Simulations-Guided Development of Custom Sorbents for Boron Capture from Coal Combustion Impoundment Leachates
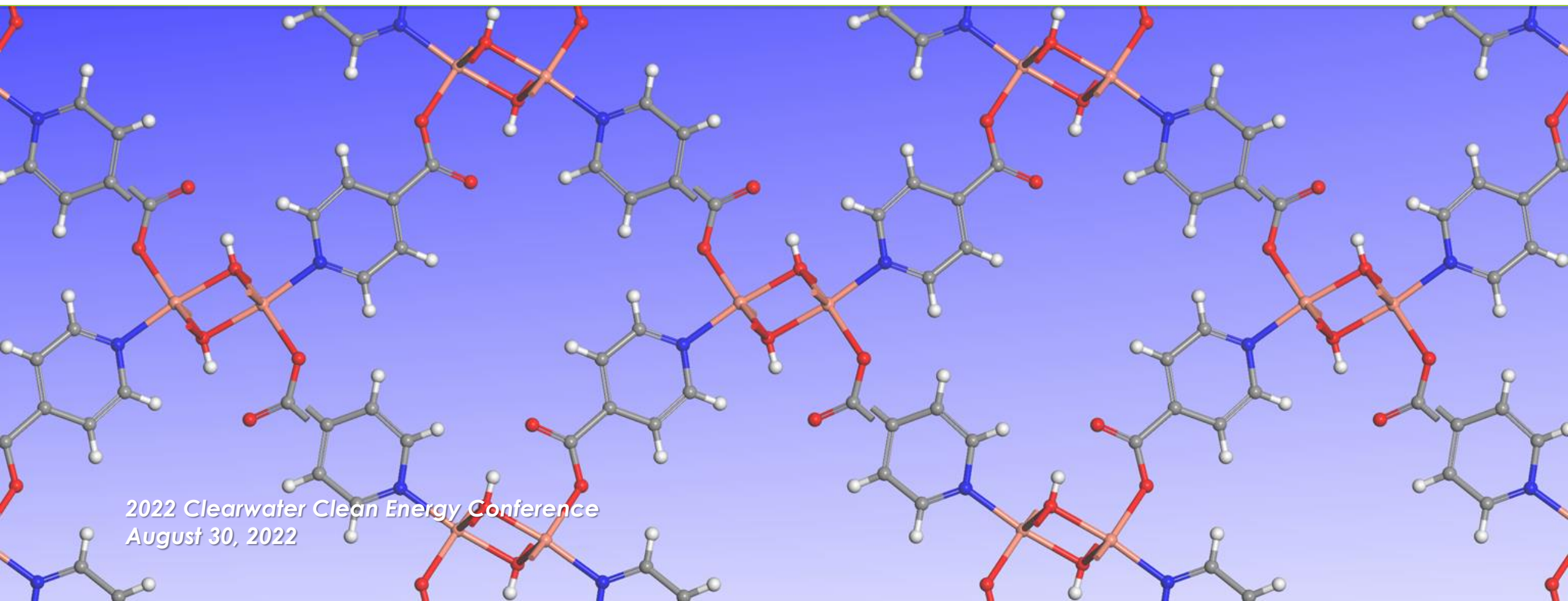
Solutions for Today | Options for Tomorrow

NETL NATIONAL ENERGY TECHNOLOGY LABORATORY

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Disclaimer

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Authors

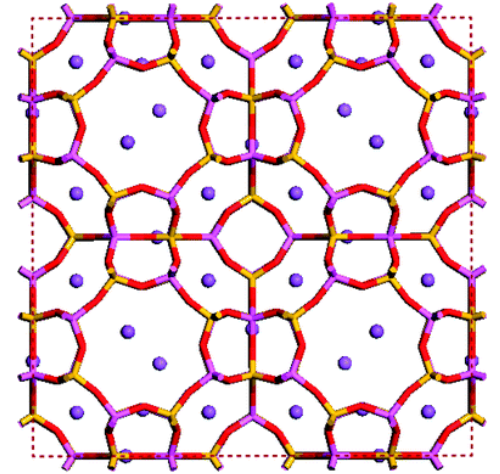**Jack Findley[1,2], Evan Granite[1], Eric Grol[1], Jan Steckel[1]**

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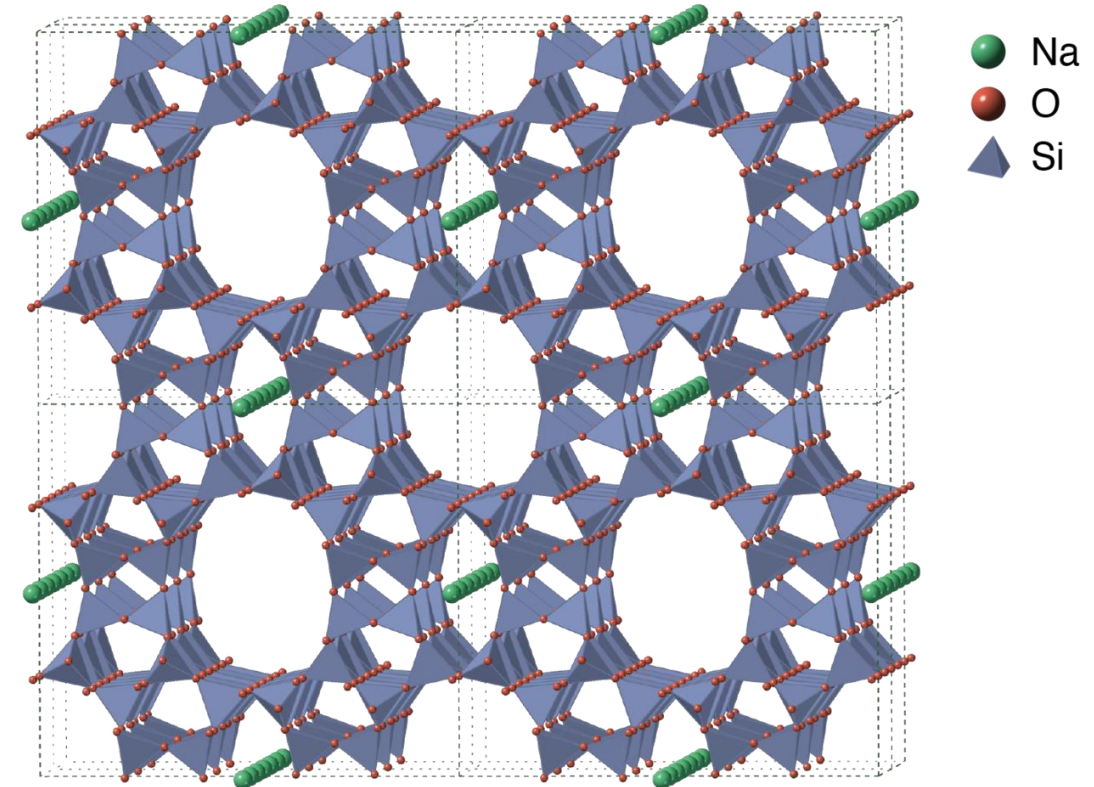
Zeolites

