Beneficial Reuse of Drill Cuttings

FWP-10224150 (Task 23)

Christina Lopano

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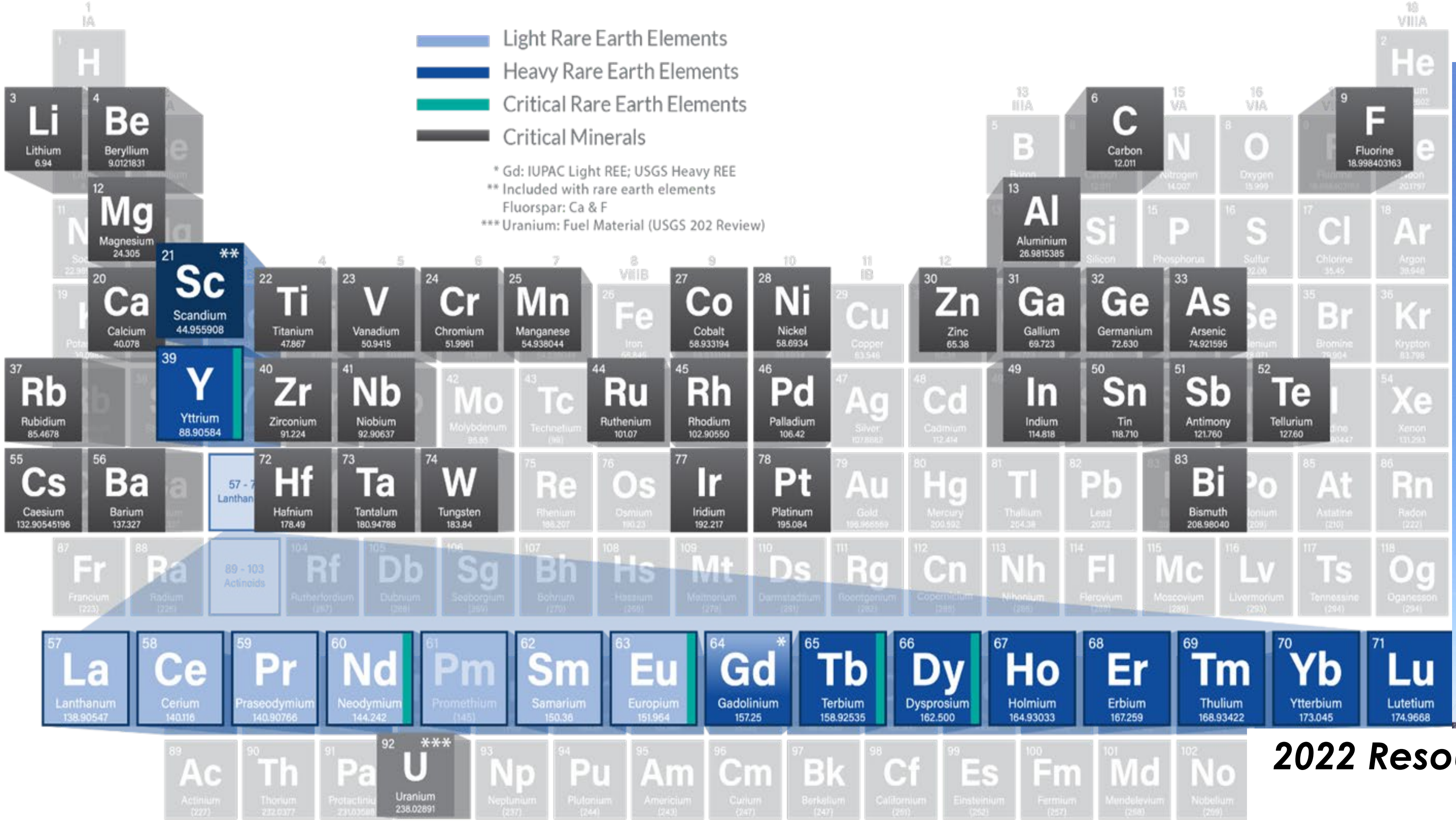

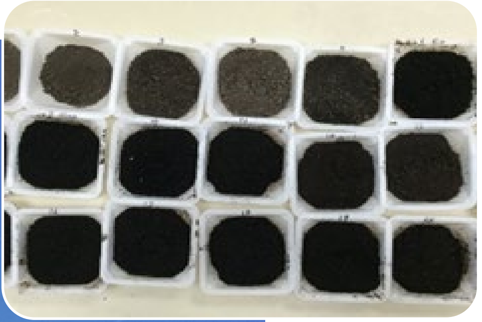

2022 Resource Sustainability Project Review Meeting

October 25, 2022

Beneficial Reuse of Drill Cuttings

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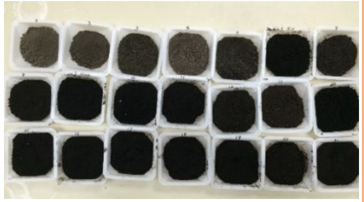
Objective

Develop an approach for identifying the most promising drill cutting chemistries (clay and organic content and metal distribution) for use as soil amendments. This work will develop novel treatments for optimizing drill cuttings for use as soil amendments and plant growth, and, as a secondary benefit, it will evaluate the potential for the recovery of critical metals (e.g. Co, Ni, Zn, V, REE) from the waste materials across U.S. basins.



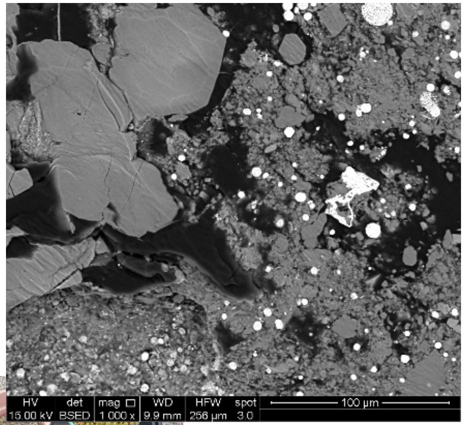
Marcellus shale Drill Cuttings

MSEEL: Horizontal drilling from WV (well 5H)

Pristine Core

Project Outline

- Identify characteristics of ideal soil amendment from potential drill cuttings (EY21).
- Explore novel treatments of drill cuttings optimized for soil carbon amendments (EY22).
- Test and optimize soil amendments as growth media (EY23–EY24).



Task Team Members

- PIs: Christina Lopano, Mengling Stuckman (LRST)
- Other Key Personnel: Maximilian Barczok (LRST), Meghan Brandi (LRST), Wei Xiong (LRST), Tom Paronish (LRST), Sean Sanguinito (LRST), Dustin Crandall

Approach & Goals

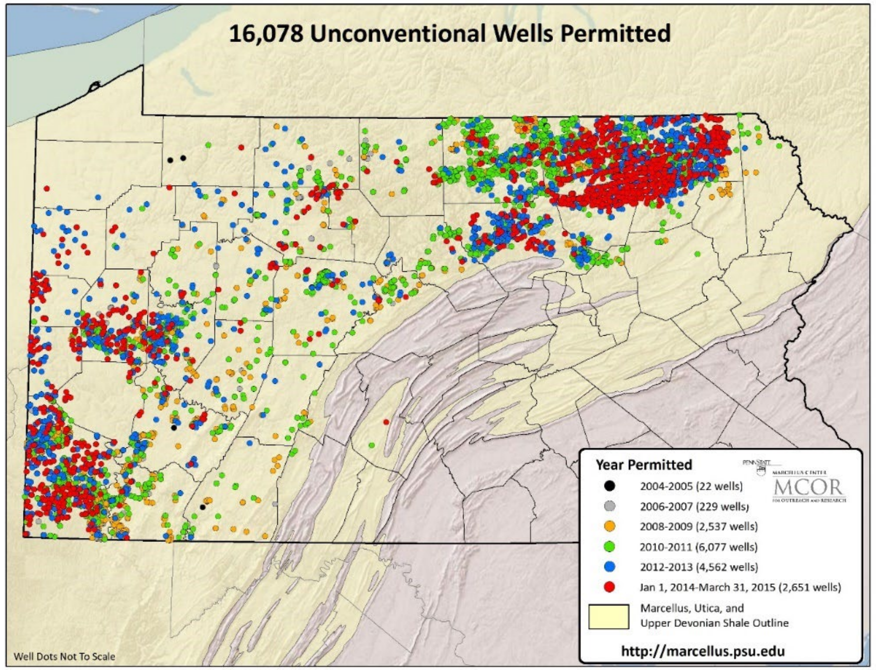
~ 3-4 year project, starting April 2021

1. Explore data collected on Marcellus Shale drill cuttings during <u>previous years</u> to identify geochemical characteristics that may make geological horizons more amenable and economical for use as soil amendments;
2. Apply geochemical trends noted in the first goal to determine <u>what/if any horizons</u> from different basins and DOE FLs (core-logged and described by NETL researchers in Task 22.0), might be ideal for testing as soil amendments;
3. Develop <u>novel method(s)</u> for treatment of key horizons drill cuttings to convert the cuttings to suitable soil ameliorants for carbon sequestration and soil health benefits;
4. Determine if <u>critical metals may be recovered</u> from the cuttings for additional economic benefit from what was previously, solely a waste material
5. Test treated drill cuttings as <u>soil amendments</u> in small batch or green-roof setting.

