Advanced Processing of Rare Earth Elements and Critical Minerals from Acid Mine Drainage Feedstocks

DE-FE0032120

Aaron Noble, PE, PhD

Virginia Tech

U.S. Department of Energy

National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
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Project Overview

Project Overview

- Funding
  - USDOE: $199,997
  - Cost Share: $50,000

- Project Performance Dates
  - 1/14/2022 – 4/13/2023

- Project Participants
  - West Virginia University (Ziemkiewicz)
  - Virginia Tech (Noble)
  - L3 Engineering, LLC (Larochelle)

Project Overview

The overall objective of this multi-phase project is to design, develop, and deploy innovative process technologies to produce salable rare earth metals and critical minerals from AMD feedstocks.

Key Sub-objectives:

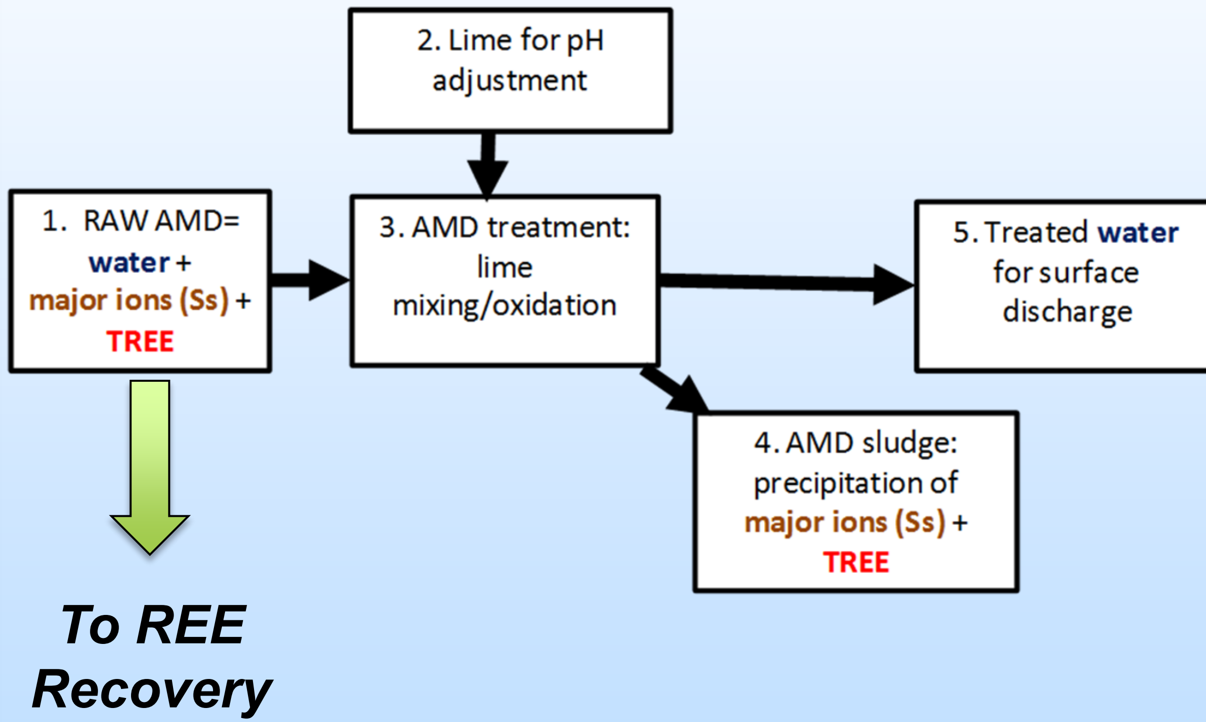
- Teaming plan development
- Resource assessment
- Preliminary process development
- Techno-economic analysis
- Research plan development

Advisory Committee

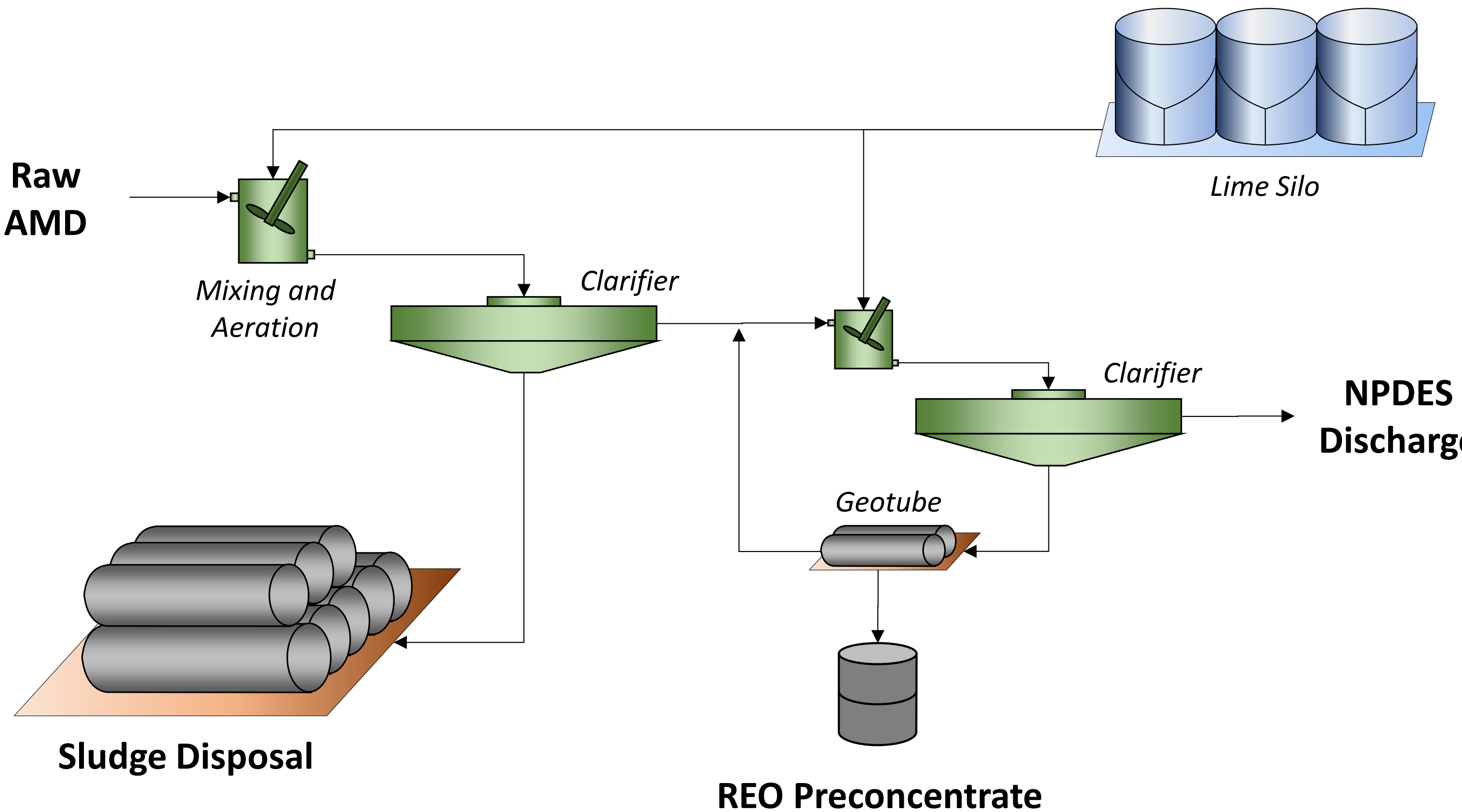
Member	Role
WV Department of Environmental Protection	Resource owner, facility operator, regulatory agency
Rockwell Automation	OEM-Automation provider
Endress and Hauser	OEM-Instrumentation provider
Hela Novel Metal	Refiner
Northrup Grumman	Purchaser/End User
Rivian	Purchaser/End User

