Application of Supported Liquid Membranes for Extraction of Rare Earth Elements from Acidic Coal Mine Drainage

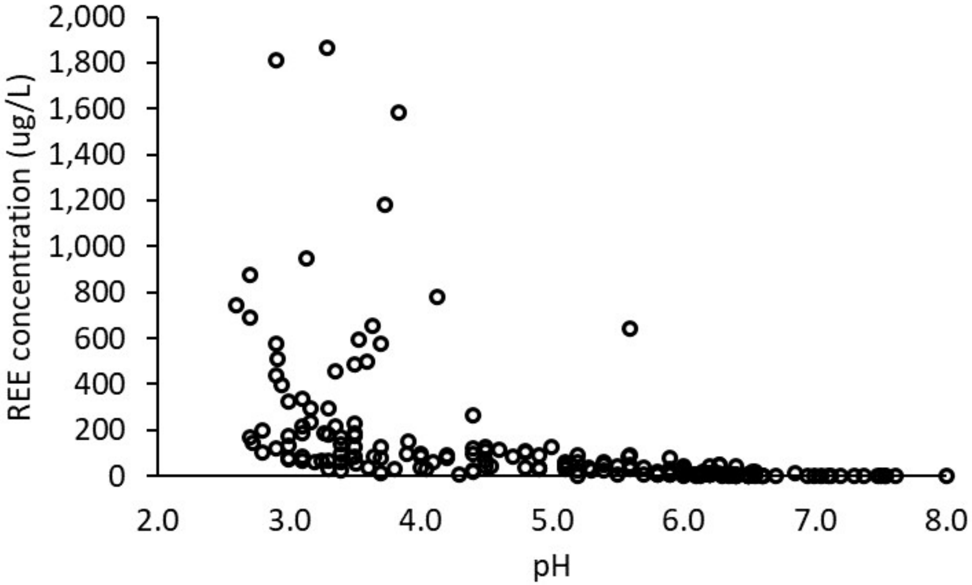
Helen Hsu-Kim, Andrew Middleton
Civil & Environmental Engineering
Duke University

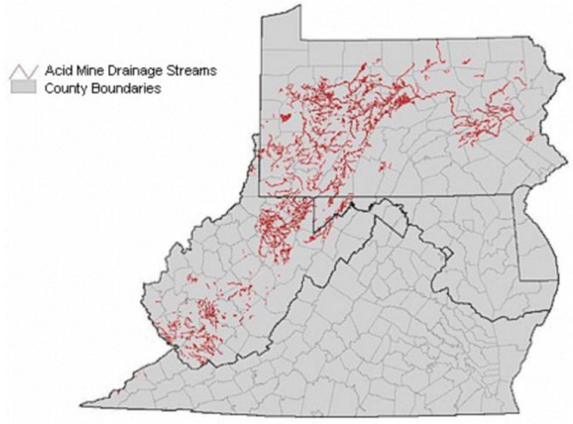
Benjamin Hedin
Hedin Environmental Inc.

Duke | DEPARTMENT OF Civil & Environmental Engineering

Acid Mine Drainage as a Rare Earth Element Resource

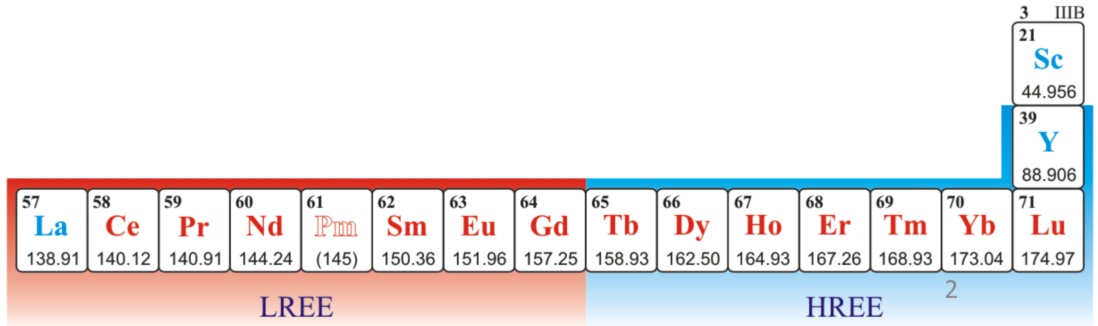
Enrichment of REE in certain types of AMD:





In Northern Appalachian region:

800-3000 tons REE per yr from AMD



Cravotta *Appl Geochem* 2008
Stewart et al., *Intl J Coal Geol* 2017
Vass et al., *Mining, Metalurg, Explor.* 2019

Duke | Department of Civil & Environmental Engineering

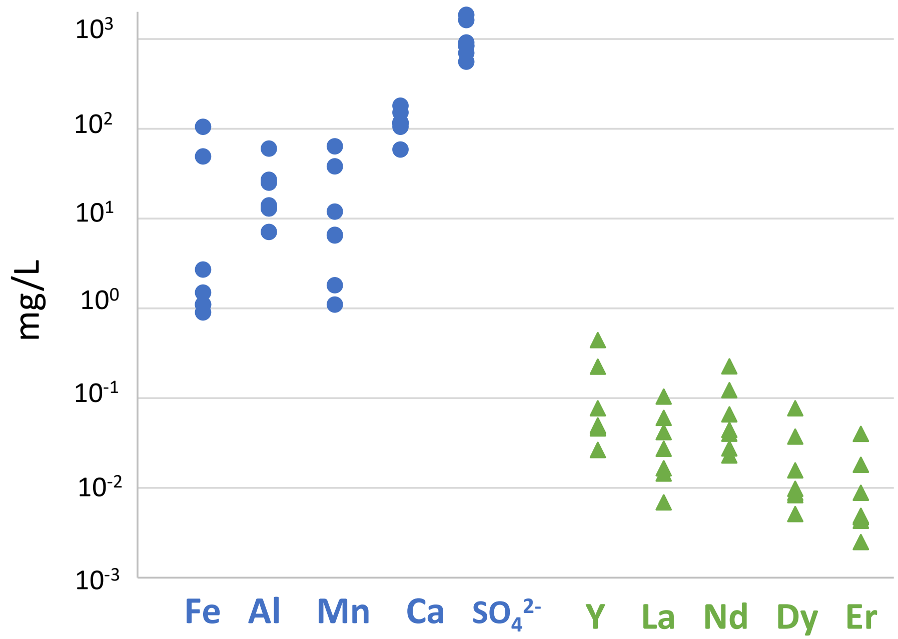
REEE recovery from Acid Mine Drainage (AMD)

Scope of this study:
To extract REE directly from drainage fluids with supported liquid membranes

Challenges for REE extraction:

