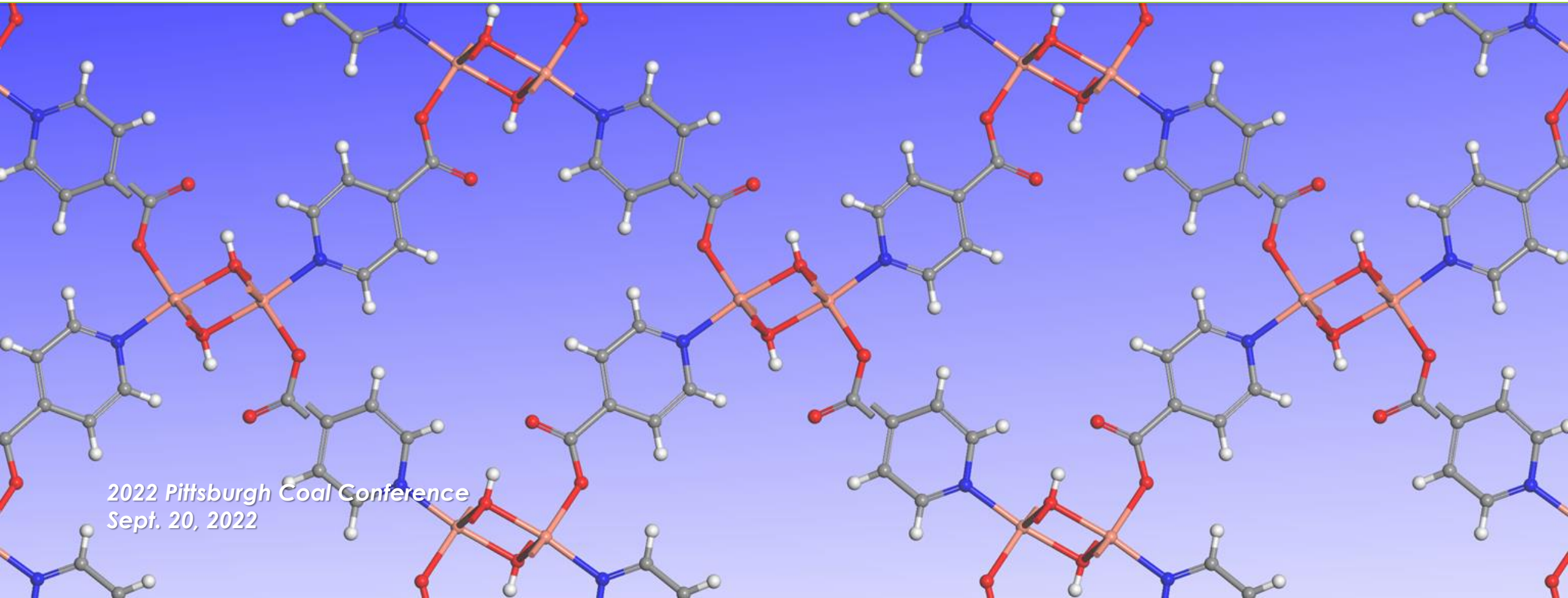
Development of Sorbents for Boron Capture from Coal Combustion Impoundment Leachates

NATIONAL ENERGY TECHNOLOGY LABORATORY

Solutions for Today | Options for Tomorrow

Jack Findley
Research Scientist
NETL Support Contractor



2022 Pittsburgh Coal Conference
Sept. 20, 2022

Disclaimer

This project was funded by the U.S. Department of Energy, National Energy Technology Laboratory, an agency of the United States Government, through a support contract.

Authors

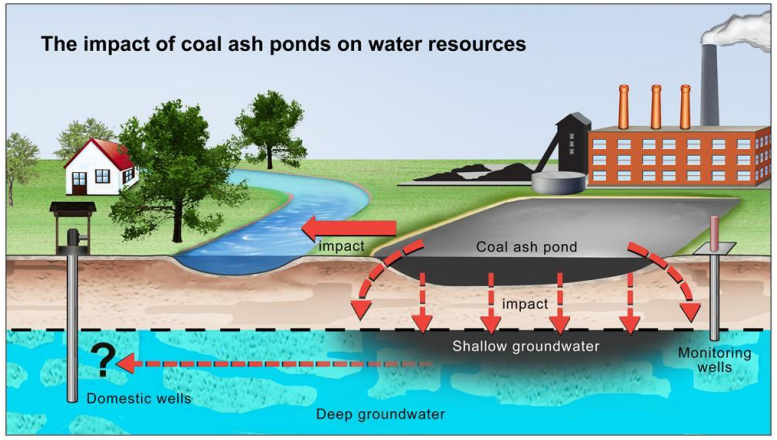
Jack Findley[1,2], Evan Granite[1], Eric Grol[1], Jan Steckel[1]

[1]National Energy Technology Laboratory, 626 Cochran Mill Road, Pittsburgh, PA 15236, USA

[2]NETL Support Contractor, 626 Cochran Mill Road, Pittsburgh, PA 15236, USA

Impoundment Sites

- Landfills to prevent the release of coal combustion products into the environment
  - Contain contaminants such as As, B, Hg, Se, Sr, etc.
- Boron: Present in impoundment sites
  - Primarily in the form of H_3BO_3 (acidic) or $B(OH)_4^-$ (basic)
- Zeolites: can be synthesized from fly ash
  - Have shown usefulness in removing contaminants
  - Topological variability
  - Tunable composition
- Which zeolite should be used for contaminant removal?