Technology Background

Conventional AMD Treatment



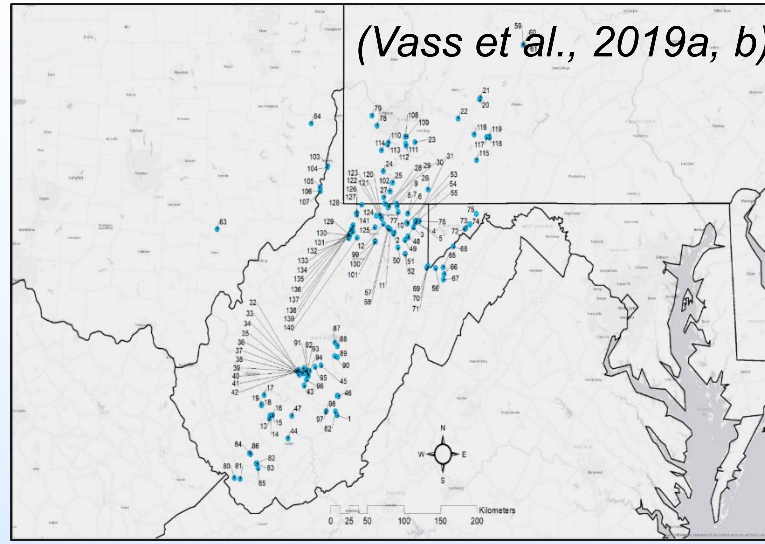
Upstream REE Preconcentration

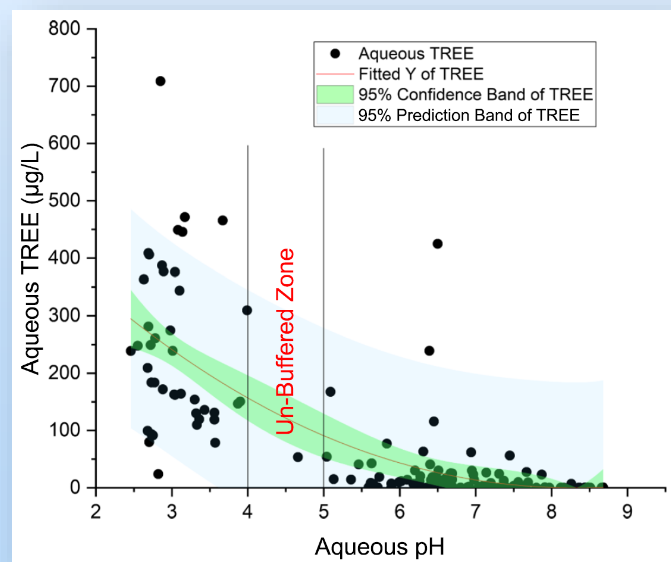


US Patent #10,954,582

Supply Chain Integration

- AMD is an abundant but disperse resource for REEs.
- No single AMD site is large enough to justify a full refining plant to final product.
- As such, the natural solution was to break the process into two operations
  - **Upstream**: initial pre-concentration that occurs at the individual AMD sites
  - **Downstream**: additional processing and refining needed to produce saleable products (e.g. oxides or metals)