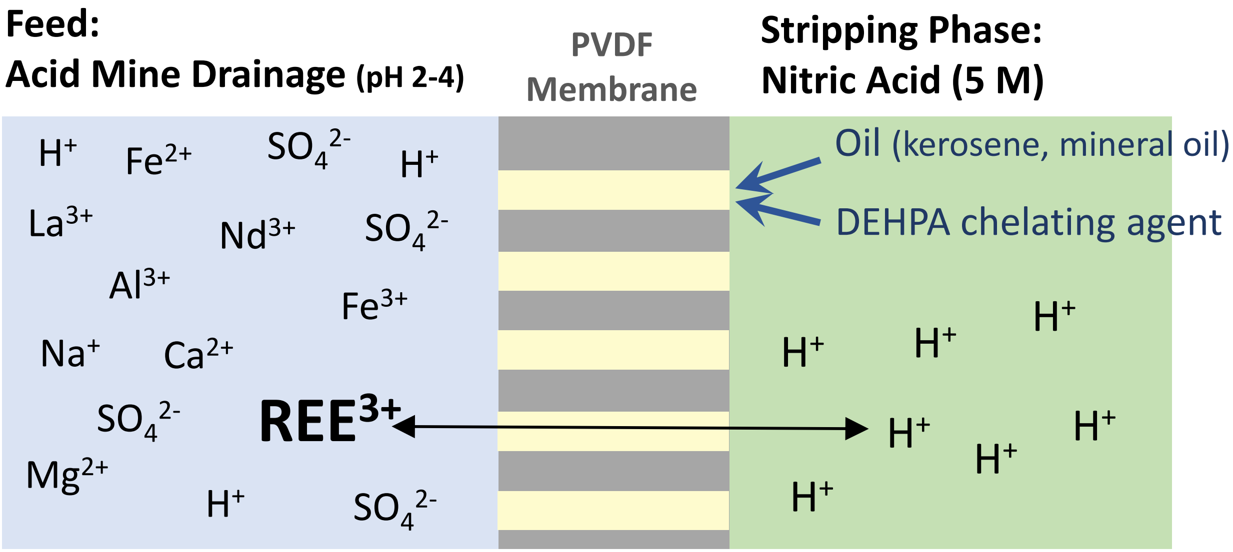
- Other major elements in AMD:
  Fe, Al, Ca, Mg, SO_4^{2-}
- Selectivity for REE ions:
  $10^2 – 10^5$-fold selectivity
- Relatively dispersed resource

Solute composition in Acid Mine Drainage
(pH 2-4)



Duke | DEPARTMENT OF Civil & Environmental Engineering

Supported Liquid Membranes

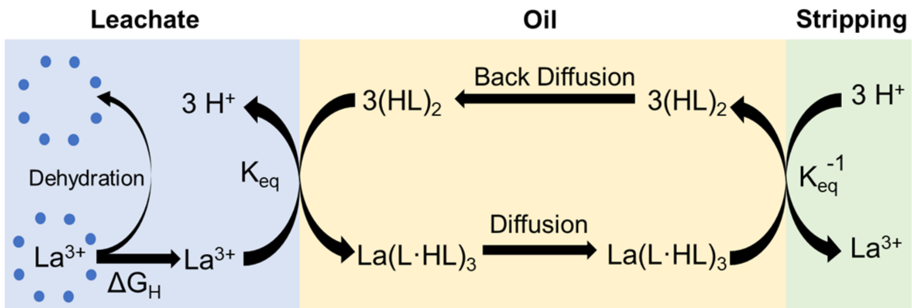


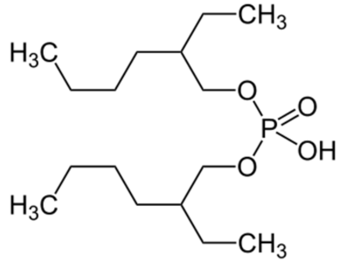
Advantages:

- Reduced solvent usage
- Modular process design

Key unknowns:

- Efficacy for dilute and variable feedstocks
- Mass transfer rates and selectivity?



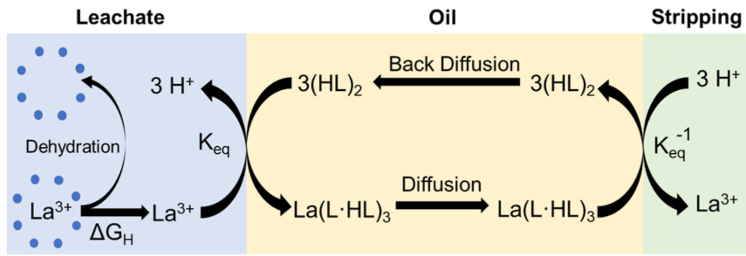


di(2-ethylhexyl)phosphoric acid
(DEHPA)

Duke | DEPARTMENT OF Civil & Environmental Engineering

Supported Liquid Membranes for REE Recovery from AMD

Overall objective: To quantify the efficacy of SLM for REE recovery from AMD feedstocks



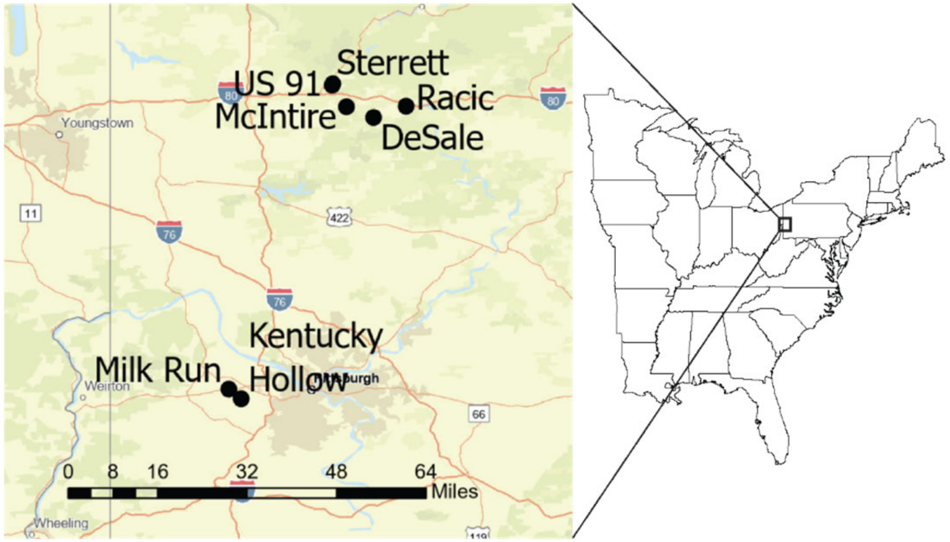
Approach:

1. Measure REE extraction flux vs. AMD composition
2. Establish trends in metal ion selectivity (e.g., competition between Nd^{3+} and Fe^{3+})
3. Quantify product purity and yield rate

Study Design

Drainage collected from 7 abandoned coal mines in southwestern Pennsylvania

Raw AMD, mostly at inlet of treatment systems



AMD site locations (May 2022)

Duke | DEPARTMENT OF Civil & Environmental Engineering

Study Design

AMD site locations:

Grouped according to drainage composition

Group 1- low pH, high metals

Group 2- medium pH and metals

Group 3- high pH, low metals

AMD Site Name	pH	Fe mg/L	Al mg/L	Mn mg/L	Ca mg/L	Cl^- mg/L	SO_4^{2-} mg/L	Total REE mg/L	Flow Rate L/min
McIntire	2.98	105	60	38	115	57	1629	1.5	143
DeSale	3.08	49	14	64	180	21	1864	0.78	--
Racic	3.19	1.1	7.1	12	59	76	913	0.17	--
Kentucky Hollow	3.24	2.7	13	6.5	152	124	848	0.24	582
US 91	3.27	1.5	27	6.6	105	19	831	0.38	64
Milk Run	3.30	1.1	13	1.1	118	3.51	698	0.12	1220
Sterrett	3.52	0.9	25	1.83	115	2	556	0.23	378

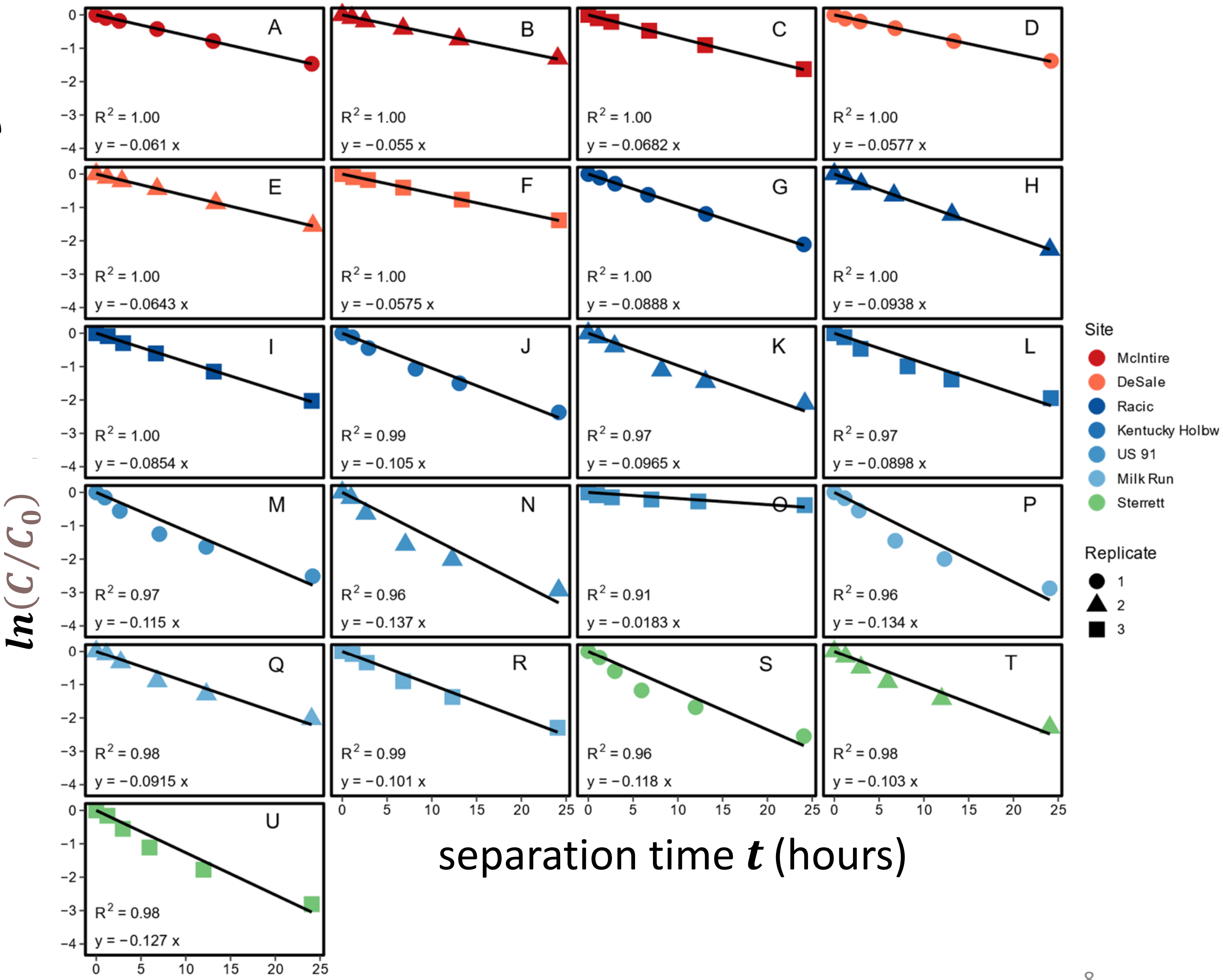
**Also note the wide rate of flowrates!

Neodymium flux across the membrane

$$\ln\left(\frac{C}{C_0}\right) = -\frac{A}{V}\boldsymbol{P}t$$

Permeability coefficient *P* (L m^{-2} h^{-1})