Introduction

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

- Composed of AlO_4 and SiO_4 tetrahedra
  - Substitution of Al for Si leads to charge imbalance
  - Extra-framework cations (Na^+, K^+, Ca^{2+}, 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

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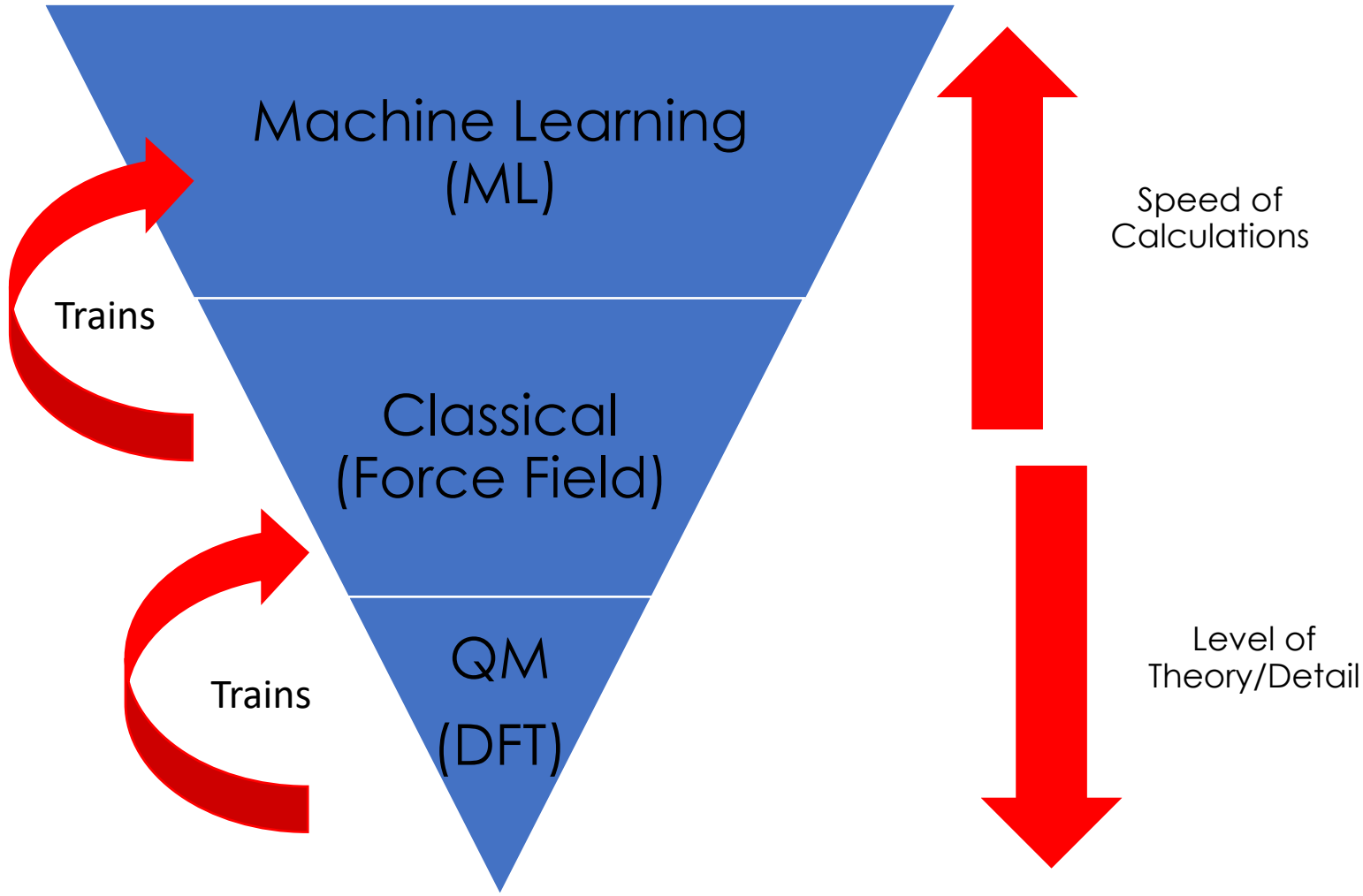
Methodology

Overall Strategy

1. Construct a collection of sorbent structures and Sorption Conditions

2. Construct appropriate model potentials

3. Carry out computations to **estimate sorption** in a **representative subset** of the sorbent structures

4. Use AI/ML techniques to exploit relationships to **screen / design tailored sorbents** for impoundments

- Na
- O
- Si

Mordenite (MOR framework)

Machine Learning for Materials Design

Overall Strategy

- **Machine Learning (ML)**:
  - Accuracy depends on training set
  - Can be used for screening or design
  - Fastest of the three

- **Classical Simulations (FFs):**
  - Accuracy may vary
  - Can study macroscopic properties
  - Useful for screening

- **Quantum Mechanical (QM) simulations**:
  - We are using density functional theory (DFT) as our QM method
  - Accurate
  - Based on first-principles calculations
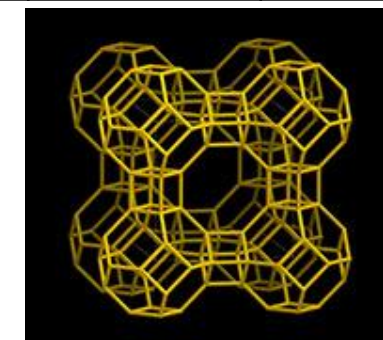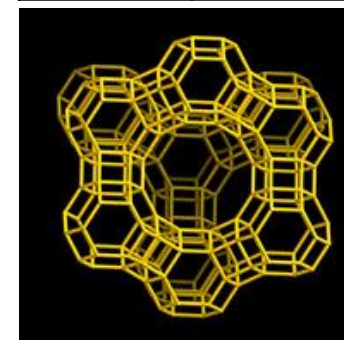 - Cannot study macroscopic properties

