Overview of Emissions Control R&D at NETL

FECM Spring R&D Project Review Meeting
Emissions Control Session
Eric Grol, Technical Portfolio Lead
May 3, 2022

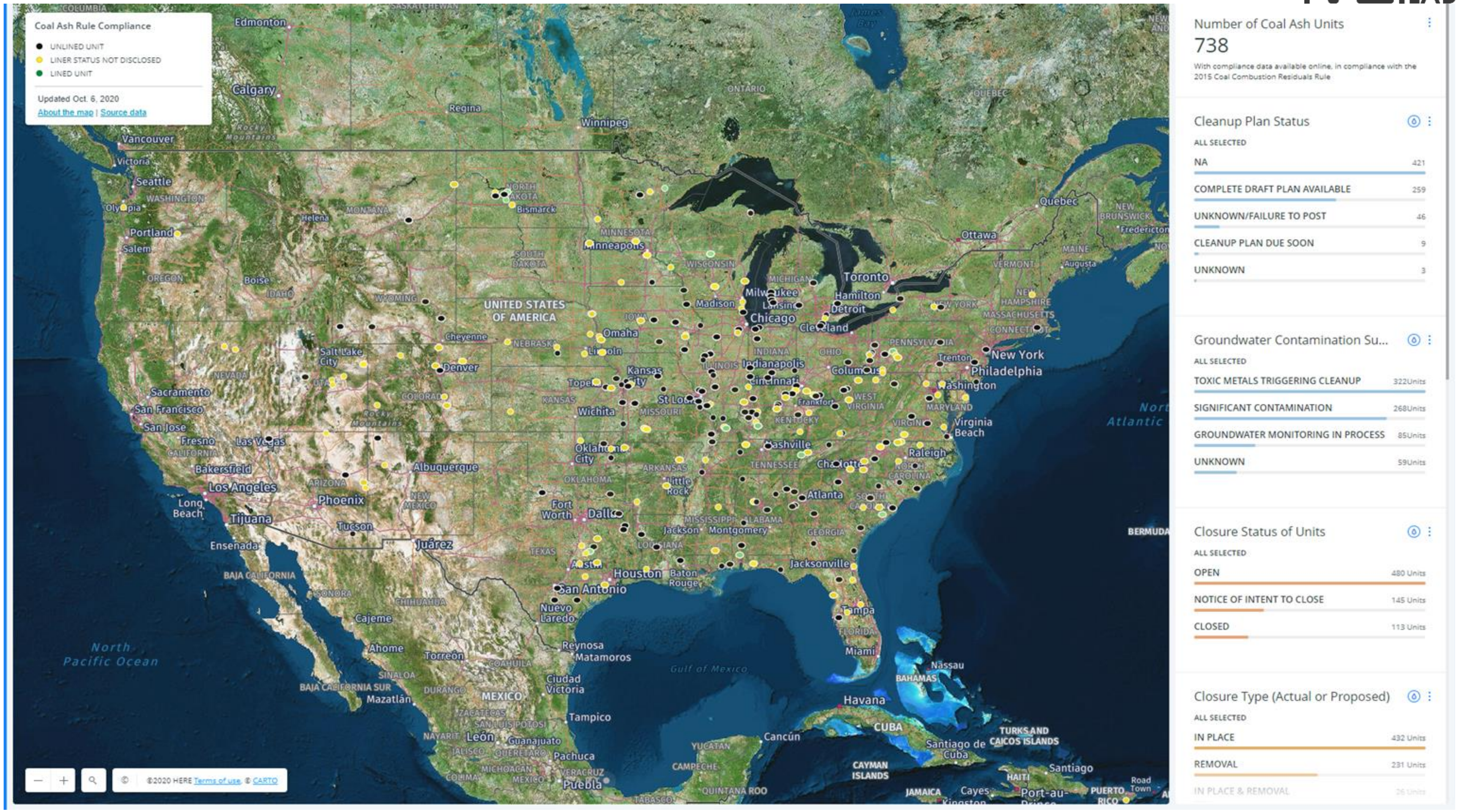
Emissions Control Field Work Proposal

Program Goal

The Emissions Control Field Work Proposal (FWP) supports Fossil Energy and Carbon Management's (FECM) mission of achieving secure, affordable, environmentally sound fossil energy supply by developing technologies that can reduce the generation of coal combustion residuals (CCR), increase beneficial utilization of CCR, and improve the environmental performance of long term CCR storage

