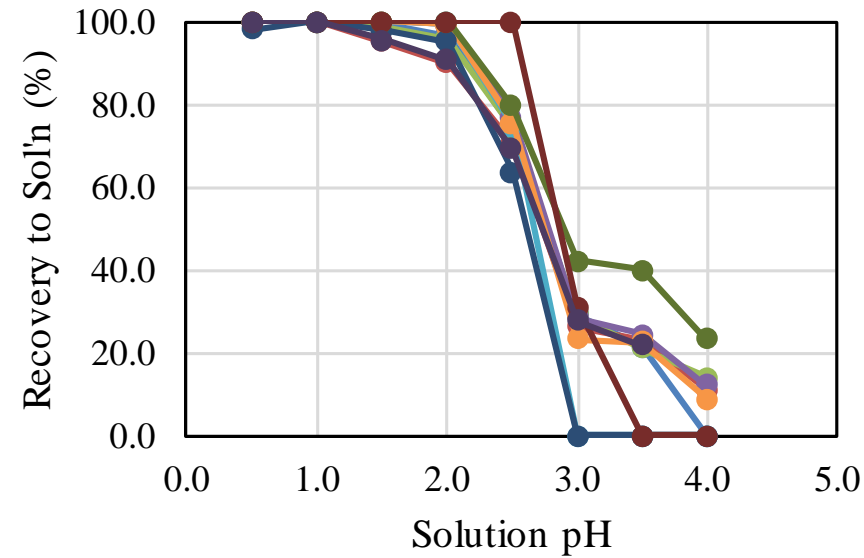
Feedstock

Light Rare Earths

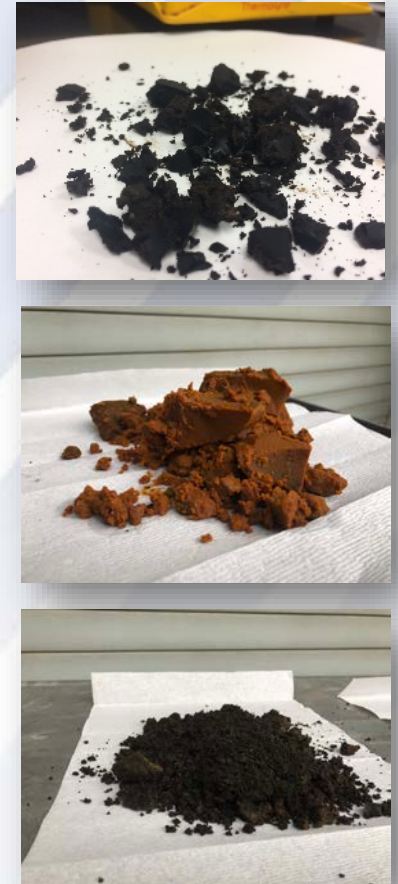


● La ● Ce ● Pr
● Nd ● Sm ● Eu

Heavy Rare Earths



● Tb ● Dy ● Ho ● Er
● Tm ● Yb ● Lu ● Y
● Sc ● Gd



Solvent Extraction-Batch Tests

Distribution Coefficients (D)

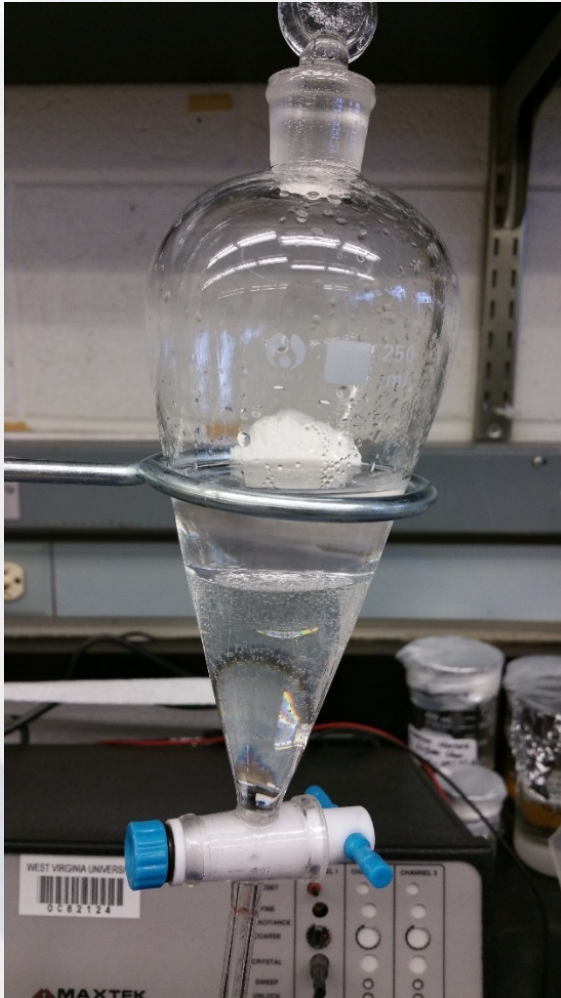
- REE = **17.7** (as high as 100+ for some elements)
- Gangue Metal = **0.023**

$$D = \frac{M_o}{M_{Aq}}$$

Separation Factor (SF)

- SF=17.7/0.023=**770**

$$SF = \frac{D_{REE}}{D_{gangue}}$$



Construction Bench-Scale, Continuous Flow Plant



SUMMARY



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Summary

Acid from coal spoils, tailings, and underground mines tends to leach REEs from the surrounding rock.