Methodology

1. Construct a Collection of Sorbent Structures and Sorption Conditions

- **Framework symmetry:**
  - The framework symmetry controls geometrical features such as pore limiting diameters or how large the cavities are inside the zeolite.
  - Seven framework symmetries – zeolites with these symmetries have been synthesized from fly ash.
  - An additional five symmetries were chosen because they are common frameworks.
    - DDR, FER, MEL, MFI, TON
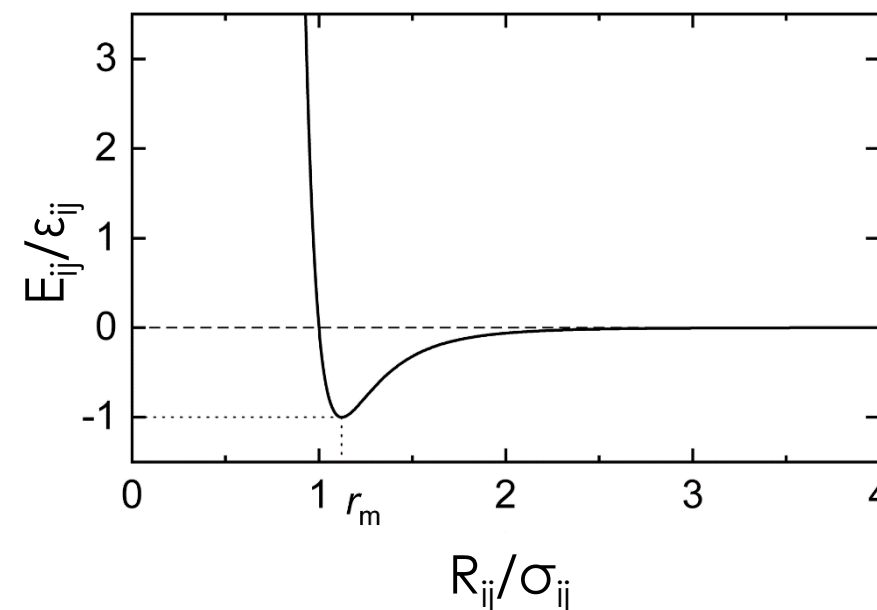 - **Expanded list of framework symmetries: 12**

IZA Code	Alternate Names	PLD (Å)	LCD (Å)
ANA	Analcime	2.43	4.21
CHA	Chabazite Hershelite (Na-form) K-chabazite (K-form)	3.72	7.37
FAU	Faujasite Zeolite X (Si/Al < 2) Zeolite Y (Si/Al >= 2)	7.35	11.2
GIS	Zeolite P1 NaP1	3.32	4.97
LTA	Zeolite 4A Zeolite 5A Zeolite A Linde Type A	4.21	11.05
LTF	Linde Type F	7.5 (z-direction)	8.16
LTL	Linde Type L Perlialite	7.5 (z-direction)	10.01
PHI	Phillipsite	3.69	5.40
SOD	Sodalite	2.53	6.32

Force Fields

2. Construct Appropriate Model Potentials

- Analytical function that describes interaction energies
  - 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

- Often parametrized based on **experimental data** or **QM calculations (DFT)**

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

Methodology

2. Construct Appropriate Model Potentials

- **Model potentials will be needed for calculations**

    - Zeolite – Cation energy
    - Zeolite – Adsorbate (H_3BO_3) energy
    - Zeolite – Water energy
    - Cation – Adsorbate (H_3BO_3) energy
    - Cation – Water energy
    - Adsorbate (H_3BO_3) – Water energy
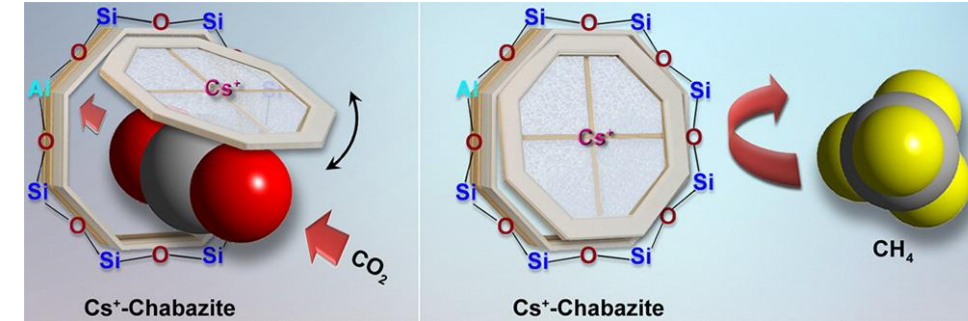
- **Key assumptions:**

    - No bonds broken or formed
    - Rigid Framework: Zeolite Si, Al, and O are held fixed

- **Buckingham + Coulomb Potential:** $E_{ij} = A_{ij}e^{-B_{ij}R_{ij}} - \dfrac{C_{ij}}{R_{ij}^6} + \dfrac{q_i q_j}{4\pi\varepsilon_0 R_{ij}}$

    - A, B, C are fitted parameters
    - q are **"partial atomic charges"** assigned to each atom based on DFT calculations
    - Good at describing repulsion in solids

- **Lennard-Jones + Coulomb Potential:** $E_{ij}(R_{ij}) = 4\varepsilon_{ij}\left[\left(\dfrac{\sigma_{ij}}{R_{ij}}\right)^{12} - \left(\dfrac{\sigma_{ij}}{R_{ij}}\right)^6\right] + \dfrac{q_i q_j}{4\pi\varepsilon_0 R_{ij}}$

