Optimizing Zeolites for Carbon Capture

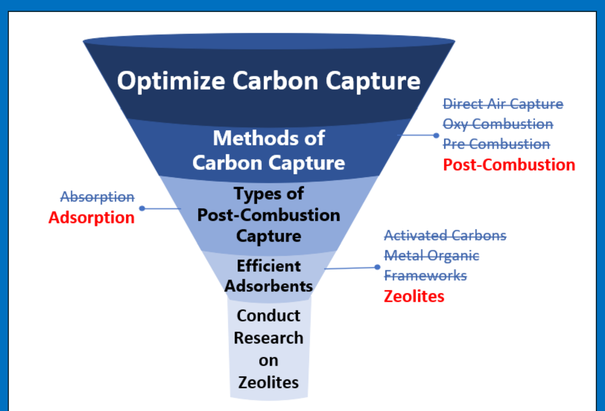
Introduction

Effects of Climate Change

Severe Storms	Worse Droughts	Rising Sea Level
Warmer water results in stronger hurricanes, typhoons, and tropical cyclones	Warmer temperatures causes excessive evaporation, leaving little moisture	Warming oceans lead to more ice melting, raising the sea level and causing more floods

Scientists agree that we are only **.5 degrees Celsius** away from the global temperature threshold that will cause **irreversible and catastrophic environmental damage**.
The largest contributor to global warming is CO2 emissions.

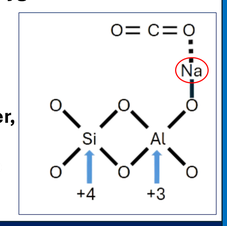
Background Research



Zeolites

Zeolites are a group of aluminosilicate crystals that are composed of silicon and aluminum oxygen tetrahedral

Extra Framework Cations:
Less electronegative cations lead to higher zeolite basicity and stronger interactions with acidic CO2. However, less electronegativity means weaker interaction with CO2, and larger ionic radii that may block zeolite cages.



CO2 Interaction

Physisorption – Molecules attach to a surface without forming chemical bonds (20 – 40 kJ/mol)
Chemisorption – Molecules attach by forming chemical bonds (40+ kJ/mol)

Evaluation Metrics

Adsorption Capacity	**Kinetics**
Adsorption Selectivity	**Longevity**
Adsorption Working Capacity	**Thermal and Structural Stability**
Adsorption Enthalpy	**Synthesizing Costs**

Industry Standard Zeolites

Zeolite 13X – FAU Framework, 1.5 Si/Al Ratio, Na Cations
Zeolite 5A – LTA Framework, 1 Si/Al Ratio, Ca + Na Cations

Simulation Types

Density Functional Theory (DFT)

Quantum computational method to model electronic structure in atoms and molecules, high computational cost.

Molecular Dynamics (MD)

Predicts how atoms and molecules move and interact as a function of time, mild computational cost.

Grand Canonical Monte Carlo (GCMC)

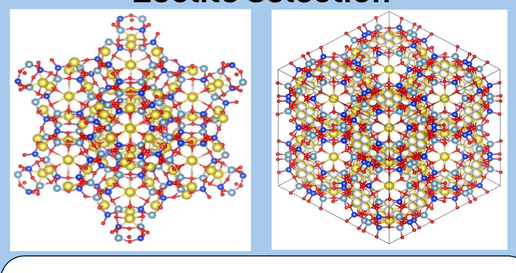
A statistical mechanical simulation for specifically solving adsorption equilibrium, low computational cost.

Hypothesis

Changing the properties of zeolites will reveal a more optimal solution than current industry standards.

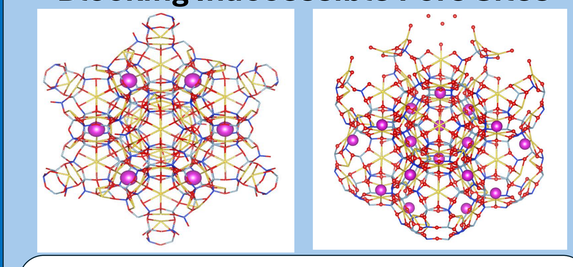
Methodology

Zeolite Selection



The 2 zeolites chosen were of the Faujasite and Linde Type A frameworks. This is because the industry standard zeolites 13X and 5A possess these frameworks.