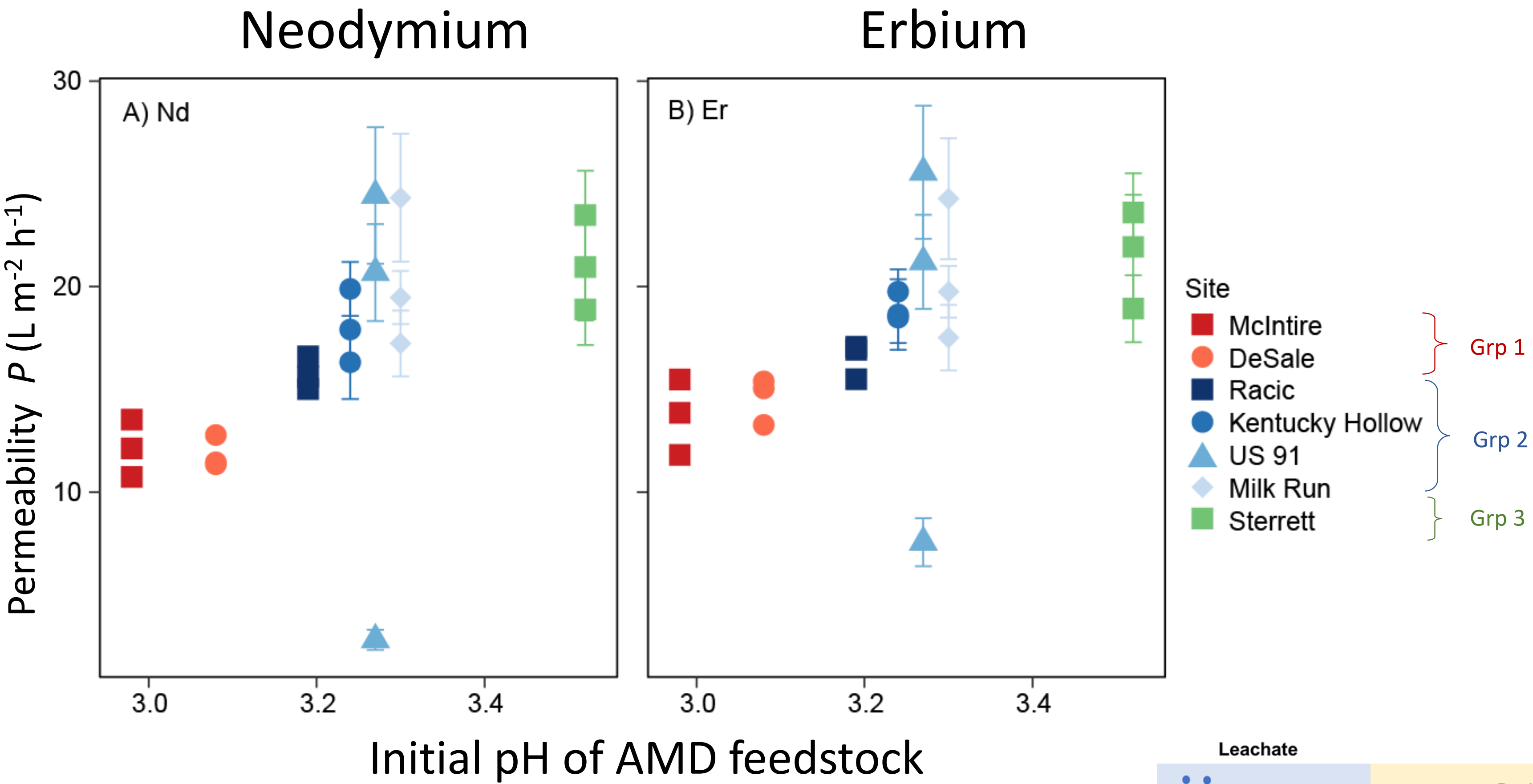
A=membrane area
V=feedstock volume



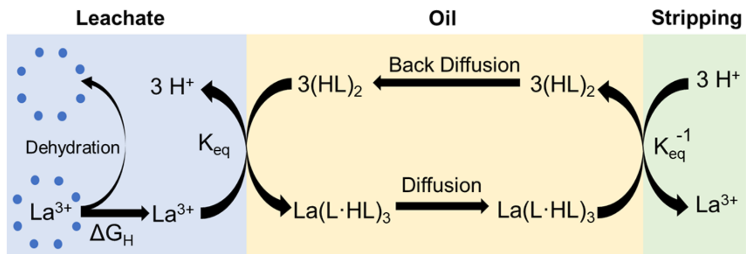
Middleton *et al. ES&T* 2024

Duke | Department of Civil & Environmental Engineering

REE flux increases with pH of AMD feed



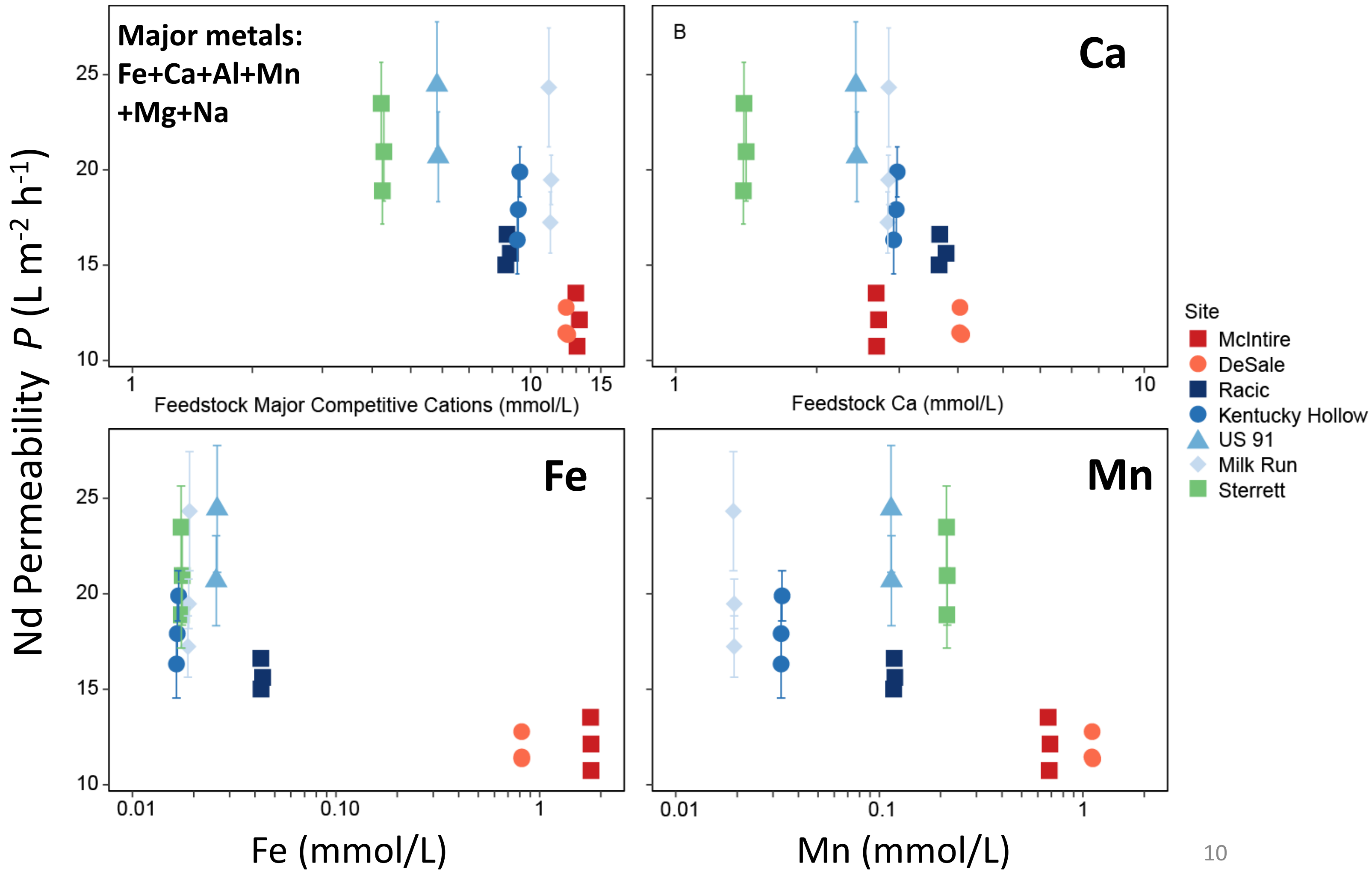
Middleton *et al. ES&T* 2024



Duke | DEPARTMENT OF Civil & Environmental Engineering

Major metal cations in AMD

Neodymium permeability decreases with metals in AMD (esp. Fe, Ca, Mn)