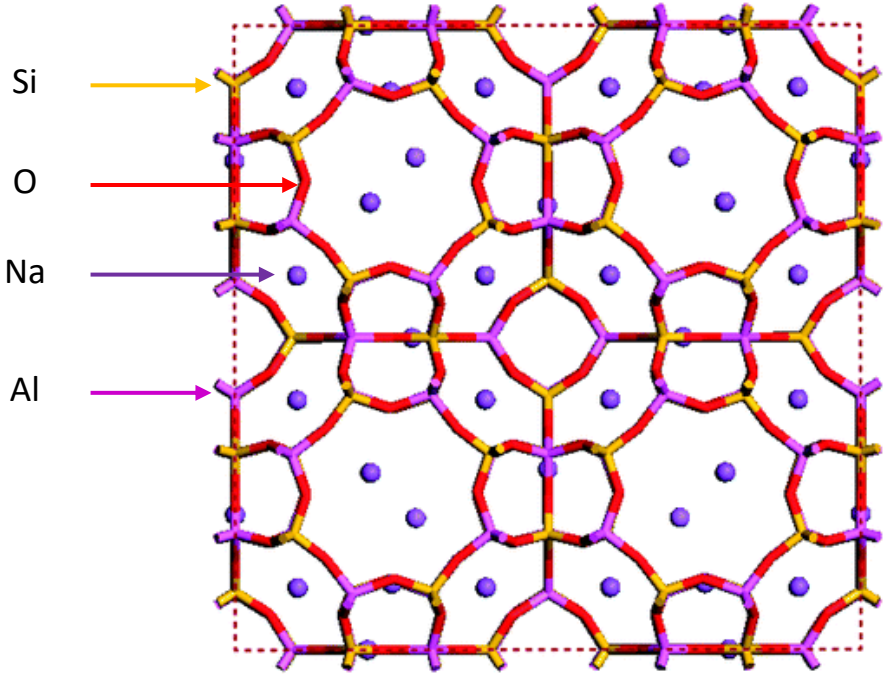


IZA Code	Alternate Names	PLD (Å)	LCD (Å)
ANA	Analcime	2.43	4.21
CHA	Chabazite Hershelite (Na-form) K-chabazite (K-form)	3.72	7.37
FAU	Faujasite Zeolite X (Si/Al < 2) Zeolite Y (Si/Al >= 2)	7.35	11.2
GIS	Zeolite P1 NaP1	3.32	4.97
LTA	Zeolite 4A Zeolite 5A Zeolite A Linde Type A	4.21	11.05
LTF	Linde Type 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

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
  - Can be synthesized from coal fly ash
  - High internal surface area for adsorption



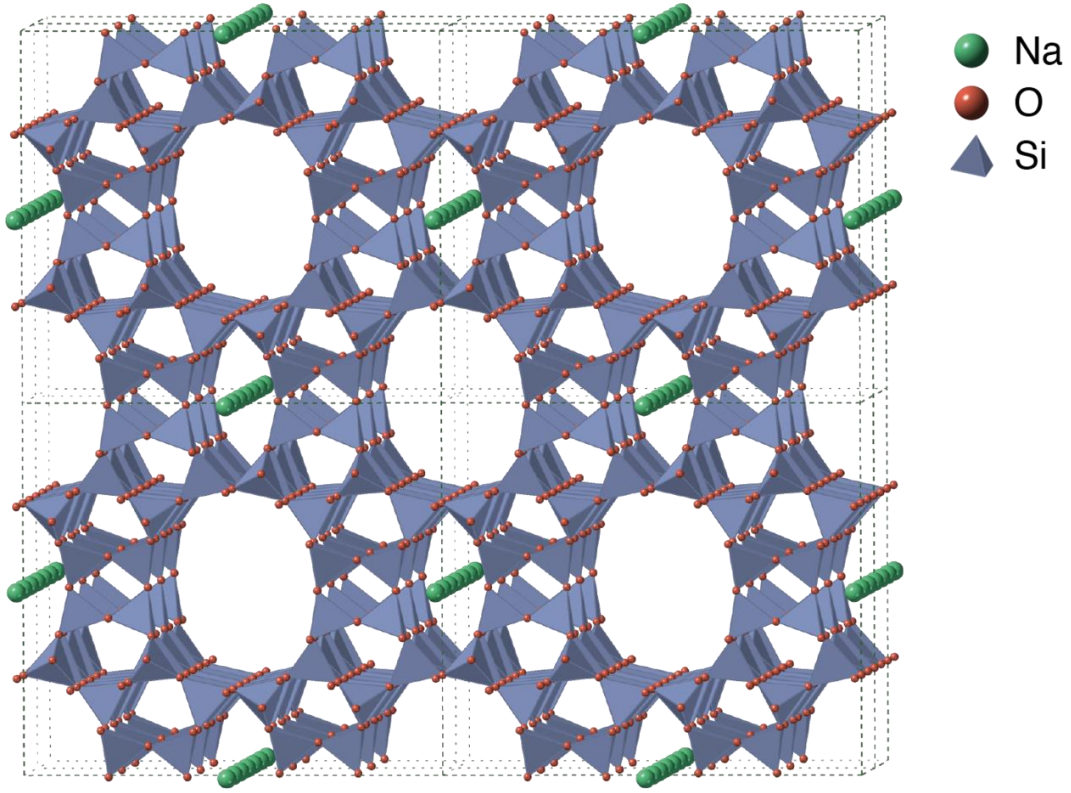
Zeolite 4A (Na-LTA)

Number of Cations	Species of Cations	Zeolite Structure (Topology)
Si/Al ratio	Modified by cation exchange Ex. Na, K, Ca, Mn(II), Fe(II)	Controls pore size, shape, and surface area