    - σ is a fitted parameter related to size
    - ε is a fitted parameter related to interaction strength
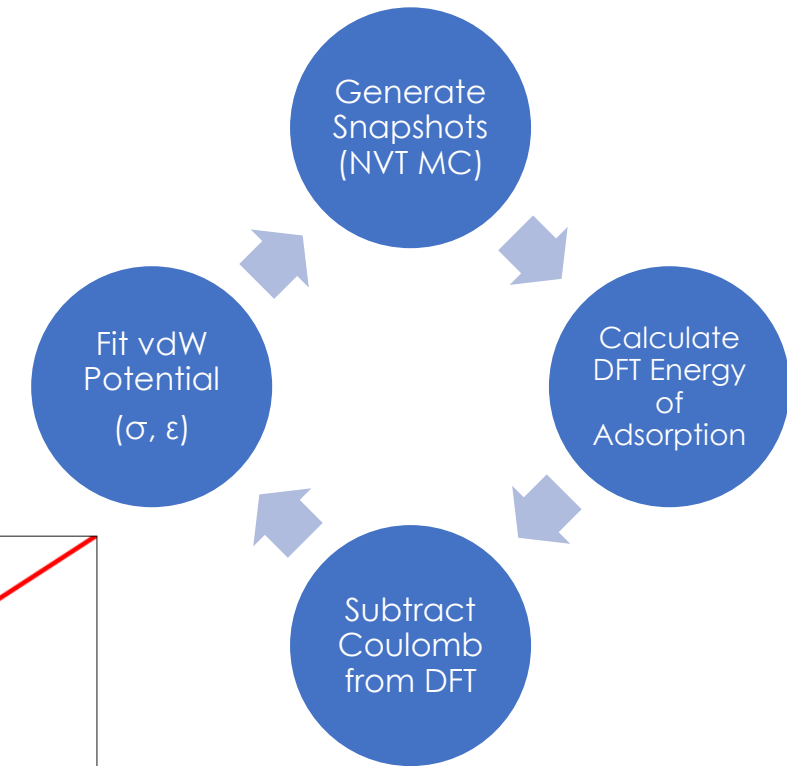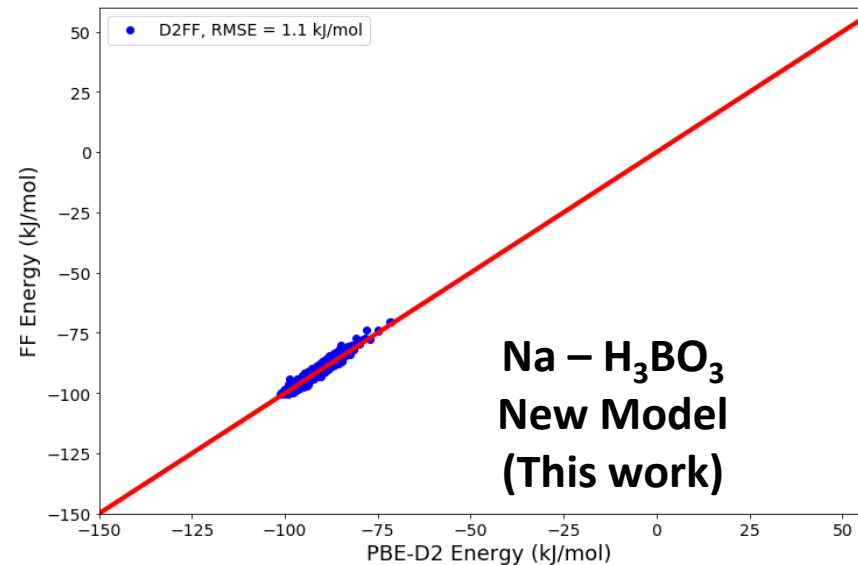   - Good at describing gasses, liquids
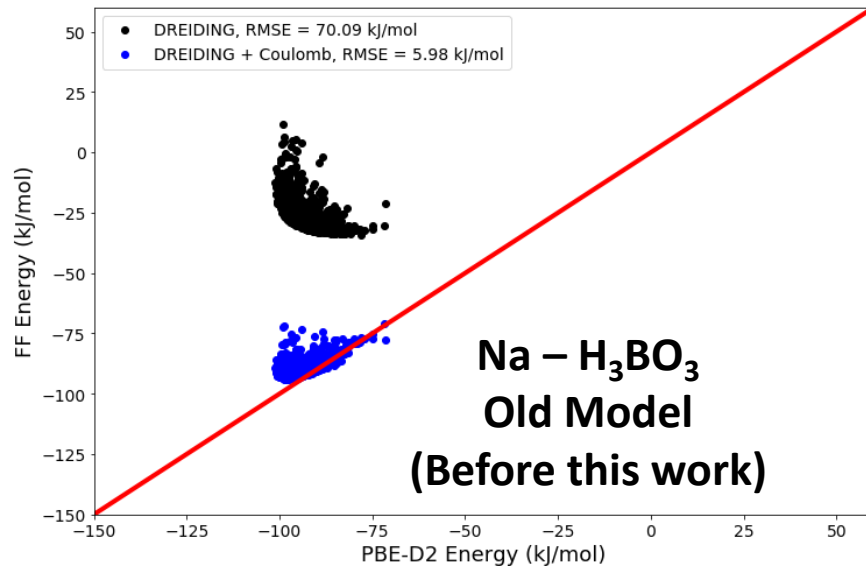
Fang, H. et al. Prediction of CO_2 Adsorption Properties in Zeolites Using Force Fields Derived from Periodic Dispersion-Corrected DFT Calculations. J. Phys. Chem. C 116, 10692–10701 (2012).

Cs⁺-Chabazite   Cs⁺-Chabazite

Fitting Adsorbate – Zeolite Interactions

2. Construct Appropriate Model Potentials

- DFT optimization showed **no chemical bonds broke** during adsorption of H_3BO_3, H_2O
  - Can use classical force fields for adsorption

- Complete for Na^+, K^+, Ca^{2+}, Mn^{2+}, Fe^{2+}

- Construct models to reproduce adsorption energies from DFT

Generate Snapshots (NVT MC)

Calculate DFT Energy of Adsorption

Subtract Coulomb from DFT

Fit vdW Potential (σ, ε)

Na – H₃BO₃ Old Model (Before this work)

DREIDING, RMSE = 70.09 kJ/mol
DREIDING + Coulomb, RMSE = 5.98 kJ/mol

FF Energy (kJ/mol) vs PBE-D2 Energy (kJ/mol)

Na – H₃BO₃ New Model (This work)

D2FF, RMSE = 1.1 kJ/mol
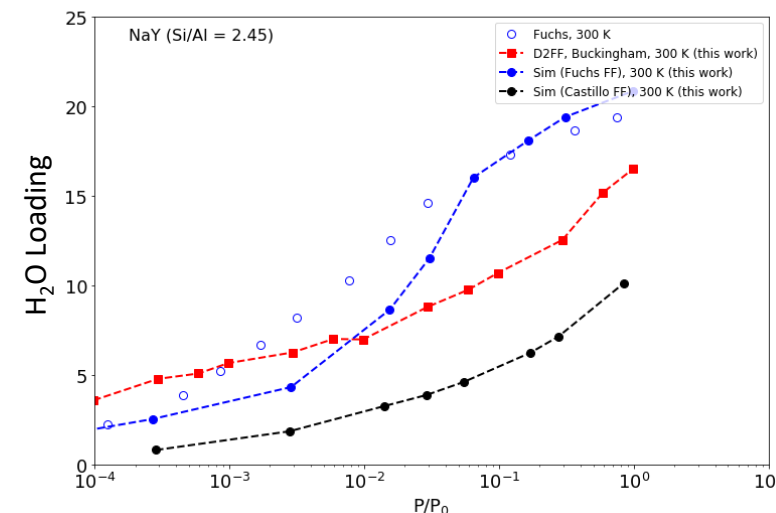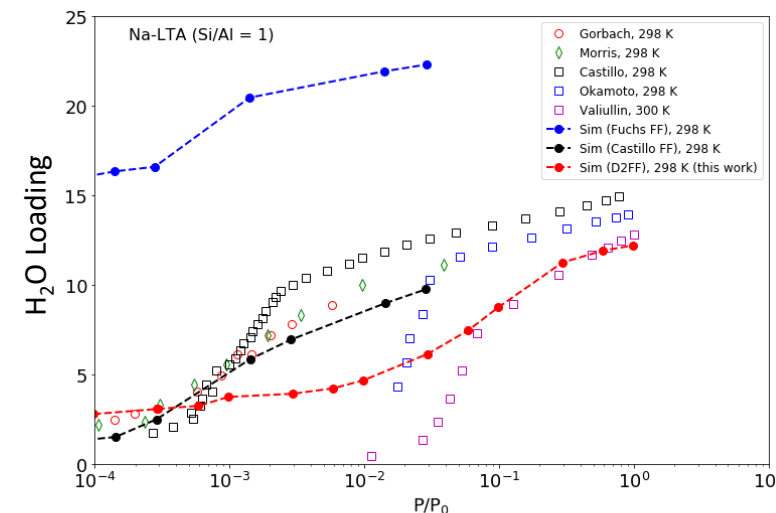
FF Energy (kJ/mol) vs PBE-D2 Energy (kJ/mol)

