Overview of Emissions Control R&D at NETL

NATIONAL ENERGY TECHNOLOGY LABORATORY

FECM Spring R&D Project Review Meeting
Emissions Control Session

Eric Grol, Technical Portfolio Lead

April 20, 2023

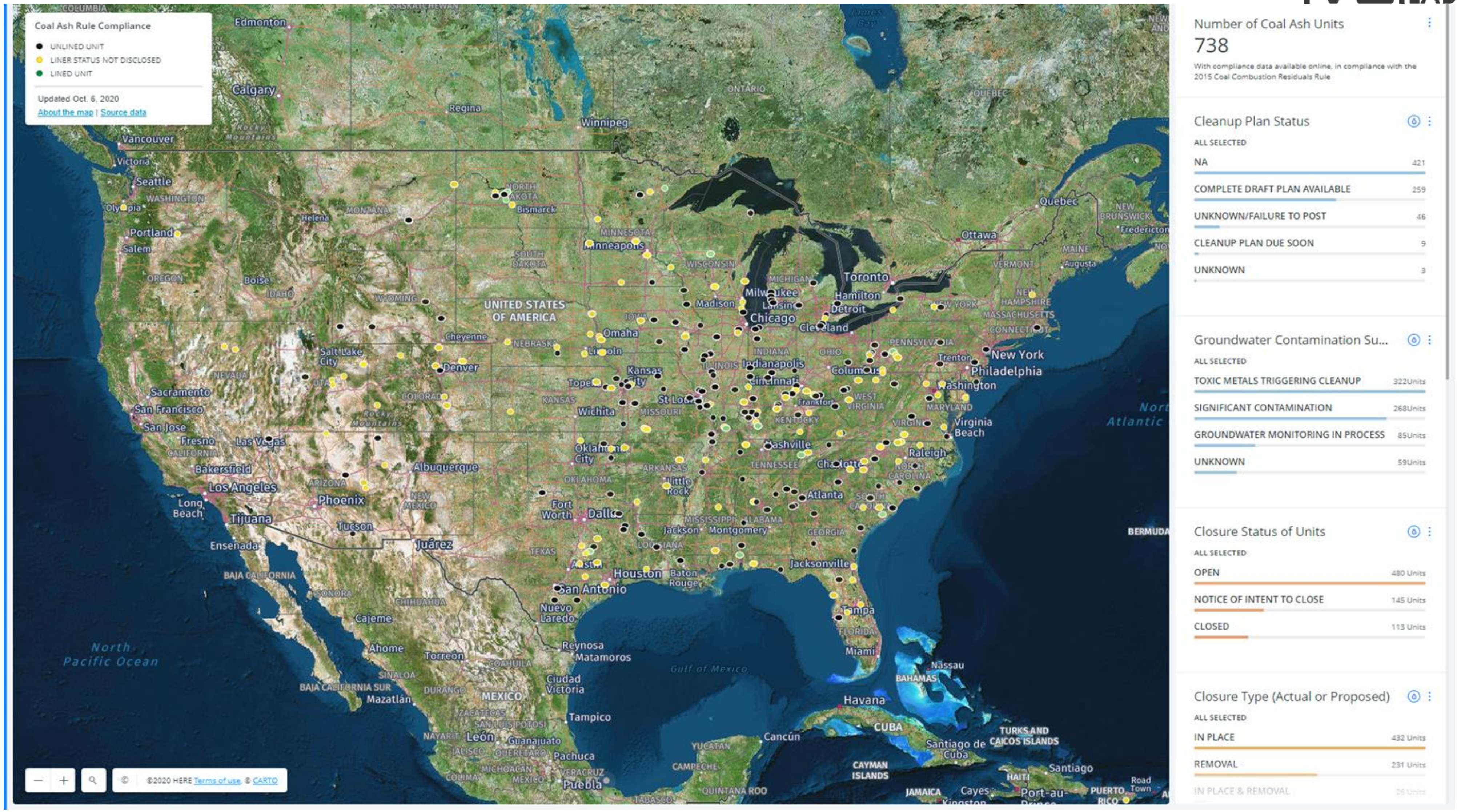
Emissions Control Field Work Proposal

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



Source: EarthJustice [Mapping the Coal Ash Contamination | Earthjustice]

Kingston Fossil Plant Ash Spill (TVA)

