Water Management for Power Systems RIC FWP: Experimental Tasks

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NETL/TDC Technology Manager: John Rogers

HQ Program Manager: Hichem Hadjeres

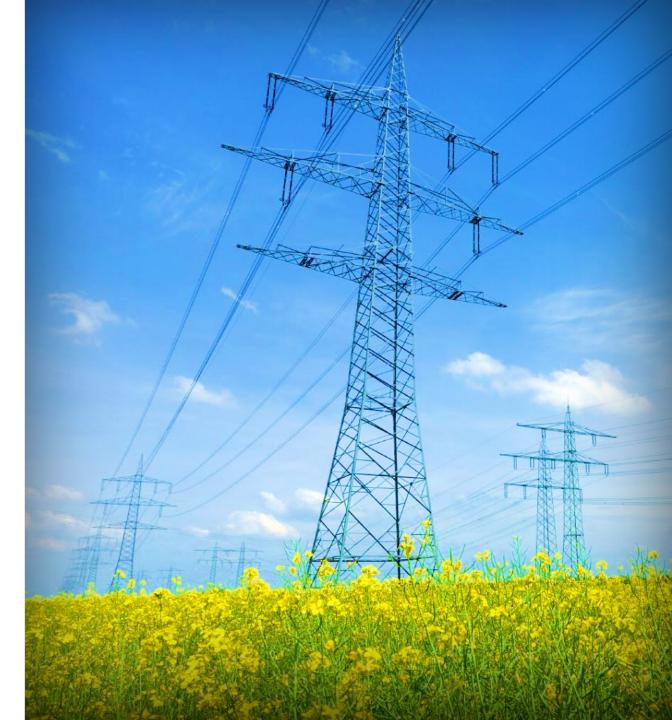
HQ Division Director: Vanessa Núñez-López



Resource Sustainability
Review Meeting
October 25th 2022



Fossil Energy and Carbon Management



Acknowledgment:



We thank the Department of Energy's Office of Fossil Energy & Carbon Management (DOE/FECM) for their support of this research.

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Water Management for Power Systems



Program Goal

The Water Management for Power Systems FWP seeks to reduce water consumption at both new and existing fossil power plants, as well as to decrease the cost of treating power plant effluent streams by converting them into valuable resources

Tasks:

- Task#2: Guiding R&D for Treatment of Fossil Power Plant Effluent Streams
- Task#3: Selective Removal of Heavy Metals from Effluent Streams
- Task#4: Concentrating Wastewater Effluent Streams & Resource Recovery
- Task#5: Impact of Water Use of Power Systems
- Task#6: Biological Treatment of FGD Effluent Streams
- Task#7: Characterization of FGD Effluent Streams
- Task#9: National Energy Water Treatment & Speciation (NEWTS) database

<u>Principal Investigator</u>

- Eric Grol /Alison Fritz
- McMahan Gray
- Nicholas Siefert
- Erik Shuster
- Djuna Gulliver
- Dustin McIntyre
- **Burt Thomas**



Motivation for Resource Recovery



Produced Water from Oil&Gas Wells and Water Consumption at Thermal Power Plants

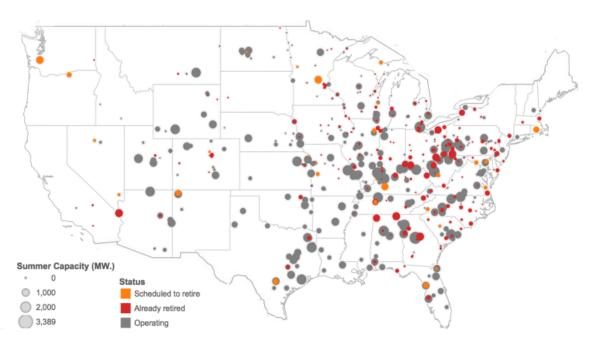
Distribution of Oil & Gas Wells

Oil Gas Oil & Gas Dry Data depict .25-mile cells.

US generates <u>4 billion</u> tons of produced water per year **2 billion** tons of produced water reinjected for EOR Remaining **2 billion** tons of produced water to SWD

Potential for ~<u>100 million tons</u> per year of salt

Capacity of Existing & Recently Retired Coal Plants



US power plants consume <u>4 billion</u> tons of fresh water per year
US power plants generate ~<u>40 million</u> tons of FGD eff per year

US consumes **50 million tons** per year of salt (\$3B/yr)



EPA ELG Final Rule: October 2020



TABLE XIV-1—LONG-TERM AVERAGES AND EFFLUENT LIMITATIONS AND PRETREATMENT STANDARDS FOR FGD WASTEWATER FOR EXISTING SOURCES (BAT/PSES)^a

