Post Combustion Carbon Capture Using Polyethylenimine Functionalized Titanate Nanotubes (FE0023040)

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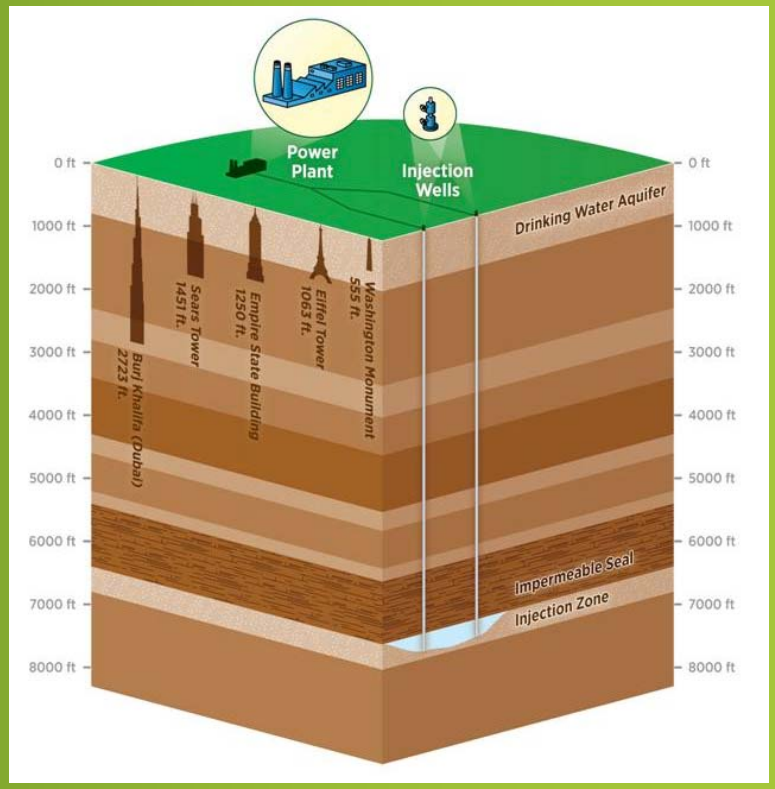
2016 Crosscutting Research & Rare Earth Elements Portfolios Review

April 18-22, Pittsburgh, Pennsylvania

Outline

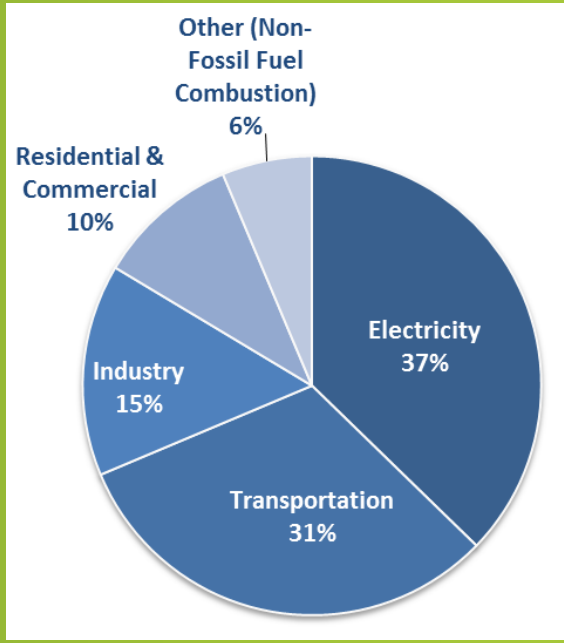
- Introduction
- Objectives
- Hypothesis
- Methodology
- Results
- Conclusions
- Future Studies
- Acknowledgements
- References



Carbon Capture and Sequestration Schematic Overview of Greenhouse Gases. (n.d.). Retrieved February 25, 2016, from http://www3.epa.gov/climatechange/ghgemissions/gases/co2.html