- DOE Program Manager: Dr. Jeff Summers
- NETL Technology Manager: Dave Lyons
- Technical Portfolio Lead: Eric Grol
- Task 2 PI: Dr. Jan Steckel (support from Dr. Jack Findley)
- Task 3 PI: Dr. Ping Wang
- Senior Leadership: Dr. Evan Granite

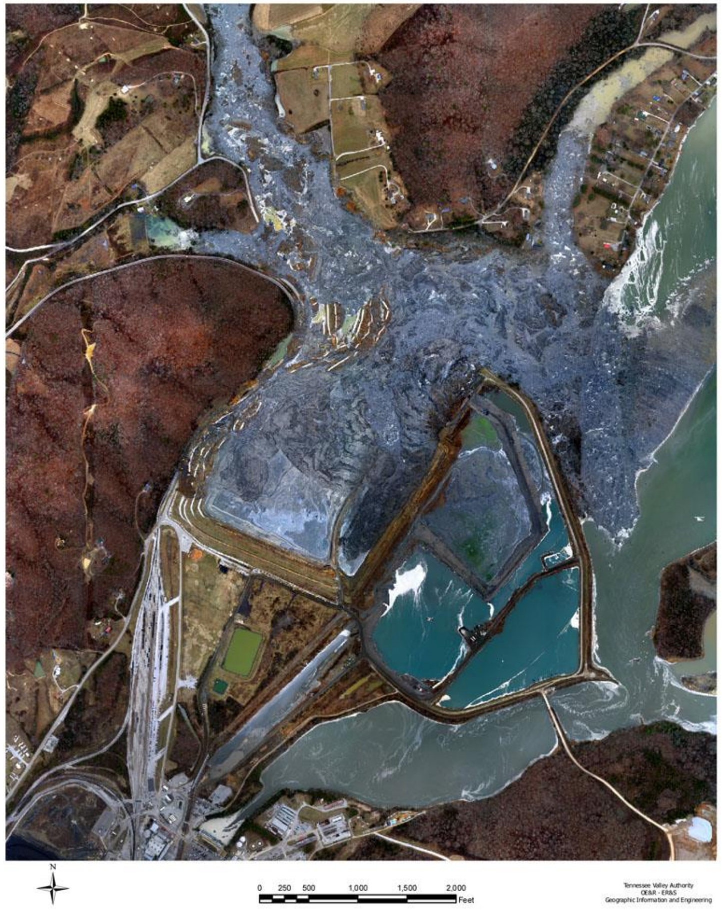
Coal Ash Impoundment Map



Kingston Fossil Plant Ash Spill (TVA)

- Tennessee Valley Authority's Kingston Fossil Plant: 1.4 GW of coal-fired capacity
- 14,000 tpd low-S coal (~140 railroad cars)
- December 22, 2008: dike failure surrounding ash dewatering pond
- Release 1.1 billion gallons of fly ash slurry covering up to 300 acres
- Discharge into Emory River and Clinch River