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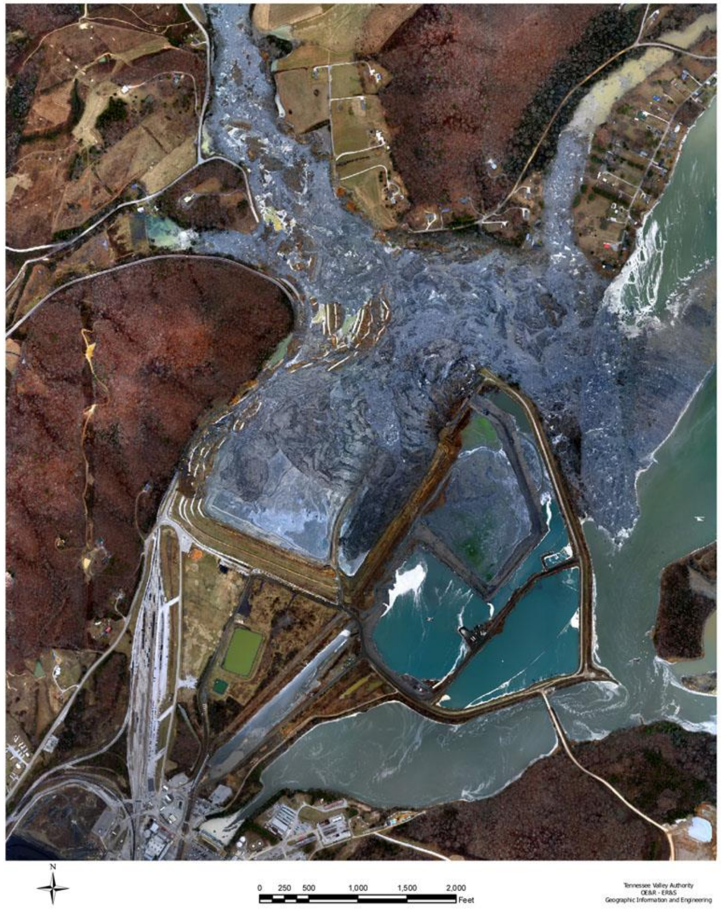
- Tennessee Valley Authority's Kingston Fossil Plant: 1.4 GW of coal-fired capacity
- 14,000 tpd low-S coal (~140 railroad cars)
- December 22, 2008: dike failure surrounding ash dewatering pond
- Release 1.1 billion gallons of fly ash slurry covering up to 300 acres
- Discharge into Emory River and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

Aerial Image Of Kingston Ash Slide 12/23/08



Dan River Coal Ash Spill

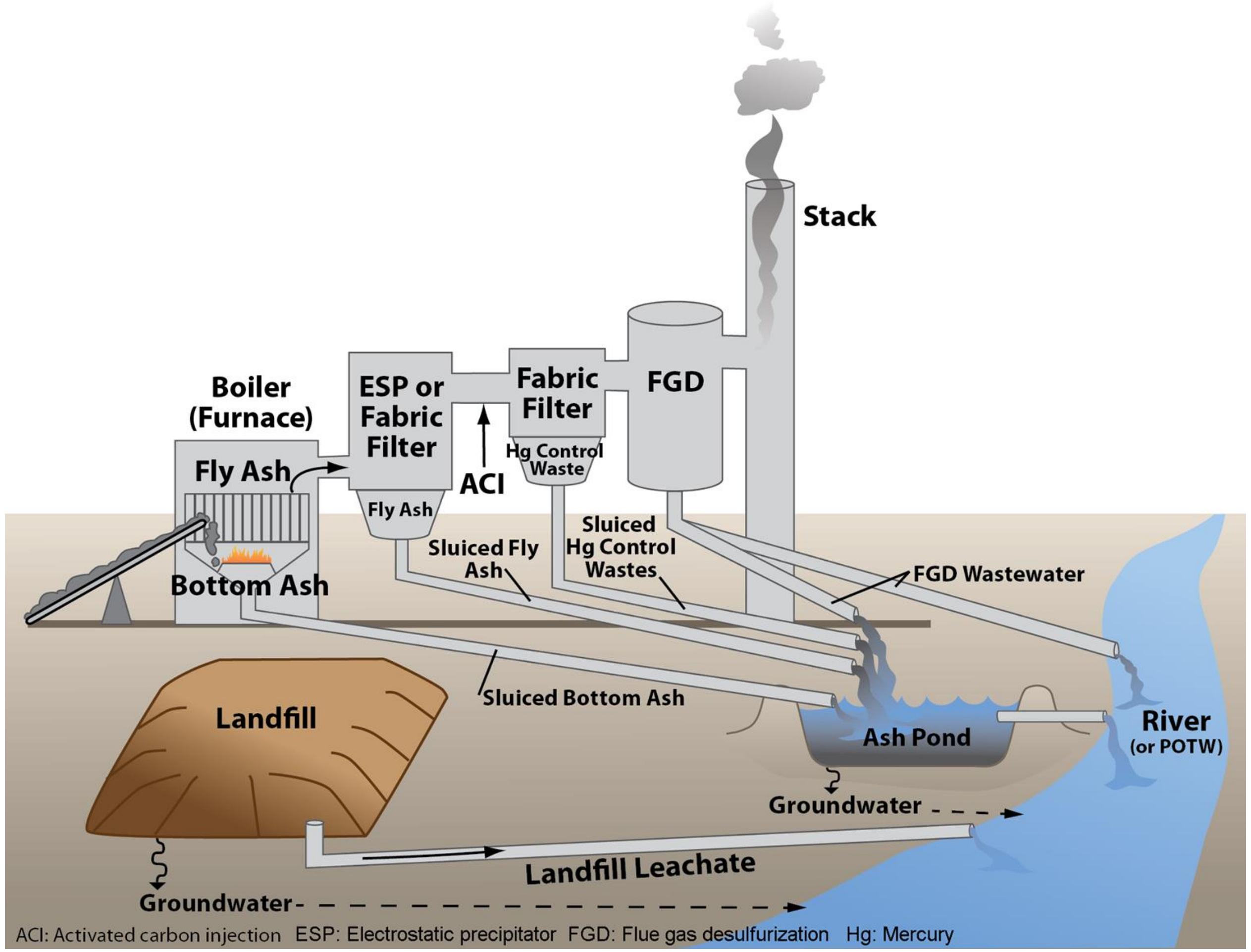
- Duke Energy's Dan River Steam Station
- 276 MW coal-fired capacity, retired in 2012
- February 2, 2014: drainage pipe burst at ash containment pond
- 39,000 tons of ash, 27 million gallons of wastewater released into Dan River