Methodology

Overall Strategy

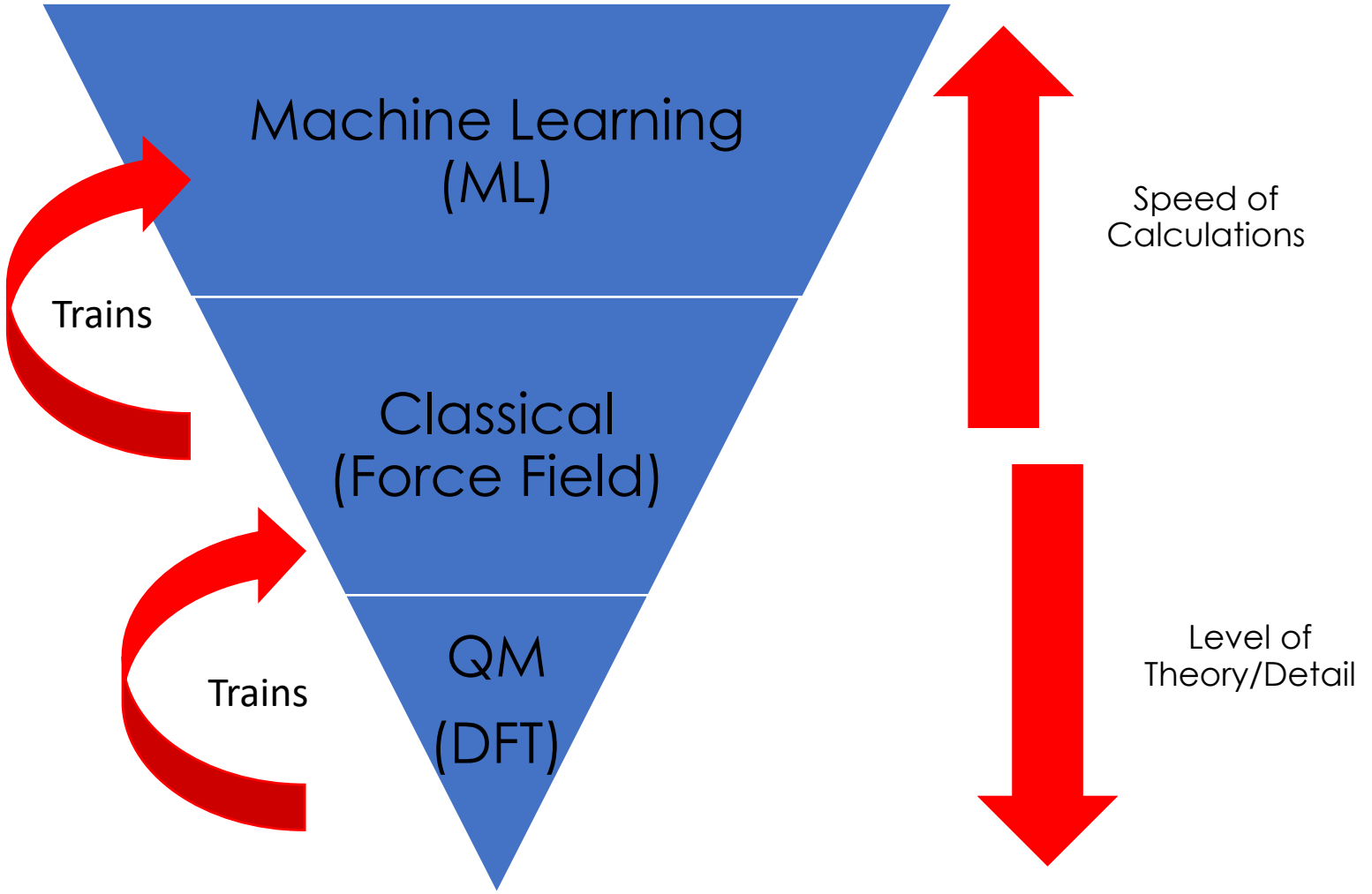
1. Construct a collection of sorbent structures and sorption conditions
2. Construct appropriate model potentials
3. Carry out computations to **estimate sorption** in a **representative subset** of the sorbent structures
4. Use AI/ML techniques to exploit relationships to **screen / design tailored sorbents** for impoundments



Mordenite (MOR framework)

Machine Learning for Materials Design

Overall Strategy



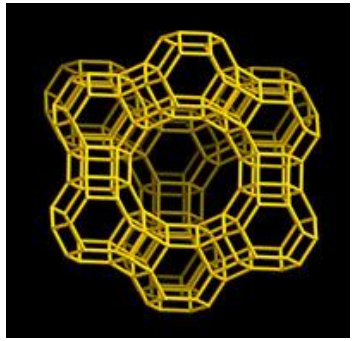
- **Machine Learning (ML)**:
  - Accuracy depends on training set
  - Can be used for screening or design
  - Fastest of these three methods
- **Classical Simulations (FFs):**
  - Molecular simulations
  - Can study macroscopic properties
  - Useful for screening
- **Quantum Mechanical (QM) simulations**:
  - Using density functional theory (DFT) as the QM method
  - Accurate
  - Based on first-principles calculations
  - Cannot study macroscopic properties

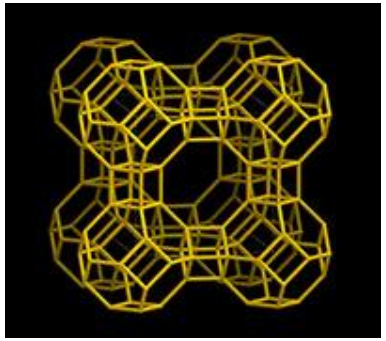
Methodology

1. Construct a Collection of Sorbent Structures and Sorption Conditions

- **Framework symmetry:**
  - The framework symmetry controls geometrical features:
    - Pore-limiting diameters
    - Cavity diameter
    - Accessible surface area
  - 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