Evaluate environmental impacts of the treatment processes

Drill Cuttings from Unconventional Wells

Background



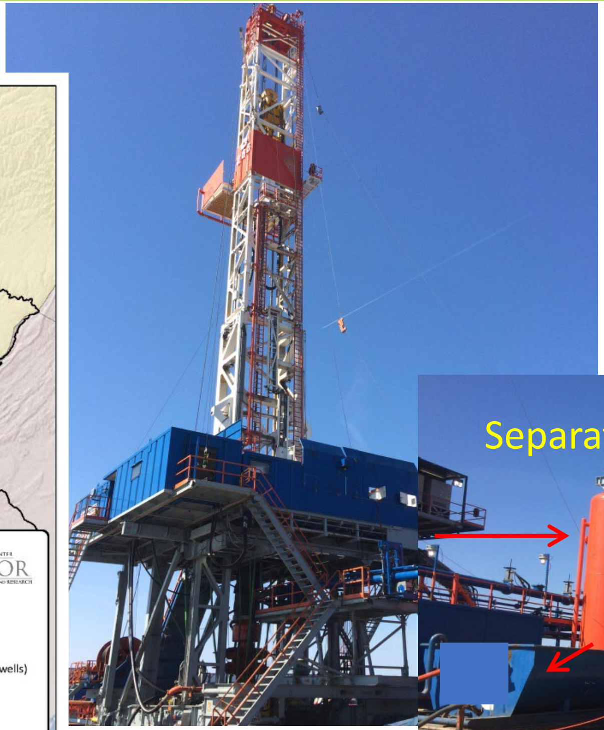
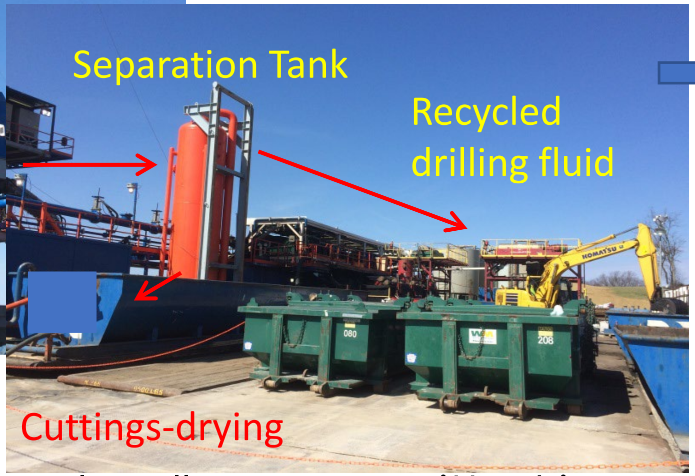


Photo: Drilling site in PA

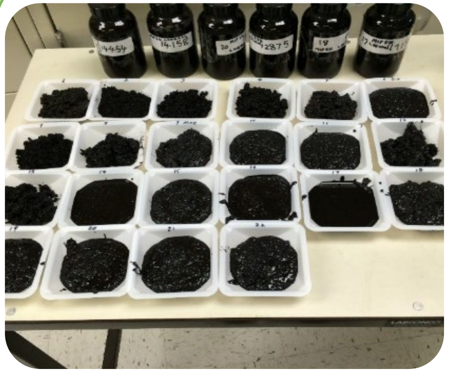


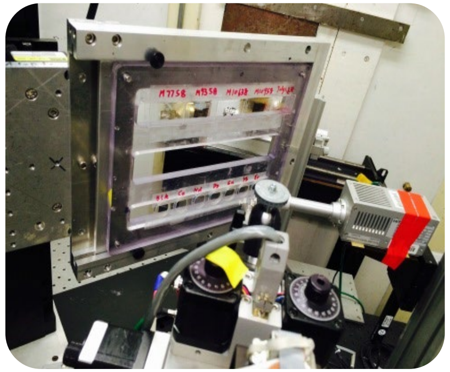
- From 2004 to March 31, 2015: 16,078 unconventional wells are permitted in Pennsylvania and 9,324 unconventional wells were drilled.
- More than 2,000 tons of drill cuttings are produced from a typical well-drilling operation (**per well**). In **2020**, state records show oil and gas drillers sent **<u>244,000 tons of drill cuttings to landfills</u>**.
- Drill cuttings contain both drilling fluids (water-/oil-/synthetic based) and shale rock cuttings

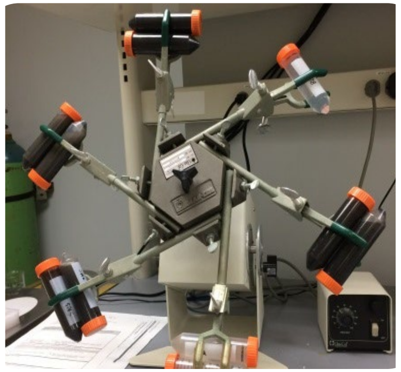
http://www.marcellus.psu.edu/images/PA%20Permit%20Map%202014-1520150331.jpg
Ball et al. , Waste Management Research, (2012)
Fact Sheet - Onsite Burial (Pits, Landfills), http://web.ead.anl.gov/dwm/techdesc/burial/

Past Work: Informing Drill Cutting Waste Management

Geochemical Factors Controlling Metal Release under variable conditions







Bulk Solid Characterization

- 22 drill cuttings and core
- Elemental Composition: ICP-MS, C and S content
-Mineralogy: XRD & XRF

Elemental Distribution

- Synchrotron micro-XRF mapping
- SEM- EDS
- BCR 4-step sequential extraction

Geochemical Leaching

- Regulatory Leaching (SPLP & TCLP):

Rain vs. Landfill

- Wet vs. Dry
- pH titration
- Long-term Effect: USEPA 1320 Multiple Extraction

Soil supplement and CM recovery (2021-2024)

- Green-roof soil amendment potential
- Explore selective extraction of CM

Stuckman M.Y., et al. (2019) *Journal of Natural Gas Science and Engineering* 68: 102922.
Stuckman M., et al. (2018), proceeding of Unconventional Resources Technology and Exposition Conference, Houston, TX, 23-25, July 2018

Environmental impacts of drill cutting disposal

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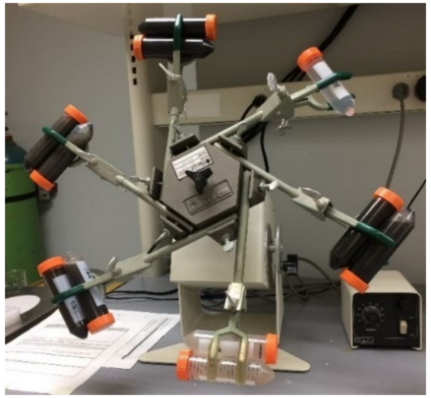
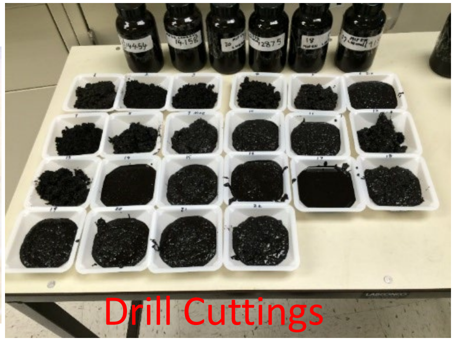
Leaching characteristics under different disposal scenarios



On-Site Burial & Road Fill

Release by rainwater

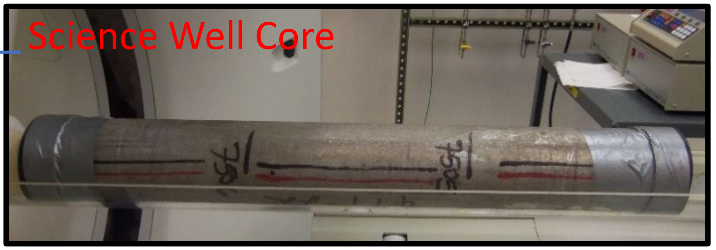
- USEPA 1311: Synthetic Precipitation Leaching Procedure (SPLP): Synthetic acid rain at pH 4.2, DI water adjusted by sulfuric/nitric acid



Landfill

Release by landfill leachate

- USEPA1312: Toxicity Characteristics Leaching Protocol (TCLP): Acetate-based synthetic leachate at pH 4.9
- USEPA 1320: Multiple Extractions



Framework Leaching

Parallel Batch Extraction for broader disposal scenarios (pH, time, L:S)

- USEPA 1313: As a function of extract pH
- Bioavailability Screening Test (Kosson, 2002): 50mM EDTA

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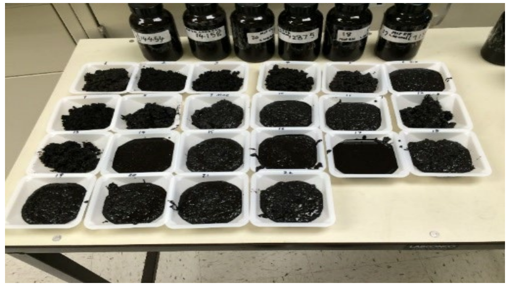
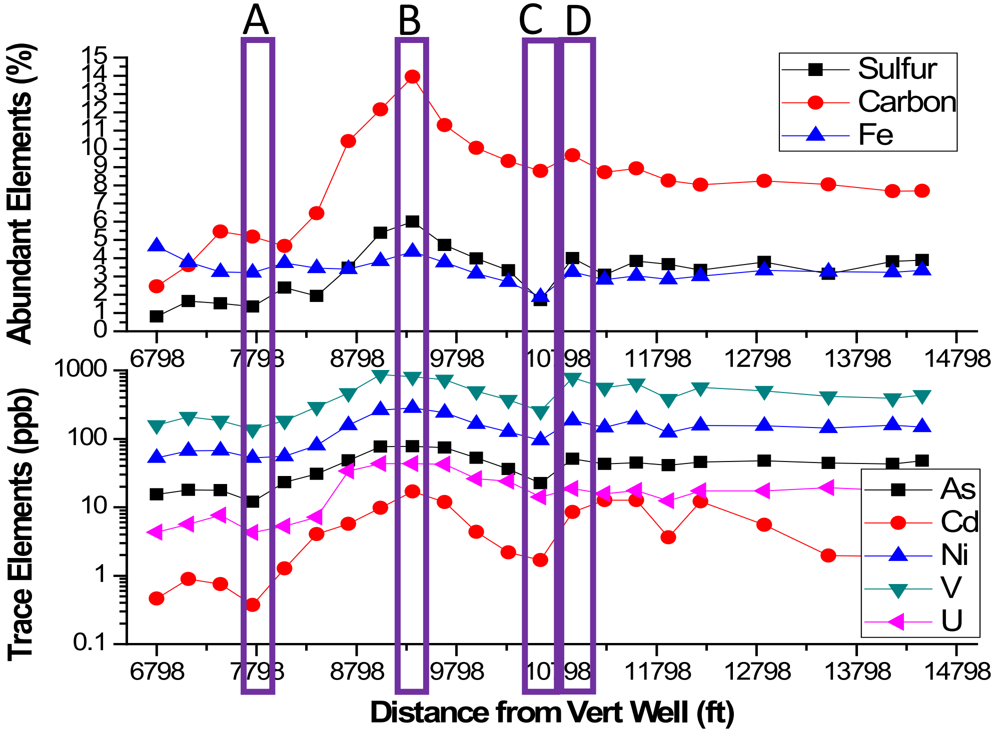
Stuckman M., et al. (2018), *proceeding of Unconventional Resources Technology and Exposition Conference*, Houston, TX, 23-25, July, 2018