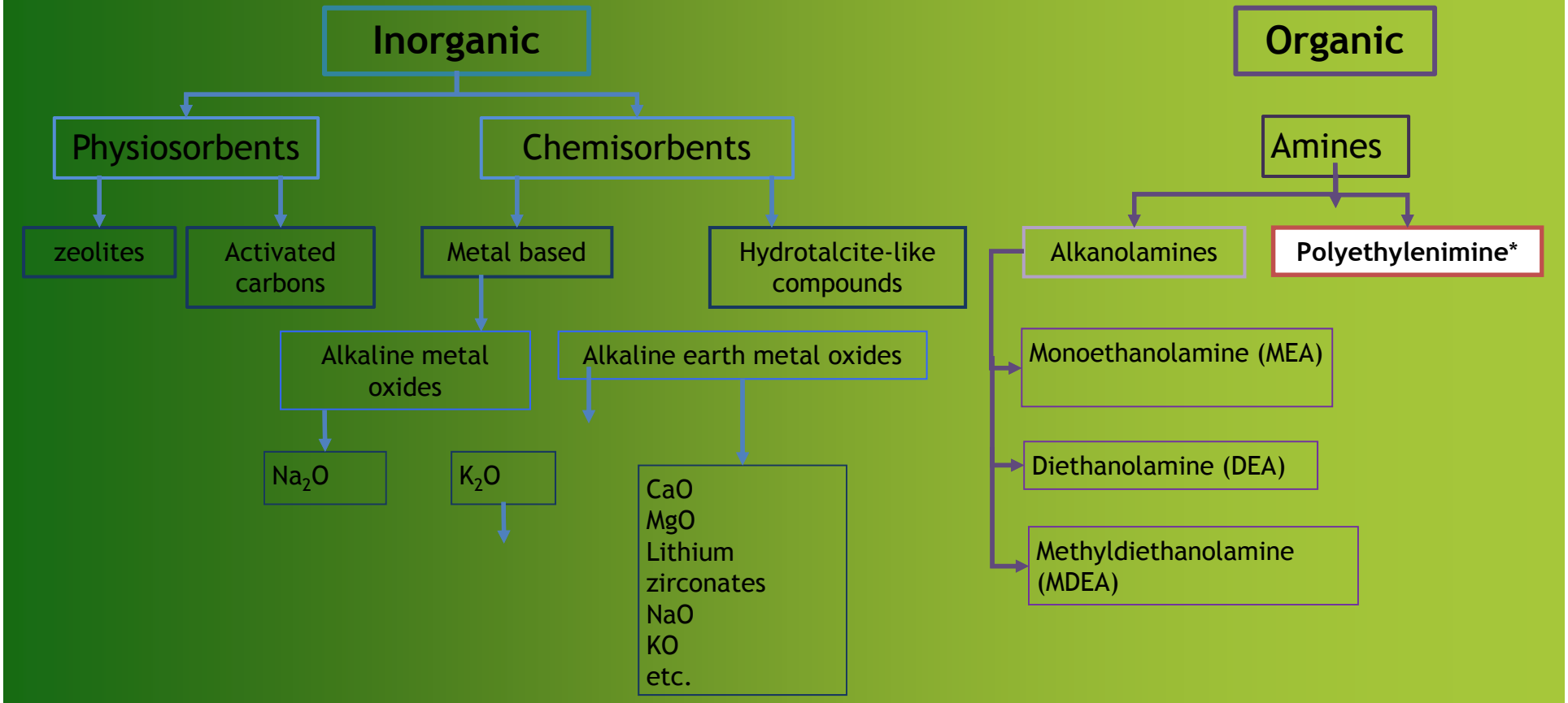
Introduction: The Importance Carbon Dioxide (CO_2)

- Atmospheric CO_2 concentration has increased by over 30% since the industrial revolution due to anthropogenic
- Is a greenhouse gas
- Multiple possible ways for reducing emissions
  - use of low carbon energy sources
  - carbon capture and sequestration
    - the most expensive part is the capture and separation of the carbon



U.S. Carbon Emissions by Source
Note: All emission estimates from the Inventory of U.S. Greenhouse Gas Emissions
and Sinks: 1990-2013.
Overview of Greenhouse Gases. (n.d.). Retrieved February 25, 2016, from http://www3.epa.gov/climatechange/ghgemissions/gases/co2.html