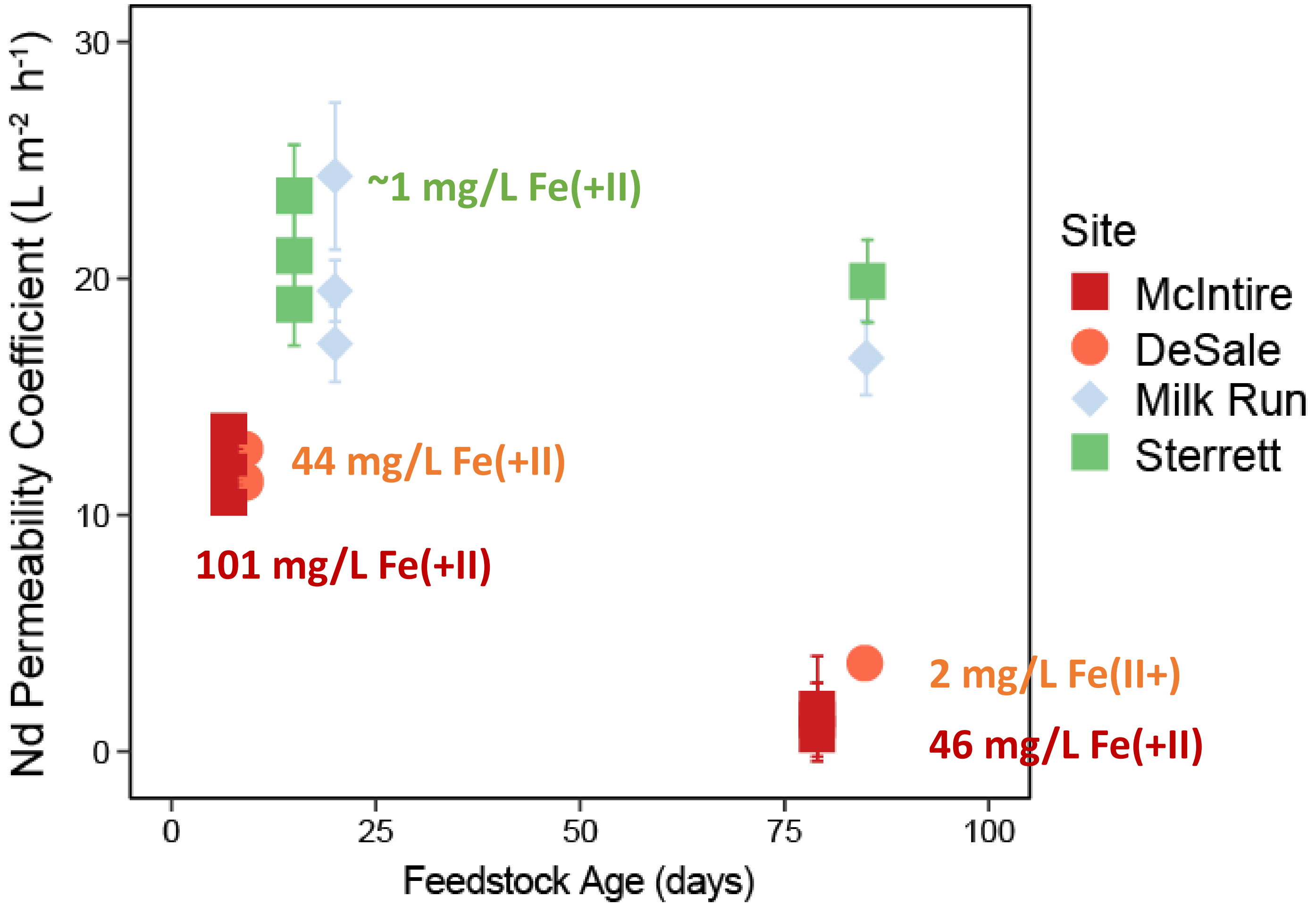


Middleton *et al.* *ES&T* 2024

Duke | Department of Civil & Environmental Engineering

Impacts of AMD aging on extraction flux

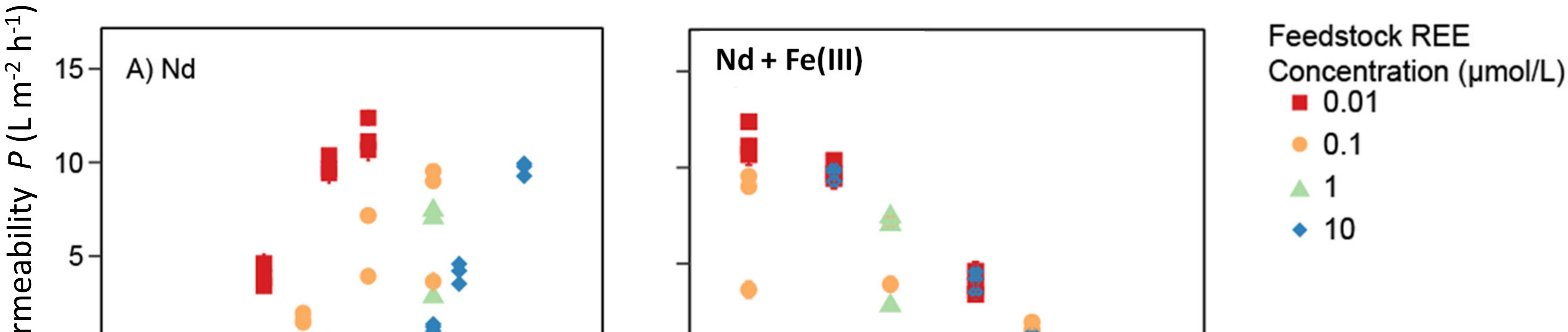
Neodymium permeability decreases with the formation of Fe(III)

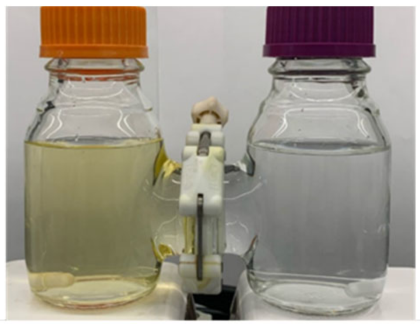


Trends in Metal Ion Selectivity

SLM separation of synthetic binary mixtures of Nd and Fe(+III):