Past work: Trace metal distribution

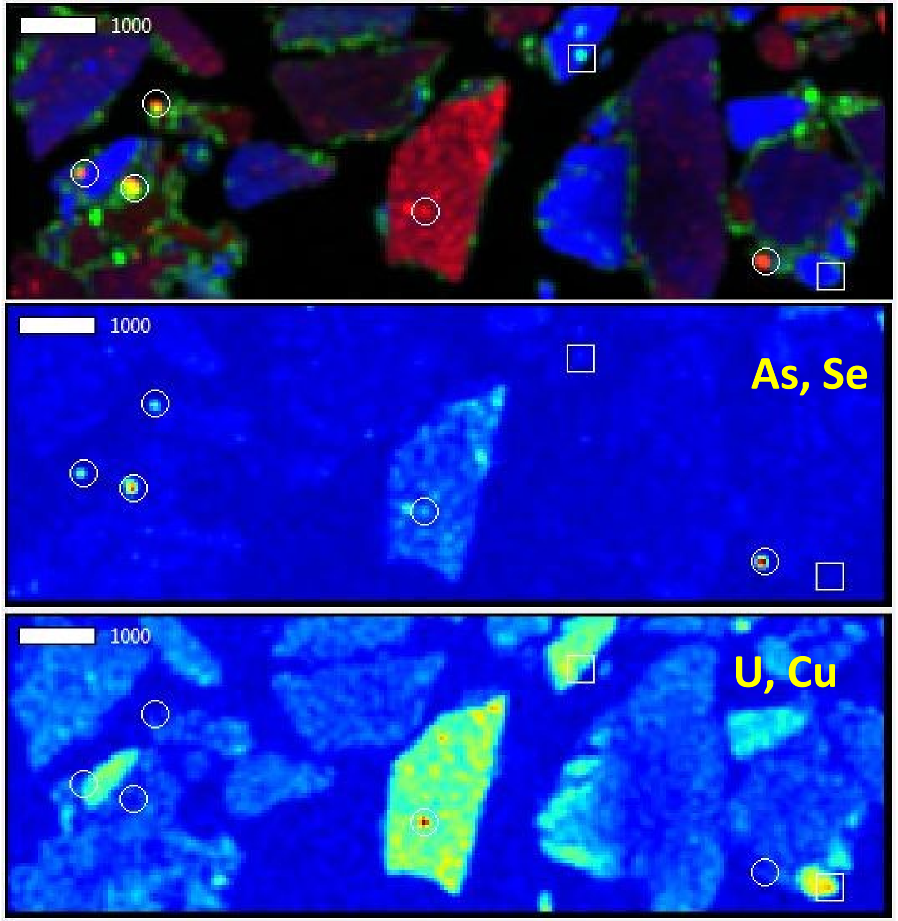
bulk and microscopic analysis



22 Marcellus Shale Drill Cuttings from 5H horizontal Well



Fe in red, Ca in blue, Ba in green



- ○ Trace metals with pyrite (e.g., As, Pb, Cu, U)
- ❑ Trace metals with calcite (e.g., U, Cu)

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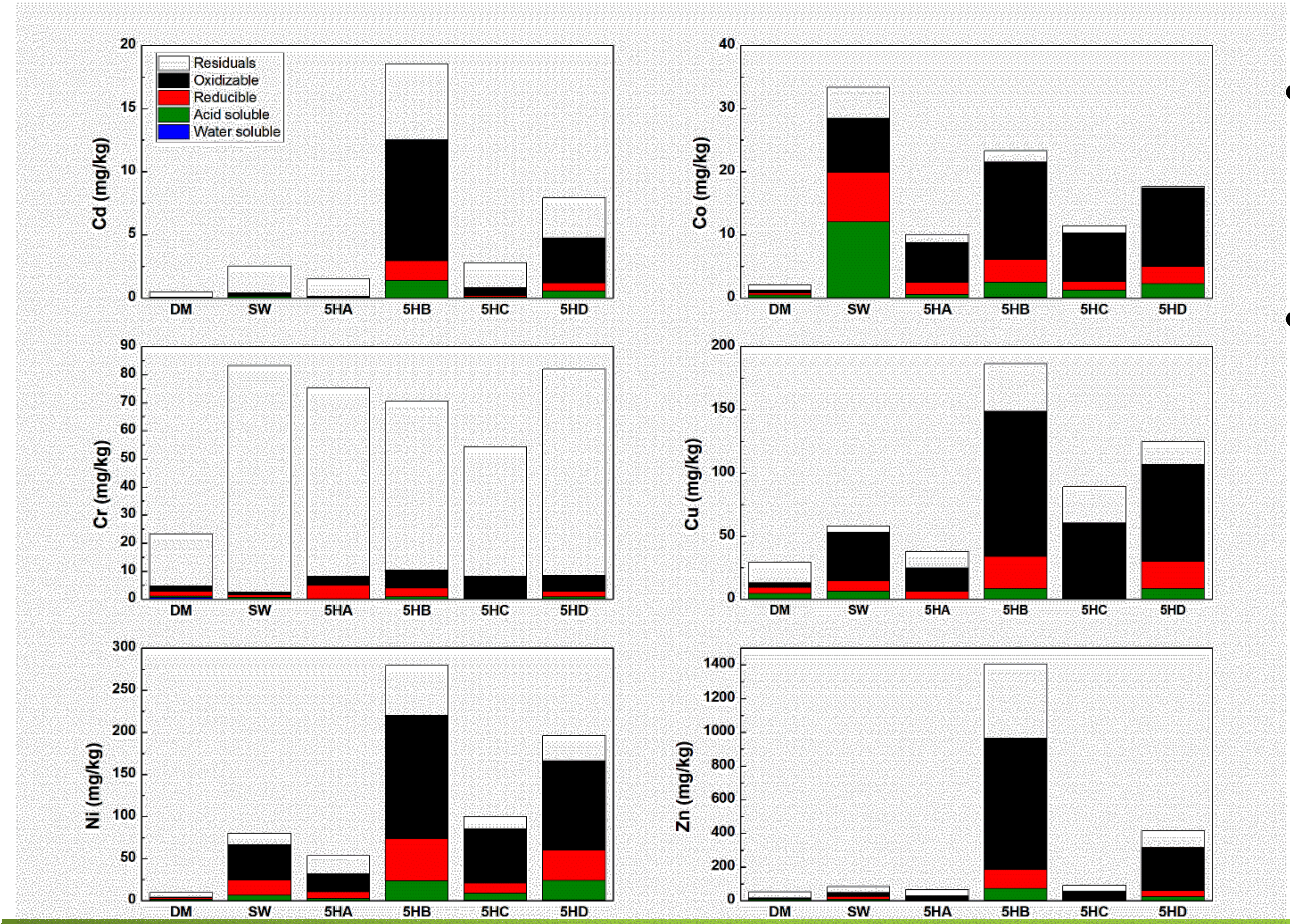
Stuckman, M. Y., et al. (2019). Journal of Natural Gas Science and Engineering **68**: 102922.