Aerial Image Of Kingston Ash Slide 12/23/08



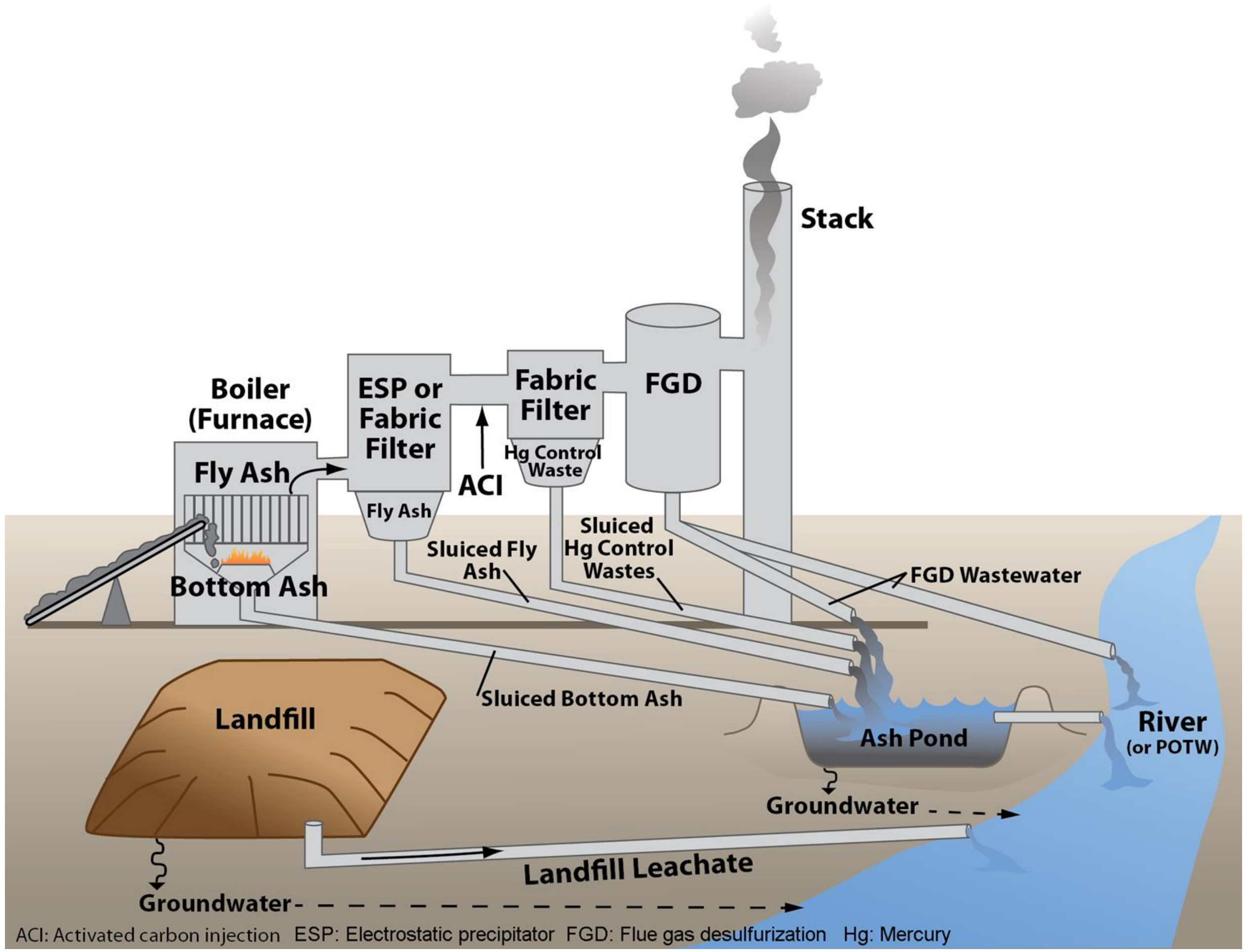
Dan River Coal Ash Spill

- Duke Energy's Dan River Steam Station
- 276 MW coal-fired capacity, retired in 2012
- February 2, 2014: drainage pipe burst at ash containment pond
- 39,000 tons of ash, 27 million gallons of wastewater released into Dan River

Landfill Leachate Wastewater Treatment

Regulatory Drivers

- Wastewater from landfills regulated by Effluent Limitation Guidelines (2015, 2020, expected fall 2022)
- Coal ash pond management regulations likely to result in wastewater streams requiring treatment



Source: EPA Steam Electric Power Generating Effluent Guidelines | US EPA

Regulations Applicable to Coal Ash Wastewater

- **Effluent Limitation Guidelines (wastewater):**
  - Combustion residual leachate
  - Combustion residuals: wastes generated from combustion, generally collected by pollution control technologies, stored at the plant in landfills or surface impoundments. Leachate includes liquid, including suspended or dissolved solids, that has drained from landfill materials or that has passed through a containment structure (example: water leaking from an ash pond)