Landfill Leachate Wastewater Treatment

Regulatory Drivers

- Wastewater from landfills regulated by Effluent Limitation Guidelines (2015, 2020, ~~expected fall 2022~~ spring 2023)

- Coal ash pond management regulations likely to result in wastewater streams requiring treatment



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

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

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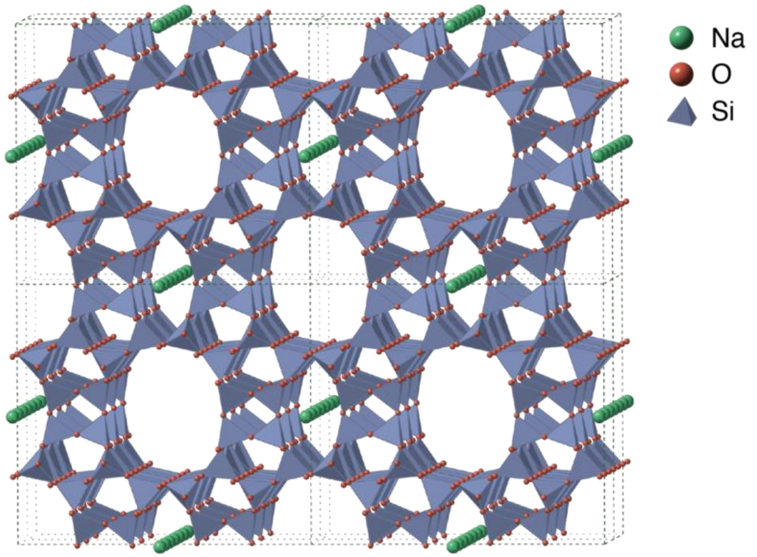
- **Objective:** Development of an artificial intelligence/machine learning (AI/ML) methodology for design of sorbents that can be used to treat wastewater from coal ash impoundments

- **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
   - Structure: considers pore structure, crystal structure features; Property: boric acid concentration
5. Use AI/ML techniques to exploit relationships to design tailored sorbents for impoundments
   - E.g., support vector machine, random forest regression



Mordenite (MOR framework)