Blocking Inaccessible Pore Sites



The purple dummy atom is assigned a repelling interaction with CO2 in the force field, preventing CO2 from spawning into the cage. The image on the left depicts the caging for the FAU zeolite, and the right the LTA zeolite.

Force Field

	ε (kcal)	σ (Å)	q
Si	.0437	2.58175	2.4
Al	0.31	4.39	1.4
O	0.1053	3.82	-1.2
Na	0.5	3.144	1
Ca	0.05	3.472	2
O_CO2	0.17	3.386	-0.05
C_CO2	0.0595	3.081	0.1
N_N2	0.0774	3.4	0
Xe	1.67e7	0	0

Mixing Equations

$\varepsilon_{A\text{-}B} = \sqrt{(\varepsilon_A * \varepsilon_B)}$

$\sigma_{A\text{-}B} = (\sigma_A + \sigma_B)/2$

Data Ranges

The range of values were centered around ambient conditions. Many different Si/Al ratios needed to be tested while managing the number of simulations . A range of 5 from the standard ratio of each Zeolite with .5 increments gives both relevant and specific data.

0.1-6 atm

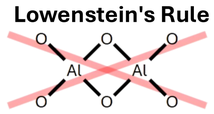
273-313 K

Si:Al 1-5

Adjusting Si/Al Ratio

1. Replace Aluminum atoms with Silicon atoms
2. Remove Extra Framework Cations to keep charge neutrality
3. Ensure Lowenstein's Rule is satisfied

Lowenstein's Rule



Aluminum Tetrahedral won't be adjacent to each other

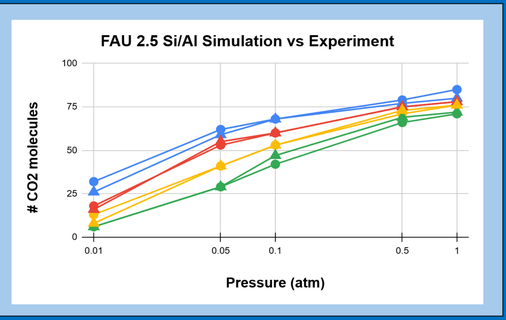
Automation

Over 1,000 simulations were needed to be run, a Java program was created to automate the entire process of preparing zeolite configurations, setting and running the simulation, and collecting data. The steps of the program are:

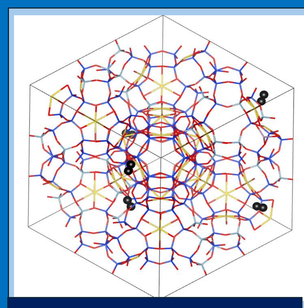
1. Block Inaccessible sites
2. Set Si/Al Ratio
3. Identify O1 and O2 Oxygen Atoms
4. Set Pressure and Temperature
5. Run the Simulation
6. Read and Record Data

Ensuring Accuracy

The blue lines are 253K, the red lines 263K, yellow 273K, and green 283K. The circles are values recorded from physical experiments. The triangle points are simulated values.
The max deviation was 6 molecules at 0.1 atm and 253K, the mean deviation was 1.8 molecules.
This reveals a high level of accuracy from the simulation.