- **Disposal of Coal Combustion Residuals (CCR) from Electric Utilities**
  - Establishes operating criteria and minimum closure standards for CCR landfills (2015)
  - Updated in 2019 to reflect change in definition for lined facilities

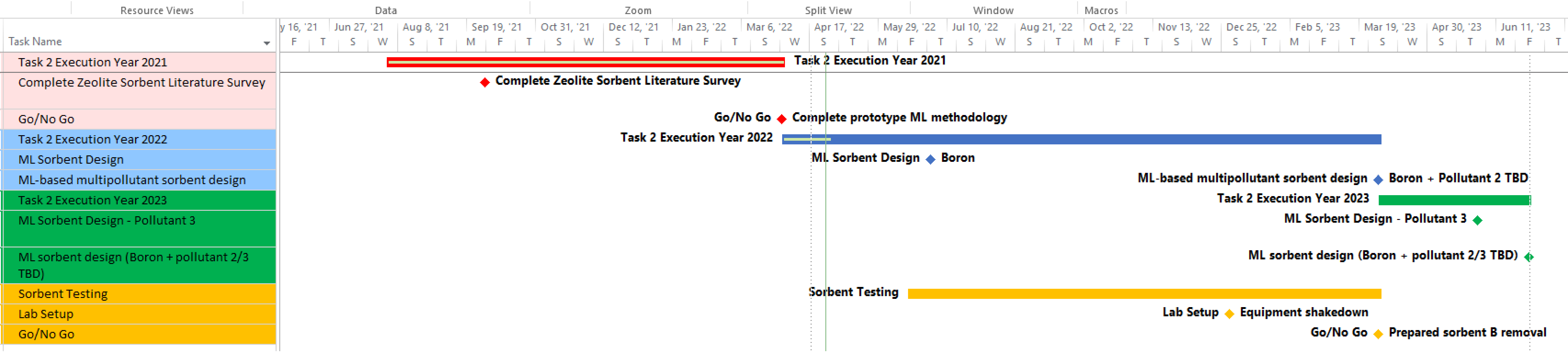
Coal Combustion Residuals Regulation

Disposal of Coal Combustion Residuals (CCR) from Electric Utilities

- **2019 regulation found that clay-lined impoundments no longer meet the definition of "lined" – applies to active impoundments and those no longer receiving waste**
- **Two compliance options given:**
  - Cap-in-place: permanently cover the impoundment, long-term groundwater monitoring, liability for 30 years once compliance is achieved post-closure
  - Clean closure (aka 'excavate and haul'): remove contents of unlined facility and move to a new, lined one; no long-term liability

Emissions Control Project Timeline

Two tasks, twenty-four months total



Task 2: Machine Learning Aided Development of Sorbents to Treat Leachates (From Ash Impoundments)

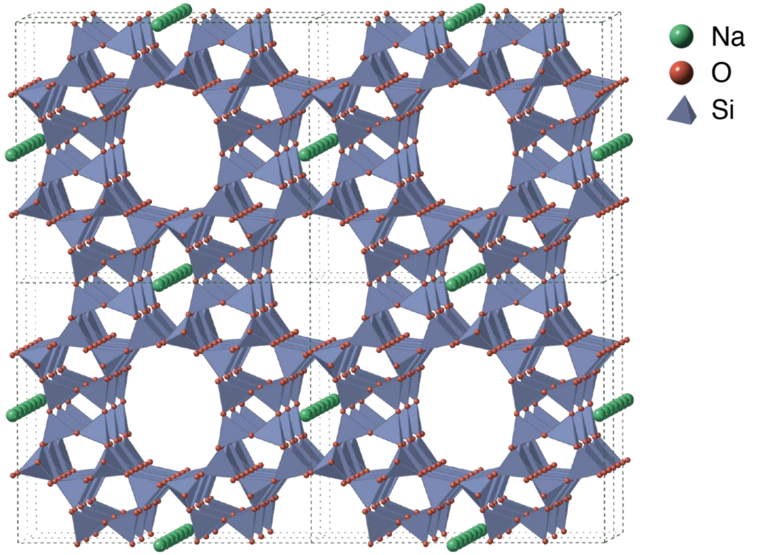
- **Objective: Development of an artificial intelligence/machine learning (AI/ML) methodology for design of sorbents that can be used to treat wastewater from coal ash impoundments**