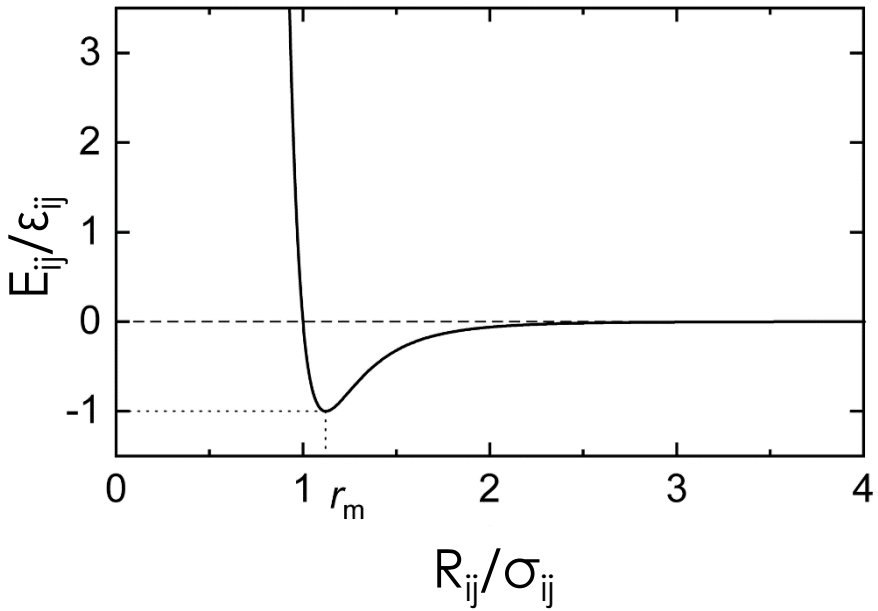


Force Fields

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

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



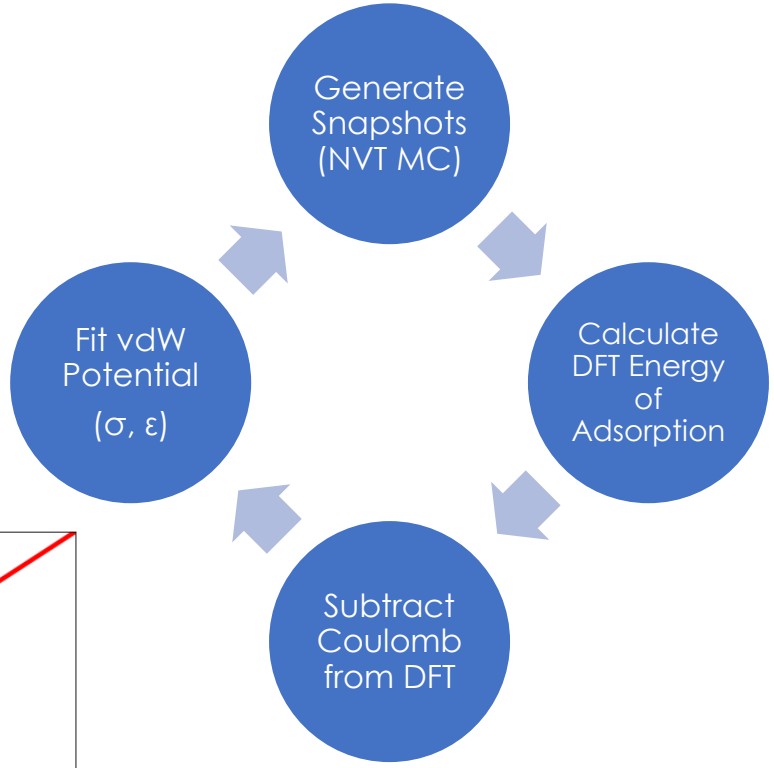
- Used with statistical mechanics to calculate thermodynamic properties
  - Fast computation of energies means more configurations and better statistics
  - Phase equilibrium, heats of adsorption, adsorption isotherms

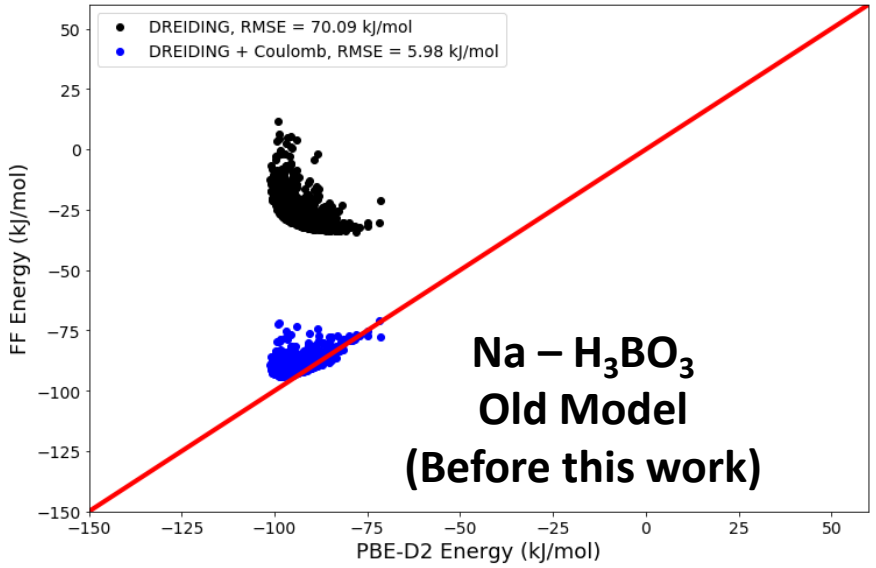
- Often parametrized based on **experimental data** or **QM calculations (DFT)**