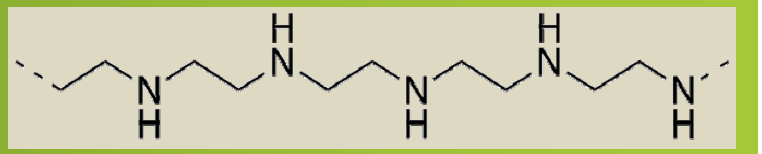
Introduction: Types of Adsorbents

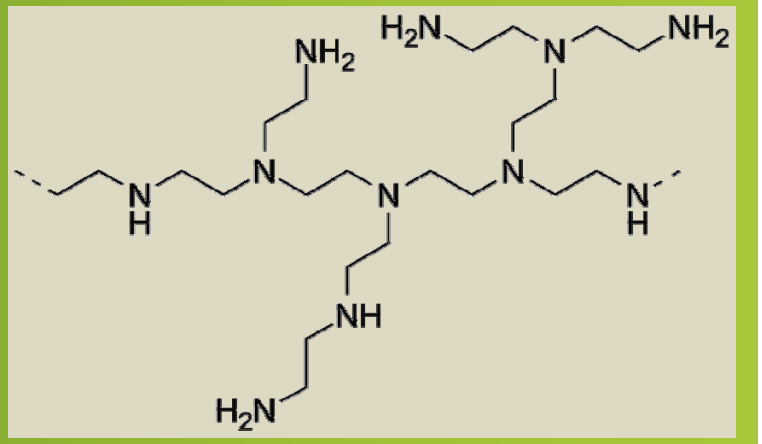


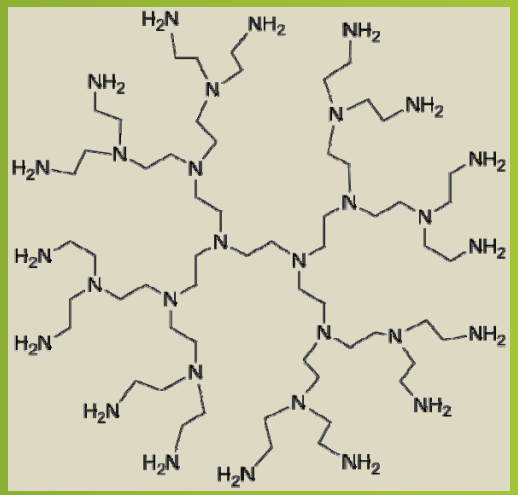
Introduction: Polyethylenimine (PEI)

- Polyethylenimine (PEI) is a polymer with repeating unit composed of the amine group and two carbon aliphatic CH_2CH_2 spacer
  - **Linear PEI fragments**
  - **Branched PEI fragments**
  - Dendrimer

- Linear PEIs contain all secondary amines, whereas the branched PEIs and dendrimers contain primary, secondary and tertiary amino groups