- **Approach: Computational design of zeolite sorbents (which can be synthesized from fly ash) that can be tuned to specific ash impoundment wastewater contaminants**

Task 2: Approach

Overall Strategy

1. Construct a Collection of Sorbent Structures and Sorption Conditions
   - Structures from International Zeolite Association database
2. Construct appropriate model potentials (as needed)
   - Adsorbate/adsorbent interaction energy – density functional theory
3. Carry out computations to estimate sorption in a representative subset of the sorbent structures
   - RASPA – Grand canonical monte carlo
4. Establish structure-property relationships that govern sorption
   - Considers pore structure, crystal structure features, boric acid concentration
5. Use AI/ML techniques to exploit relationships to screen / design tailored sorbents for impoundments
   - E.g., support vector machine, random forest regression



Mordenite (MOR framework)

Task 2: Zeolites

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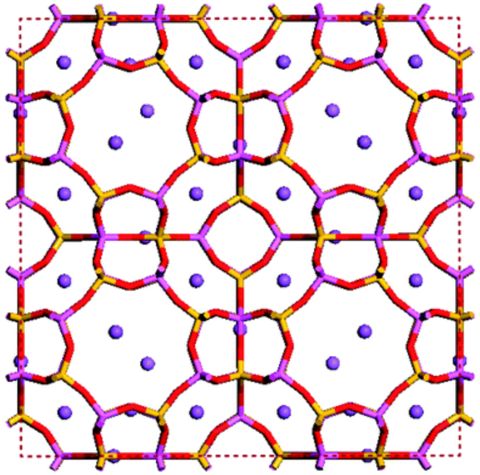
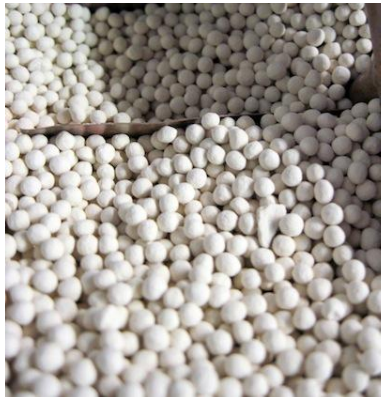
Introduction

1. Tetrahedral aluminosilicates
   - 245 distinct experimentally-synthesized topologies
   - Millions of hypothetical zeolites

2. Composed of AlO_4 and SiO_4 tetrahedra
   - Substitution of Al for Si leads to charge imbalance
   - Extra-framework cations (Na+, K+, Ca2+, etc.) balance charge
   - Cations are loosely bound, can be exchanged
   - Cations are adsorption and catalytic sites
   - Properties vary based on topology, composition, and Al distribution

3. Uses for separations and catalysis
   - Stable, inexpensive to produce
   - High internal surface area for adsorption





Task 2: Methodology

1. Construct a Collection of Sorbent Structures and Sorption Conditions

- **Si to Al ratio**
  - Zeolites from all Si are charge neutral.
  - Substitution of some Si with Al leads to charge imbalance that is balanced by loosely held, extra-framework cations.
  - IZA database has silica but not aluminosilicates; started with IZA structures and replaced silica with aluminum atoms
  - Constrained placement to prevent aluminum atoms on neighboring sites
  - Database of structures has 5 Si:Al ratios: 1, 2, 3, 4, 9
- **Cations: Na^+, K^+, Ca^{2+}, Mn^{2+}, Fe^{2+}**
  - Mixtures of Cations also included, e.g. 25% Na+, 75% K+
    - Number of cations present depends on amount of Al present
    - Number is controlled by cation charge and Si/Al ratio
    - Location is controlled by topology, cation size, and cation charge
    - Number of potential sorbent structures grows quickly but limited to twelve for this exercise
    - Cations often serve as adsorption sites