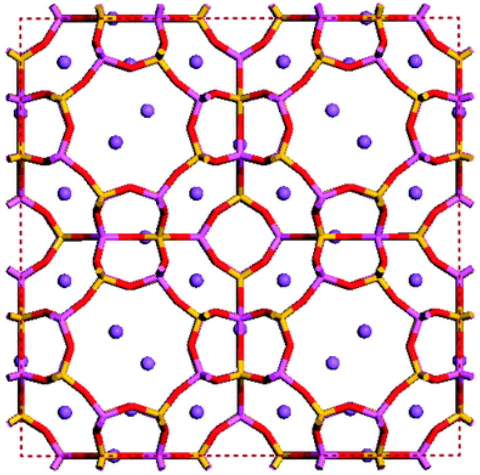
Task 2: Zeolites

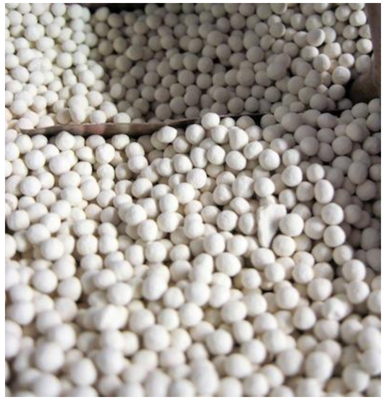
Introduction

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

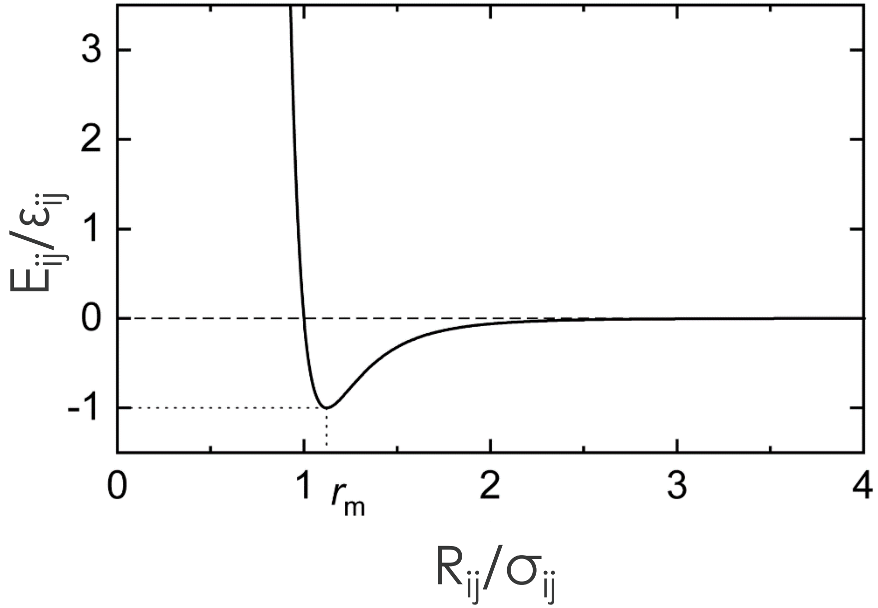
2. Construct appropriate model potentials

- Potentials are analytical functions 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

- Potentials 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

- Depending on pairs of atoms of interest, either Lennard-Jones + Coulomb potential OR Buckingham + Coulomb potential used

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



Task 2: Monte Carlo Methods

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

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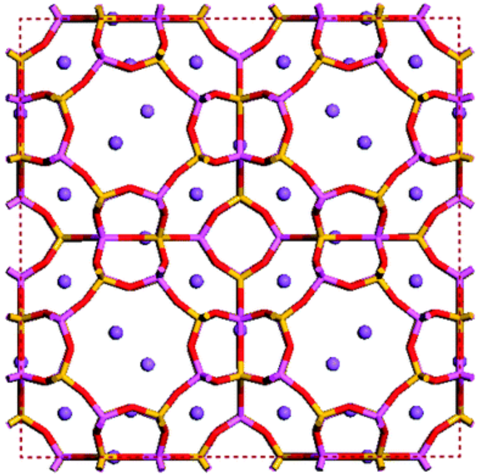
5. Use AI/ML techniques to exploit relationships* to design tailored sorbents

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



*Zeolite composition/adsorption capacity; zeolite structure/adsorption capacity

Machine Learning Model (Boron)

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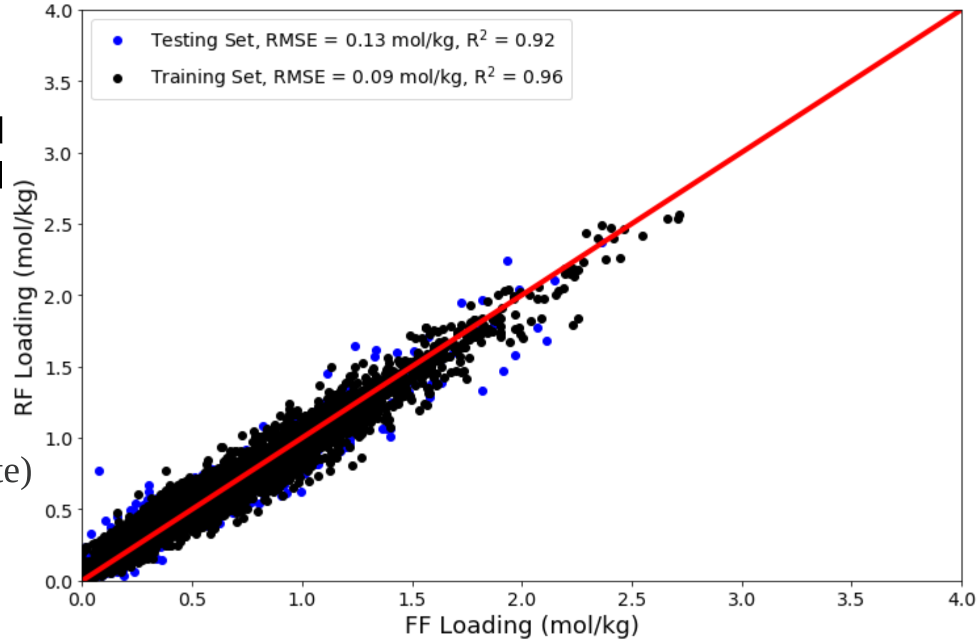
5. Zeolite Optimization (Boron)

- **Dataset:** 8000 molecular simulations of boric acid adsorption in zeolites
- **Features:**
  - Stoichiometry (Al/O, Na/O, Ca/O, Mn/O, Fe/O)
  - Structure: Radial Distribution Functions
  - Solution: B Concentration
- **Random Forest Model**
  - Hyperparameters tuned using grid search CV
  - Two most important features: Al content (Si/Al) and Ca content (strongest adsorption site)
- Used Genetic Algorithm to optimize zeolite for H_3BO_3 removal at for 3 impoundment sites
  - Concentrations from EPRI reports
  - Optimal zeolite characteristics in green
  - Optimal zeolite contains a mixture of Ca, Fe