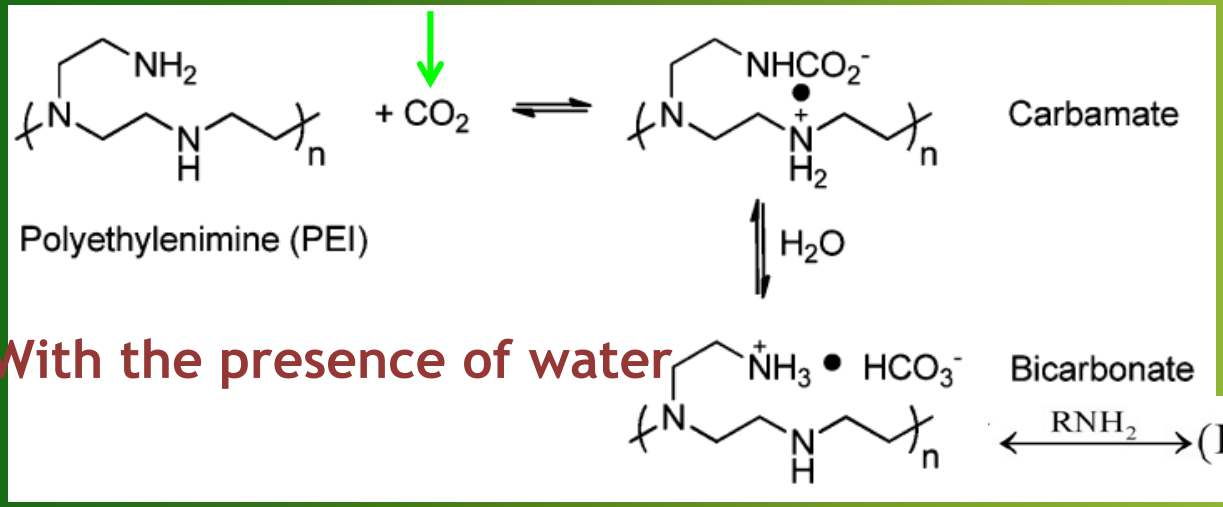






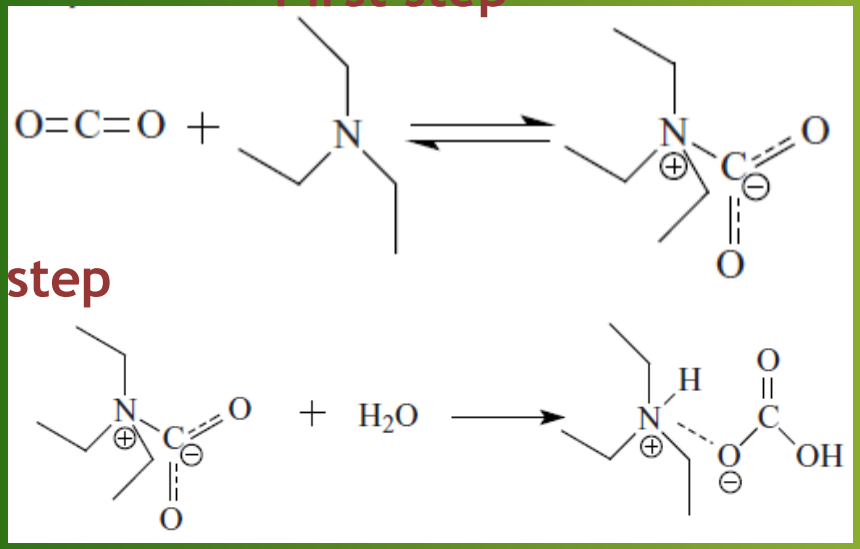
Possible Mechanisms of CO2 Reactions with Branched PEI

Without water



Goeppert, A., et al. *Journal of the American Chemical Society* **2011**, *133*, 20164-20167

First step



Second step

Reaction between CO_2, H_2O and tertiary amine

Introduction: PEI continued

- Branched PEI has about 30% of primary amine, 40% of secondary amine with the left (~30%) of tertiary amine
- PEI can be impregnated, grafted, or directly synthesized on mesoporous silica, mesoporous alumina, zeolites, carbon nanotubes, porous polymer, porous titanate nanotubes, clay and metal organic frames (MOF) for CO_2 capture
- Branched PEI is used in this study

Objectives

- To synthesize a novel CO_2 adsorbent of PEI-TNTs
- To characterize the samples using XRD, SEM and TEM
- To analyze the effects of temperature on the synthesis of PTNTs and CO_2 adsorption capacity
- To develop a geometric model for CFD simulation with a central porous section that represents the packed bed adsorption section
- Explore the opportunity to use the adsorbent for CO_2 capture in power plants.

Hypotheses

- It is hypothesized that:
  - Strong chemical bonding developed between PEI and TNTs when TNTs is protonated
  - CO_2 adsorption increases with increased nanotube size of TNTs
  - with increased synthesizing temperature, there will be increased CO_2 adsorption