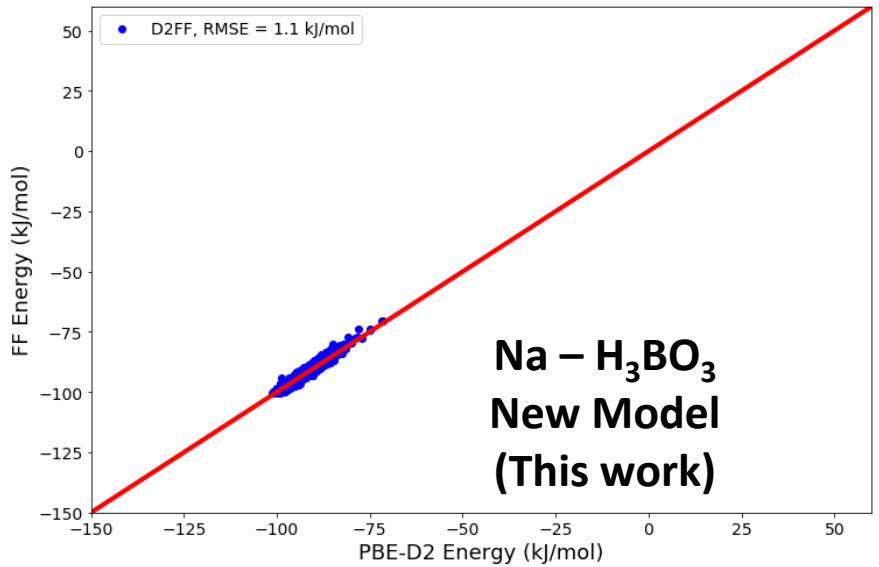
Fitting Adsorbate – Zeolite Interactions

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







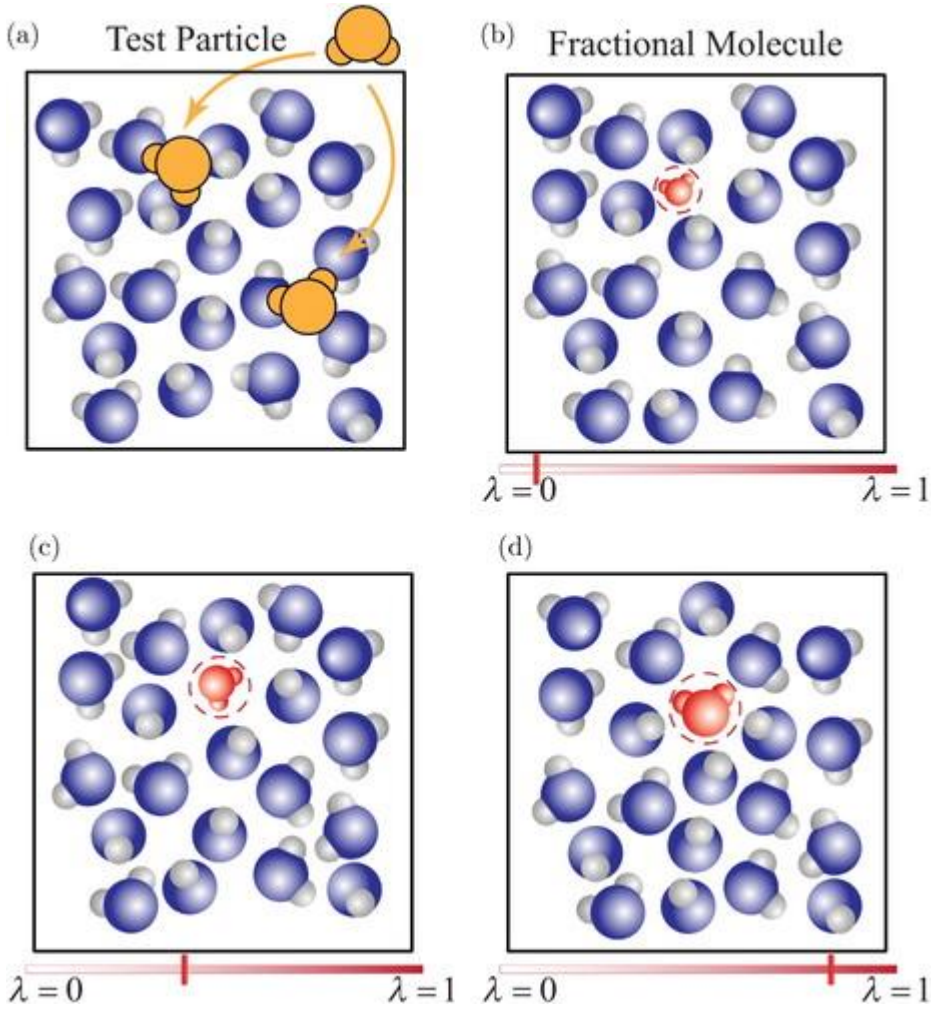
$$E_{ij}(R_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{R_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}}\right)^{6}\right] + \frac{q_i q_j}{R_{ij}}$$

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 (HSDB)
  - $K_H = \lim_{x_A \to 0} \left(\frac{f_A}{x_A}\right) = \rho k_B T exp(\beta \mu_A^\infty)$
- 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*m^3/mol)	Source
Experimental	2.65*10^{-7}	HSDB (NIH)
Sim (CFCMC-WI)	**1.29*10^{-7}**	**This work**



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)