Machine-Learned Model

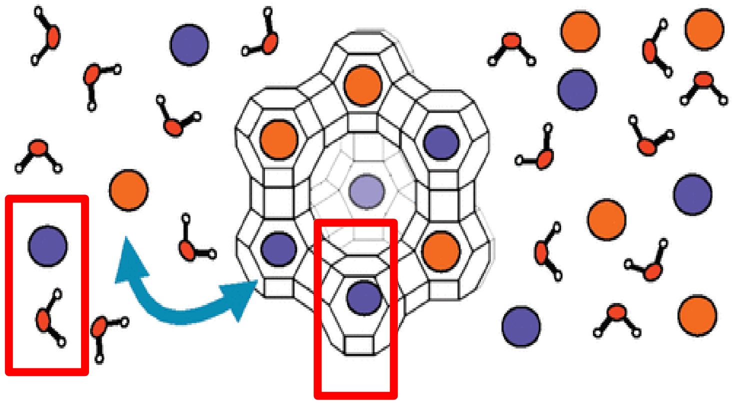


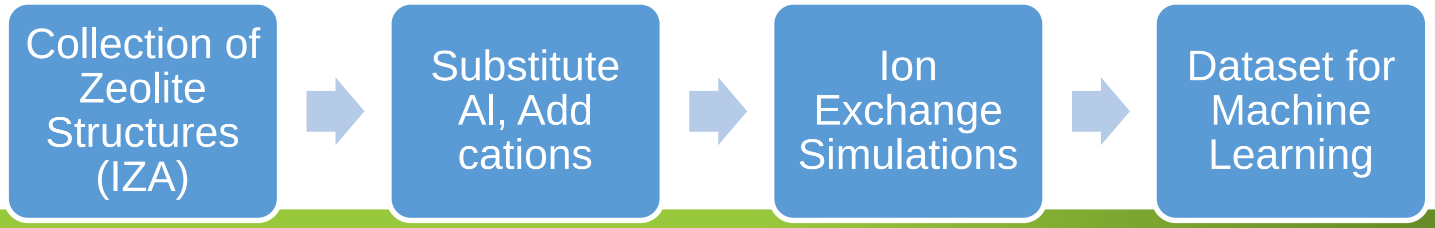
Monte Carlo Method

Impoundment Site	B Concentration (ppm)	Topology	Si/Al	Na (%)	Ca (%)	Mn (%)	Fe (%)	Predicted Boron Uptake (mol/kg)
Site 1	27.43	LTA	1	5.75	74.12	3.40	16.73	2.41
Site 2	12.84	LTA	1	7.37	70.09	6.60	15.94	2.25
Site 3	3.50	LTA	1	3.02	78.60	4.75	13.63	2.04

Dataset Generation Workflow (Barium)

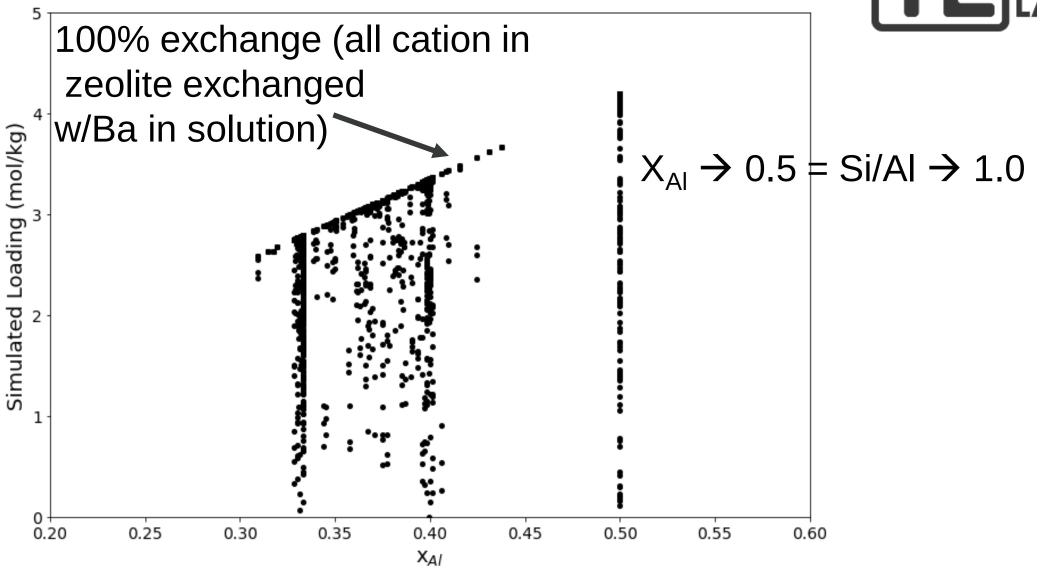
- **Structures:**
  - 130 (out of 245) topologies from International Zeolite Association
  - All previously-synthesized fly ash zeolites are included
- **Si/Al** = 1, 1.5, 2
  - Only low Si/Al: more ions to exchange
  - **Hypothesis:** This will be the most important factor for the removal of ionic contaminants
- **Extra-Framework Charge Balancing Cations:** Mg, Ca, Sr
  - Mechanism for sorbing Ba^{2+} is cation exchange of Ba^{2+} with extra-framework cations.
  - These extra-framework cations have the same charge as Ba^{2+}
    - Makes molecular simulations more straightforward
- **Impoundment Site Leachate Ba Concentrations:** from EPRI reports
  - Sorbent design expressed in terms of x_{Ba}/x_i (ratio of barium to cation of interest)
  - "x_i" is the concentration of the zeolite cation in impoundment pond
  - Max, medians, Min
- Total dataset size ≈ 3500