Subcategory	Pollutant	Long-Term average	Daily maximum limitation	Monthly average limitation
Requirements for all plants not in the VIP or subcategories specified below (BAT & PSES).	Arsenic (μg/L	4.98	18	8
,	Mercury (ng/L)	13.48	103	34
	Nitrate/nitrite as N (mg/ L).	2.14	4	3
	Selenium (μg/L)	15.87	70	29
Voluntary Incentives Program for FGD Wastewater (existing direct dischargers).	Arsenic (μg/L)	^b 5.0	5	NA
3 ,	Mercury (ng/L)	5.44	23	10
	Nitrate/nitrite as N (mg/ L).	0.89	2.0	1.2
	Selenium (µg/L)	7.35	10	NA
	Bromide (mg/L)	0.200	0.2	NA
	TDS (mg/L)	86.06	306	149
Low utilization subcategory-AND-High FGD flow subcategory (BAT & PSES).	Arsenic (μg/L)	5.98	11	8
	Mercury (ng/L)	159	788	356

^a BAT effluent limitations for EGUs that will permanently cease the combustion of coal by December 31, 2028, are based on the previously established BPT limitations on TSS and are not shown in this table. The BAT effluent limitations for TSS for these EGUs are: Daily maximum of 100 mg/L; and monthly average of 30 mg/L.

Option#1: Selective Removal

Option#2: Delayed timeline; however, the tight TDS spec effectively requires zero liquid discharge (ZLD)



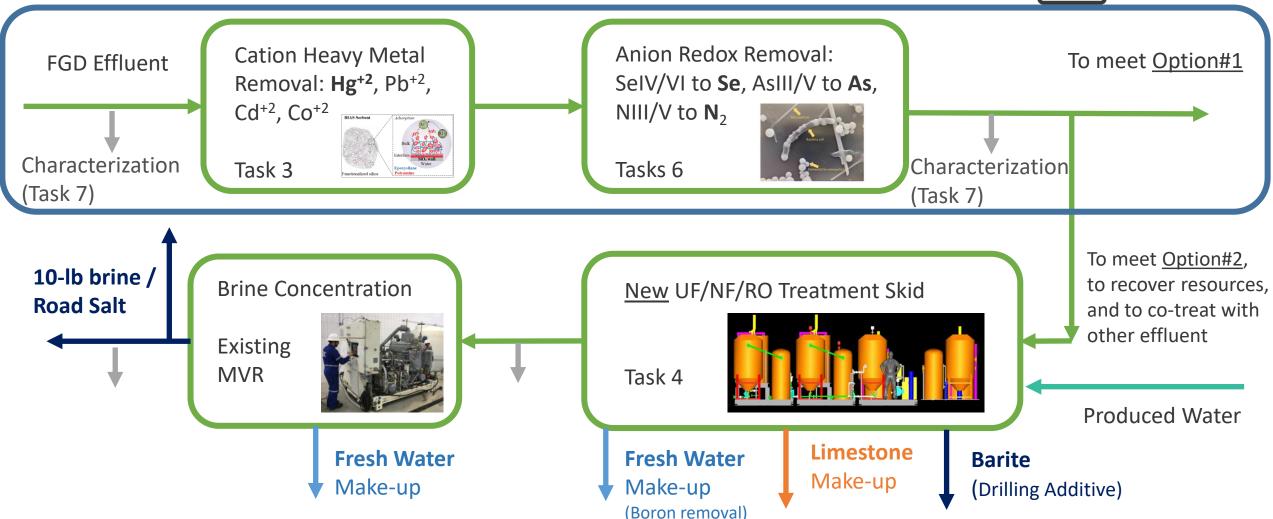
^b Long-term average is the arithmetic mean of the quantitation limitations because all observations were not detected.