Task 2: Force Fields

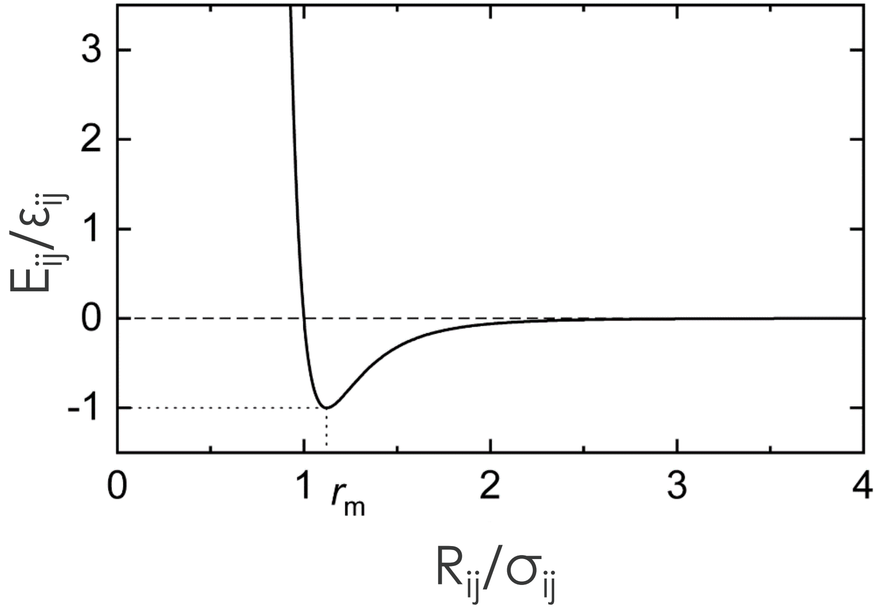
2. Construct appropriate model potentials

- Analytical function that describes interaction energies between:
  - Water/Boric acid, boric acid/zeolite, boric acid/cations, cation/zeolite, water/zeolite, water/cations
- Function of distance between a pair of atoms(R_{ij})
- Total energy of system is the sum over the atomic pairs
- Example: Lennard-Jones potential (right)
  - σ is related to average atomic size
  - ε is related to depth of potential energy well

- Used with statistical mechanics to calculate thermodynamic properties
  - Fast computation of energies means more configurations and better statistics
  - Phase equilibrium, heats of adsorption, adsorption isotherms

- Lennard-Jones + Coulomb potential OR Buckinham + Coulomb potential

$$E_{ij}(R_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{R_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}}\right)^{6}\right]$$



Task 2: Monte Carlo Methods

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3. Carry out computations to estimate sorption in sorbent structures

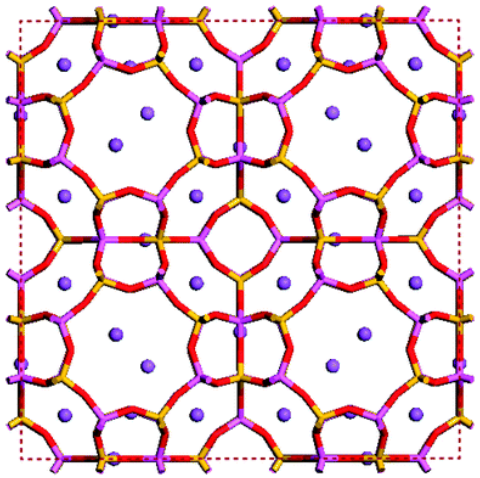
- Methods for computing equilibrium properties
  - Equations of state, adsorption isotherms, heats of adsorption
- Accept or reject trial moves based on detailed balance
  - $\pi_1 P_{1\to 2} = \pi_2 P_{2\to 1}$
    - π_i is the probability of being in state i, P is the transition probability
  - **Canonical Monte Carlo (NVT):**
    - Moves: Translation, Rotation (If necessary)
    - $P_{i\to j} = \min(1, e^{\frac{-(E_j - E_i)}{kT}})$
  - **Grand Canonical Monte Carlo (μVT):**
    - Moves: Translation, Rotation (if necessary), Insertion, Deletion
- **Classical Simulations:** E is calculated using a Force Field (function of distances)
- Determine property by taking the average over the ensemble of states
  - <N>, the average number of particles, at different fugacities (related to chemical potential)
  - Requires large number of trial moves to average over (usually on the order of 10^5 – 10^6)