Past Work: Trace metal distribution

Laboratory sequential analysis



- Trace metals enriched in 5HB with **high pyrite** and **organic carbon**.
- 70% Co, Ni, Zn, Cu extracted from "Oxidizable" – pyrite and organic phases from drill cuttings

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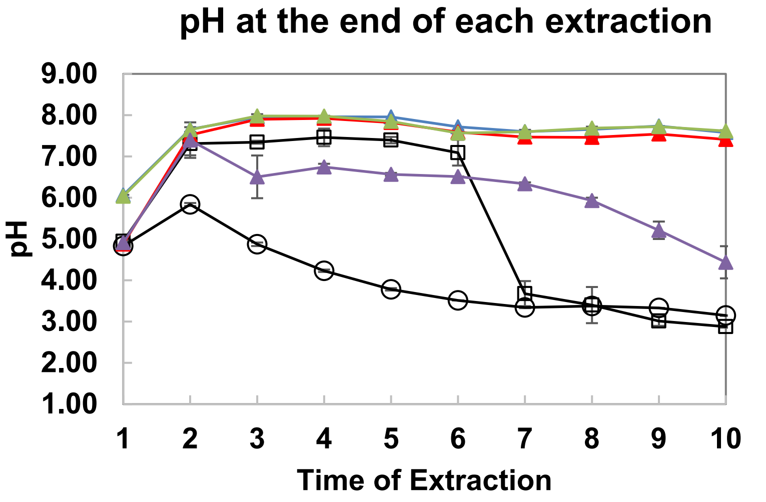
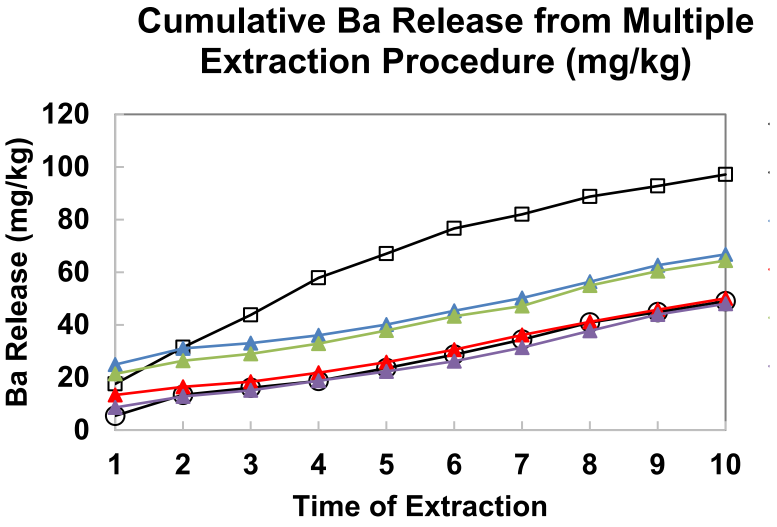
Stuckman, M. Y., et al. (2019). Journal of Natural Gas Science and Engineering **68**: 102922.

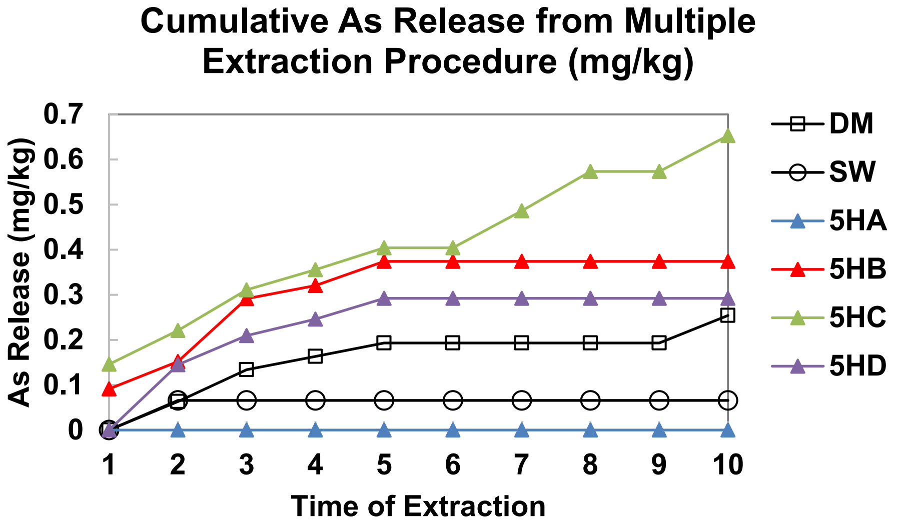
Past Work: Evaluating leaching over time

- "Simulate leaching that a waste will undergo repetitive precipitation of acid rain on an improperly designed sanitary landfill" "Reveal the highest concentration that is likely to leach in a natural environment" (EPA1320)
- Acetic Acid @ pH5 + 9 times synthetic rain @ pH 3

> ➢ Potential long-term Ba release
>
> ➢ Cumulative release of oxyanions (e.g., As, Sb, V, and Mo), due to high pH buffer capacity (pH@ 7-8)
>
> ➢ 5HD had long-term release concern for Ni, Cd, Zn and Cr, due to low buffer capacity (3% Calcite)







Stuckman M., et al. (2018), proceeding of Unconventional Resources Technology and Exposition Conference (URTEC), Houston, TX, 23-25, July 2018

Landfill Leachates Concerned Wastewater Treatment Plant

https://stateimpact.npr.org/pennsylvania/2019/09/11/how-did-fracking-contaminants-end-up-in-the-monongahela-river-a-loophole-in-the-law-might-be-to-blame/

- <u>Drill cuttings</u> consist of about 40% of solid wastes in the *Belle Vernon Municipal Authority* landfill, which can contain naturally occurring radioactive materials, salts, and metals (e.g., Ba)
- "They were killing off our bugs. Our bugs are what treats the water," said Kruppa from *Kruppa Sewage System*
- "We were discharging…into the Mon River higher than drinking water standards,"


The Westmoreland Sanitary Landfill, which accepts solid fracking waste, is shown in September 2019. Photo: Reid R. Fr
Reid R. Frazier / StateImpact P

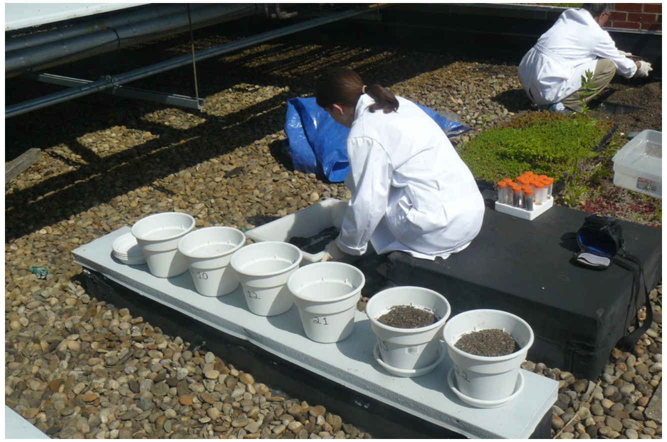
How did fracking contaminants end up in the Monongahela River? A loophole in the law might be to blame

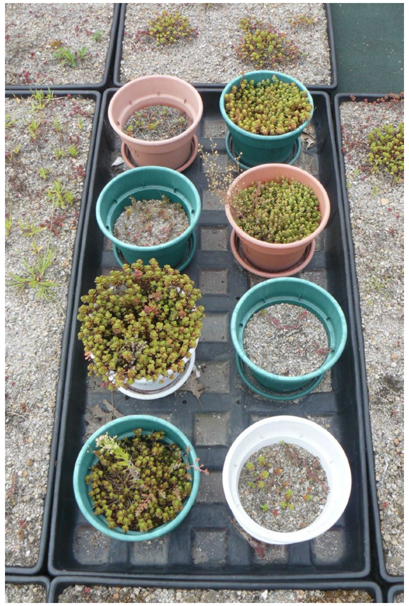
Reid Frazier

SEPTEMBER 11, 2019 | 5:00 AM

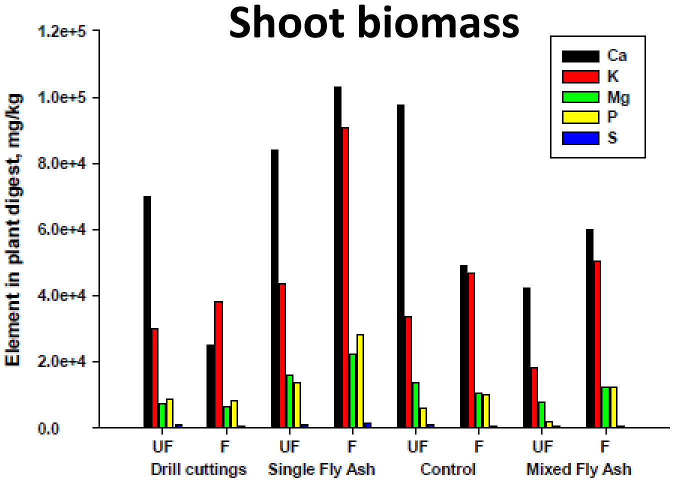
Novel Waste Management: Soil Supplements

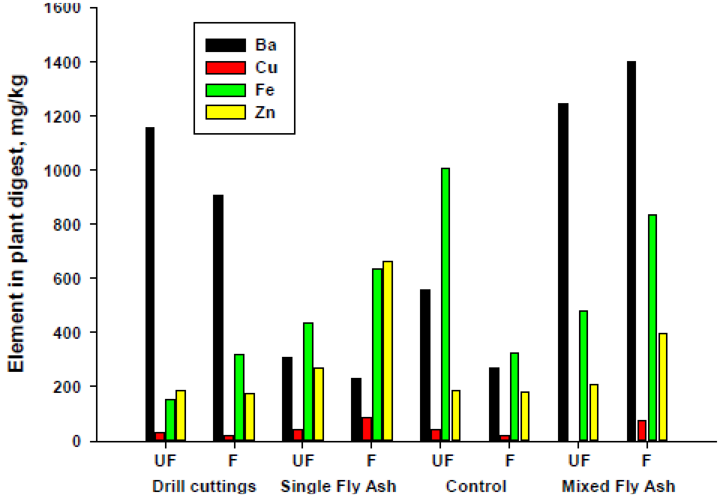
2016 Summer Project: Use of waste as green roof substrate for plant growth





Lettuce seed germination was completely inhibited at 50% cuttings/soil (v/v), due to high NaCl.