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

Model Validation

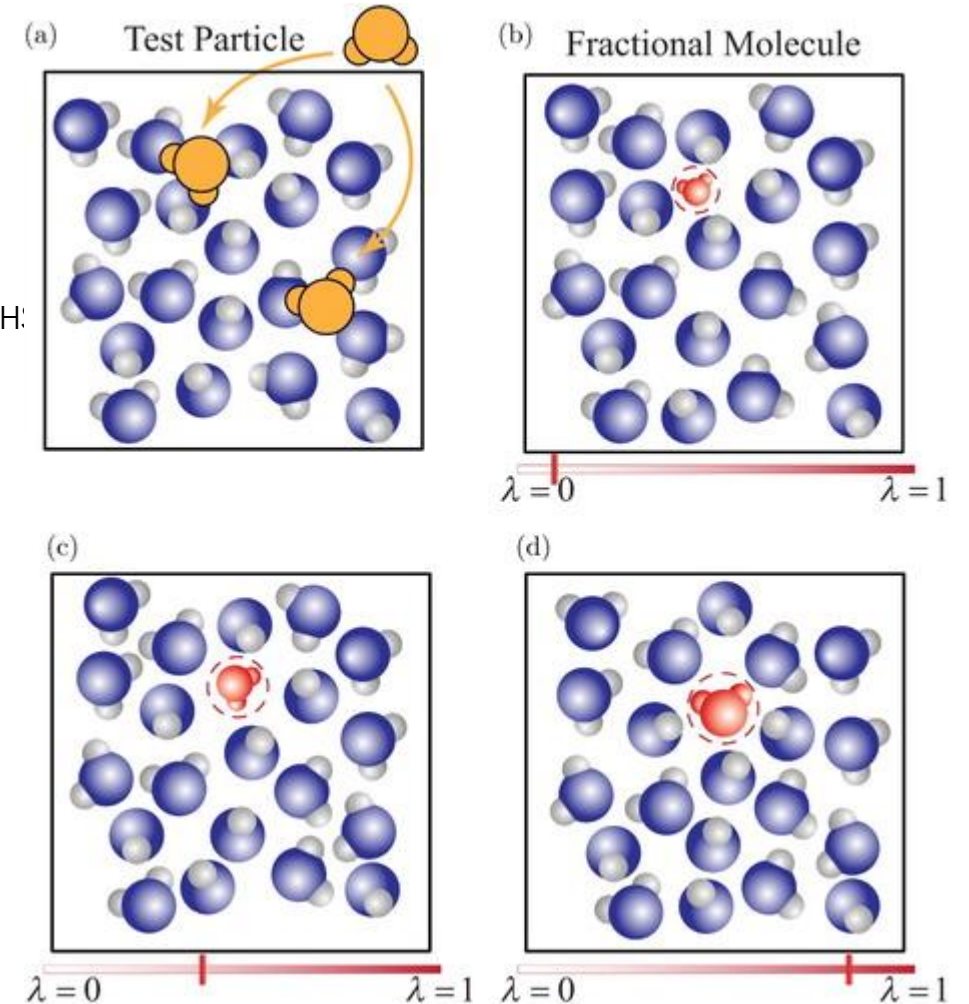## 2. Construct Appropriate Model Potentials (Validation)

- Used models developed in December to predict water vapor adsorption isotherms
  - Model parametrized by fitting to Density Functional Theory Energies (PBE-D2 to be specific)
  - Compared two different potentials
    - **Buckingham:** $E_{ij} = A_{ij}e^{-B_{ij}R_{ij}} - \frac{C_{ij}}{R_{ij}^6} + \frac{q_i q_j}{4\pi\varepsilon_0 R_{ij}}$
  - Na-LTA (Si/Al = 1, top) and NaY (Si/Al = 2.45, bottom)

- Most important ranges are:
  - **High pressure** (similar to liquid water)
  - **Low pressure** (water-zeolite interaction strength)

- **Low pressures:** Good agreement with **D2FF**
  - Our Buckingham model predicts interaction energies between the zeolite and water
  - This bodes well for our H_3BO_3 models because the fugacity of H_3BO_3 is very low for ppm-level concentrations

- **High pressure (near saturation):** Good agreement
  - Similar to liquid water inside the pores

- **Intermediate pressures:** Decent to poor agreement for **D2FF**
  - Shape of the isotherm does not completely match
  - Likely caused by imperfections in SPC/E water model (non-polarizable, only three-point charges)

- **Our Model (D2FF)** seems **sufficiently accurate** for further use

  - **Note:** Simulations (D2FF, red) performed **without** experimental input
    - Fuchs FF (blue) was fit to Fuchs experimental data (NaY)
    - Castillo FF (black) was fit to Castillo experimental data (black)

Adsorption Simulation Methods

3. Carry out Computations to Estimate Sorption in Sorbent Structures

- Adsorption from solution:
  - Reference state is now boric acid in solution
  - $f_A = \rho k_B T \left(e^{\mu_A^\infty / k_B T} \right) x_A$
    - μ_A^∞ is the excess chemical potential of infinitely dilute solute in the solvent
    - x_A is mole fraction of solute
  - Model predictions for Henry's constant match Hazardous Substances Data Bank (H
  - $K_H = \lim_{x_A \to 0} \left(\frac{f_A}{x_A} \right) = \rho k_B T \exp(\beta \mu_A^\infty)$

- Continuous Fractional Component Monte Carlo
  - Designed for dense systems: Difficult to perform insertion moves without overlap
  - Insertion of boric acid in hydrophilic zeolite
  - Inserts a "fractional" molecule
    - Scales intermolecular interactions by λ (0, 1]
  - Allows other molecules to move with fractional molecule present
  - Increases weight (λ) until full molecule is grown

	K_H (Pa*m³/mol)	Source
Experimental	2.65×10^{-7}	HSDB (NIH)
Sim (CFCMC-WI)	**1.29×10^{-7}**	**This work**