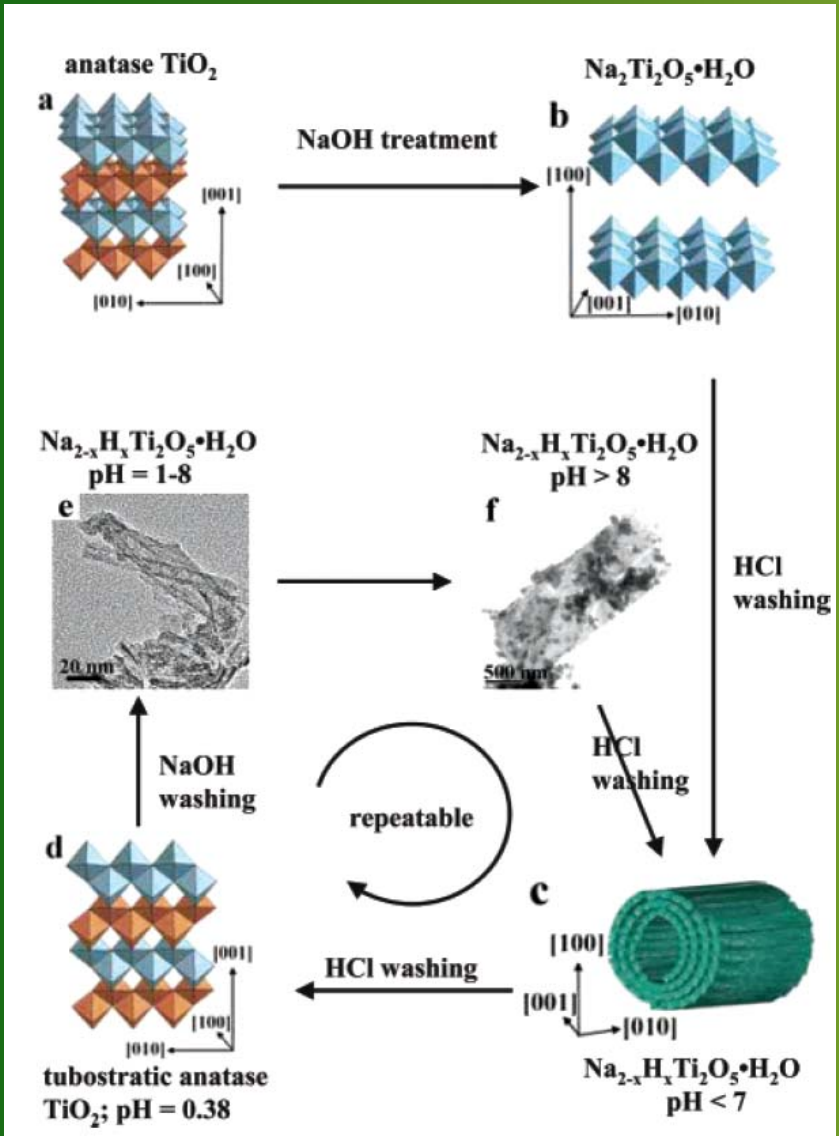
Experimental Section: PTNTs Preparation

- 3 grams (g) TiO_2 powder was added to 120 mL 10M sodium hydroxide (NaOH) solution and stirred
- The slurry was added to a polytetrafluoroethylene autoclave and treated at 130°C, 140°C and 150°C for 24 hrs.
- The precipitate was collected (excess NaOH was removed) and washed with 0.1M hydrochloric acid aqueous solution to a pH of 1.6 and subsequently rinsed to neutral pH with deionized (DI) water. The protonated titanate nanotube was obtained, named after PTNTs.
- The neutralized precipitate was dried at 100°C overnight

$$TiO_2 \text{ powder} + 10M\ NaOH \xrightarrow[130^\circ C,\ 140^\circ C,\ 150^\circ C]{\Delta} TNTs + 0.1M\ HCl + DI\ H_2O$$

$$TNTs + 0.1M\ HCl + DI\ H_2O \longrightarrow PTNTs$$

Mechanism of PTNTs Generation



*Left figure: The scheme for the formation and transformation of nanotubes generated by the NaOH hydrothermal treatment and the post-treatment washing.

- **After NaOH treatment, some Ti-O-Ti bonds are broken, some intermediates including Ti-O-Na and Ti-OH are developed.**
- **After washing with HCl above pH 8, some nano-sheets are formed.**
- **Continue washing to pH below 7, nanotubes are achieved through Na^+ exchange with H^+ in the post acid washing.**