UF: unfertilized; F: fertilized

Preliminary Findings

- Preliminary evidence suggests that drill cutting serves a good growth substrate once NaCl is leached, but may result in high concentrations of <u>Ba in plant biomass</u>
- All drill cutting amended soils supported sedum growth over 16 months

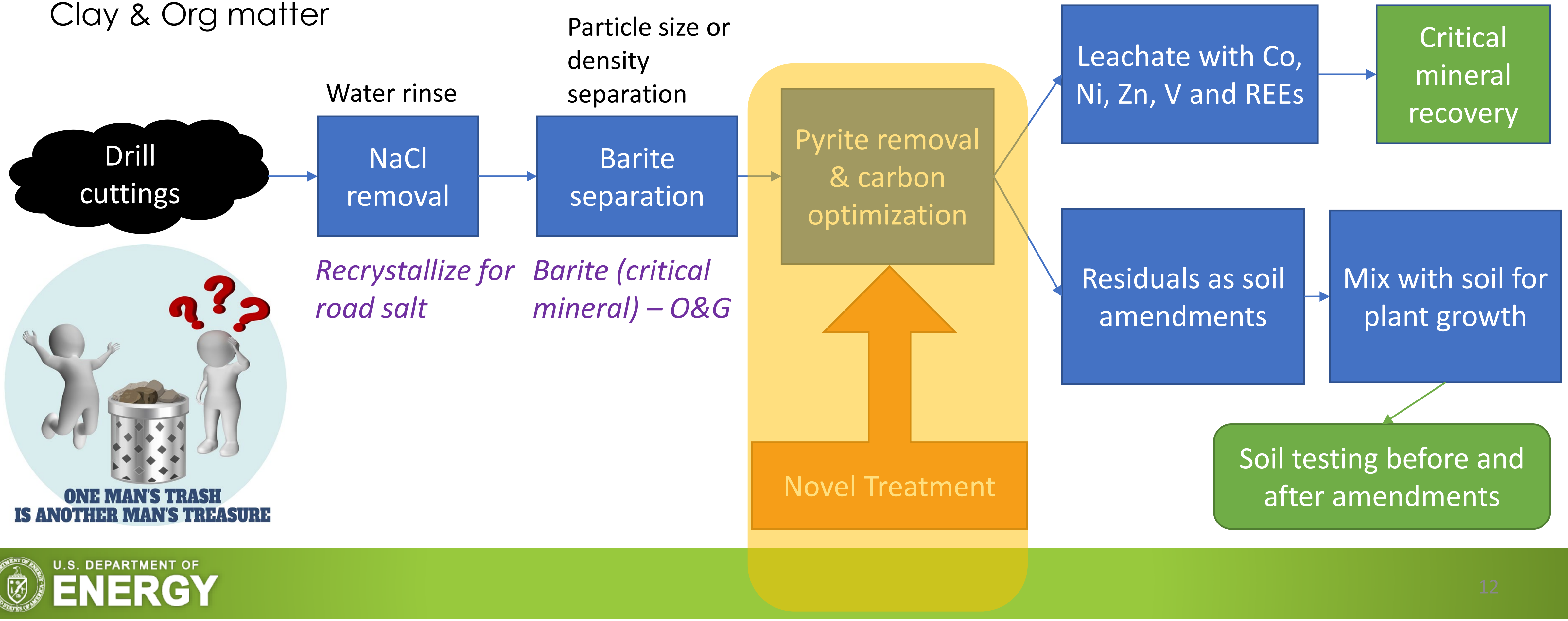
Edenborn, H. M., and Jinesh N. Jain. No. NETL-PUB-20276. National Energy Technology Lab.(NETL). In-house Research, 2016.

Reimagining Cutting Use: Soils & REE/CM

Pending NETL characterization informed CM recovery:

- Barite
- Transition metals (Co, Ni, Zn)
- Vanadium
- Rare Earth Elements (REE)
- Clay & Org matter

Tentative schematic of drill cutting conversion



Year 1 (2021-2022) Reviewing Data

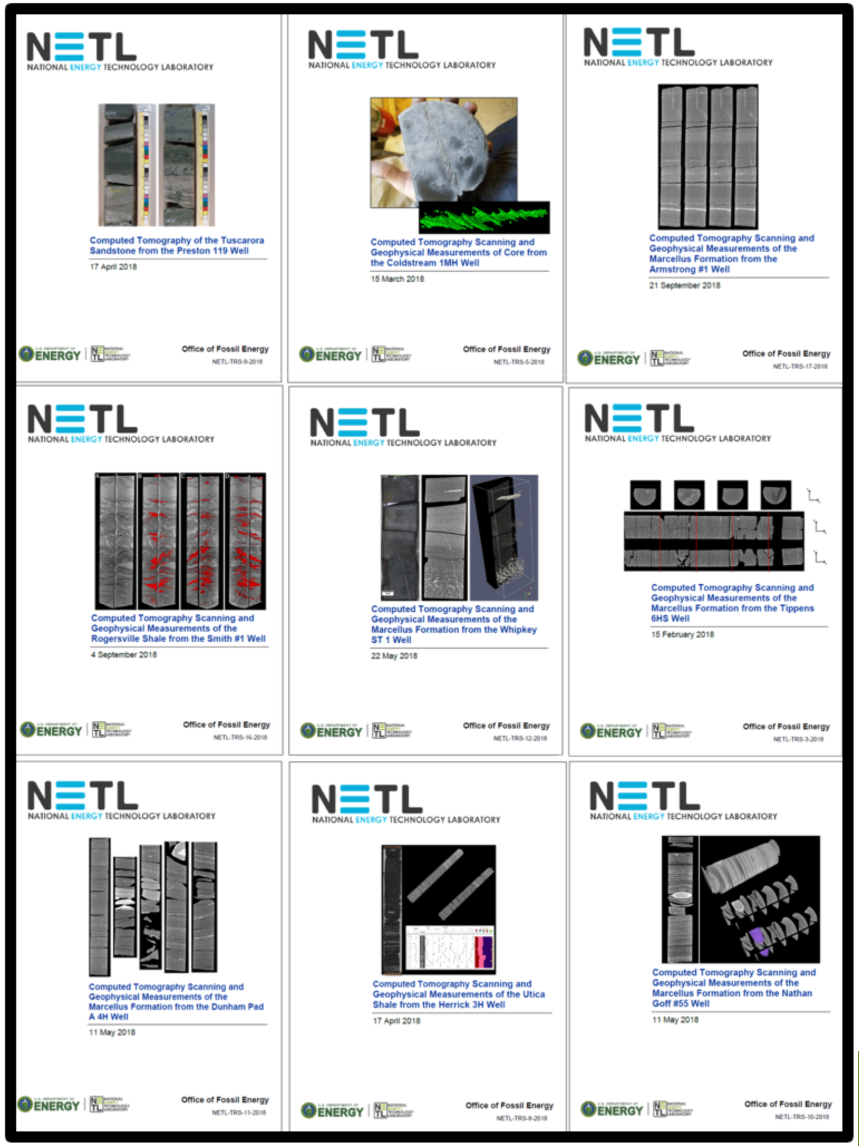
Identify characteristics of drill cuttings amenable to amendments

Data from previous RIC projects will be leveraged to determine geochemical trends of interest.

- Marcellus Shale Drill cuttings work (Stuckman et al 2018, 2019) & in prep
- Core-logging activities (Task 22) were used to determine high potential cuttings for additional testing
  - Marcellus Shale
  - Bakken Shale
  - Wolfcamp Shale

Stuckman M.Y., et al. (2019) *Journal of Natural Gas Science and Engineering* 68: 102922.
Stuckman M., et al. (2018), proceeding of Unconventional Resources Technology and Exposition Conference, Houston, TX, 23-25, July 2018

https://edx.netl.doe.gov/group/core-characterization



Studying drill cutting and core library at NETL

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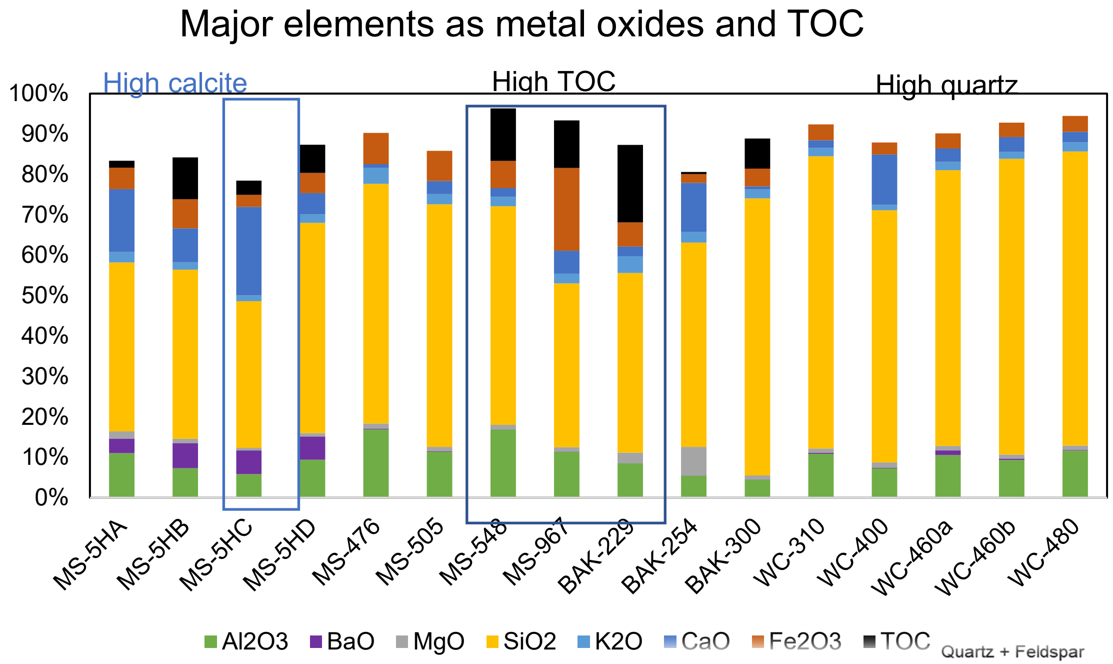
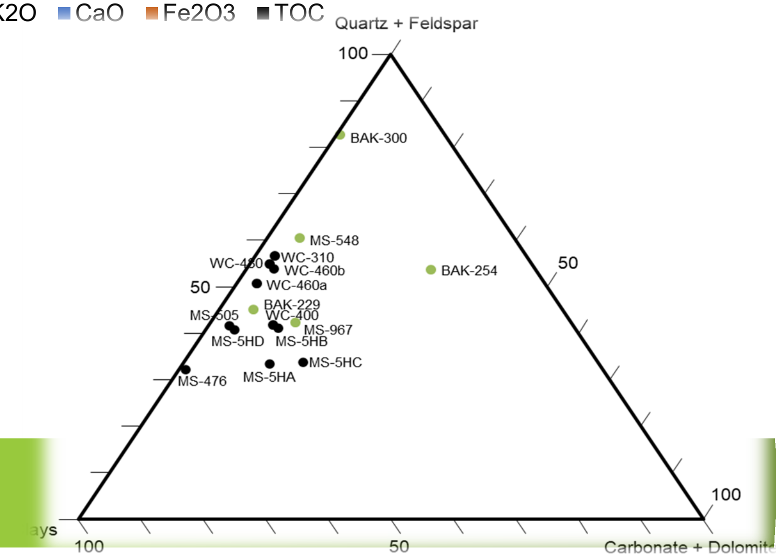
16 drill cutting and shale samples selected from Marcellus, Bakken and Wolfcamp Shale library