(a) Test Particle (b) Fractional Molecule $\lambda = 0$ $\lambda = 1$
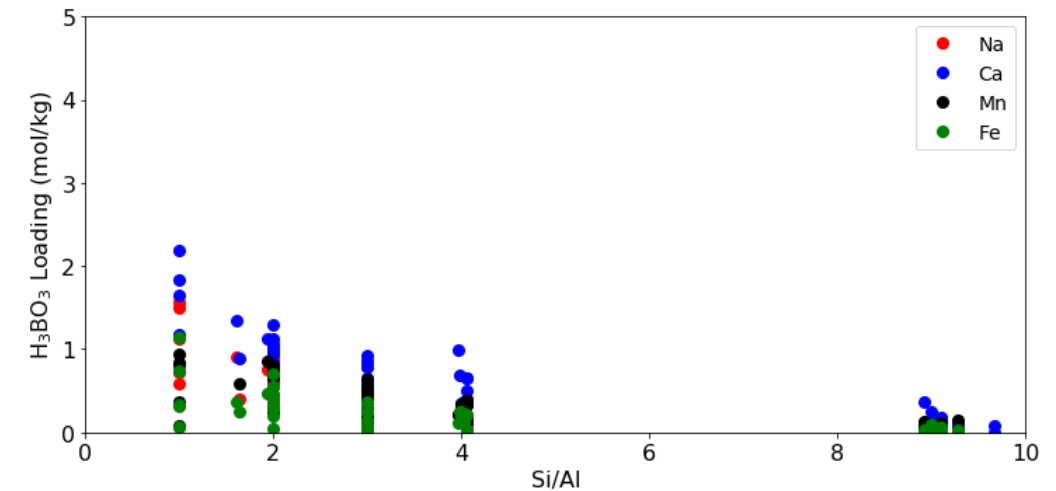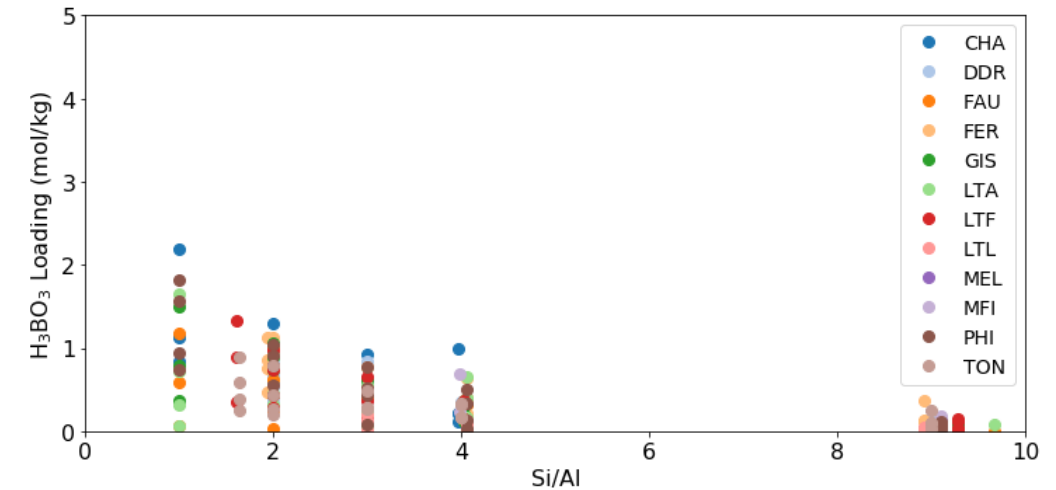(c) $\lambda = 0$ $\lambda = 1$ (d) $\lambda = 0$ $\lambda = 1$

Rahbari, A., et al. "Recent advances in the continuous fractional component Monte Carlo methodology." *Molecular Simulation* 47.10-11 (2021): 804-823.
Xiong et al. Alcohol Adsorption onto Silicalite from Aqueous Solution Journal of Phys. Chem. C (2011)

Initial Dataset (1 ppm)

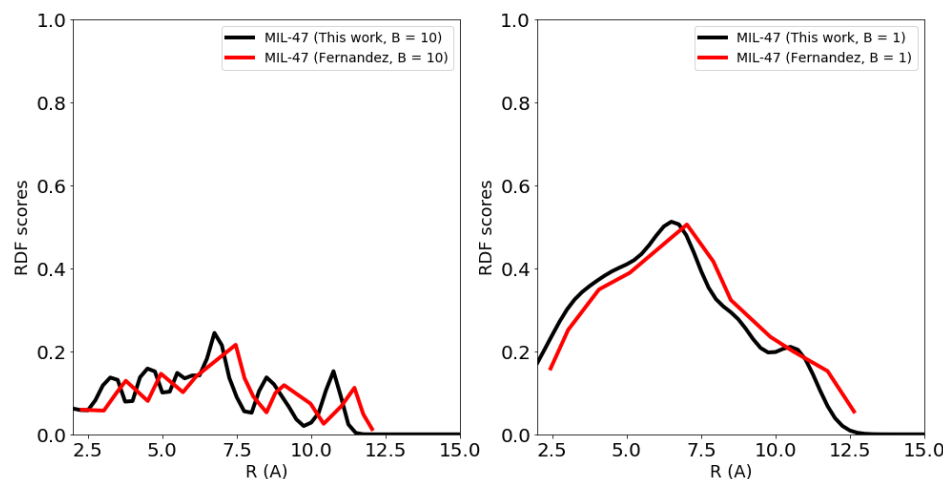## 3. Carry out Computations to Estimate Sorption in Sorbent Structures

- Results for 1 ppm H_3BO_3 solution

- Ca, Na-exchanged zeolites were top performers
  - Largest charge (Ca)
  - Most cations per unit cell (Na)

- Low Si/Al ratios performed best
  - Most cations per unit cell

Zeolite Structure Encoding (RDFs)

5. Use AI/ML Techniques to Exploit Relationships to Design Tailored Sorbents

Atomic Property Weighted Radial Distribution Functions

- RDF analysis is a crystallographic technique sensitive to both short- and long-range structural correlations.
- The RDF is the interatomic separation histogram representing the weighted probability of finding a pair of atoms separated by a given distance.
- The RDFs can be weighted to fit the requirements of the chemical information to be represented, by introducing the atomic properties, P_i.
- Electronegativity, polarizability, and van der Waals volume.
- Encoded RDFs for all IZA zeolites.

$$\mathrm{RDF}^{P}(R) = f \sum_{i,j}^{\text{all atom pairs}} P_i P_j \, e^{-B(r_{ij}-R)^2}$$

Fernandez, M.; Trefiak, N. R.; Woo, T. K. Atomic Property Weighted Radial Distribution Functions Descriptors of Cation–Organic Frameworks for the Prediction of Gas Uptake Capacity. J. Phys. Chem. C **2013**, 117 (27), 14095–14105.