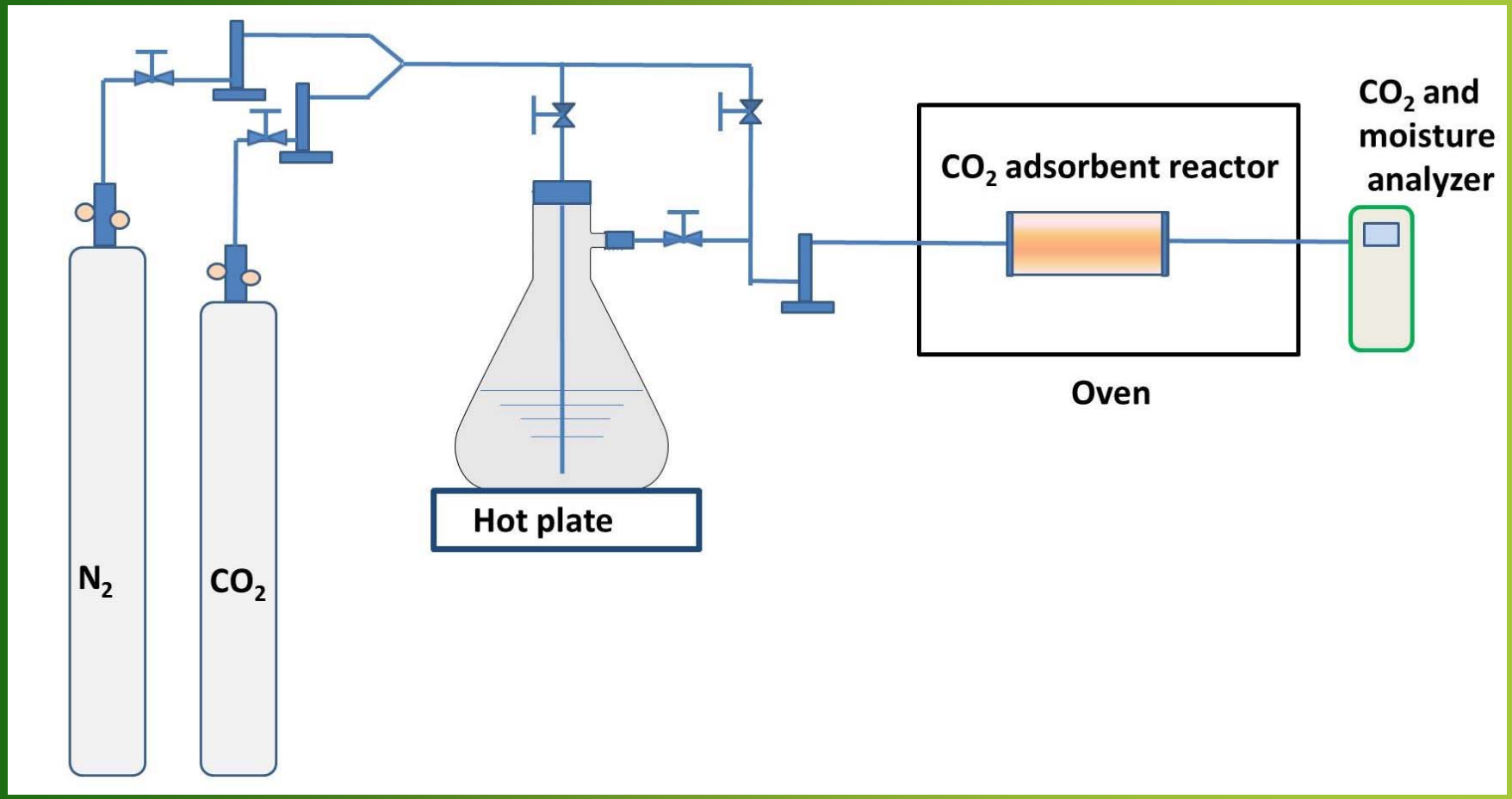
*Chien-Cheng Tsai and Hsisheng Teng, Structural Features of Nanotubes Synthesized from NaOH Treatment on TiO2 with Different Post-Treatments, *Chem. Mater.* **2006**, *18*, 367-373

PEI-PTNTs Preparation

- 3 g PEI was dissolved in 120mL methanol and the PTNTs was added to this solution for a wet impregnation of the PEI into the PTNTs
- The mixture was stirred in a covered beaker for 2hrs. and then stirred uncovered for another 8hrs.
- The recovered residue was dried at 100°C overnight
- The resulting product was denoted as PEI-PTNTs-wt% according to the PEI loading