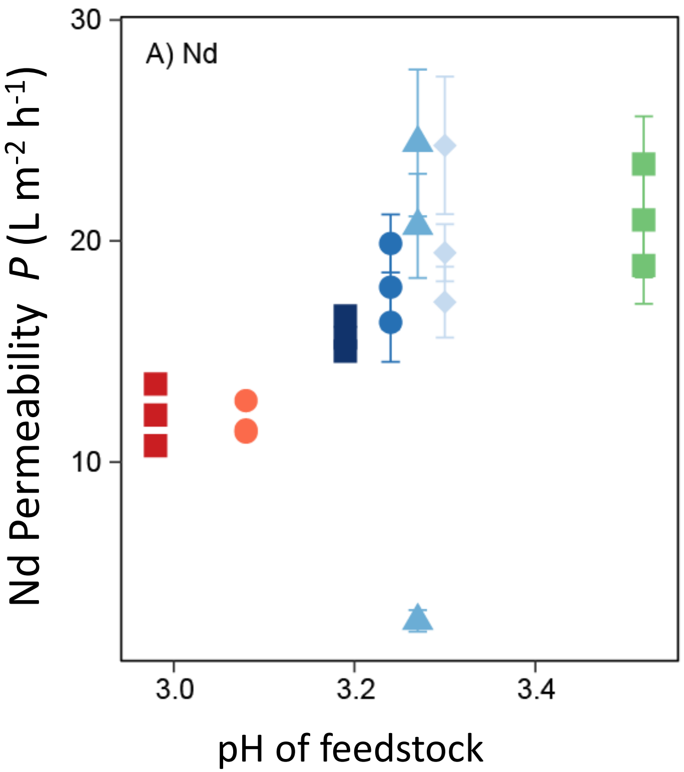
Middleton & Hsu-Kim, *ACS ES&T Engr*, 2023

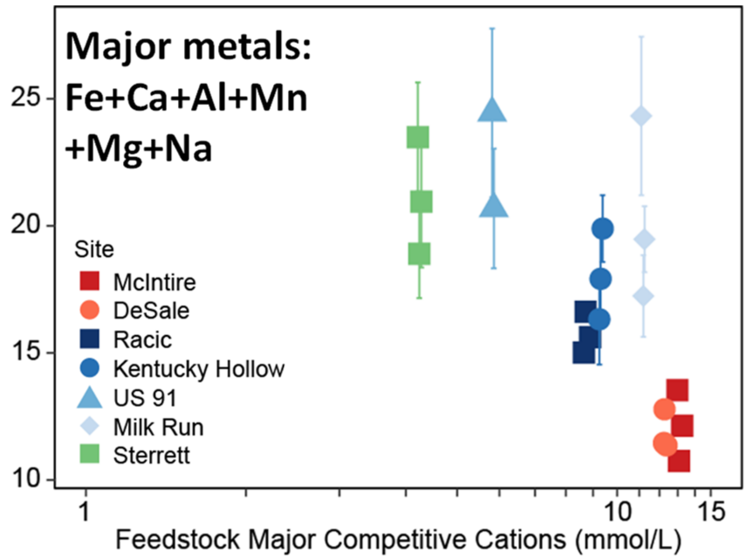




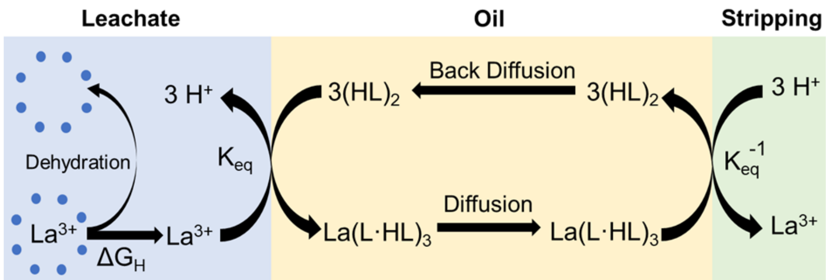
Duke | DEPARTMENT OF Civil & Environmental Engineering