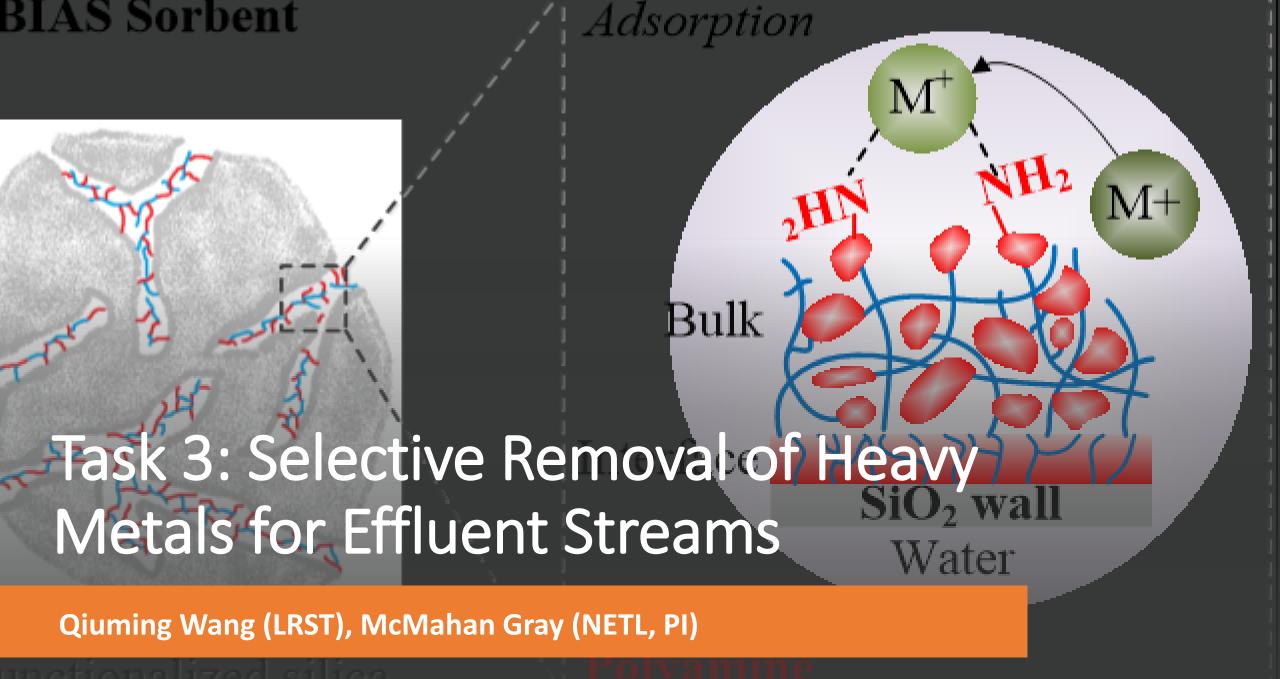
^cLimitation is set equal to the quantitation limit for the data evaluated.

d Monthly average limitation is not established when the daily maximum limitation is based on the quantitation limit.

Overview of RIC's Experimental Efforts



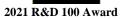


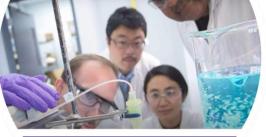


Task 3: Selective Removal of Heavy Metals from Effluent Streams











(From Left to Right)

2022 Edison Award, Bronze

2021 Secretary of Energy's Achievement Team Award

Members of the NETL team that developed MUST are (top row from left)



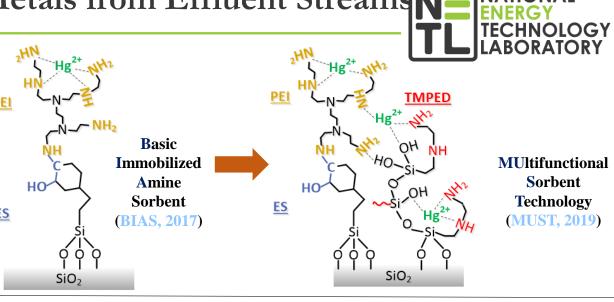








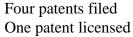
- Scalable
- Solvent Recyclable
- Sorbent Regenerable



Sorbent Formats

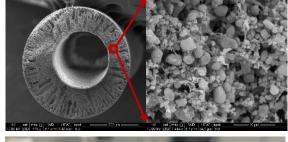
Particle Sorbent







One patent filed





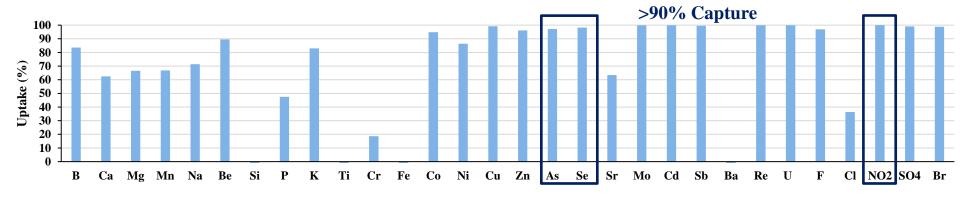


Task 3: Selective Removal of Heavy Metals from Effluent Streams

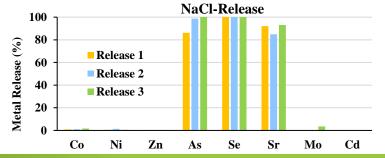


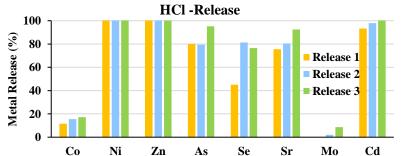
Identifier	Expected Completion	Description	Status
EY22.3.M	6/30/2022	Develop sorbent materials with high affinity to NO ₃ -/NO ₂ - with the specific aim of affecting removal by at least 90%.	Completed
EY22.3.N	9/30/2022	Develop a pretreatment process for CFPPs with high salinity and complicated Se species with the specific aim to remove Se and other heavy metals to least 90%.	Completed
EY22.3.O	12/31/2022	Develop a regeneration protocol to extend sorbent lifetime.	In Process
EY22.3.P	3/31/2023	Develop a module process for the capture of NO ₃ -/NO ₂ -, As, Se, and Hg from FGD coal waste streams. Pending removal of travel restrictions, a pre-pilot or pilot sorbent module field test will be initiated on a split stream of Longview FGD.	In Process