Task 2: ML Development Procedure

5. Use AI/ML techniques to exploit relationships to design tailored sorbents

QM (DFT) → Train → Classical (FFs) → Train → Machine Learning

- Goal: Preserve accuracy at each step
  - QM trains "force field" model
  - "Force field" model (e.g. Lennard Jones + Coulomb) computes adsorption data
  - Adsorption data trains ML model
    - y=f(x): y=adsorption capacity, x = zeolite structure, composition, boric acid concentration, Al/Si ratio, cation type, etc
- Ensures accurate training set



Task 2: Proposed Machine Learning Model

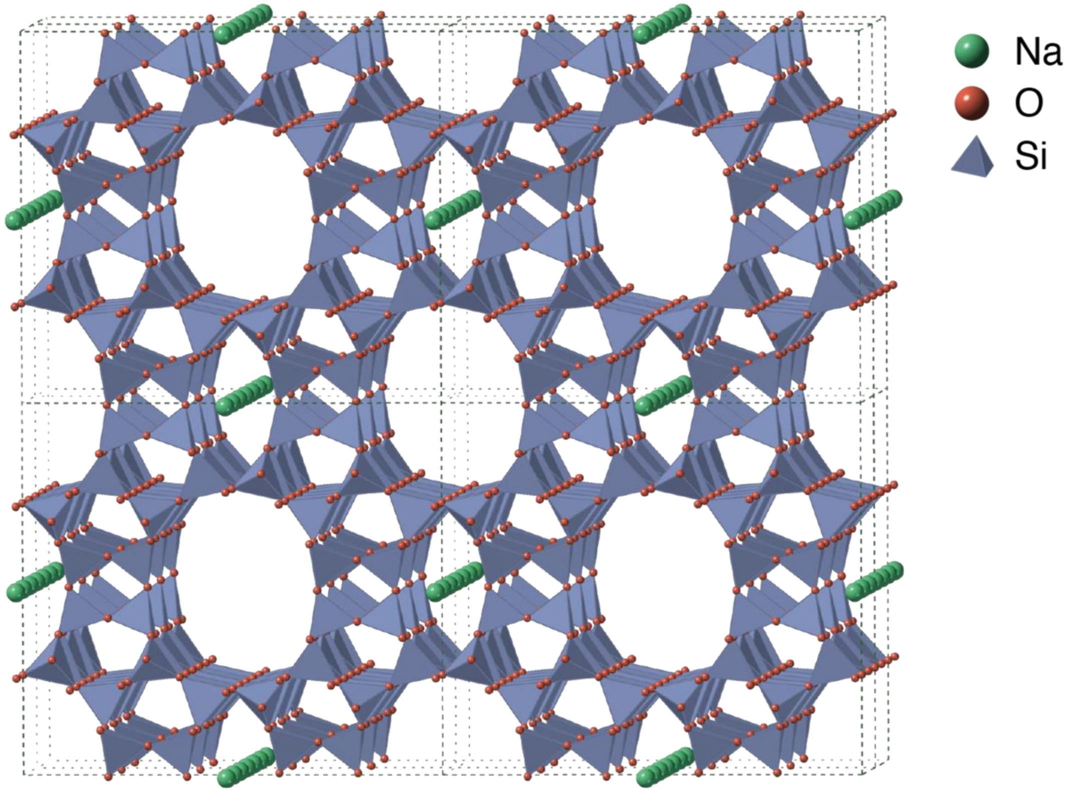
5. Use AI/ML techniques to exploit relationships to design tailored sorbents