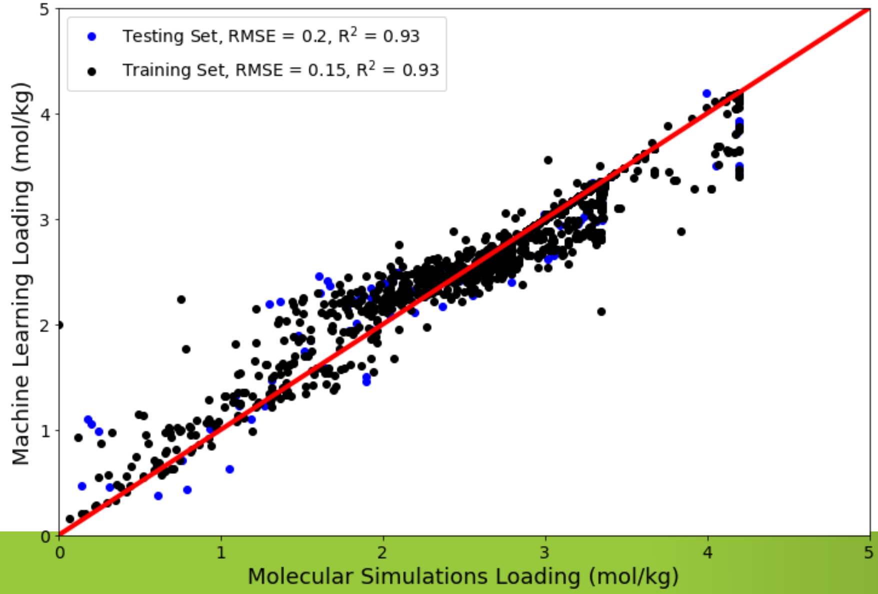


Dataset Summary and Machine Learning (Barium)

- Si/Al ratio critical to performance
  - Linear relationship between Al content and Ba loading(charge balance) for best zeolites



- Random Forest Regression
  - Tuned hyperparameters using grid search cross-validation (5-folds)
  - Good agreement between simulations and ML Model (bottom)



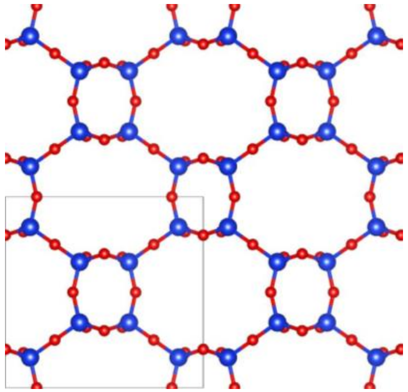
Machine-Learned Model

Monte Carlo Method

Site-specific Optimization (Barium)

- Optimized zeolites based on concentrations from EPRI reports
- Used ML model for adsorption predictions (mol Ba per kg of sorbent)
  - Optimized zeolites using genetic algorithm
  - Ca-GIS (Si/Al = 1) was an optimal zeolite for all cases

    *Sometimes Ca-LTA and Ca-FAU were tied (to 3 decimal places)



GIS Zeolite

Impoundment Site	Ba (ppm)	Mg (ppm)	Ca (ppm)	Sr (ppm)	Optimal Zeolite (Structure*)	Optimal Zeolite (Si/Al)	Optimal Zeolite (Cation)	Predicted Uptake (mol/kg)
Site 1	1	1	1	1	FAU, GIS, LTA	1	Ca	4.199
Site 2	1	10	100	1	FAU, GIS, LTA	1	Ca	4.199
Site 3	10	100	1000	10	GIS	1	Ca	4.199
Site 4	1	100	1000	10	GIS	1	Ca	4.199