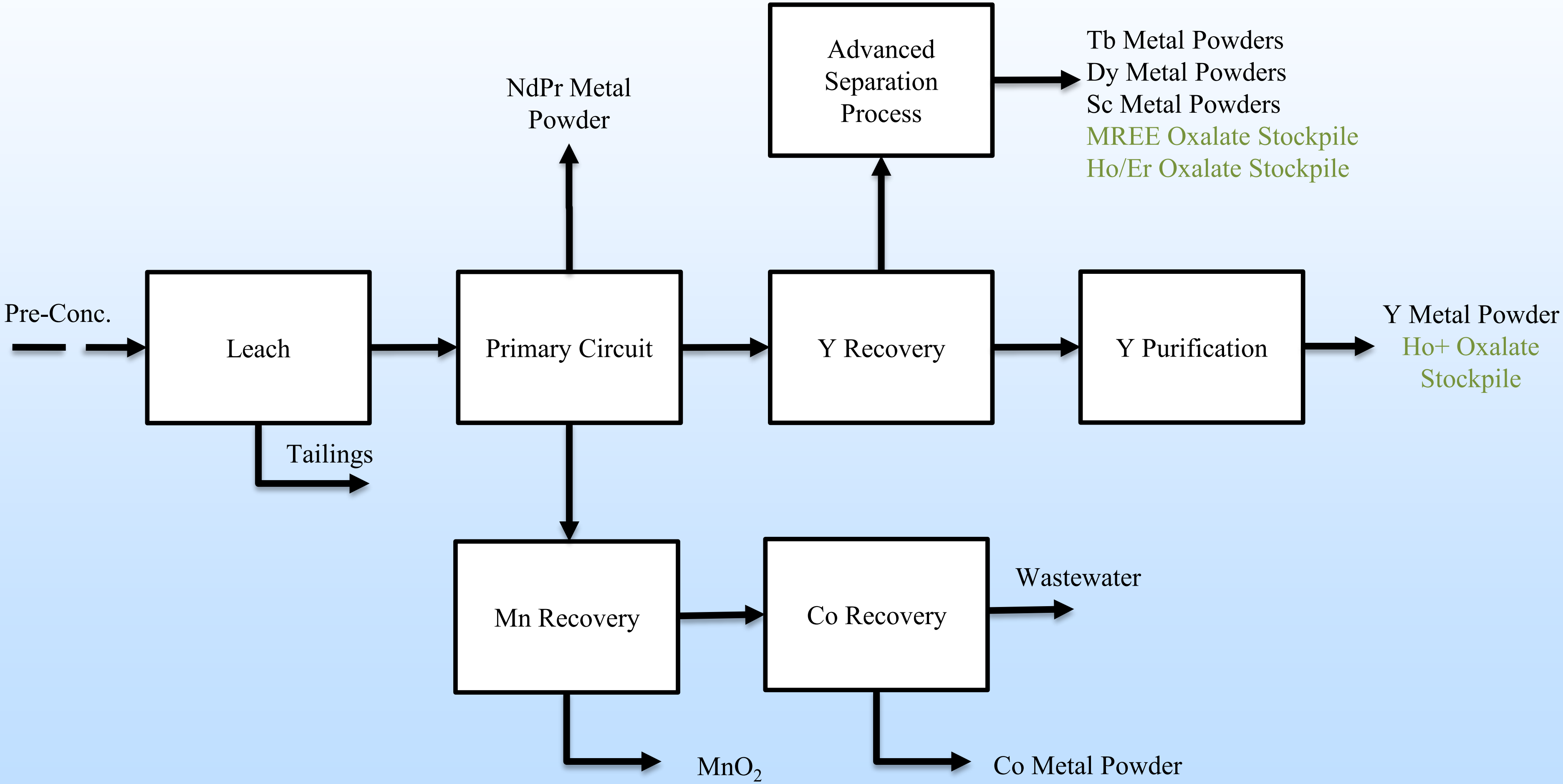




Technical Approach

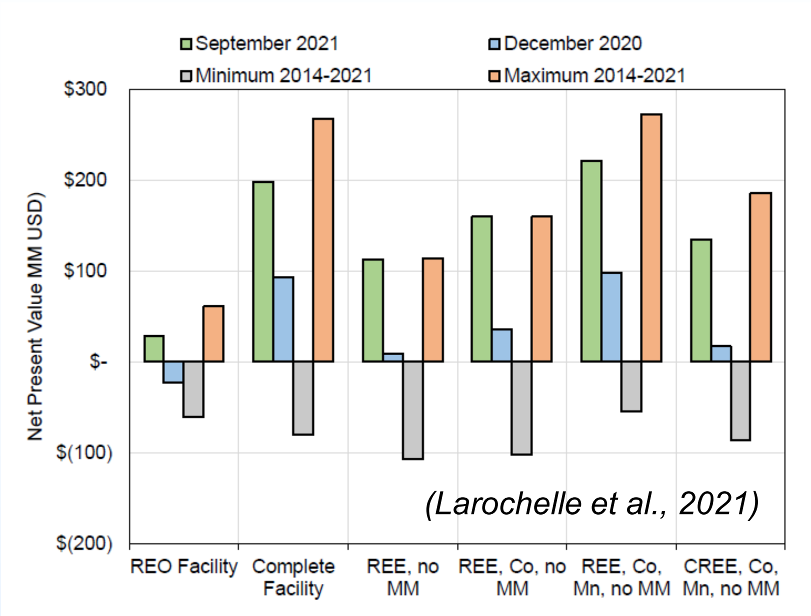
Downstream Separation BFD

1-3 TPD Separation and Refining Facility

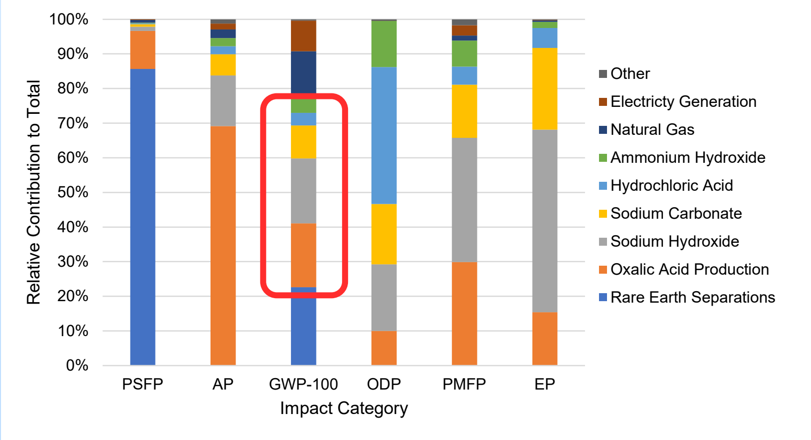


Preliminary TEA and LCA

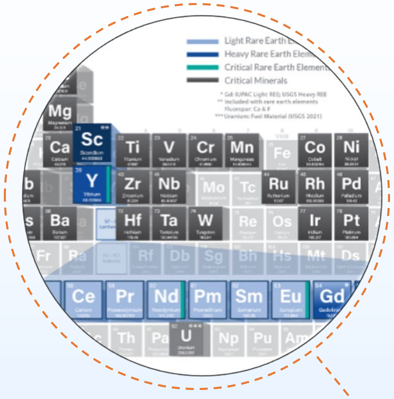
- TEA conducted under various operational configurations and REE pricing scenarios.
- Results showed favorable economics, with capital cost and stripping acid being major sensitive factors.



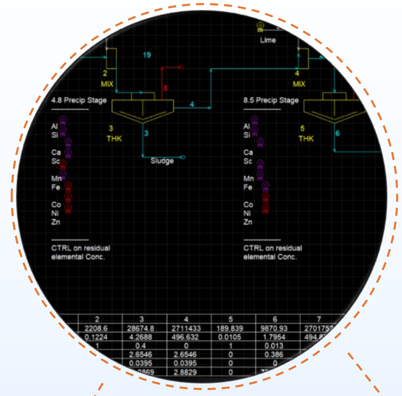
- LCA indicated that embodied CO_2 is approximately 50% relative to conventional monazite and bastnaesite production routes.
- Reagent use was the major contributing factor (cf. energy and transport).