Machine Learning Model

5. Use AI/ML Techniques to Exploit Relationships to Design Tailored Sorbents

- ML Model requires:
  - **Descriptors:**
    - Crystal structure (topology)
    - Composition (both zeolite and solution)
  - **Adsorption data:**
    - Little experimental data available (not enough for ML)
    - Can predict adsorption using molecular simulations
      - Accuracy depends on models and level of theory
    - Can use molecular simulations to generate a large, robust training set
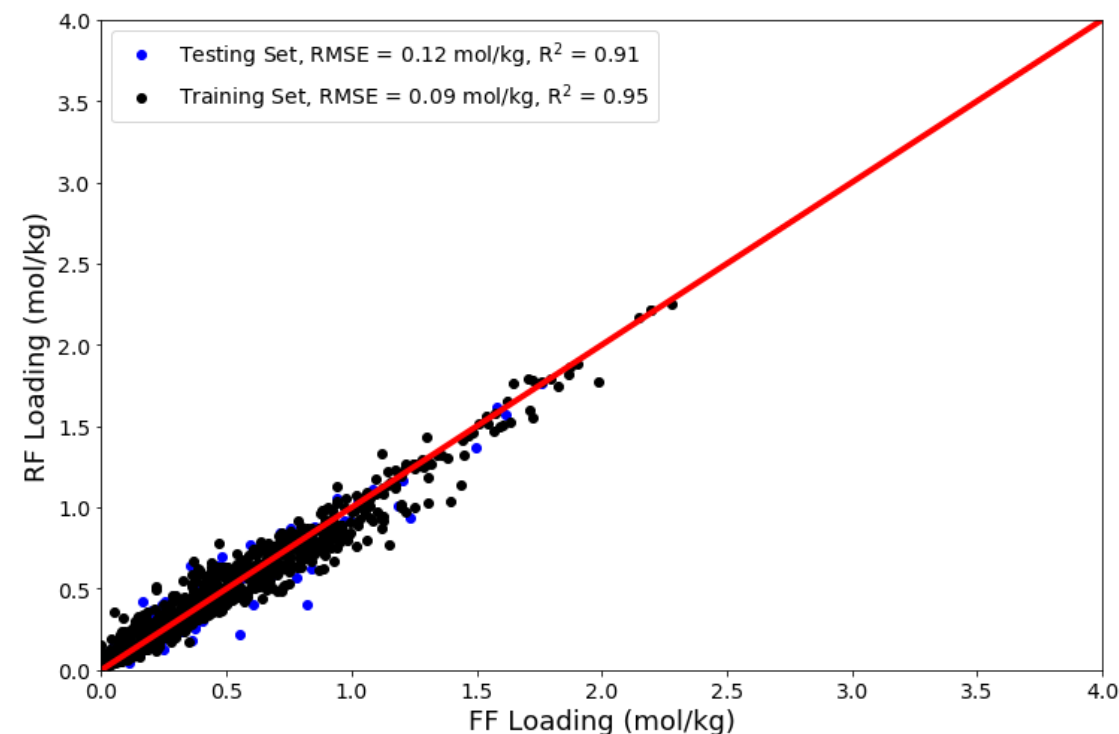
Amount Adsorbed	Si/Al	Na/O	K/O	Ca/O	Mn/O	Fe/O	RDF_PC1	RDF_PC2	Concentration

$$y = F(x_1, x_2, \ldots, x_n)$$

First Pass ML Model

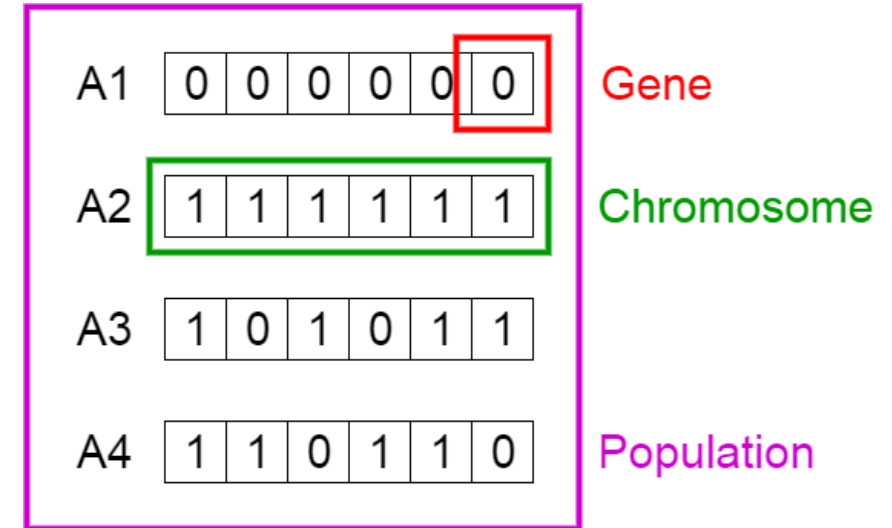## 5. Use AI/ML Techniques to Exploit Relationships to Design Tailored Sorbents

- **Prediction:** H_3BO_3 uptake from 1-20 ppm H_3BO_3 solution

- **Features:**
  - Stoichiometry (normalized by number of O atoms)
  - Six principal components for weighted RDFs (weighted by charge, electronegativity)
  - H_3BO_3 Concentration in solution

- **Model**: Random Forest Regression
  - Max depth = 9
  - N trees = 15
  - Tuned using gridsearchCV

- **Conclusions:**
  - Good quality of fit
  - Adding more data (mixed-cation)

Legend: Testing Set, RMSE = 0.12 mol/kg, R^2 = 0.91; Training Set, RMSE = 0.09 mol/kg, R^2 = 0.95. X-axis: FF Loading (mol/kg); Y-axis: RF Loading (mol/kg).

Genetic Algorithms – Zeolite Optimization

5. Use AI/ML Techniques to Exploit Relationships to Design Tailored Sorbents

- **"Survival of the fittest"**
  - Optimization technique

- **Genes:** Features
  - Examples. Si/Al, Al/O, RDF_PC1

- **Chromosome:** Set of genes
  - Example: Na-LTA with Si/Al = 1

- **Population:** Group of potential solutions

- **Fitness function:** Affects the probability of selection for "reproduction"
  - Predicted H_3BO_3 uptake

- **Crossover:** Swapping a set of genes between two chromosomes and adding the offspring to the population