Adsorption into ACE Sorbent



Regeneration of ACE Sorbent

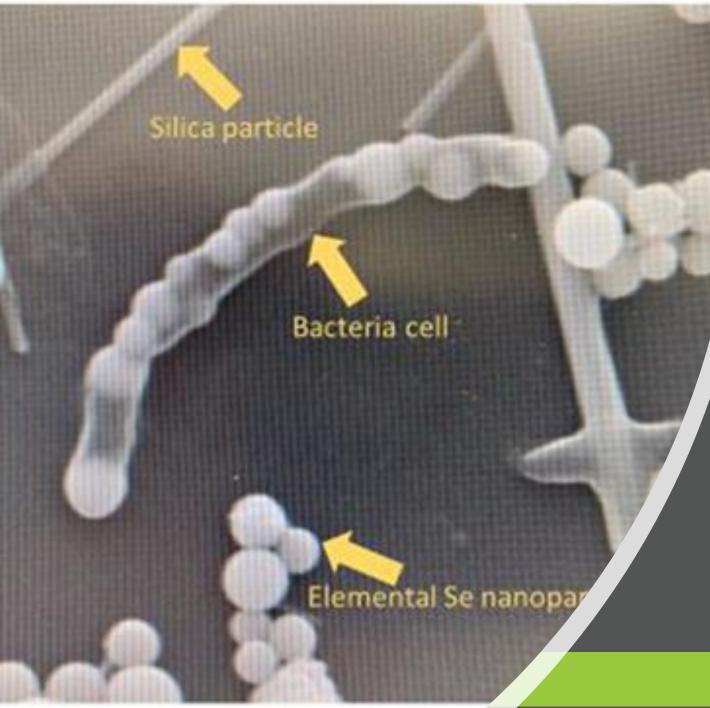






Effective Removal of Trace Levels of Toxic Heavy
Metals from Flue Gas Desulfurization Wastewater

Stable Immobilized Amine Sorbents for Heavy
Metal Removal from Industrial Wastewaters





Task 6: Biological treatment of FGD effluent streams

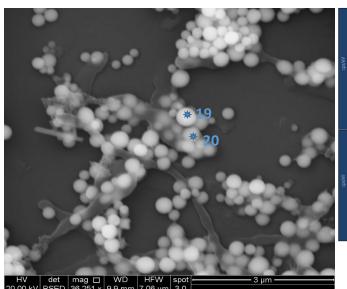
Preom Sarkar (LRST), Gregory Lowry (CMU), Djuna Gulliver (NETL, PI)

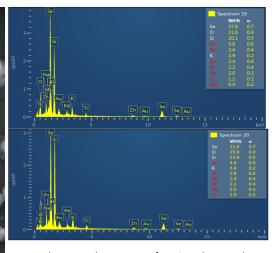
Water Management of Power Systems

TL TECHNOLOGY LABORATORY

Task 6.0 Biological Treatment of FGD Effluent Streams

Selenate Enrichments

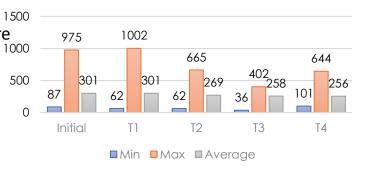




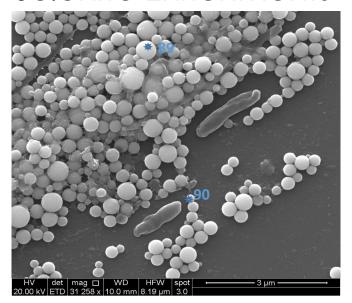
Based on XRD data, we are forming elemental selenium, predominantly amorphous and hexagonal allotropes.

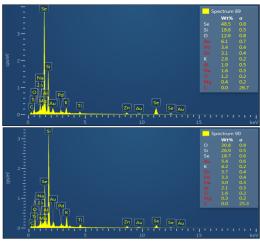
Selenate Enrichments Particle Size

Particles formed by microbes are relatively large. Could be useful 1000 to stimulate the microbes to 500 make bigger particles to avoid the use of RO to remove Se colloids.