Keys to the Technical Approach

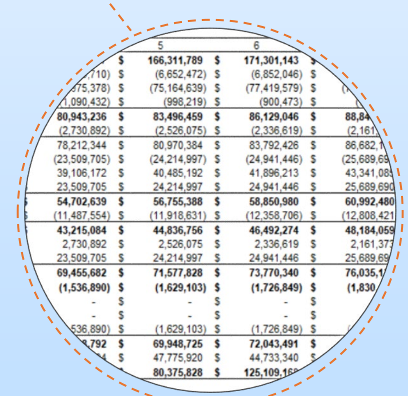


Identify target CMs, redefine BFD



Evaluate technical performance with METSIM

Assess novel separations, namely ionic liquids



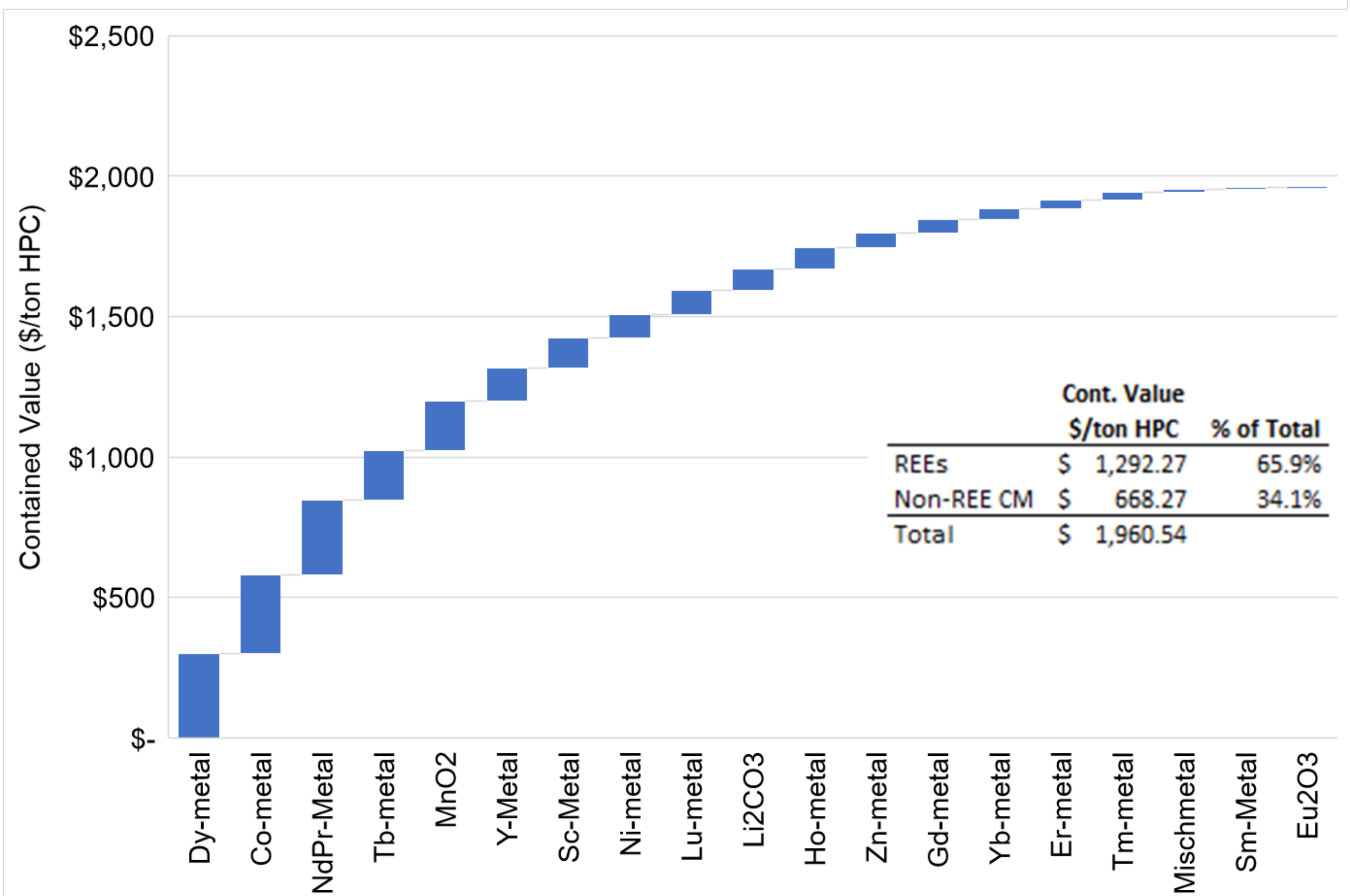
Conduct final TEA

Current Progress

Evaluation of Candidate Elements

	A	B	A x B	*Conc factor
	ug/L		Value	AQ to OXP
AQ65	22'0651	$/kg	index	^mg/kg
Rb	35.4	82,700	2,924,272	3,556
In	256.0	360	92,160	25,745
Pd	1.3	27,650	35,116	128
Ge	14.0	1,358	19,012	1,408
Be	11.0	630	6,930	1,106
Li	293.0	14	4,073	29,466
Pt	0.0	30,865	123	0
As	37.0	2	74	3,721
V	2.0	11	23	201
Ta	0.1	193	11	6
Hf	0.2			
Sn	<0.081			
Sb	<0.030			
Cr	<0.015			
Ir	<0.014			
Ga	<0.009			
Ru	<0.006			
Cs	<0.004			
Rh	<0.002			
Ti	<0.001			

AMD PC Contained Value (w/ CMs)

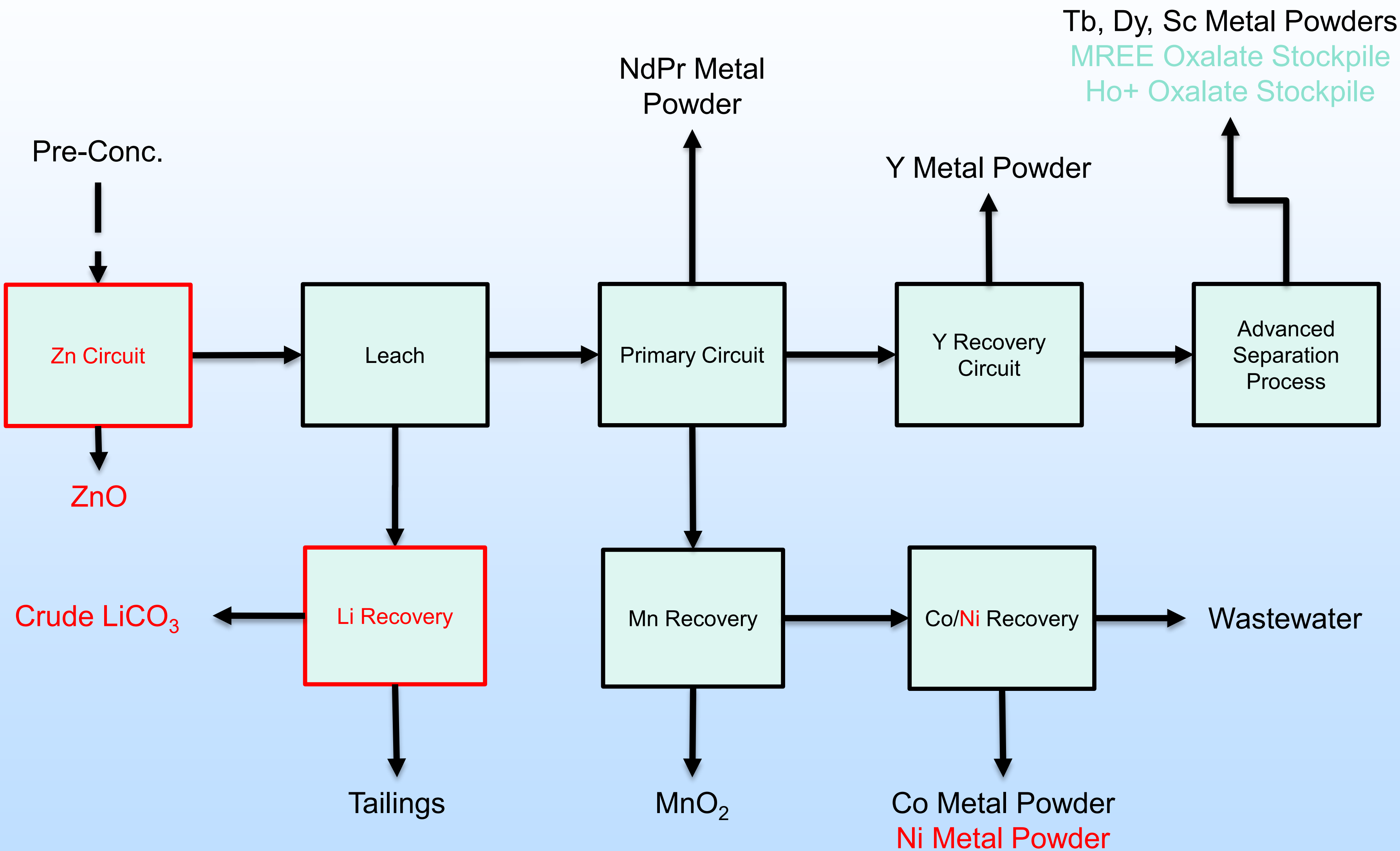


	Cont. Value $/ton HPC	% of Total
REEs	$ 1,292.27	65.9%
Non-REE CM	$ 668.27	34.1%
Total	$ 1,960.54	

	Avg Conc mg/kg	% of TREE
Sc	32.3	0.3%
Y	2,908.4	30.7%
La	629.8	6.6%
Ce	1,572.2	16.6%
Pr	302.8	3.2%
Nd	1,592.2	16.8%
Sm	459.4	4.8%
Eu	115.0	1.2%
Gd	688.6	7.3%
Tb	95.6	1.0%
Dy	521.9	5.5%
Ho	96.3	1.0%
Er	250.4	2.6%
Tm	30.3	0.3%
Yb	166.6	1.8%
Lu	24.6	0.3%
TREE	9,486.4	

Non-REE CM	
Co	4,765.9
Ni	4,730.1
Mn	56,124.3
Li	2,865.0
Zn	17,555.3

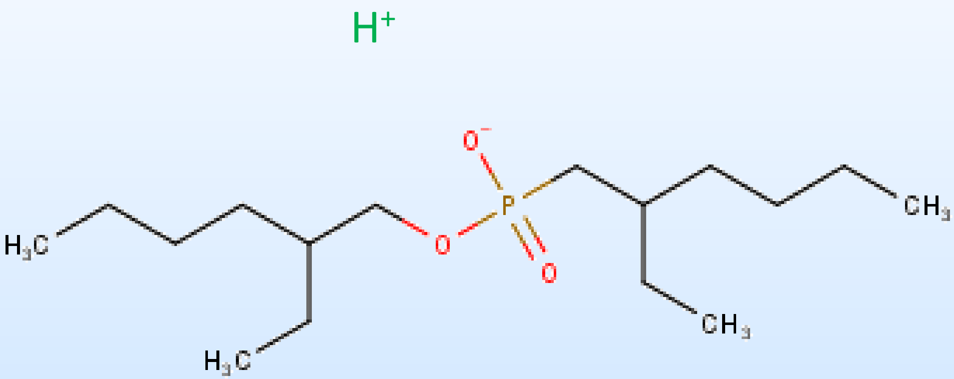
Updated BFD


Tb, Dy, Sc Metal Powders
MREE Oxalate Stockpile
Ho+ Oxalate Stockpile
NdPr Metal Powder
Pre-Conc.
Y Metal Powder
Zn Circuit
Leach
Primary Circuit
Y Recovery Circuit
Advanced Separation Process
ZnO
Crude $LiCO_3$
Li Recovery
Mn Recovery
Co/Ni Recovery
Wastewater
Tailings
MnO_2
Co Metal Powder
Ni Metal Powder