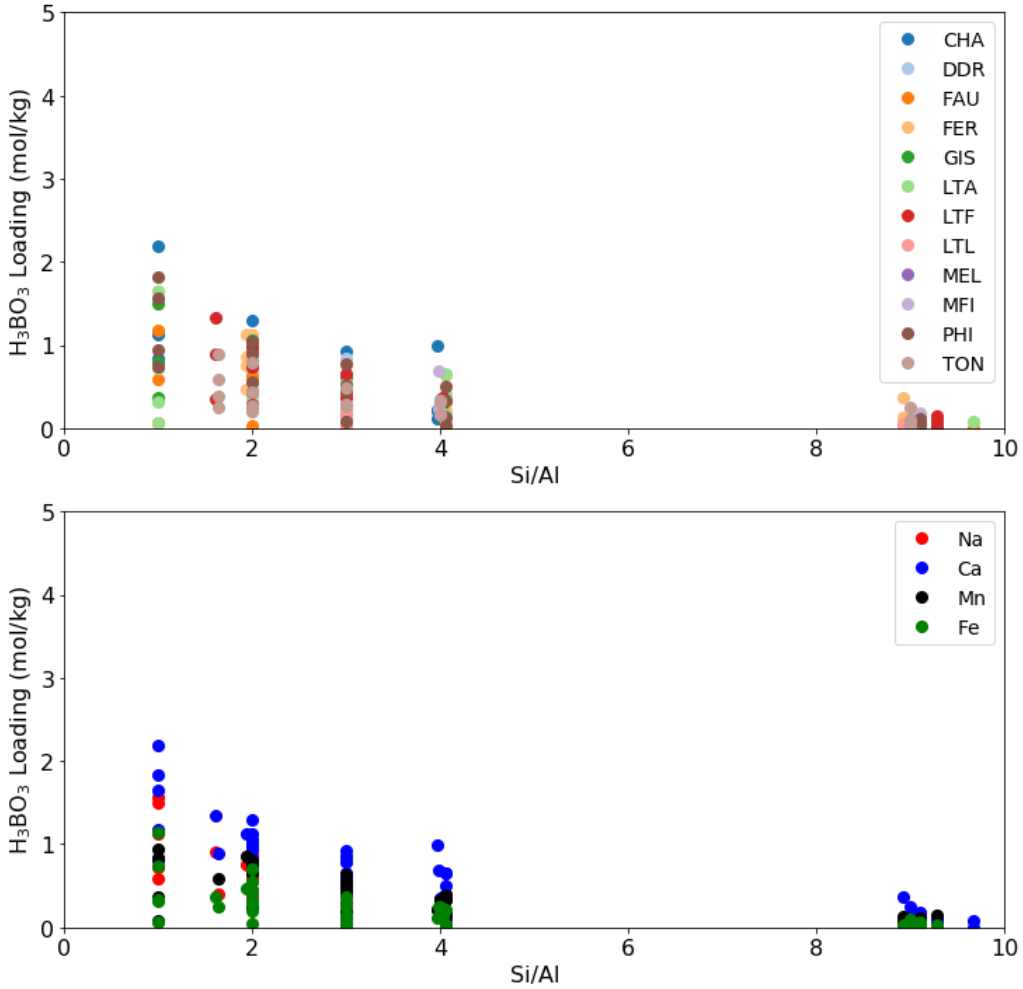
Initial Dataset (1 ppm)

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

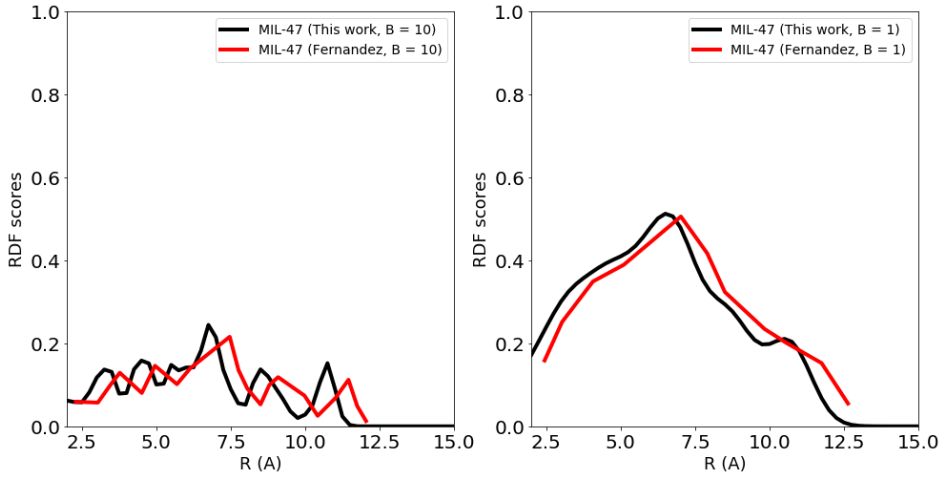


Zeolite Structure Encoding (RDFs)

4. 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.



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

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

4. 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

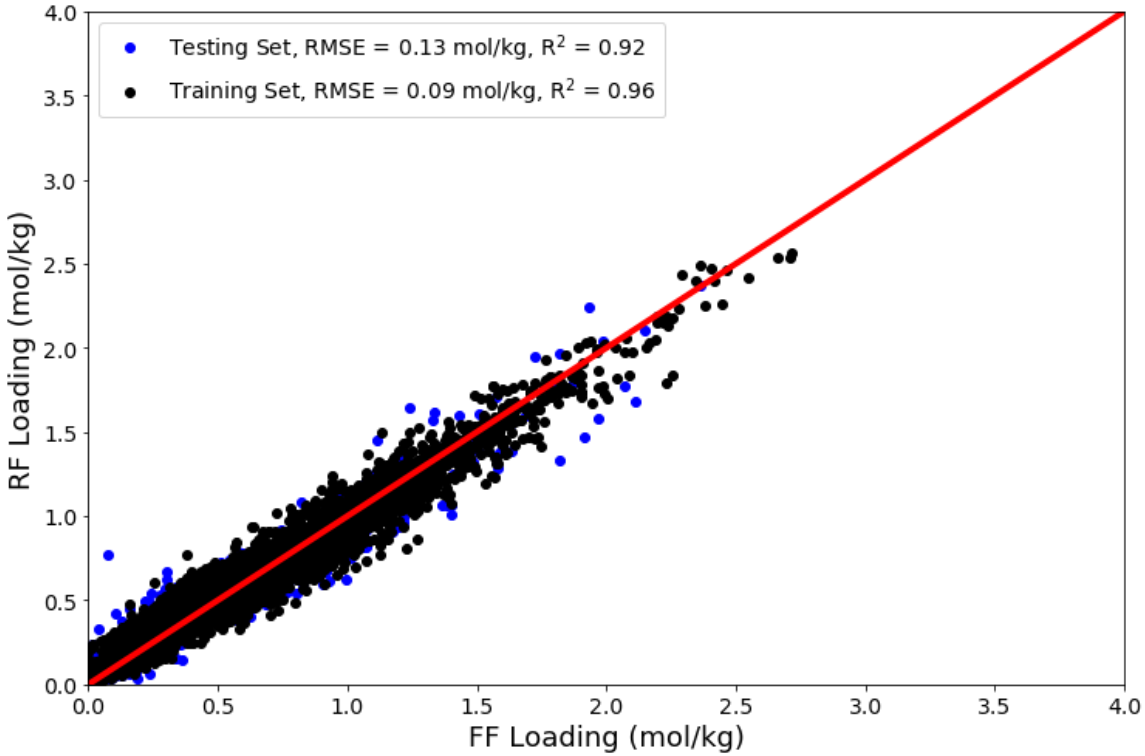
Target	Number of Cations	Species of Cations				Zeolite Structure Encoding		Solution
Amount Adsorbed	Al/O	Na/O	Ca/O	Mn/O	Fe/O	RDF_PC1	RDF_PC2	Boric Acid Concentration