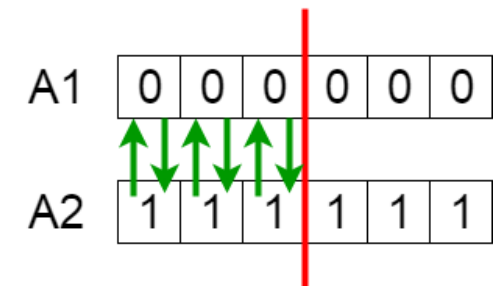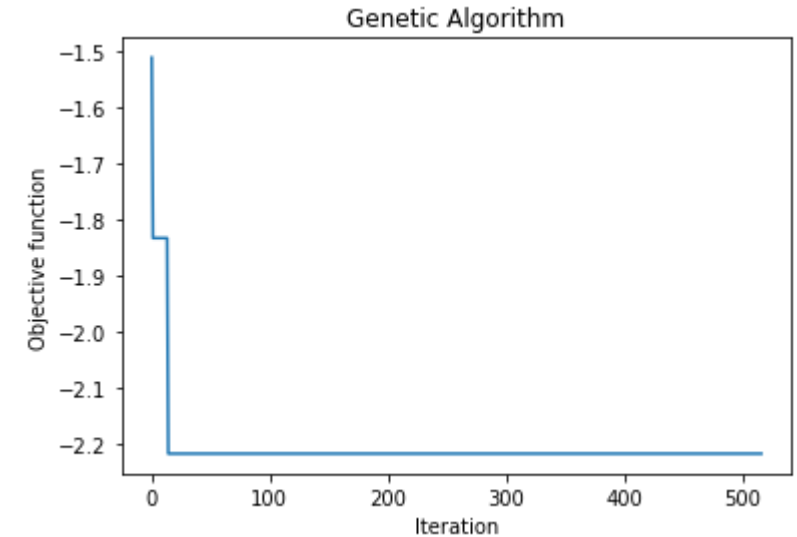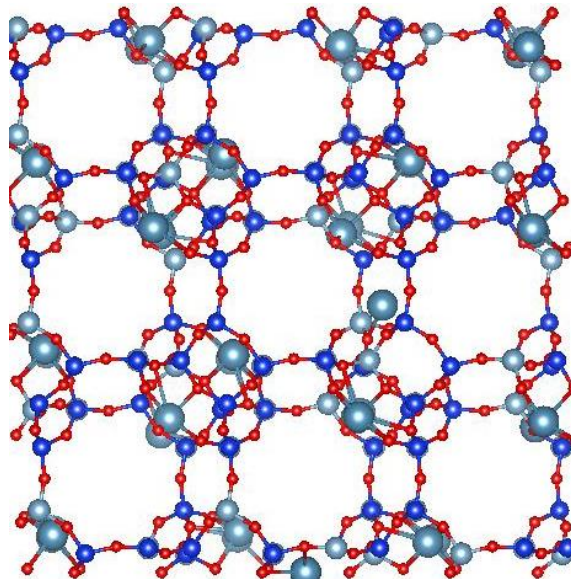- **Mutation:** Altering the set of genes in an offspring

Genetic Algorithms – Zeolite Optimization

5. Use AI/ML Techniques to Exploit Relationships to Design Tailored Sorbents

- Used GA for optimization of zeolite topology and composition

- Optimized zeolite for adsorption from 3 ppm H_3BO_3 solution

- Predicted optimal zeolite is CHA (Si/Al = 1.01) with almost 90% Ca exchange

Concentration	3 ppm
Loading (mol/kg)	2.20
Topology	CHA
Si/Al	1.01
Na (%)	2.9
Ca (%)	89.1
Mn (%)	1.3
Fe (%)	6.7

Next Steps

- Model enhancement
  - Mixed cation zeolites
  - Differing concentrations
  - Model pH effects

- Add additional contaminants to models (As, Se)

NETL Resources

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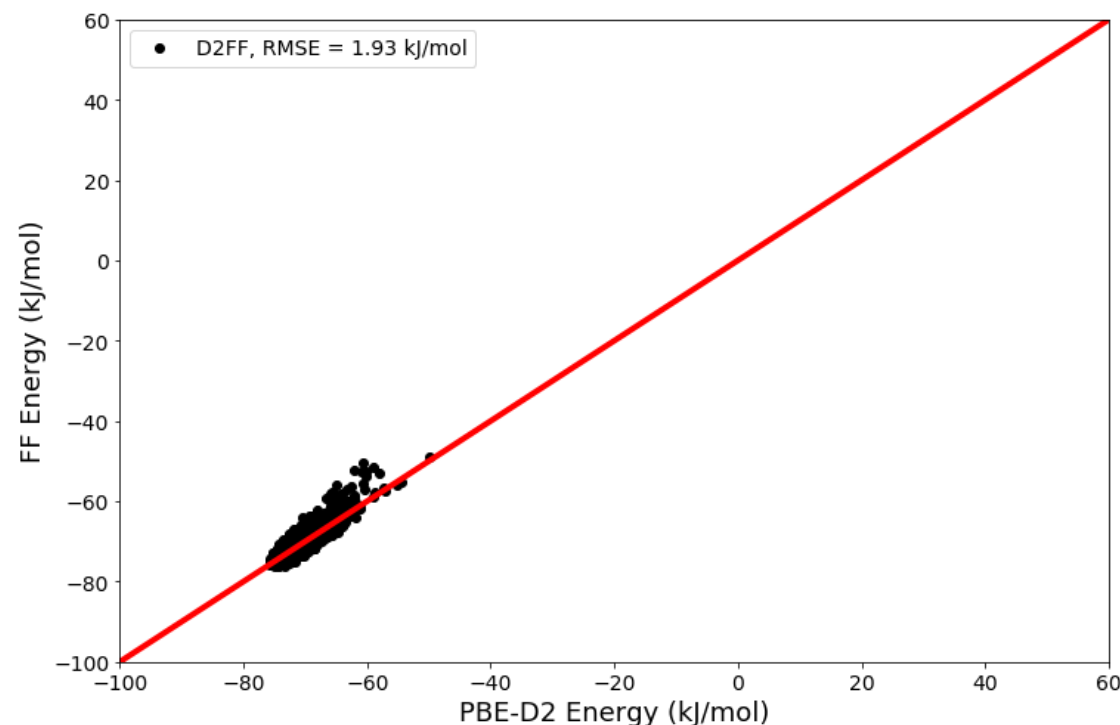
CONTACT:
John Findley
John.Findley@netl.doe.gov

Addition of K

2. Construct appropriate model potentials

- Fit new models (when necessary) K interactions with zeolite framework (finished), H_2O (finished), H_3BO_3 (finished, pictured)

Atomic Pair	A_{ij} (K)	B_{ij} (Å^{-1})	C_{ij} ($K*\text{Å}^6$)	q_M (-e)	Source
K – Oz	$6.23*10^7$	3.43	$2.29*10^6$	0.990	Fang et al.
K – O (H_2O)	$3.50*10^6$	2.55	0	0.990	This work

Atomic Pair	ε_{ij} (K)	σ_{ij} (Å)	q_M (-e)
K – O (H_3BO_3)	348	2.87	0.990