Conventional Extractants

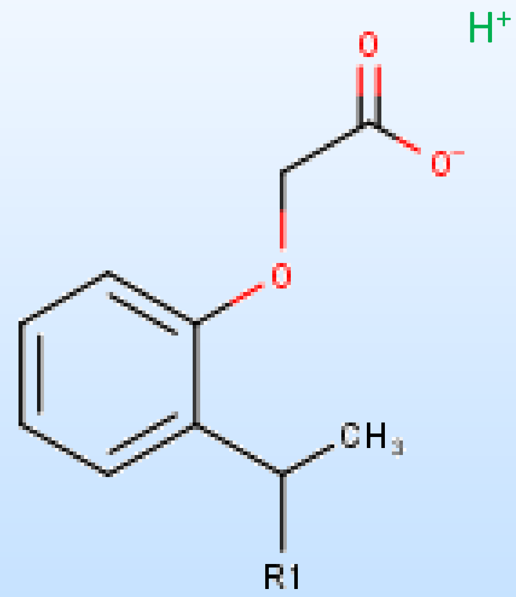
Primary Circuit – EHEHPA

$Ln^{3+} + 3\ \text{H-EHEHP} \rightarrow Ln(\text{EHEHP})_3 + 3\ H^+$



Yttrium Circuit – SOPAA

$Ln^{3+} + 3\ \text{H-SOPA} \rightarrow Ln(\text{SOPA})_3 + 3\ H$



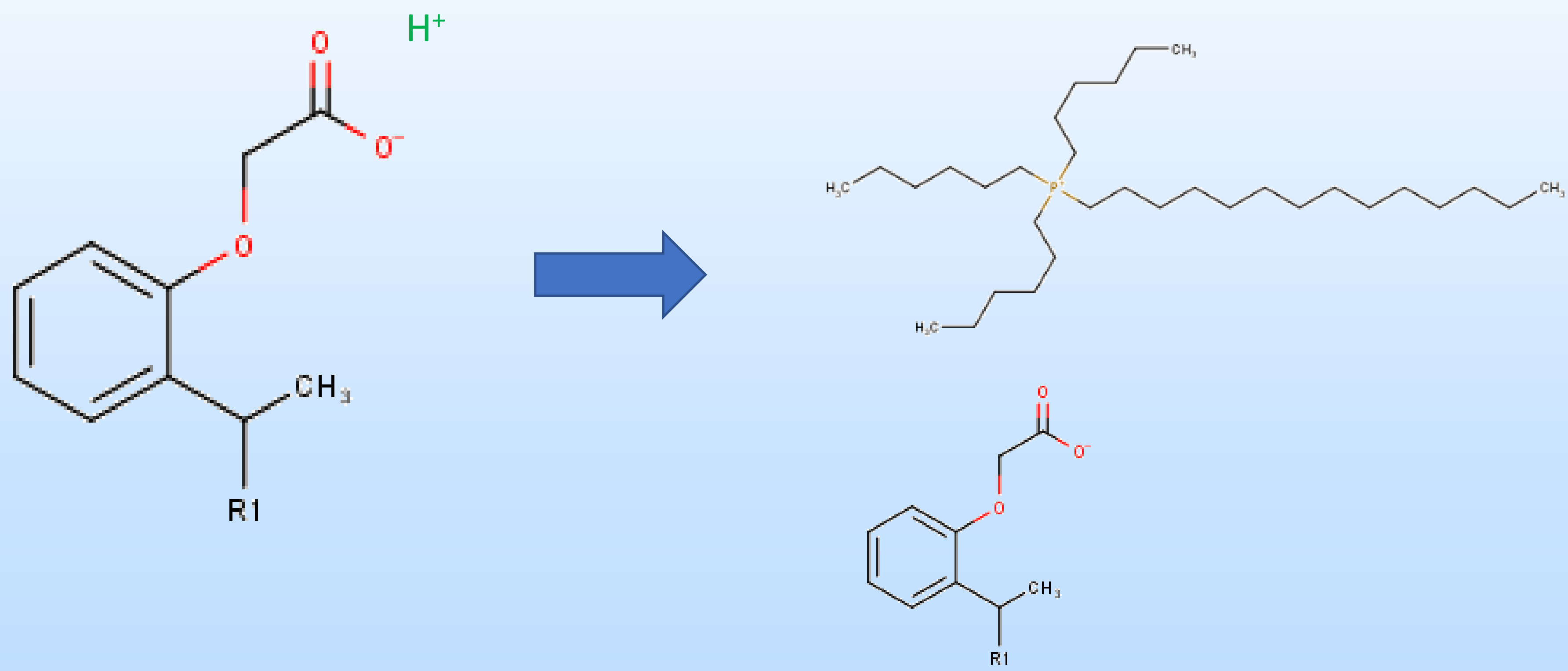
Ionic Liquid Extractants – Y Circuit

SOPAA

Ln^{3+} + 3 H-SOPA -> $Ln(SOPA)_3$ + 3 H

[P66614][SOPA]

LnCl3 + [P66614][SOPA] -> [SOPA][LnCl3][P66614]



Ionic Liquid Extractants – Y Circuit

Separation Factors (from literature)

Extractant	Ho/Y	Er/Y	Tm/Y	Yb/Y	Lu/Y
SOPAA	1.74	1.68	1.35	1.27	1.08
$[P_{66614}]$[SOPA]	1.94	1.94	2.78	4.17	5

[P66614][SOPA] has 4x the loading capacity of SOPAA

(Huang et al., 2017)

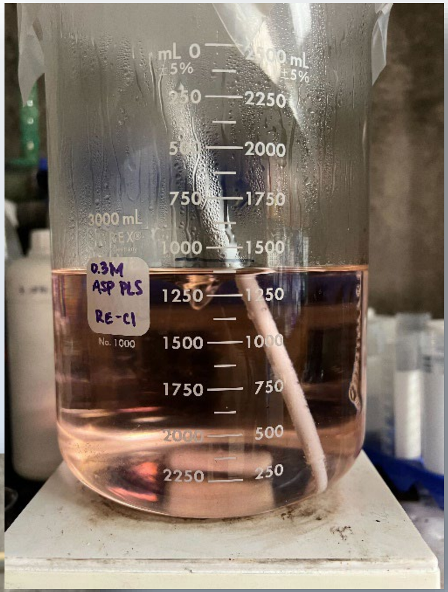
Ionic Liquids Literature Survey

ID	H	[N88]	[N888]	[N1888]	[N888DOPE]	[N1444]	[N2222]	[N4444]	[N8888]	[N6222]	[N444Bn]	[P66614]	[P8884COOH]	[P81R
[D2EHP]	G	[137]		[112]			[134]	[134]	[134]					
[EHEHP]	G			[112]			[134]	[134-171]	[134]					
[C272]			[124]	[213-496]	[D-012]			[171]	[124]	[100 - 124]		[229]		
[P227]	[365]			[365]										
[C572]														[373]
SPEx														
PF6														
ND	[D-002]			[D-002]										
N														
[SNPAA]														
[SOPAA]				[030]								[259]		
[NOPAA]				[030]										
[DMHPAA]	[268]			[268]										
[IOPAA]												[411]		
[BDOAC]														
MA											[D-015]			
DDA											[D-015]			
[BA]												[200]		
[Cl]/[NO3]													[z009]	