Selenite Enrichments

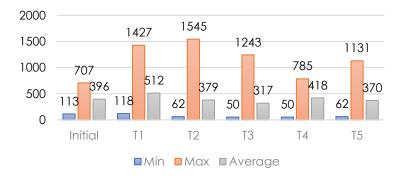




Based on XRD data, we are forming elemental selenium, predominantly amorphous and hexagonal allotropes.

Selenite Enrichment Particle Sizes

Particles formed by selenite enrichments are slightly larger than those created by selenate enrichments.

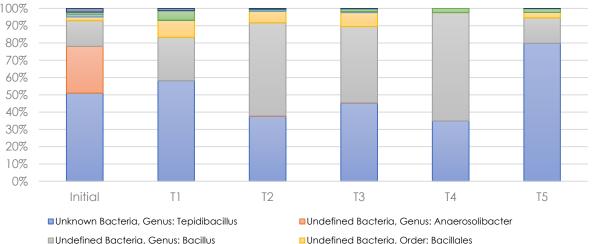




Water Management of Power Systems

Task 6.0 Biological Treatment of FGD Effluent Streams

50/50 Selenium Oxyanion Mix



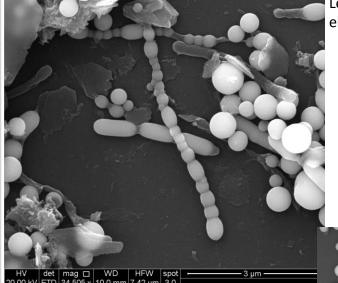
■Undefined Bacteria, Genus: Clostridium sensu stricto 9 ■Undefined Bacteria, Family: Thermotaleaceae

■Other

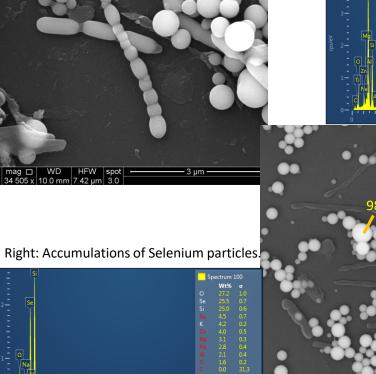
Selenium Oxyanion Measuements after Incubation mmol of Se

Much like the selenate and selenite enrichments, we see the rise of Tepidibacillus which is a selenite reducer. Another major player is the Bacillus, which is a selenate reducer.

Microbial community able to reduce 80% selenate and 99% of selenite in 7 days.



Left: Likely a bacteria with internal elemental selenium accumulations

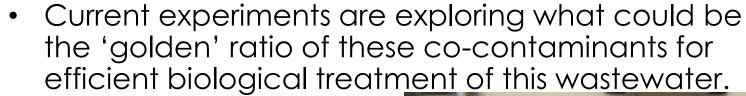




Water Management of Power Systems

Task 6.0 Biological Treatment of FGD Effluent Streams

Identifier	Type ¹	Expected Completion Date	Description (What, How, Who, Where)
EY21.6.C	Major	03/31/2022	Completed. Microbial profile and baseline efficacy
			values of biocatalyst treatment for FGD effluent
			streams.
EY22.6.D	Progress	03/31/2023	Assessment of biocatalyst performance at varying FGD
			effluent conditions.



 Nitrate appears to stimulate Se removal

 Low and medium concentrations of sulfate stimulate Se removal, but high sulfate inhibits selenium removal.

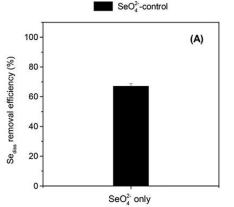


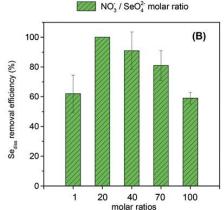


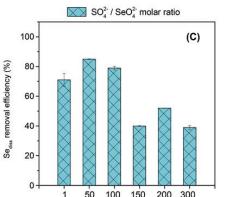
Table 1 Se-laden wastewater composition (co-contaminants) from different industrial sources

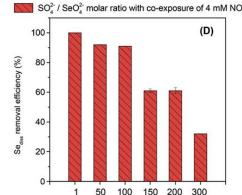
Wastewater	Se (mM)	SO ₄ ²⁻ (mM)	NO ₃ (mM)
Mining-impacted ^{7,38}	0-0.2	5-72	4
Se refinery plant ³⁹	Up to 8	0-2	n.i. ^a
Flue gas desulfurization ^{38,40}	0-2	31-209	0-7
Agricultural ^{12,38}	~0.01	6-106	0-4

^a n.i. – no information.