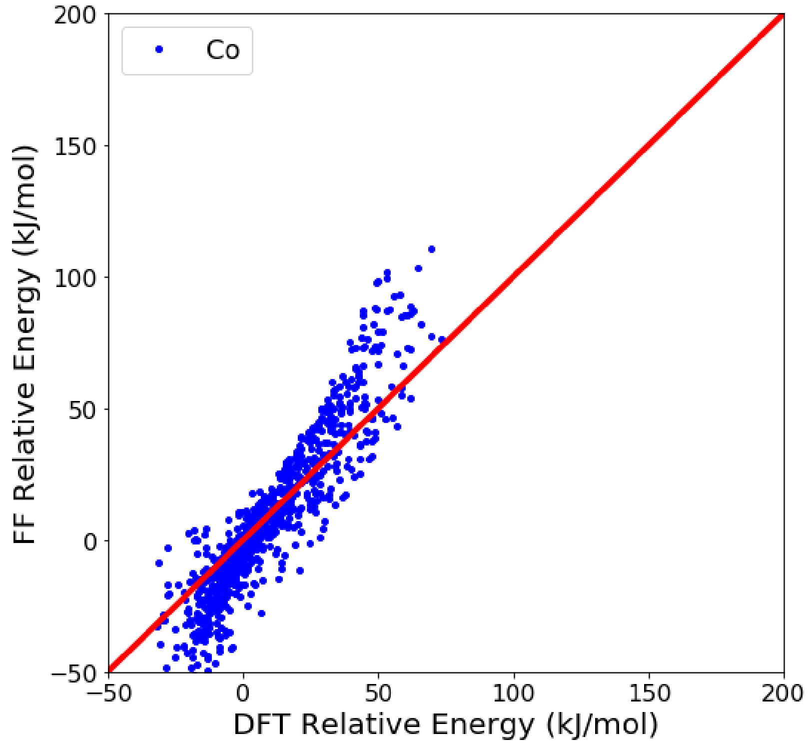
Next Contaminant – Co(II)

Cation-Framework Interactions

$$E_{ij} = A_{ij}e^{-B_{ij}r_{ij}} - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

Buckingham Parameters	A (K)	B (Å)	C (K*Å^6)	q_M (|e$^-$|)
Co(II) – Oz	3.545e+06	2.457	8.457e+05	1.348

- Can cause health problems
- Based on data, large subset of impoundment ponds exceeding expected Co regulatory limits
- Can be removed by using zeolites as ion exchangers
    - Large number of accessible cations on inner surface
- Force field model (for molecular simulations) is complete



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

- **Objective:**

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

- **Task started fall 2022**

- **Approach:**
  - EY22 studied removing Boron (B) from wastewater by purchasing a commercially available zeolite, demonstrate ability to promote based on Task 2 modeling results, and testing its adsorption performance
  - EY23 will focus on exploring transformation of coal fly ash (CFA) to the promoted zeolite and testing its adsorption performance to remove B from wastewater

Task 3 Experimental Setup

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

Task 3: Milestones and progress status

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- Shaken down synthesis and adsorption systems (12/30/2022) ***Completed***
- Purchase zeolites and evaluated them in model synthetic wastewater with boric acid (3/31/23) ***Completed***
- Initiate development of processes for transforming Coal Fly Ash (CFA) to the sorbents for treating leachates from ash impoundments, which focus on discussion of the anticipated research issues/challenges for potential future study ***Completed***
- Synthesize zeolite from CFA using hydrothermal method and microwave assisted hydrothermal method ***In progress***

Task 3: Characterization of Purchased and Fe-Modified Zeolites

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- Purchased commercial zeolites of 5A, CaX, Chabazite and 13X
- Prepared Fe-modified ZSM-5 zeolite sorbents with 2.5 wt% and 5 wt % Fe loading (2.5%Fe ZSM-5 and 5%Fe ZSM-5) using wet impregnation method
- Characterized zeolite composition using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)
- Analyzed Brunauer-Emmett-Teller (BET) surface areas of the zeolites
- Evaluated X-ray diffraction (XRD) crystal structure of the Fe-modified zeolites that showed Identical XRD patterns with parent zeolite
- Examined Fe distribution of the Fe-modified zeolite using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) that illustrated even distribution of Fe

Group	Name	Source	Type	Si/Al mole ratio	Nominal Cation Form	Na_2O Weight %	CaO Weight %	Surface area (m^2/g)
Purchased	5A	Zeochem	LTA	1.01	Ca, Na	18	82	561
Purchased	CaX	Zeochem	FAU X	1.32	Ca, Na	12	88	732
Purchased	Chabazite	Gelest	CHA	2	Ca, Na	--	--	432
Purchased	13X	Gelest	FAU X	1.23	Na	100	--	695
Available in NETL	ZSM-5	Zeolyst	MFI	11.5	NH_4	0.05	--	391
Modified NH_4 to Fe	2.5%Fe ZSM-5	Prepared	MFI	11.5	Fe	--	--	247
Modified NH_4 to Fe	5%Fe ZSM-5	Prepared	MFI	11.5	Fe	--	--	243

Task 3: Batch Adsorption Procedure and test conditions

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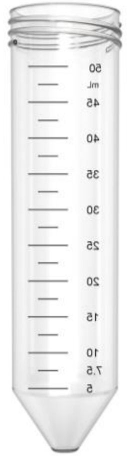
~35ml Boron solution

B concentration (6 to 20ppm)

pH (3.5 -11)

1.4g zeolite (adsorbent dose (40g/L)

ICP-MS, BET, XRD, SEM



Adsorption

Initial pH (3.5 to 11)
Initial B concentrations (6 to 20ppm)
Adsorbent dose (20 to 40g/L)
Temperature (25°C)
Time (~24hr)
Rolling speed (80rpm)