- Very High Interest
- High Interest
- Med Interest
- Low Interest
- No interest

Ionic Liquids Scoping Tests

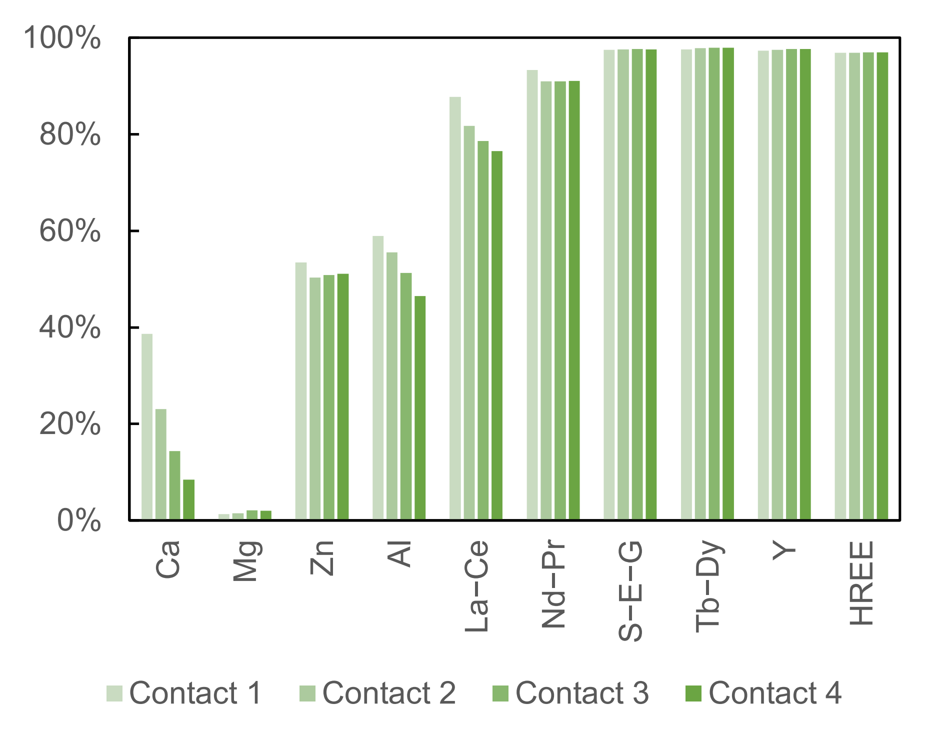
- Common extractants and corresponding ionic liquids evaluated in a comparative test program:
  - D2EHPA + TBP
  - EHEHPA
  - C572
  - [c101][D2EHP]
  - [c101][EHEHP]
  - [c101][C572]



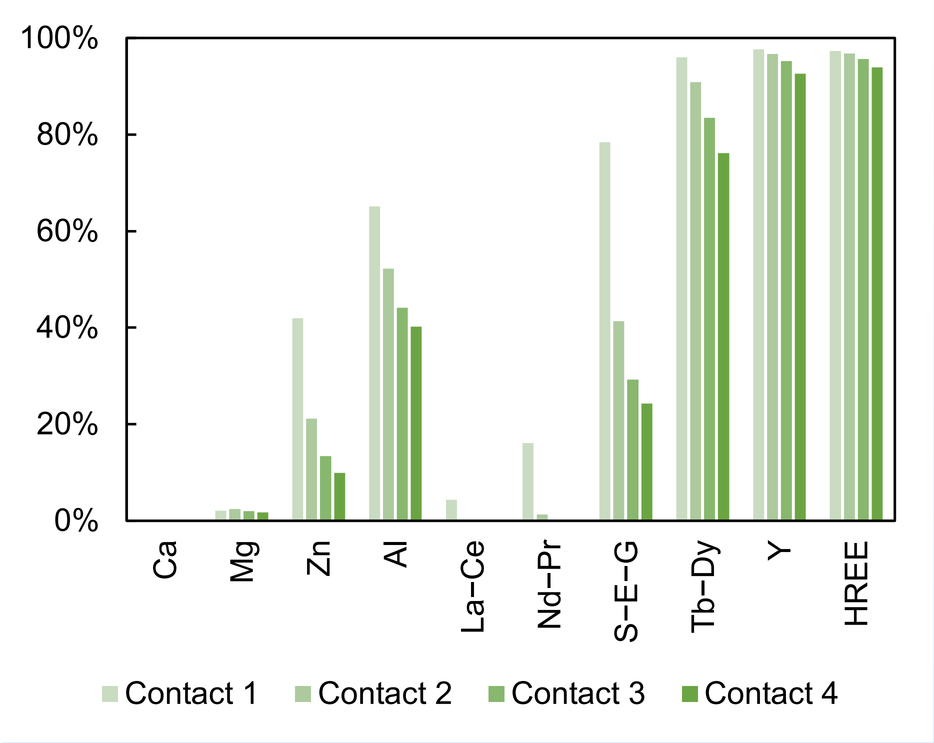
(Larochelle et al., 2022)