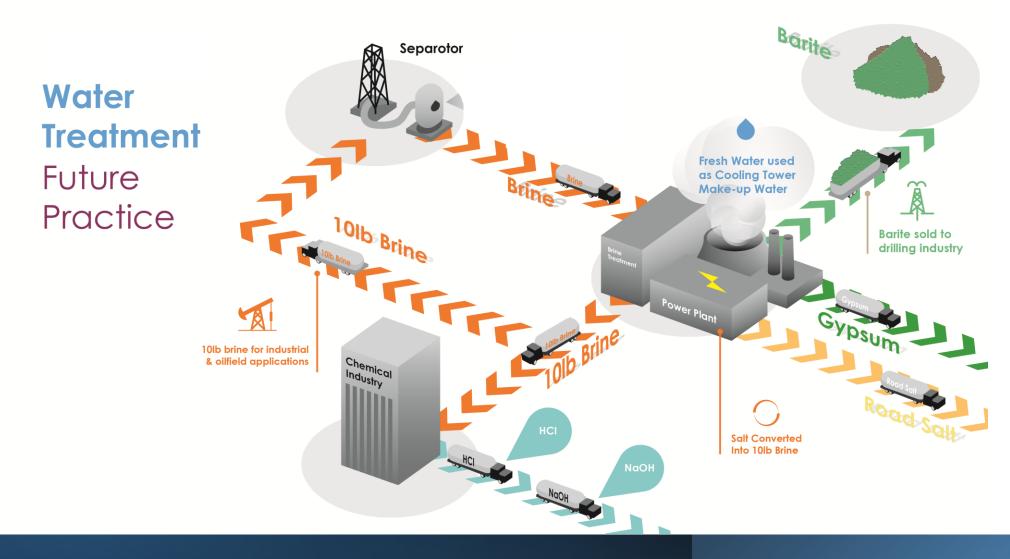












Task 4: Concentrating Wastewater Effluent Streams & Resource Recovery

Nicholas Siefert (NETL, PI)

Kevin Resnik (LRST)

Lance Lin (WVU)

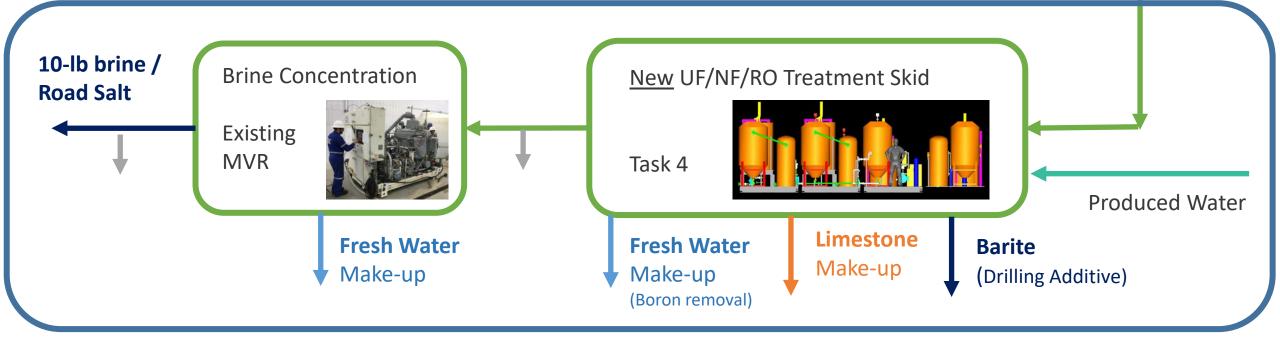
Marc Kurz (UND EERC)

Task 4 High Level Overview and Milestone



Identifier	Type ¹	Expected Completion Date	Description (What, How, Who, Where)
EY22.4.2.1.A	Project	12/31/2022	Demonstrate > 40 hrs of operation of 3-gpm UF/NF/RO skid at WVU co-treating FGD effluent and produced water.