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

ML Model

4. 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 = 10
  - N trees = 200
  - Tuned using gridsearchCV (5-fold)
- **Conclusions:**
  - Good quality of fit
  - Most important features: AlO (Si/Al ratio), CaO (cation type)

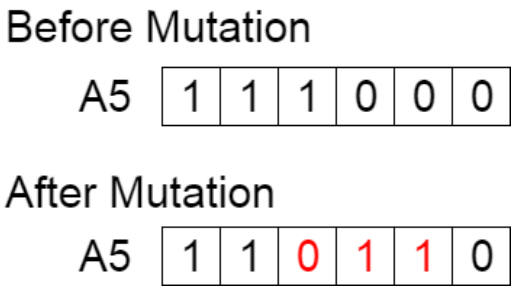


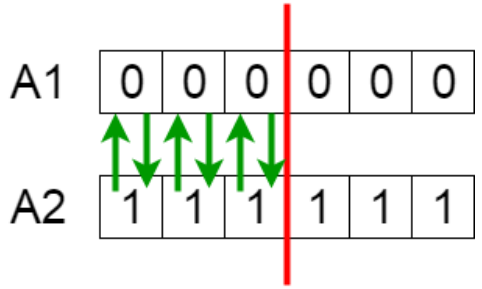
Genetic Algorithms – Zeolite Optimization

4. 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 (a zeolite)
  - 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

Gene	Values	Meaning
Topology	[0 to $N_{topologies}$]	Assigns structure encoding
AlO	[0, 1]	Si/Al ratio
NaO	[0, 1]	Na%
CaO	[0, 1]	Ca%
MnO	[0, 1]	Mn%
FeO	[0, 1]	Fe%





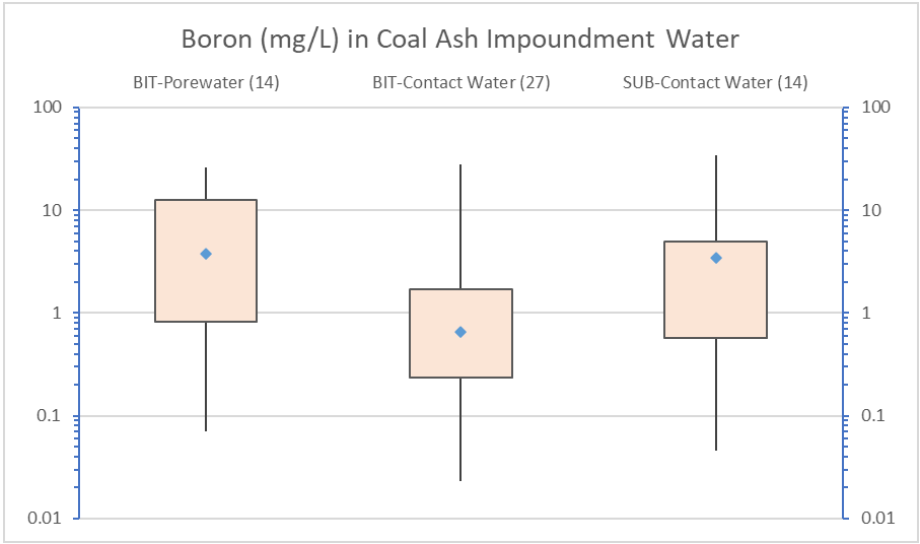
Genetic Algorithms – Zeolite Optimization

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

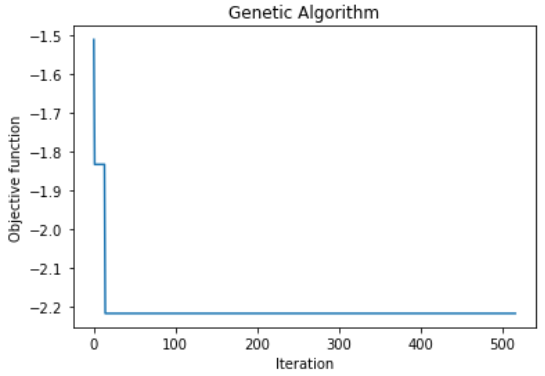
- Selected boron concentration data from Electric Power Research Institute (EPRI) report

- Designed tailored zeolites using GA optimization
  - **Case 1:** Fly ash zeolite topologies, all Si/Al are valid
    - Broader search
  - **Case 2:** Fly ash zeolite topologies, minimum Si/Al based on literature search
    - Searches zeolites that are "easier" to make

- CHA and LTA topologies are ideal for boric acid removal
  - Si/Al = 1, partially Ca-exchanged



Type	Percentile	Concentration (mg/L)	Case	Loading (mol/kg)	Topology	Si/Al	Na (%)	Ca (%)	Mn (%)	Fe (%)
BIT-Porewater	75	12.84	Case 1	2.5	CHA	1	42.82	49.98	2.29	4.92
			Case 2	2.25	LTA	1	7.37	70.09	6.60	15.94
BIT-Contact Water	100	27.43	Case 1	2.5	CHA	1	49.27	46.25	3.24	1.24
			Case 2	2.41	LTA	1	5.75	74.12	3.40	16.73
SUB-Contact Water	50	3.50	Case 1	2.5	CHA	1	29.47	68.49	0.39	1.66
			Case 2	2.04	LTA	1	3.02	78.60	4.75	13.63



Next Steps

- **Model enhancement**
  - Model pH effects

- **Add additional contaminants to models (such as As, Hg, Ni, Se)**
  - Hg, Ni: ion-exchange
  - As, Se: adsorption

Questions?