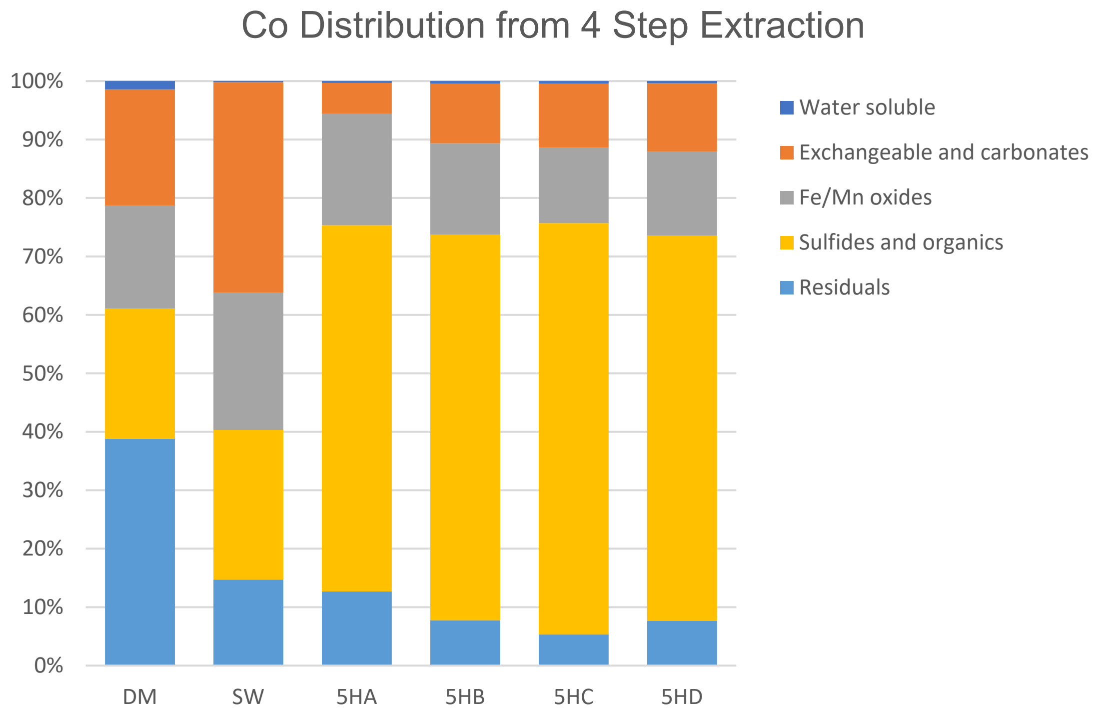
- High pyrite and total organic carbon samples (TOC, 10-19 wt. %): **MS-5HB**, MS-548, MS-967 and BAK-229
- High clay samples (**MS-5HA** and MS-476)
- High quartz: WC samples, Bak-300
- High calcite: **MS-5HC** and Bak-254
- Only MS drill cuttings have high barite



Data Collection and Observations

Identify characteristics of drill cuttings amenable to amendments

- Characterization of cuttings (on-going)
  - SEM & Synchrotron Imaging
  - XRD/XRF, TOC
  - Laboratory Leaching tests (sequential extractions & regulatory tests)
- Key horizons/cuttings (preliminarily **clay, pyrite and organic rich horizons**) will be determined and collected where feasible for method validation and for future amendment experiments.
- Preliminary results with some novel extractions already show promise for removing REE and critical minerals

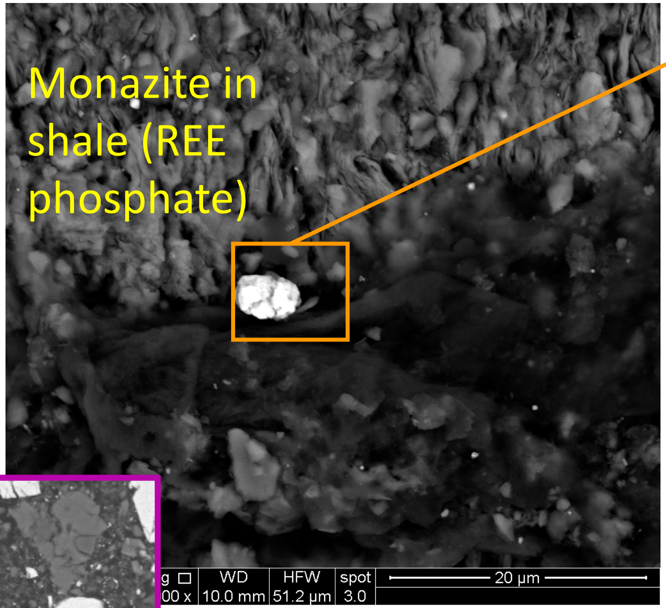


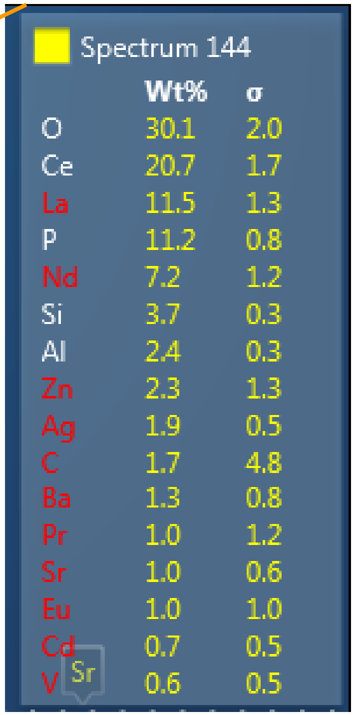
- 70% of Co can be extracted targeting sulfide and organic matter phases.
- Treatment designed to extract the CM; the rinsed solid safe for landfill disposal or green roof material

Novel Waste Management: Critical Mineral Recovery

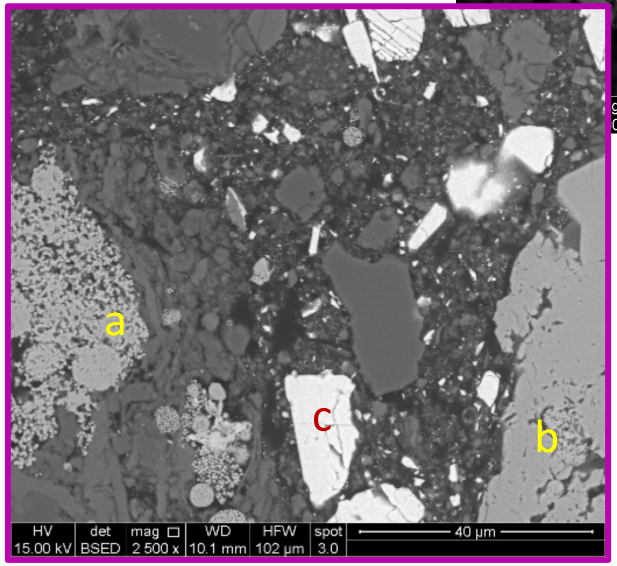
NETL Characterization Efforts - Inform CM & Soil Supplement potential

- Transition metals (Cr, Ni, Zn up to 2,500 mg/kg)
- Vanadium (up to 1,500 mg/kg)
- Lithium
- Barite
- Rare Earth Elements (REE)




Spectrum 144

	Wt%	σ
O	30.1	2.0
Ce	20.7	1.7
La	11.5	1.3
P	11.2	0.8
Nd	7.2	1.2
Si	3.7	0.3
Al	2.4	0.3
Zn	2.3	1.3
Ag	1.9	0.5
C	1.7	4.8
Ba	1.3	0.8
Pr	1.0	1.2
Sr	1.0	0.6
Eu	1.0	1.0
Cd	0.7	0.5
V	0.6	0.5



SEM-EDS
Marcellus Shale drill cutting:
Framboidal (a) and euhedral (b) **pyrite** with Co, Zn and REEs (c) **Barite** with heavy REE (3.5% Lu, 1.6%Tb)