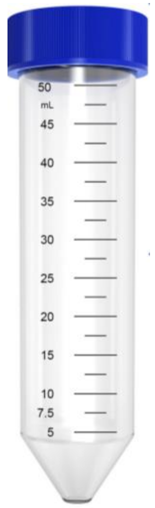
Roller mixer

Separation

Centrifuge

Treated water

B concentration (ICP-MS)



Used zeolite

ICP-MS
BET
XRD
SEM

Task 3: Boron Removal Performances of Zeolites

- Measured B concentrations in the initial and final solutions of the adsorption using ICP-MS in the Pittsburgh Analytical Laboratory (PAL)
- Evaluated B adsorption performances
  - Removal efficiency (R%)

    $$R = (C_0 - C)/C_0 \times 100 \qquad (1)$$

  - Adsorptive capacity (q mg/g)

    $$q = (C_0 - C)/m \times V_0 \qquad (2)$$

- pH strongly impacts adsorption performance because the forms of boron present in an aqueous solution depend on the pH of the solution
- Initial B concentration (6 and 20ppm) and adsorption dose (20 and 40 g/L) influences adsorption performance
- To improve the applicability of adsorption technology using zeolites, the addition of boron-specific chelating functional groups will be investigated

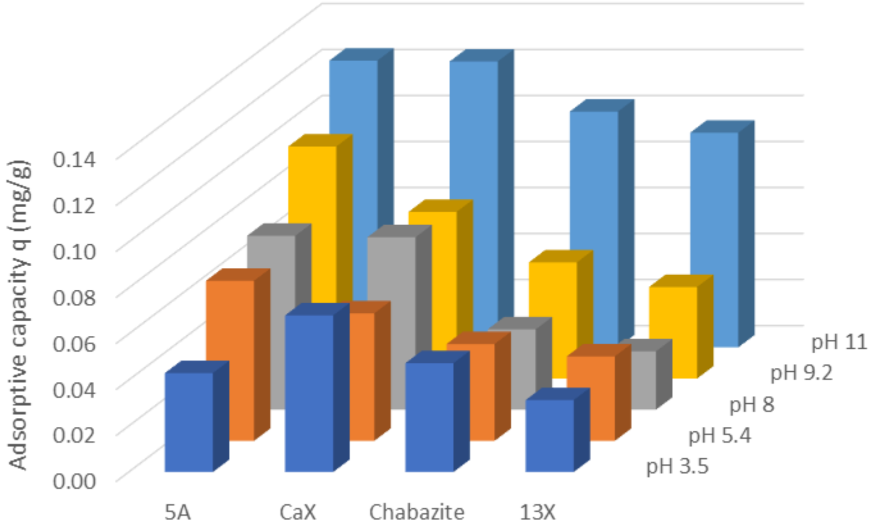


Fig 1. Effect of pH on adsorptive capacity of zeolites at initial B 20ppm and adsorbent dose 20g/L

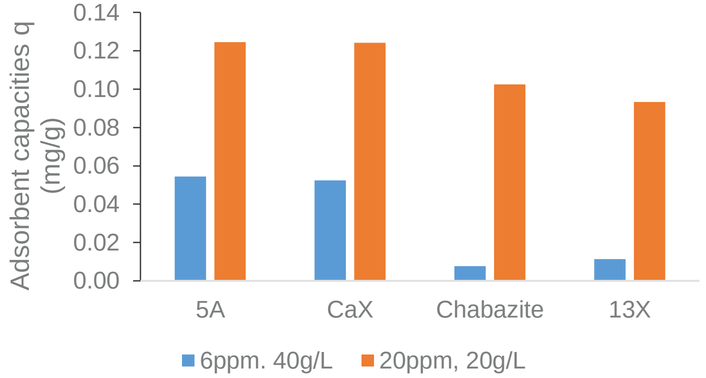


Fig 2. influence of initial B concentration (6 and 20ppm) and adsorbent dose (20 and 40g/L) on adsorptive capacity of zeolites at pH 11

Task 3: Synthesize Zeolite from CFA

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- Obtained CFA sample
- CFA main composition

Ash yields (% day basis)	97.15
Na (ppmw)	4003
Mg	4509
Al	157321
Si	285408
K	18540
Ca	21767
Mn	399
Fe	158558
Ba	148

Si/Al: 1.7

- Purchasing sodium aluminate to adjust Si/Al
- Identified suitable available equipment for synthetization
- Microwave are novel energy and dramatically decrease reaction times due to the influences on the induction periods and nucleation

Characterize synthesized zeolites
- Composition using ICP-MS
- BET surface areas
- XRD crystal structure
- SEM and EDS morphology

Initial develop synthesize method

Small scale (50ml reactor)

Hydrothermal methods

Improve synthesize method

Scale up (100ml reactor) Microwave assisted hydrothermal method

Generate zeolites for B adsorption test (8X100ml reactor)

Shaking water bath (80-100^{o}C)

Perkin Elmer Titan MPS microwave digester