NETL Resources

VISIT US AT: **www.NETL.DOE.gov**

@NETL_DOE

@NETL_DOE

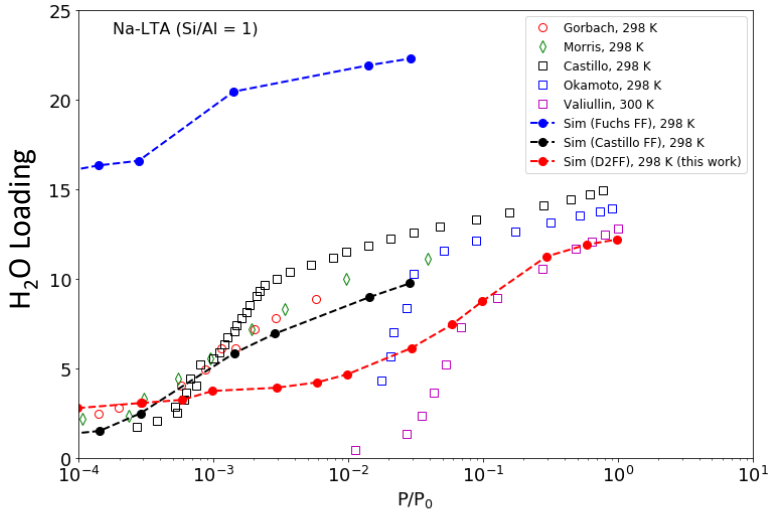
@NationalEnergyTechnologyLaboratory

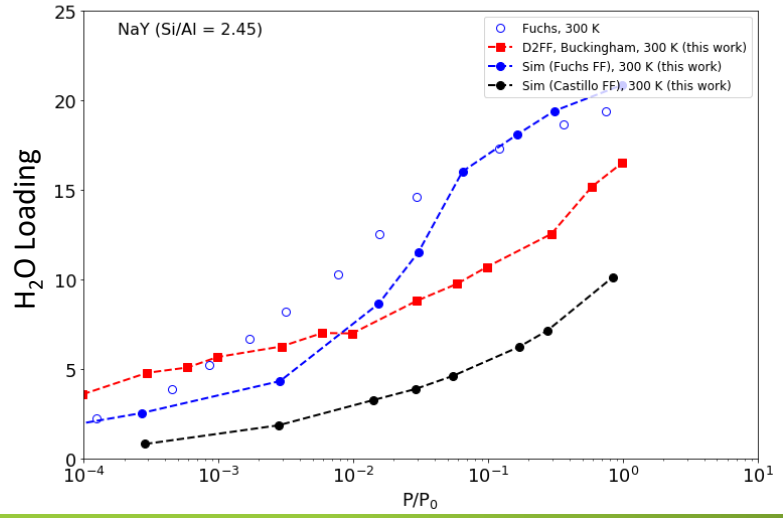
CONTACT:
John Findley
John.Findley@netl.doe.gov

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)

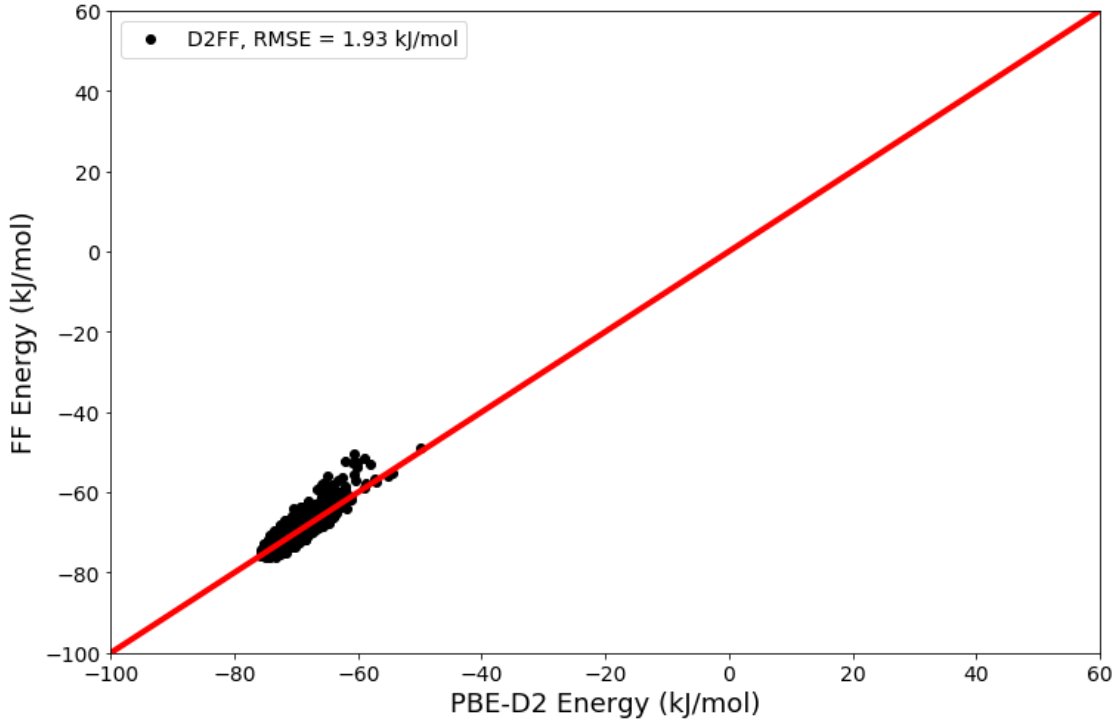




Addition of K

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*$Å^6$)	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