PEI + Methanol + PTNTs → PEI-PTNTs

Schematic of Adsorption Apparatus



Adsorption/ Desorption Cycle

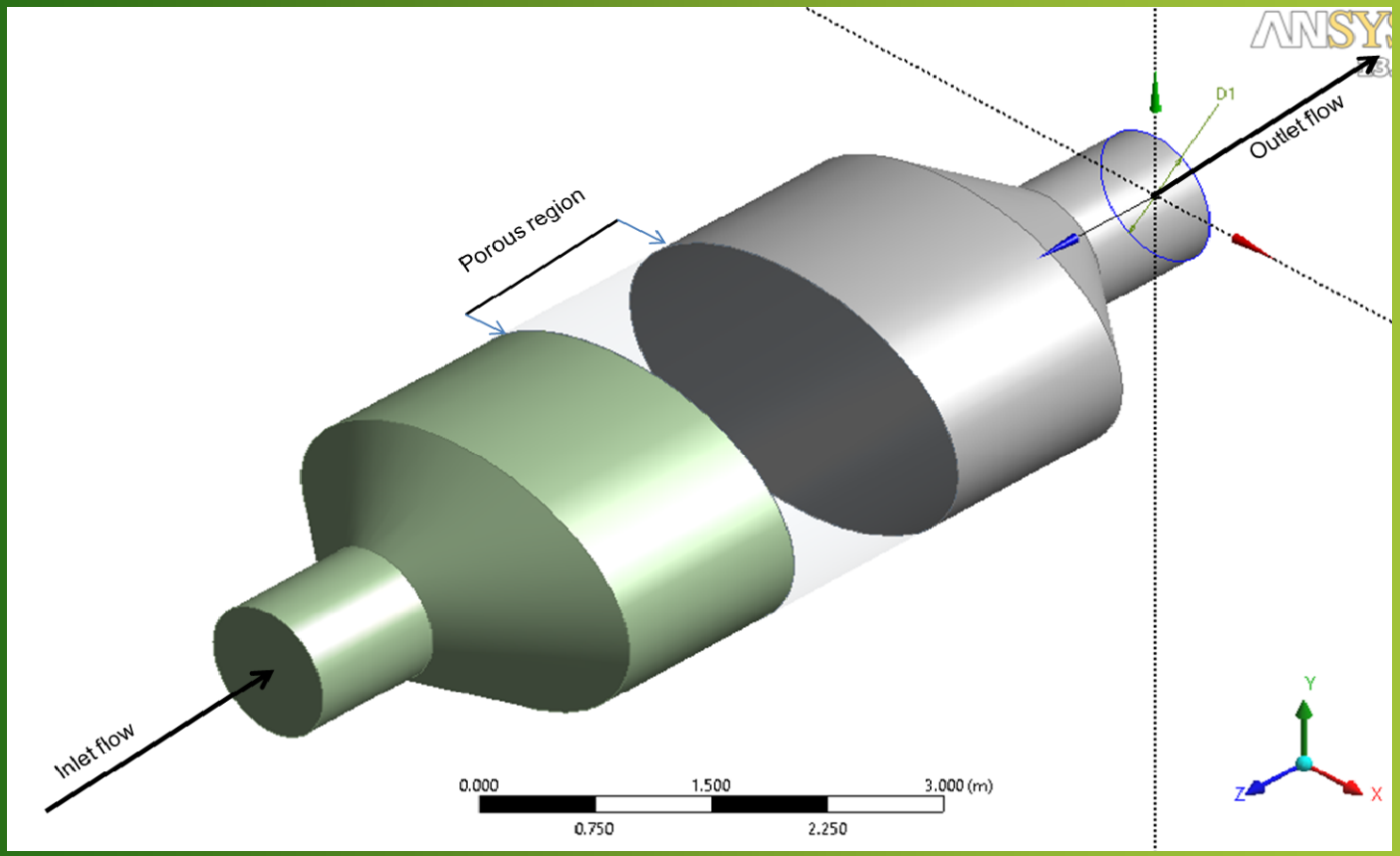
- Adsorption capacity was determined using weight differential in adsorbent
- 1 g adsorbent was pretreated at 150°C with pure nitrogen (N_2) gas at 120 mL/min for 30mins and the weight recorded
- A mixture of nitrogen and carbon dioxide (N_2/CO_2) was passed through the adsorbent at 120 mL/min flow and at 100°C for 30mins and the weight recorded
- The steps above were repeated and the weight differential between each set of adsorption/ desorption were calculated with the difference being regarded as the CO_2 adsorbed capacity