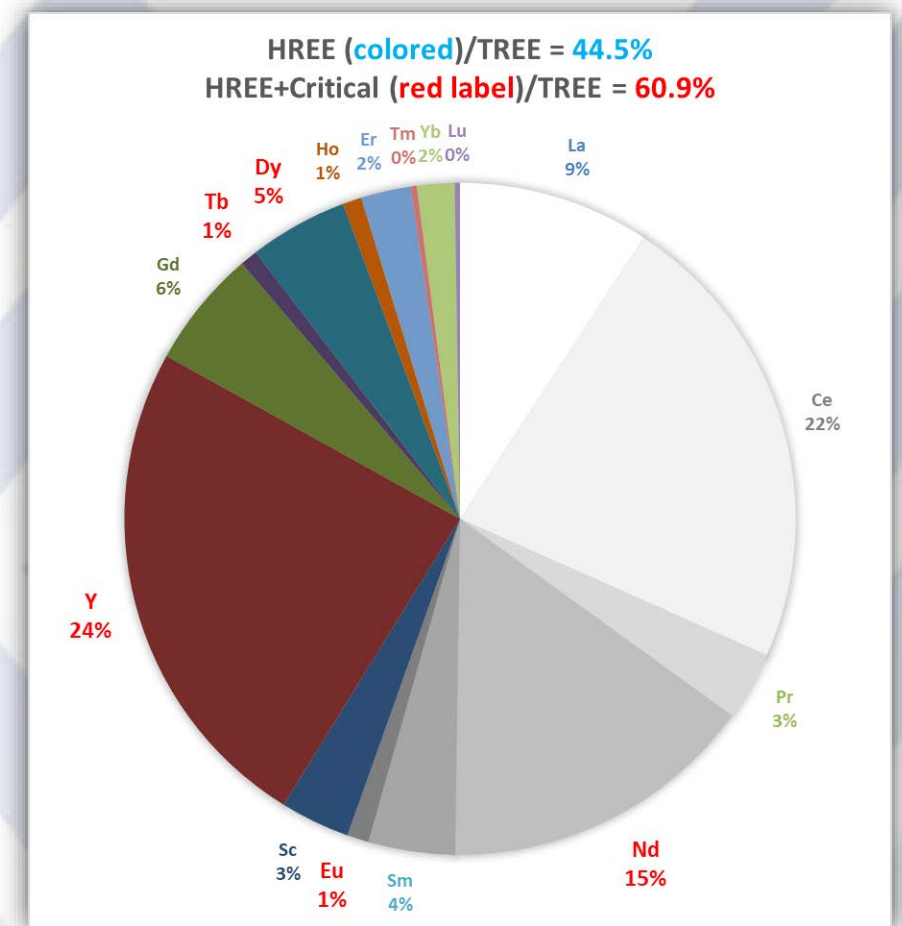
Conventional AMD treatment captures nearly 100% of the REEs and concentrates them by a factor of 2600x.



Summary

AMD sludge has a mean REE concentration of 420 g/t, with a fairly consistent elemental distribution. Excluding the lowest grades raises the average to >700 g/t.

High proportion of heavy and critical REEs



A continuous, bench scale ALSX unit is currently under construction. Operational early June 2018



Revenue potential: two scenarios

(we are in the early stages of optimizing the modular plant)

Parameter	modular plant 6.25 t/hr	Centralized plant 2100 t/day
sludge feed grade	425 g/t, 65% moisture	
overall process recovery	87.20%	
weighted average metal quotation	\$225/kg REE	
inherent value	\$96/t plant feed	
realization	\$6100/t concentrate	
REE concentrate production	1.36 t/day	29 t/day
internal rate of return	10%	46%
payback period (operating years)	18.5 years	2.5 years
Net present value (1=10%)	\$ 47,217	\$ 63,454,000



Risk: REO, SREO

High confidence

- REE distribution
- REE grade
- Regional/local resource dimension
- Prediction based on site conditions

Low confidence

- Elemental separability through ALSX
- REO distribution through ALSX
- Processing costs
- Market
- Valuation



For more information, please
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