Cation competition and REE extraction rates from AMD

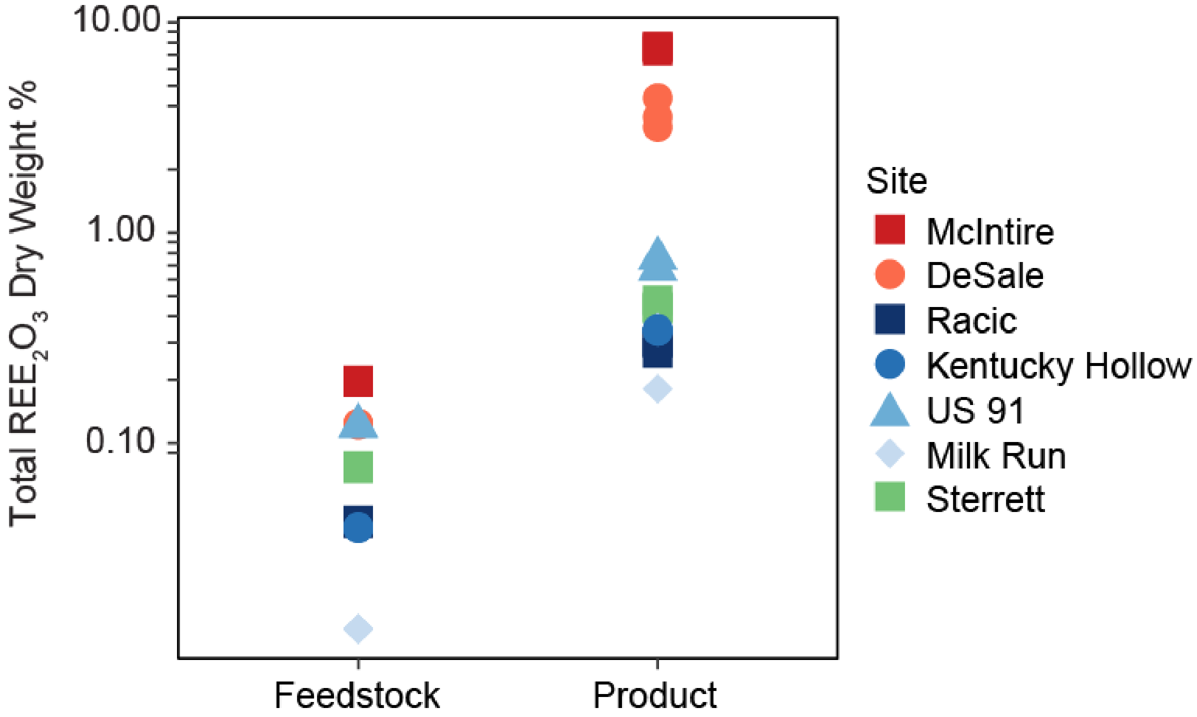




Bi-directional cation competition effect

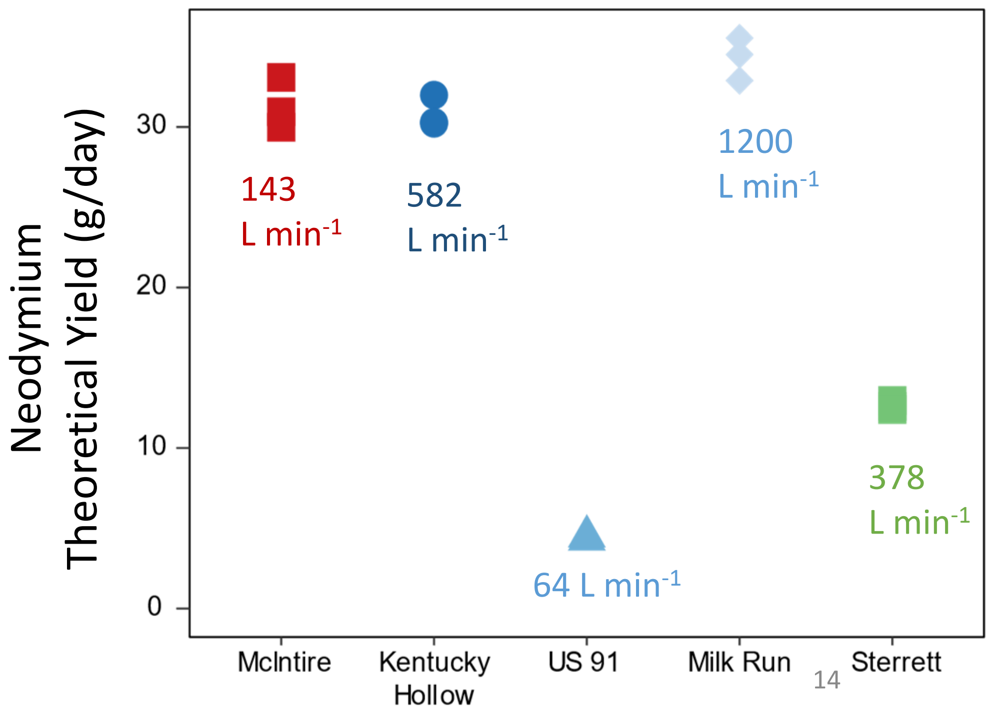


Product purity and daily yield



5- to 25-fold enrichment of REE after SLM extraction

REE yield depends on drainage flow rates



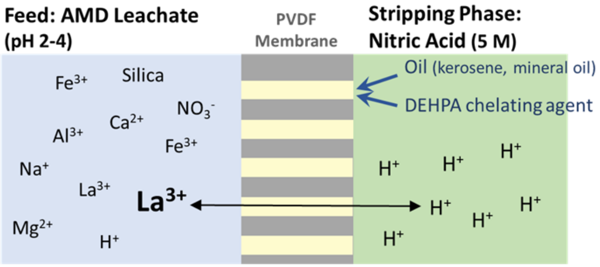
Unit Processes in the Extraction REE from Wastes

Acidic Feedstock → **Selective precipitation** (**pH adjustment**, **(bio)oxidation**) → **REE Extraction** (**Solvent Extraction**, **Ion Exchange**, **Supported Liquid Membrane**) → **Mixed REE product** (ore-grade)

Selective precipitation → Fe residuals

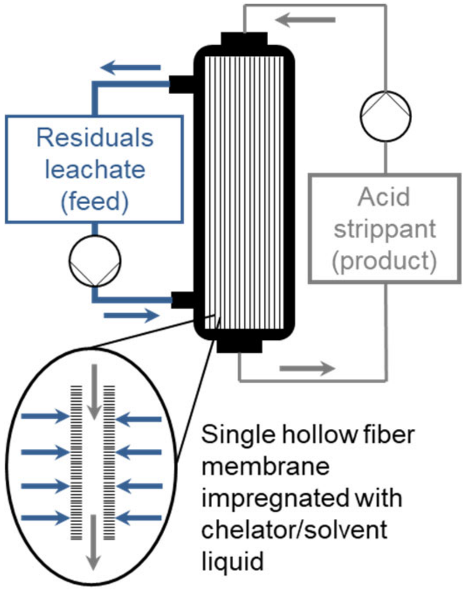
Supported Liquid Membranes would allow for reduced solvent usage in the REE extraction step

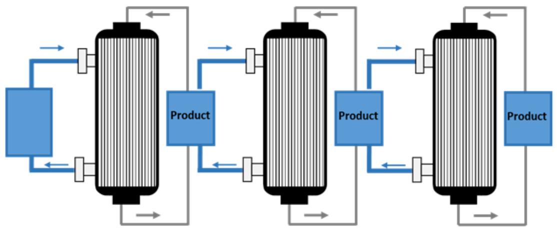
Scaling up SLM for AMD Feedstocks



Feasibility of SLM for REE Recovery:

- Membrane configuration
- Type of membrane and carrier
- Longevity and reusability of the liquid membrane
- Waste disposal



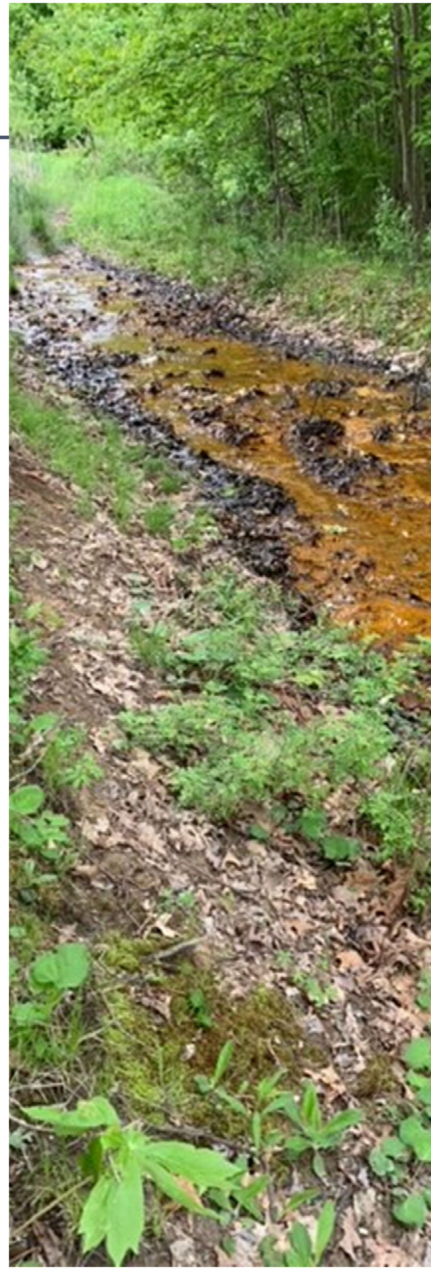


Duke | DEPARTMENT OF Civil & Environmental Engineering

Summary

Supported Liquid Membrane Extraction of REE from Acid Mine Drainage

- Wide variation of AMD composition (REEs and major solutes)
- SLM extractions: increased REE flux with high pH, low metals
- Cation competition effect: controls selectivity and REE recovery efficiency
- Yield rate and purity depends on AMD flow rates and relative REE concentrations



Duke | DEPARTMENT OF Civil & Environmental Engineering

NSF U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

Trends in Metal Ion Selectivity

Adsorption of REE to suspended colloids?