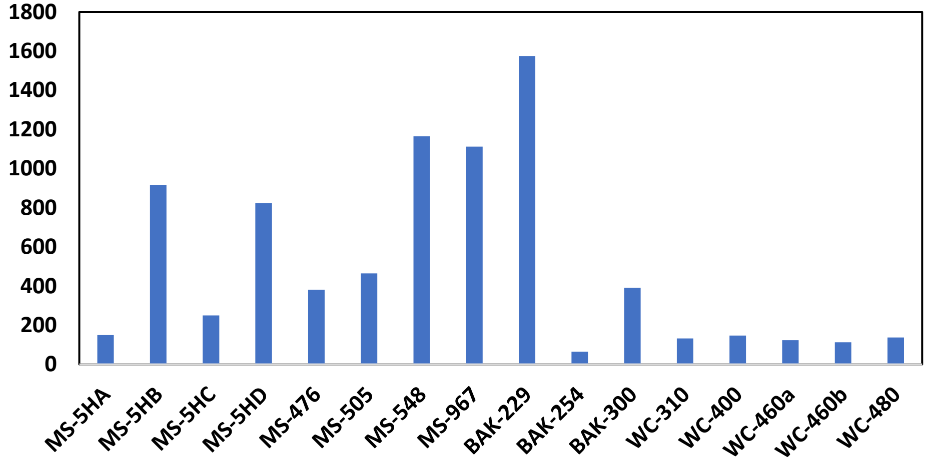
Stuckman, M., et al. (In prep), "Beneficial Reuse of Drill Cuttings as Soil Supplements and as Critical Mineral Recovery Resources," NETL Technical Report Series

Example: Vanadium

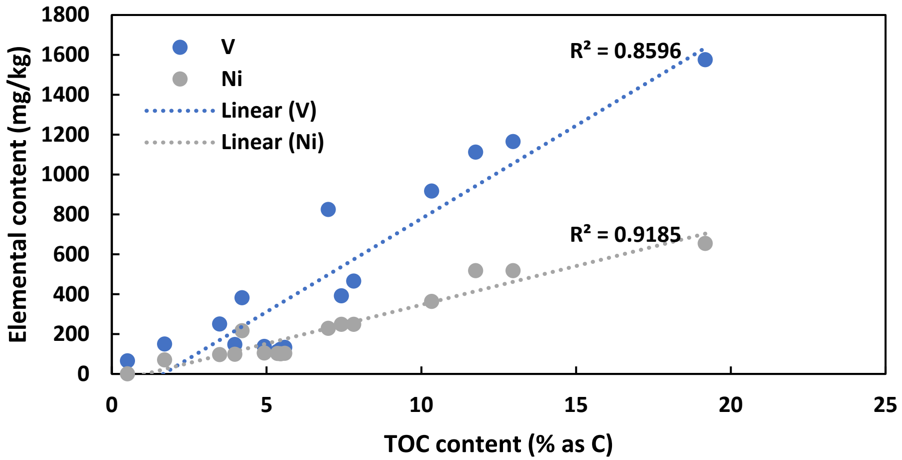
- Used in steel alloys and green applications, 50% supplied by China
- Vanadium up to 1,500 mg/kg in collected shale samples
- Often related to organic and sulfides in black shale resources
- Enriched in oil refinery wastes

https://www.ferro-alloy.com/en/vanadium/TTP%20Squared%20market%20summary%203%20April%202020.pdf

V (mg/kg) in shale



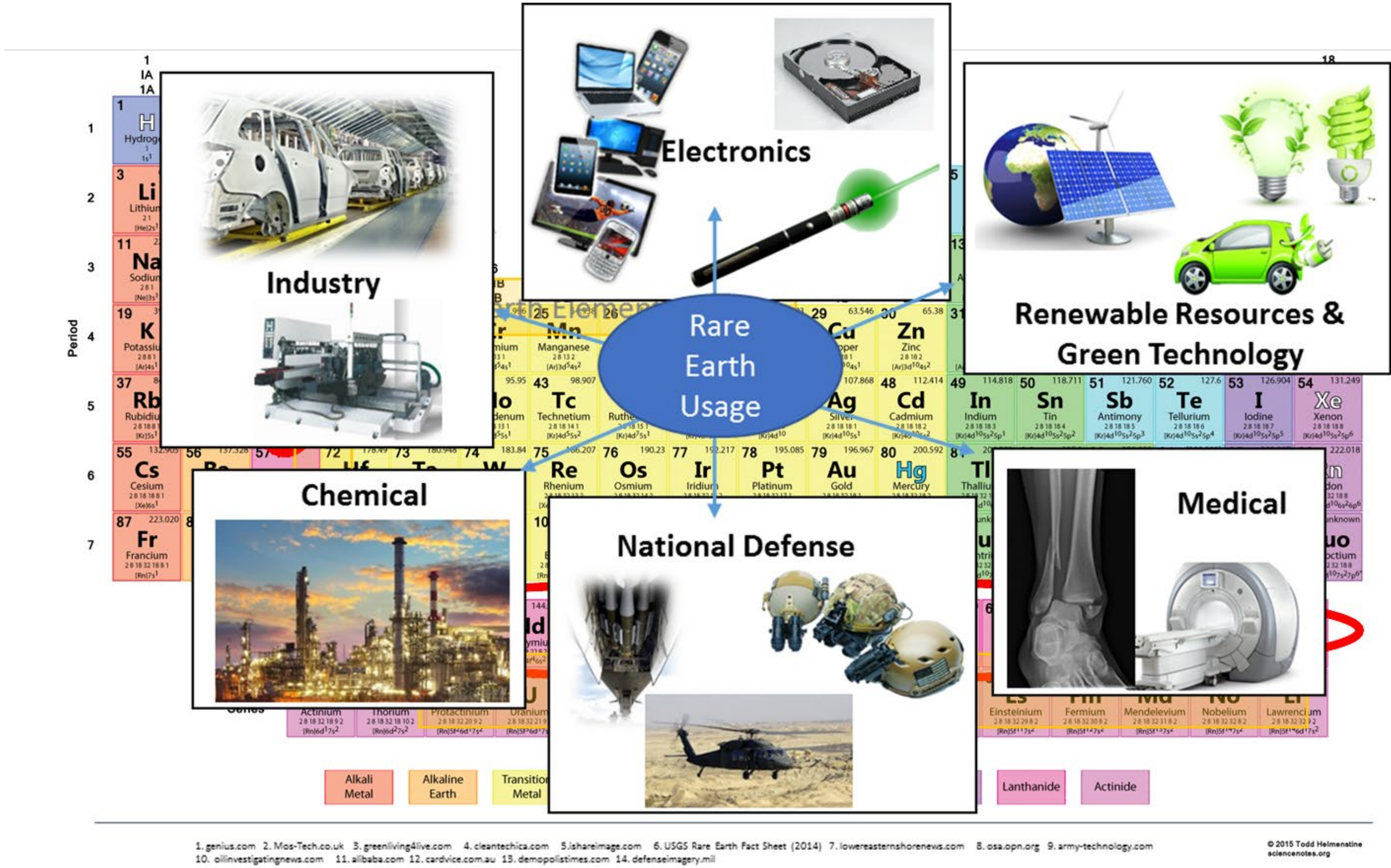
Org C correlates with V and Ni in shale



Stuckman, M., et al. (In prep), "Beneficial Reuse of Drill Cuttings as Soil Supplements and as Critical Mineral Recovery Resources," Technical Report Series

Rare Earth Element (REE) Use: Marcellus

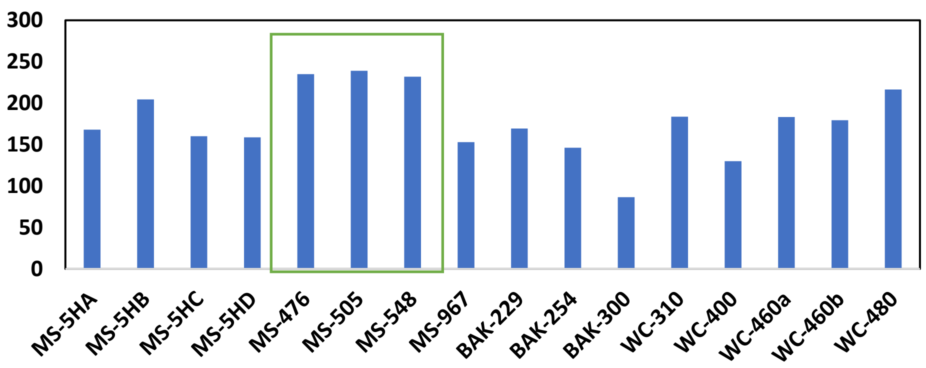
- REE: Sc, Y, 15 lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu)
- 80% global supply from China



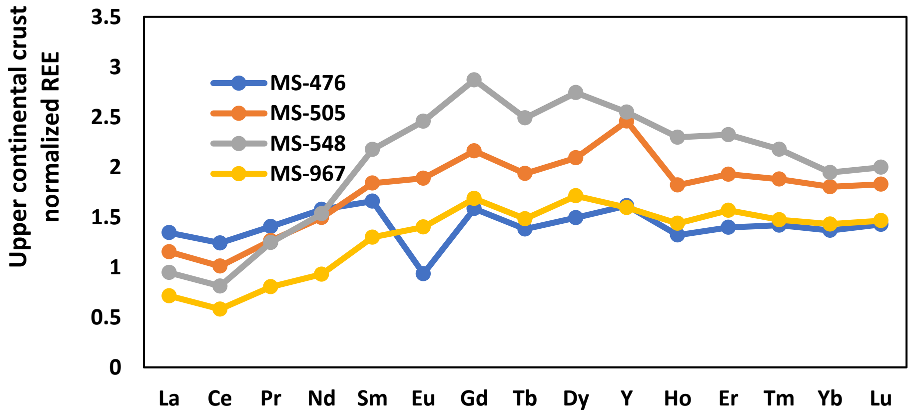
From Summers et al. (2020) IPCC

Source: USGS

REE up to 250 mg/kg in Marcellus Shale at 7476-7548 ft



Marcellus shale: Middle to Heavy REE enriched



Stuckman, M., et al. (In prep), "Beneficial Reuse of Drill Cuttings as Soil Supplements and as Critical Mineral Recovery Resources," Technical Report Series

Take-away Thoughts

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characteristics of drill cuttings amenable to amendments

Findings

- Trace metals in drill cuttings are co-localized with pyrite, organics, & calcite; and become less mobile when pH is buffered by minerals in drill cuttings.
- When drill cuttings are disposed of after drying, release of Ba, V, Mo, Sr, and Sb become two–ten times greater compared to wet drill cuttings.
- Green roof plants were inhibited by high NaCl concentrations and accumulated Ba over time.