To meet Option#2, to recover resources, and/or to co-treat with other effluent

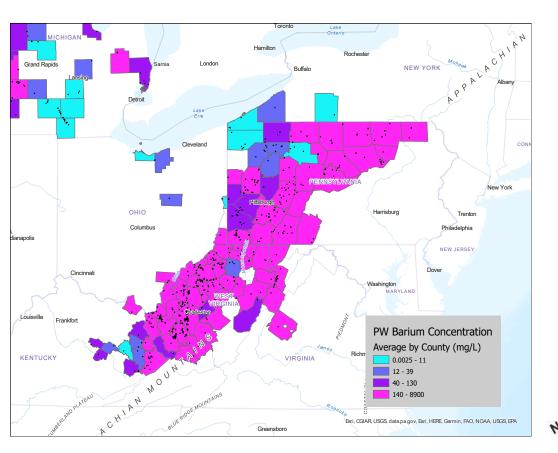


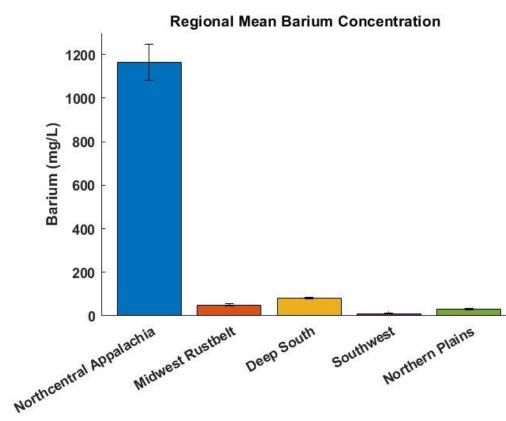


Co-treatment Opportunities in Appalachia



- Appalachia Produced Water has high barium concentrations
- Co-management of FGD and produced water can generate USGS critical minerals, such as API grade barite





API 4.2 = Density: >4.20 g/cubic cm

API 4.1 = Density: >4.10 g/cubic cm



Barite Specs (api.org)



Synergies between PW and FGD Effluent



- Produced water is high in divalent cations (Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺)
- Power plant FGD effluent is rich in sulfate (SO₄²-)

Potential to make up to 0.4 million tons per year of Barite (~\$70 M/yr)

- Produced water has reducing species (NH₄⁺, Fe²⁺, C₂H₃O₂⁻)
 - FGD biological treatment reactor need these reducing species
- Power plant FGD effluent has oxidizing species that need to be reduced NO₃-, NO₂-, SeO₄²-, SeO₃²-, CrO₄²-
- Synergies make co-treatment advantageous



Synergies between PW and FGD Effluent



Sulfate in FGD effluent can combine with Barium and Strontium in PW to make C.M. Barite

		FGD <u>High</u> Salinity After Phys/Chem/Bio		PW Marcellus <u>High</u> Salinity
	mmol/L	mmol/L	mmol/	L mmol/L
H ₂ O	55,241	55,071	54,19	52,230
CI-	121	307	1,27	3,187
SO ₄ ²⁻	12	59		_
Na ⁺	5	57	82	2,132
Ca ²⁺	52	26	15	344
Mg ²⁺	20	160	2	7 66
Sr ²⁺	-	-	1	47
Ba ²⁺	-	-	1	67
Li+	-	-		7 NM
Fe ²⁺	-	-		2 NM
B(OH) ₃	6	33		1 2
TDS (g/L)	8.7	26	76	191
Osmotic Pressure (atm)	4.9	15	61	183



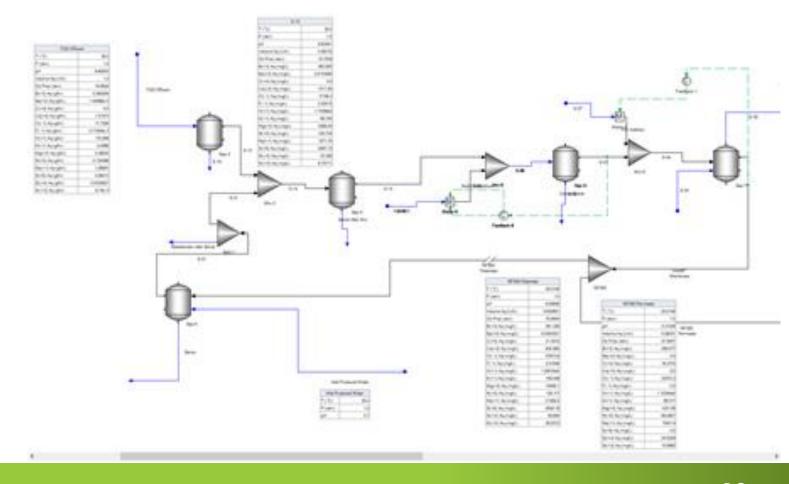
Process Flow Modeling



• Co-treatment process was first modeled in Dupont Wave and the simulated in OLI Flowsheet