Cumulative Extraction – 4 Contacts

1 M D2EHPA + TBP

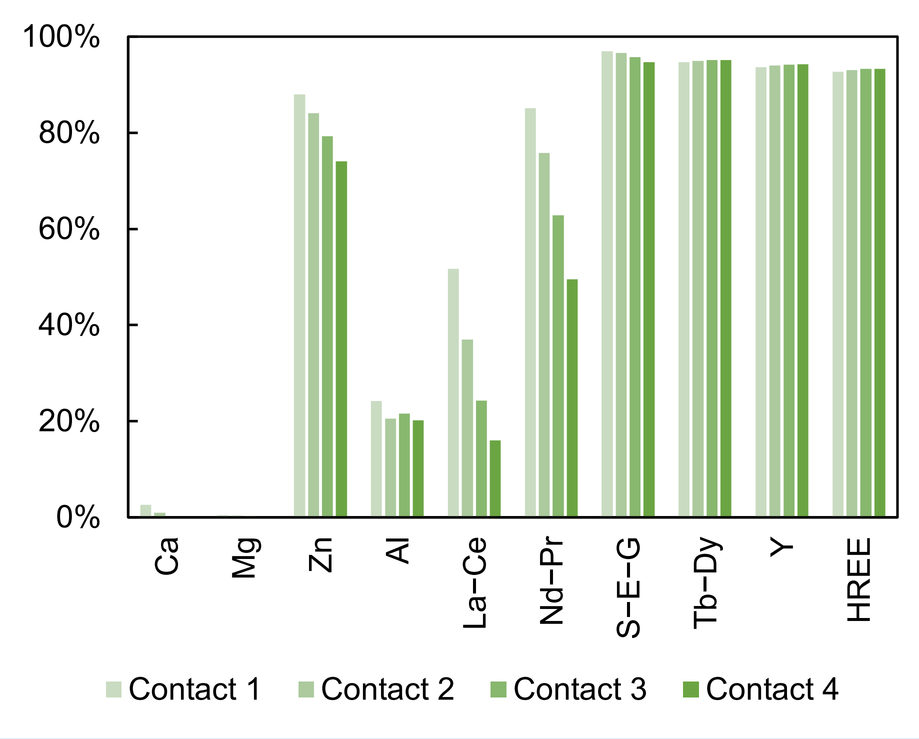


1 M [c101][D2EHP]

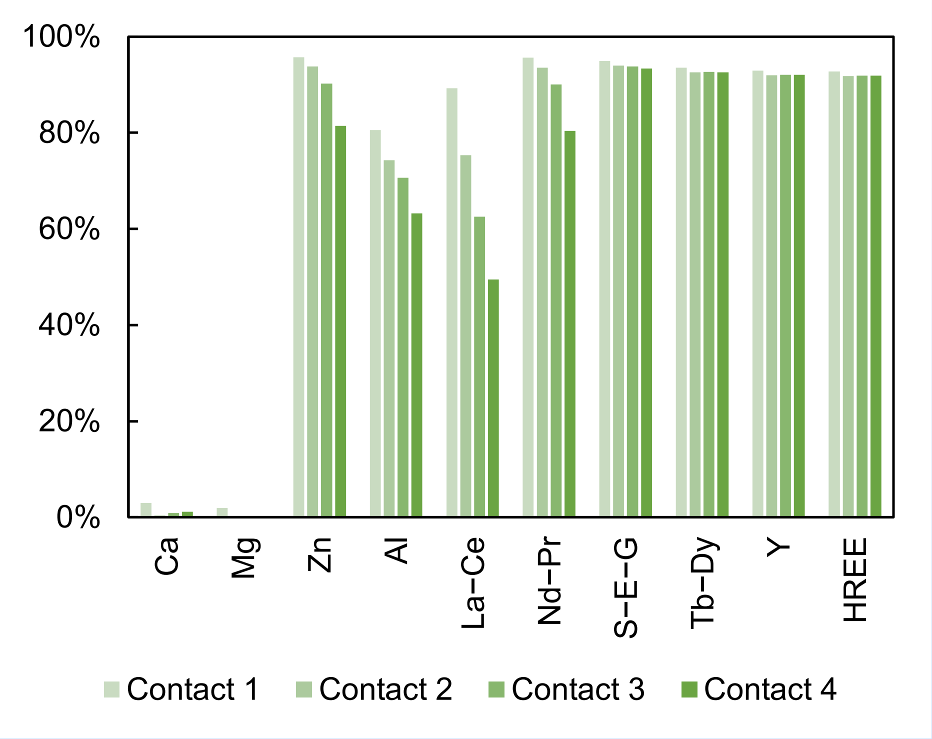


Cumulative Extraction – 4 Contacts

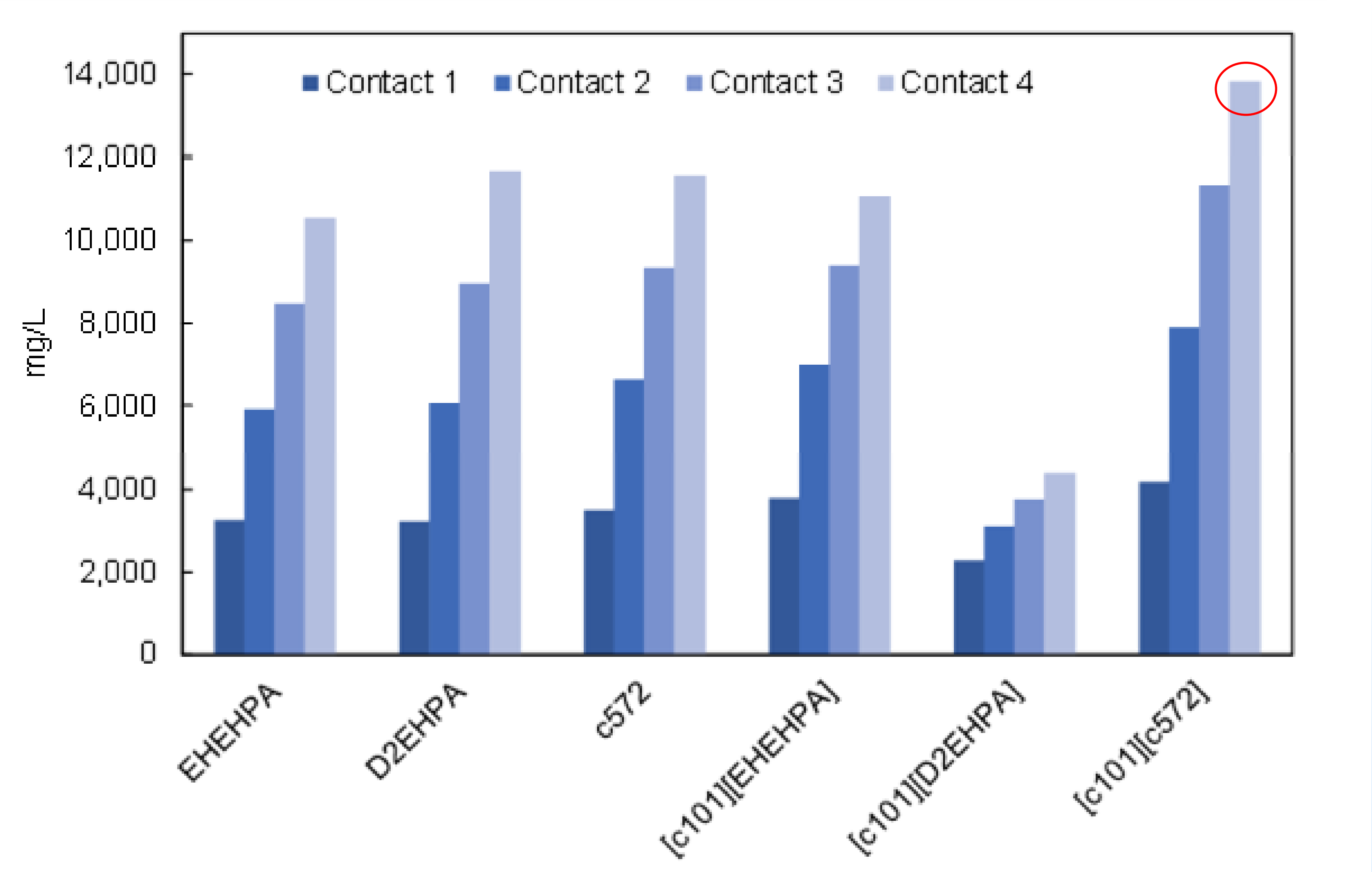
1.05 M C572



1 M [c101][C572]



Total Organic Loading



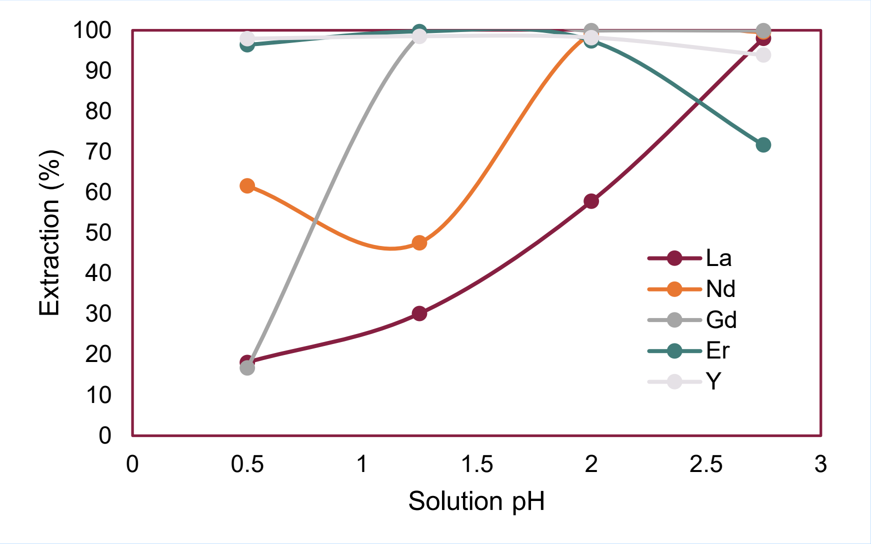
Separation Factors

Element Pair	0.1M EHEHPA	0.1M [c101][EHEHP]	0.1M D2EHPA	0.1M [c101][c572]
Al / Pr	1.38	4.26	2.24	1.81
Zn / Pr	3.89	3.67	0.55	1.81
Ce / La	2.04	1.10		1.28
Pr / Ce	0.91	0.81	1.90	0.93
Nd / Pr	1.43	1.47	1.38	1.31
Sm / Nd	2.25	0.80	2.63	1.14
Eu / Sm	1.49	1.03	1.18	1.00
Gd / Eu	1.32	1.44	1.07	1.27
Tb / Gd	1.89	**2.29**	1.31	**2.27**
Dy / Tb	1.29	**2.01**	1.17	**1.94**
Ho / Dy	1.19	1.92	1.11	1.70
Y / Ho	1.17	1.70	1.15	1.50