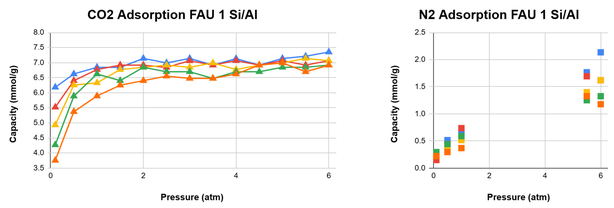


Results

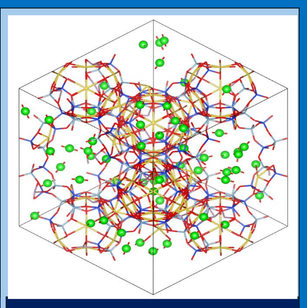


FAU 1 at N2 Adsorption Equilibrium

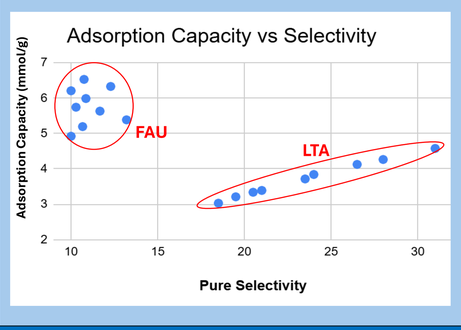
Blue = 273K Red = 283K Yellow = 293K Green = 303K Orange = 313K



The isotherms were collected for each Zeolite configuration



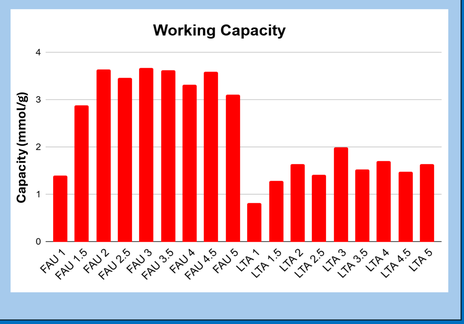
FAU 1 at CO2 Adsorption Equilibrium



Pure Selectivity:
mol CO2/ mol N2 at 1.0 atm

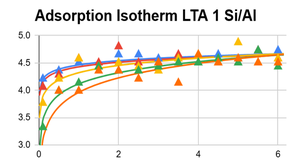
Working Capacity:
CO2 at 1.0 atm – CO2 at 0.1 atm

- **LTA 1 had the Highest Selectivity of 31**
- **FAU 1.5 had the Highest Capacity of 6.53**
- **FAU 3 had the highest Working Capacity of 3.67**

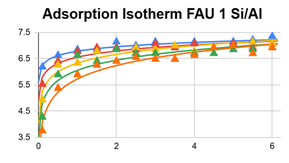


Statistical Analysis

Logarithmic Trend Fitting



Mean R^2 for FAU Configurations **.8859**



Mean R^2 for LTA Configurations **.7668**

These trends were used to verify the reliability of isotherm data points, ensuring individual points agreed with the overall isotherm behavior.

Conclusion

Carbon Dioxide Adsorption is a very promising field in Carbon Capture Storage.
FAU Zeolites feature higher adsorption capacities, while LTA emphasizes on selectivity.
General trends in data showed increase in SI/Al ratios led to decrease in performances.
My research had proved my hypothesis correct, different configurations led to higher performances than Zeolite's 13X and 5A.

3 Takeaways

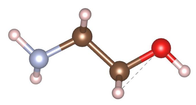
1. **Current Carbon Capture technology is too costly**
2. **This research succeeded in discovering configurations that show promise in outperforming current industry standard zeolites in Carbon Capture**
3. **Reduced costs will facilitate the mass implementation of Carbon Capture**

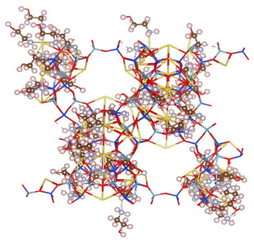
Future Work

Future objectives include:
- Expanding the input variables
- Measuring kinetics through MD Simulation
- Conduct Physical Experiments of promising zeolite configurations
  - Lifetime
  - Thermal and Structural Stability
  - Synthesizing Costs

Zeolites can undergo amine activation to improve their adsorption performance. The addition of amines as an input variable would open a doorway to thousands of more testable configurations. A program has been made that inserts the amines into the zeolites. Geometry optimization and a suitable force field still need to be obtained before simulations can begin.

Ethanolamine:





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