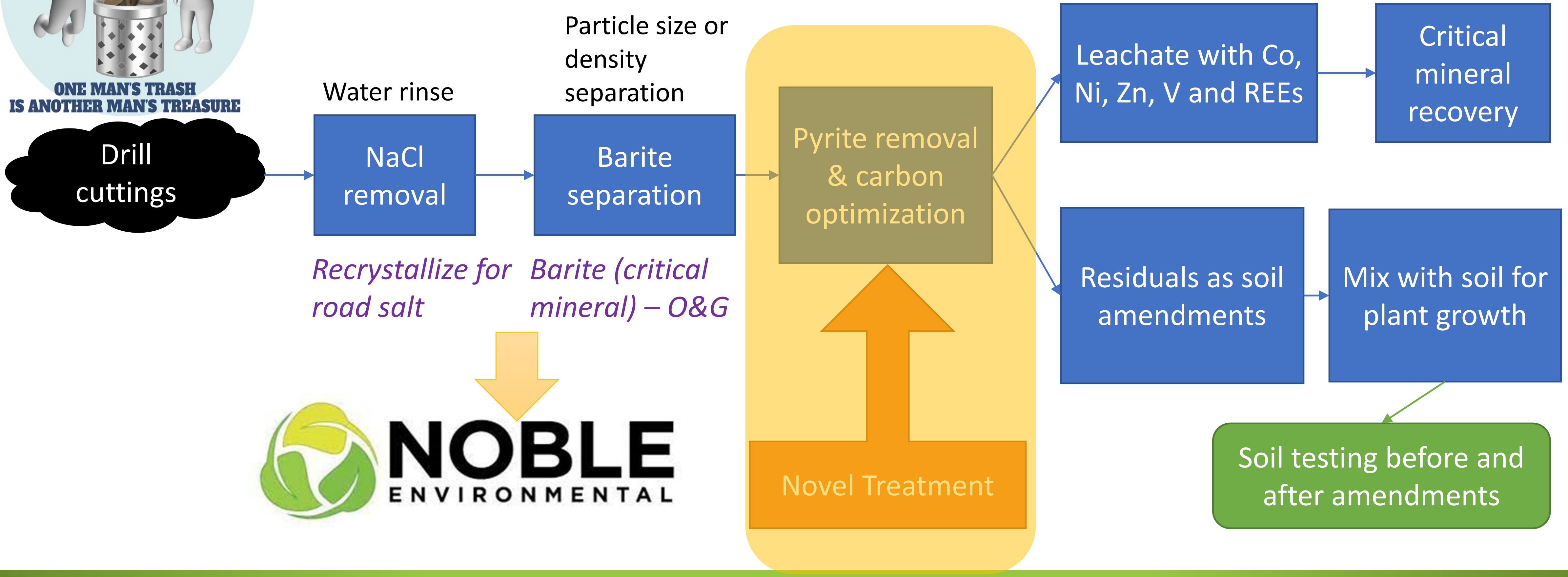
Management Suggestions

- Low content of pyrite and high content of calcite in drill cuttings are of low environmental concern; whereas high pyrite and organic content will host more **CMs** for potential recovery.
- Cuttings will need to be treated prior to use as soil growth substrates
- **Novel treatments** to break up carbon chains (more bio-available) and recover CMs
- **Barite** might be separated and purified from drill cuttings.

Up Next

Experimental work removing metals & optimizing carbon

Tentative schematic of drill cutting conversion



Acknowledgements

Just keep swimming

- Hank Edenborn (RIC, ret) – Green roof testing
- Christine Thomas (USGS, ORISE-NETL)– intern drill cutting & green roof testing
- Samantha Berry (ORISE) – Summer intern extraordinaire
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- Shikha Sharma – WVU and MSEEL liaison
- Alexandra Hakala – GES Senior Fellow, NETL-RIC
- Eilis Rosenbaum – co-TPL Rem. Reuse Onshore Resources, NETL-RIC
- Burt Thomas – TPL CM NETL-RIC

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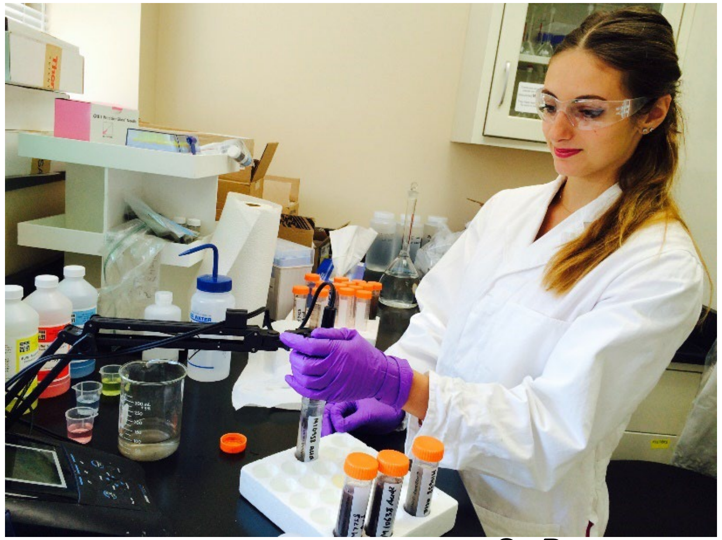

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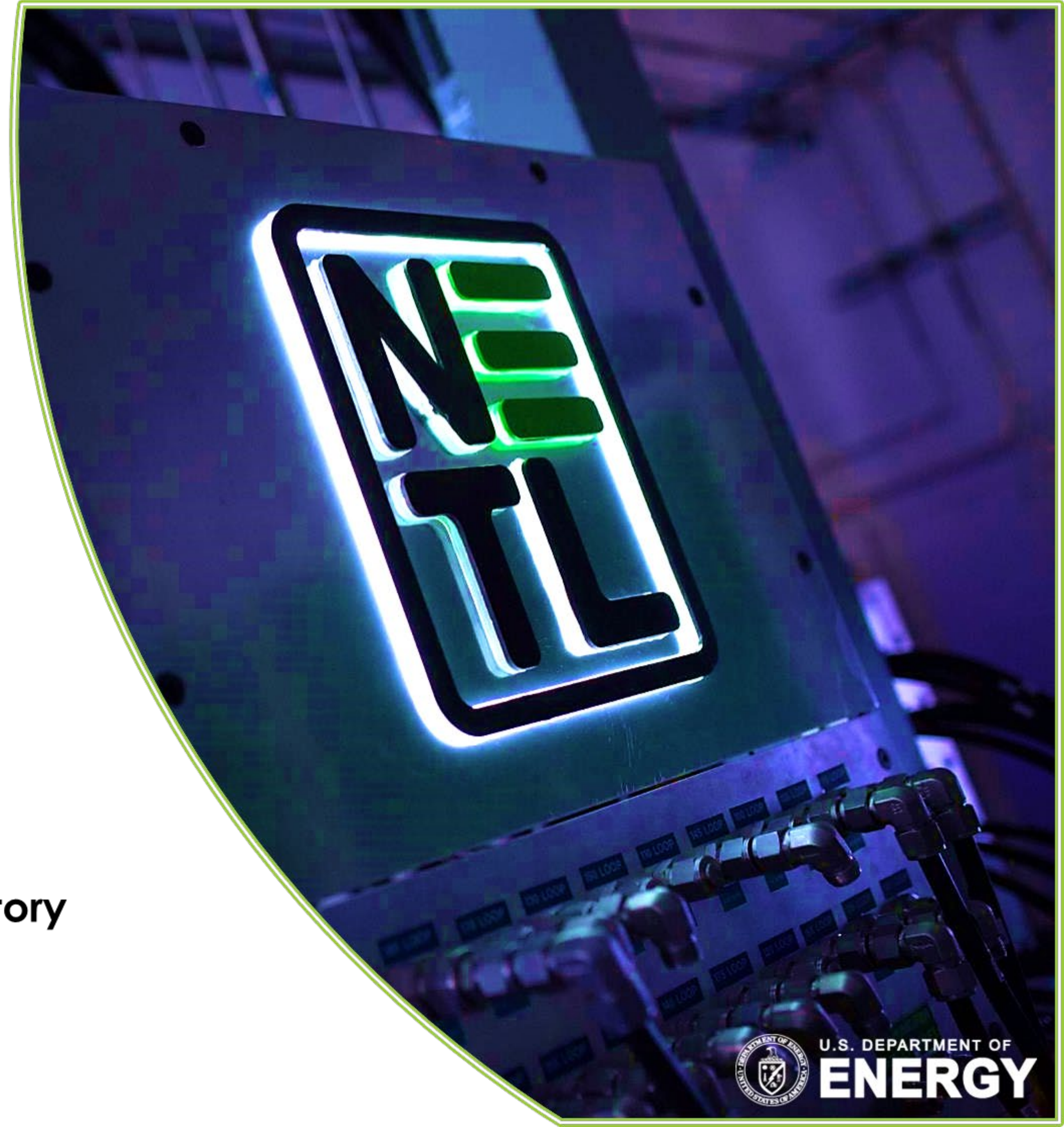

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