New Acidic Extractants

Advantages

- Easy to synthesize
- High acidity
- Many possible conformations
- High potential for transition to ionic liquid



Weaknesses

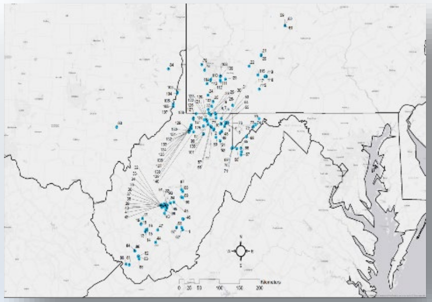
- High Acidity
- Unproven
- Optimum molecular structure not yet identified.

Future Work and Summary

Future Plans

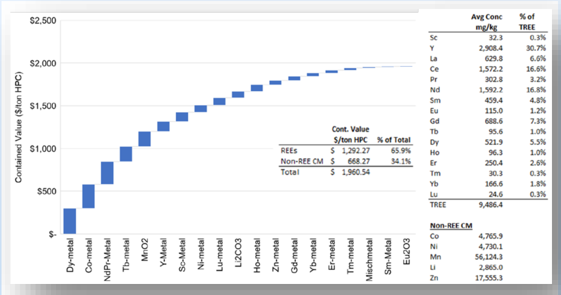
- **Laboratory Verification**
  - Stripping tests
  - Performance verification
- **Process Design**
  - Reevaluate process model
  - Conduct final TEA
- **Scale-Up**
  - Identify knowledge gaps
  - Conduct pilot trials

Summary



AMD is a disperse but promising source of REEs. Keys to the approach include an upstream preconcentration technology and a downstream refinery.

Co, Mn, Ni, and Zn recovery can be readily incorporated into the existing process and have the potential to add significant value.



We have synthesized and tested a range of ionic liquids for REE separations. Several candidates merit further study and optimization.

Questions?

For more information, please contact:

Aaron Noble

Aaron.noble@vt.edu

Paul Ziemkiewicz

pziemkie@wvu.edu

Tommee Larochelle

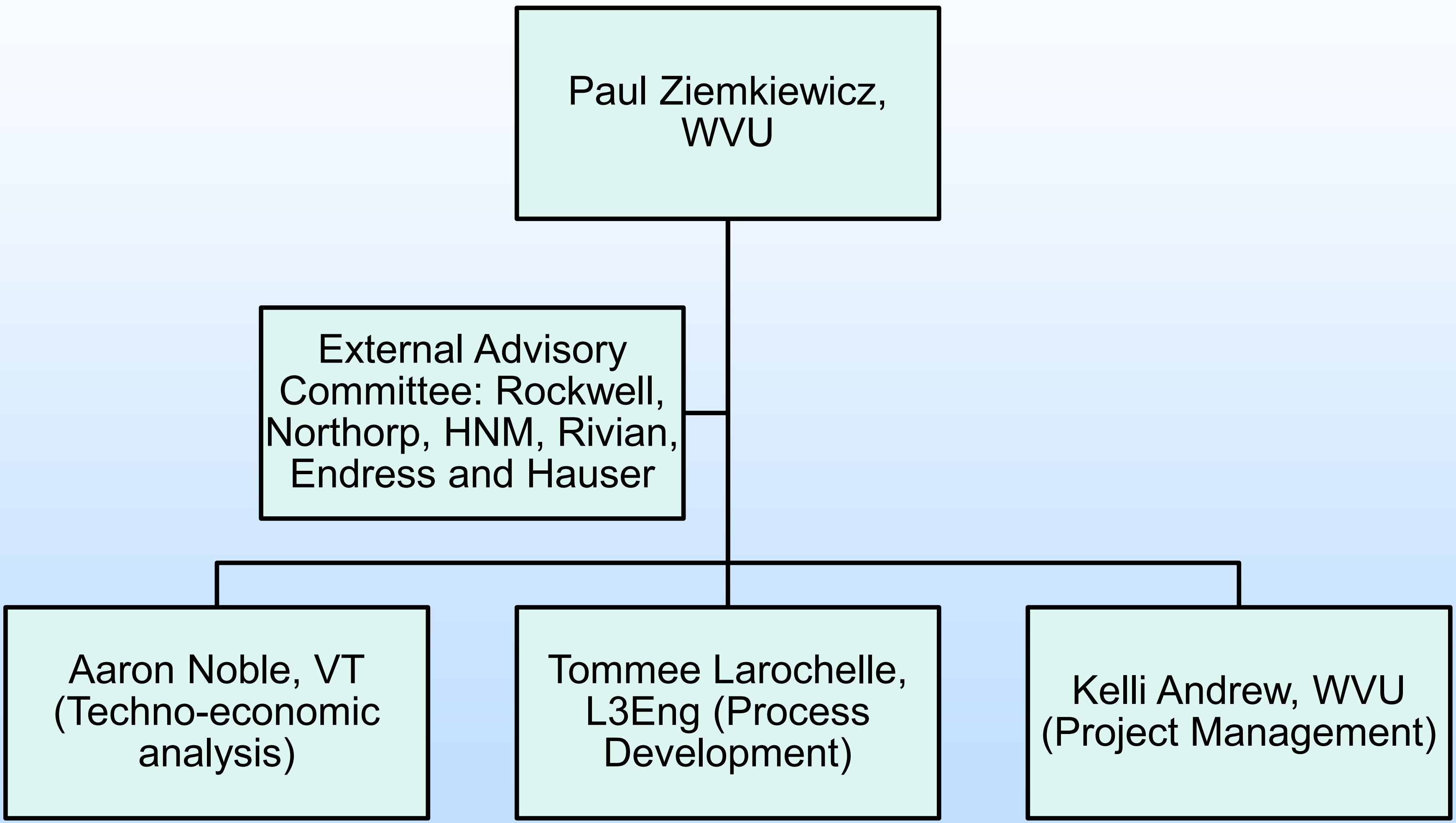
Tommee.Larochelle@l3eng.com

Appendix

Acknowledgements

The authors would like to thank Allie Ahn, Kris Strickland, James Constant, David Hoffman, and Caitlin Glasock who contributed to the studies in this report.

Organizational Chart



Schedule

			Project Month								
ID	Task	Lead	1	2	3	4	5	6	7	8	9
1.0	Project Management and Planning	Ziemkiewicz, Andrew									
2.0	Team Coordination and Market Research	Ziemkiewicz									
3.0	Resource Assessment and Feedstock Selection	Ziemkiewicz									
4.0	Preliminary Process Development	Larochelle									
4.1	Process Technical Analysis	Larochelle									
4.2	Process Synthesis and Modeling	Larochelle									
4.3	Process Techno-Economic Analysis	Larochelle									
5.0	Technical Research Plan Development	Noble									
5.1	Project Risk Assessment	Noble									
5.2	Technical Research Plan Formulation	Noble									
			Sept	Oct	Nov	Dec	Jan	Feb	Mar	Ap	May
			2021				2022				