- **First Pass Model**
  - **Biggest Issue:** Treating the metal cation positions (unknown prior to molecular simulations or experimental measurements). Cations are also nonbonded, which causes issues for crystal graphs
  - **Features (x on previous slide):**
    - O-O RDF (binned using the methods of Fernandez et al.)
    - Stoichiometry (including info on Si/Al, number of each cation)
    - Solution composition
  - **Initial ML Approach:** SVM (support vector machine) or Random Forest Regression
  - **Reasoning:** In the actual sorbent design, only the topology for each zeolite is known beforehand. Need to optimize composition.
  - **Possible Improvements:**
    - Weight RDF with electronegativities or DDEC3 (density derived electrostatic and chemical method – method for assigning charges to atoms) atomic charges.
      - This will improve accuracy but reduce "predictive power"
    - Two attached ML models: One predicts cation distribution, other predicts adsorption given the cation distribution

Task 2: Progress

Overall Strategy

1. Construct a Collection of Sorbent Structures and Sorption Conditions ← **Complete**
2. Construct appropriate model potentials (as needed) ← **Complete**
3. Carry out computations to estimate sorption in a representative subset of the sorbent structures ← **Ongoing**
4. Establish structure-property relationships that govern sorption ← **Ongoing**
5. Use AI/ML techniques to exploit relationships to screen / design tailored sorbents for impoundments ← **Ongoing**



Mordenite (MOR framework)

https://en.wikipedia.org/wiki/Zeolite, François-Xavier Coudert

Task 3: Experimental Development of Sorbents for Treating Leachates from Ash Impoundments

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- **Objective: Prepare promoted zeolite sorbent(s) informed by computational modeling, capable of removing contaminants from ash impoundment leachate**

- **Approach: Using a purchased zeolite, chemically modify with optimized cations (based on computational modeling results) and demonstrate ability to remove contaminants present in landfill leachate (initially boron)**
  - Start with commercially available sorbent and demonstrate ability to promote based on Task 2 modeling results

- **Expected to start fall 2022**

Task 3 Experimental Setup

Reaction Kinetics Lab in PGH
B94#404 (0230)
RP: Ping Wang

Backup slides

Effluent Limitation Guidelines (wastewater)

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Combustion Residual Leachate - New Source Standard (2015)

Federal Register / Vol. 80, No. 212 / Tuesday, November 3, 2015 / Rules and Regulations **67871**

TABLE XI–2—LONG-TERM AVERAGES AND STANDARDS FOR FGD WASTEWATER, GASIFICATION WASTEWATER, AND COMBUSTION RESIDUAL LEACHATE FOR NEW SOURCES

Wastestream	Pollutant	Long-term average	Daily maximum limitation	Monthly average limitation
FGD Wastewater (NSPS & PSNS)	Arsenic (µg/L)	[a] 4.0	[b] 4	([c])
	Mercury (ng/L)	17.8	39	24
	Selenium (µg/L)	[a] 5.0	[b] 5	([c])
	TDS (mg/L)	14.9	50	24
Gasification Wastewater (NSPS & PSNS)	Arsenic (µg/L)	[a] 4.0	[b] 4	([c])
	Mercury (ng/L)	1.08	1.8	1.3
	Selenium (µg/L)	147	453	227
	TDS (mg/L)	15.2	38	22
Combustion Residual Leachate (NSPS & PSNS)	Arsenic (µg/L) [d]	5.98	11	8
	Mercury (ng/L) [d]	159	788	356

[a] Long-term average is the arithmetic mean of the quantitation limits since all observations were not detected.
[b] Limitation is set equal to the quantitation limit.
[c] Monthly average limitation is not established when the daily maximum limitation is based on the quantitation limit.
[d] Long-term average and standards were transferred from performance of chemical precipitation in treating FGD wastewater.

Effluent Limitation Guidelines (wastewater)

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Combustion Residual Leachate - Existing Source Standard (2015)

- **Standards on total suspended solids, oil & grease established in 2015**

Pollutant or pollutant property	BPT Effluent limitations	
	Maximum for any 1 day (mg/l)	Average of daily values for 30 consecutive days shall not exceed (mg/l)
TSS	100.0	30.0
Oil and grease	20.0	15.0