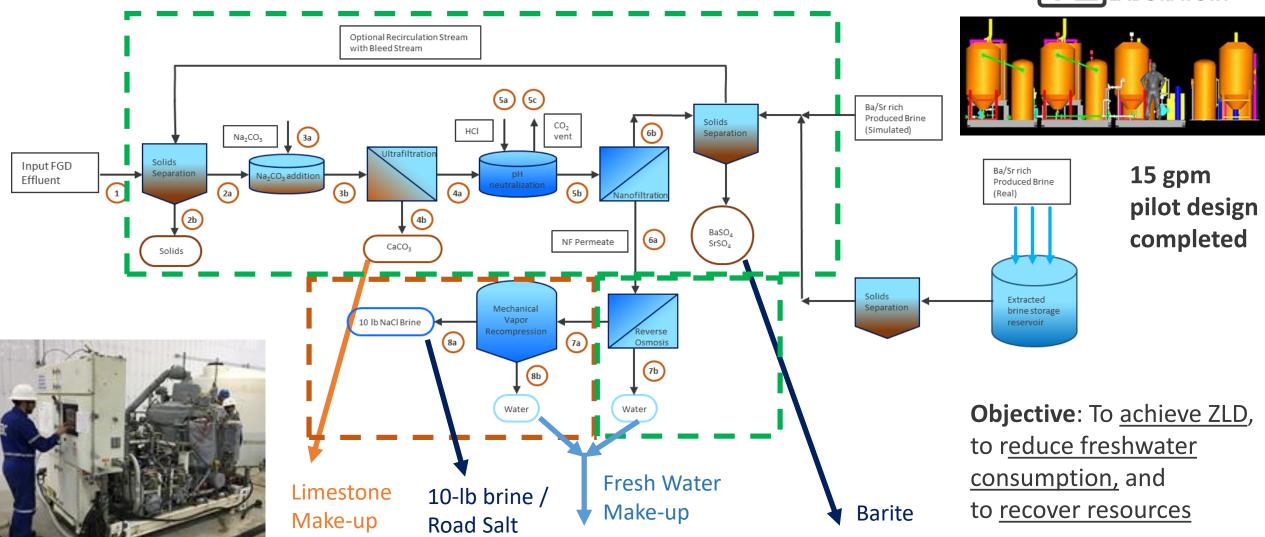






Pilot Skid Designed to Operate on FGD Effluent

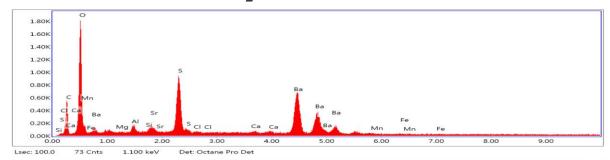






Laboratory Scale Demonstrations at WVU



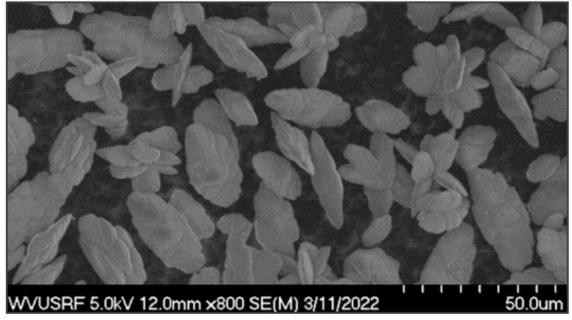




Laboratory at WVU I Dr. Lance Lin Builds off previous FECM/NETL grant: Co-treating Cooling Tower Blowdown and Produced Water, Dr. Harry Finklea, Co-Pl



Recovered BaSO₄/ SrSO₄ density >4.1 g/cm³. **Meets API Spec**.



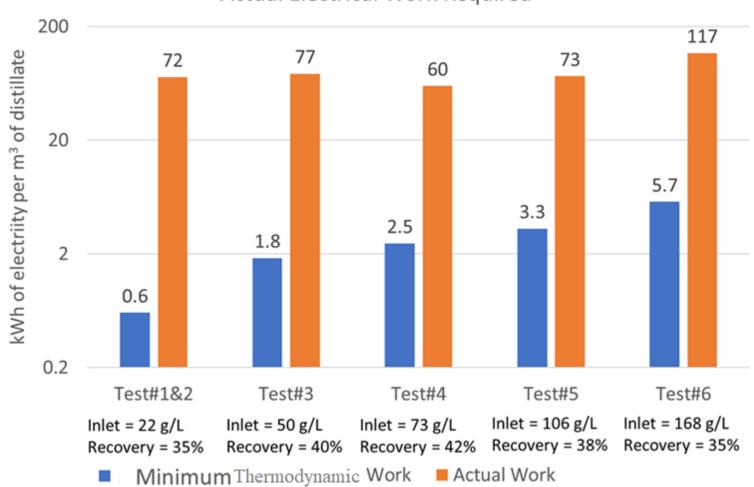
Barite mineral generated from the co-treatment process. Barite's high density makes it an ideal weighting additive to drilling fluids and concrete



Concentrating Wastewater Effluent Streams



Comparison between Minimum Thermodynamic Work and Actual Electrical Work Required





Additional MVR baseline testing in 2023 at UND EERC BEST with options for shipping brines from across US



Acknowledgment:



We thank the Department of Energy's Office of Fossil Energy & Carbon Management (DOE/FECM) for their support of this research.

NETL/TDC Technology Manager: John Rogers

DOE/FECM HQ Program Manager: Hichem Hadjeres

DOE/FECM HQ Advanced Remediation Technologies Division: Vanessa Núñez-López

HQ Director FECM-30: David Alleman

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