Middleton & Hsu-Kim, *ACS ES&T Engr*, 2023

10^{-5} mM Nd
+ 18 mM Fe(III)

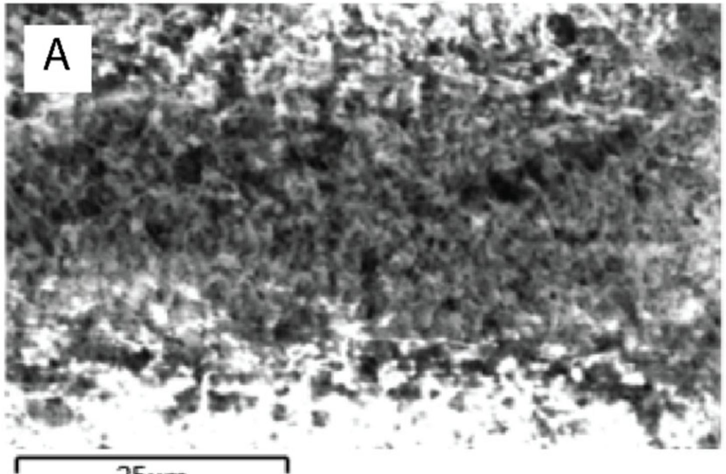
Ultracentrifuge +
Filter (0.02 μm Anodisc)

95-105% of Nd remains in the aqueous phase

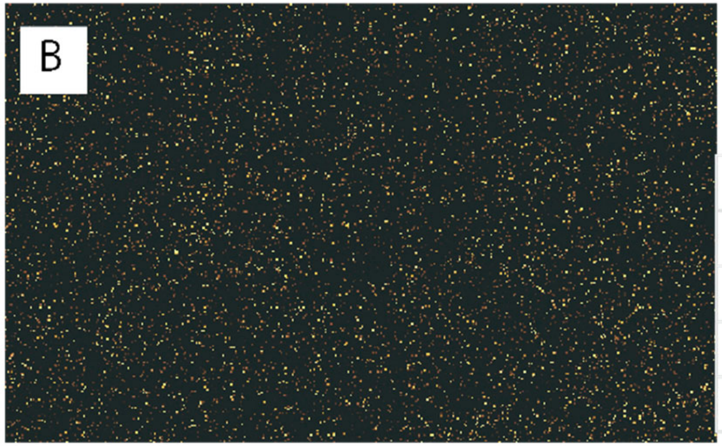
Trends in Metal Ion Selectivity

Fe colloids on membrane surface

surface of 'spent' PVDF membrane



Scanning electron microscopy



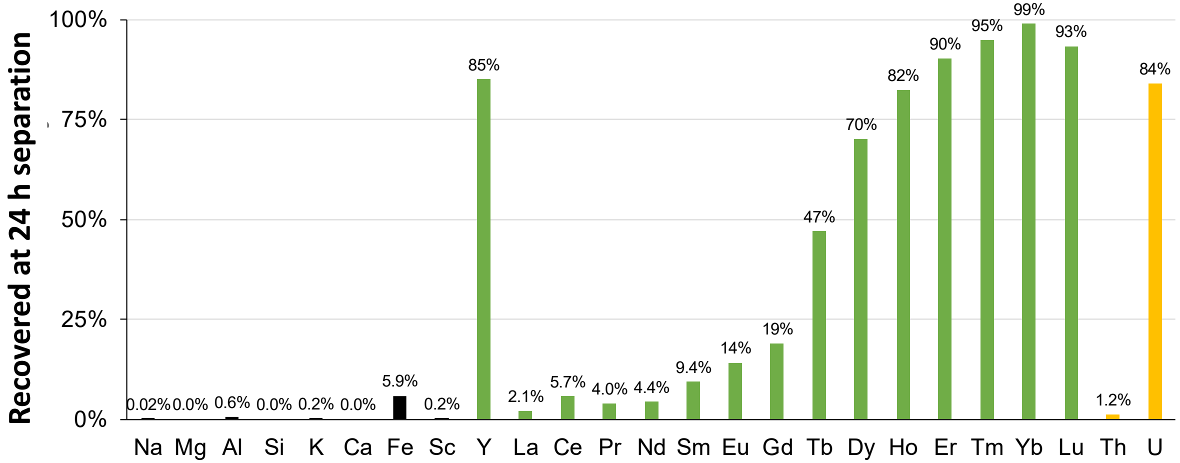
Fe intensity
(EDS mapping)

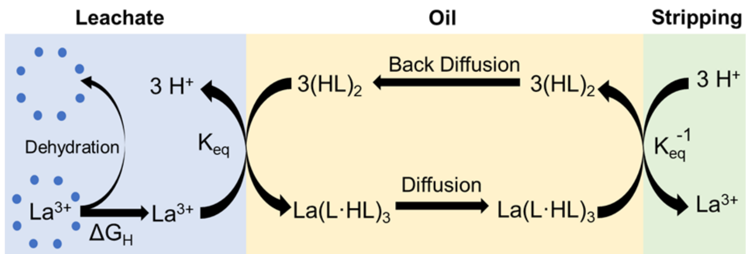
Element	Weight %
C	59.87
F	38.8
P	1.1
Fe	0.23

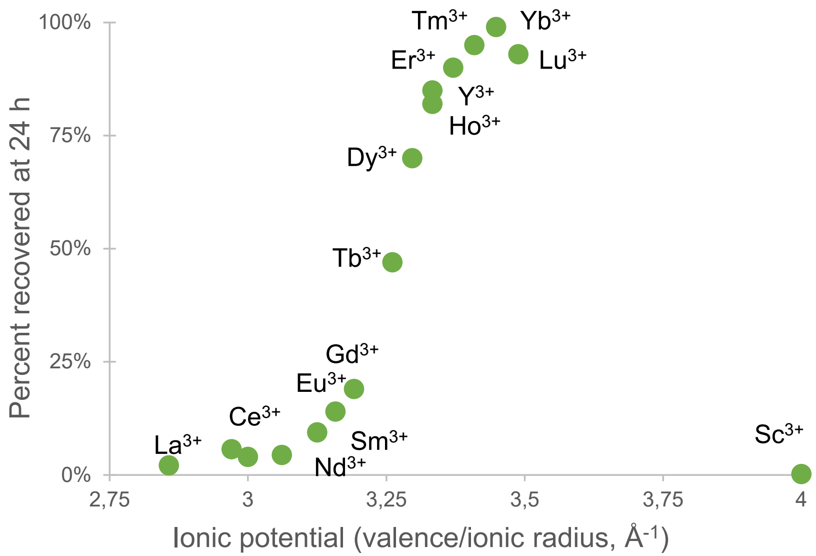
Trends in Metal Ion Selectivity

flux controlled by metal-ligand competition at the membrane interface

A different example with coal fly ash leachate:







Smith *et al.*, *ES&T*, 2019

Duke | DEPARTMENT OF Civil & Environmental Engineering