XRD, SEM and TEM Characterization of Nano Materials

- The crystal samples were analyzed using a Bruker D8 Advanced diffractometer with CuKα radiation and the following:
  - Scattering angle: 2θ
  - Step Size: 0.015
- JEOL JSM-7500F field emission scanning electron microscope (FE-SEM)
  - Acc. voltage:
    - 0.5 to 30kV (SEM mode)
    - 10 V steps from 0.5 to 2.9 kV
    - 100 V steps from 2.9 to 30 kV
- Transmission Electron microscopy (TEM) performed at Texas A&M University

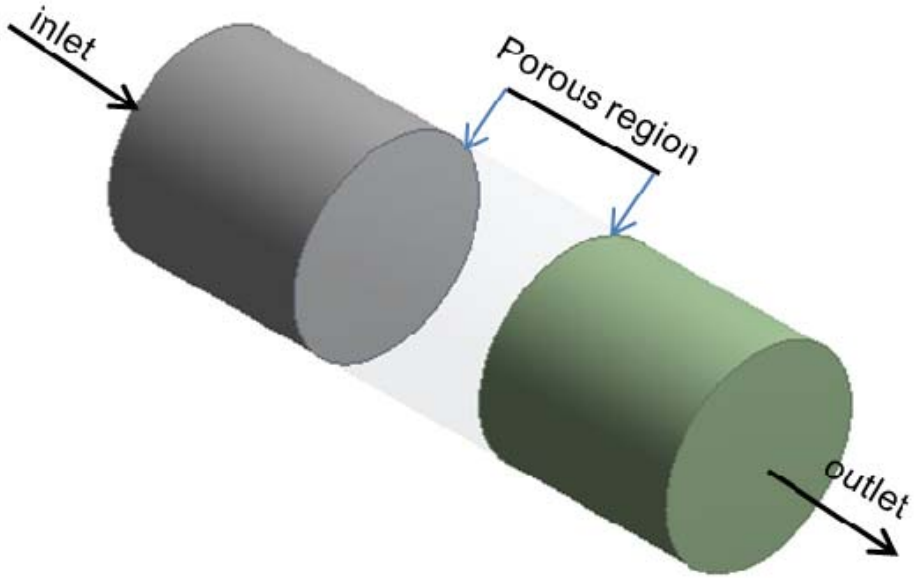
CFD Model Geometry of Carbon Capture Device

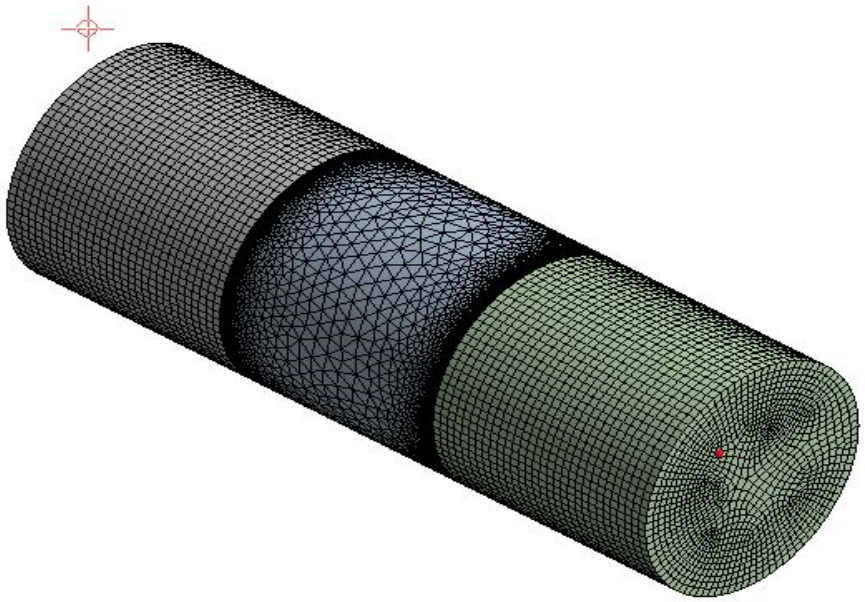
- Total length is 4m with the porous region being 1.5m
  - Middle transparent region is porous



Simplified Geometry & Meshing of Carbon Capture Device

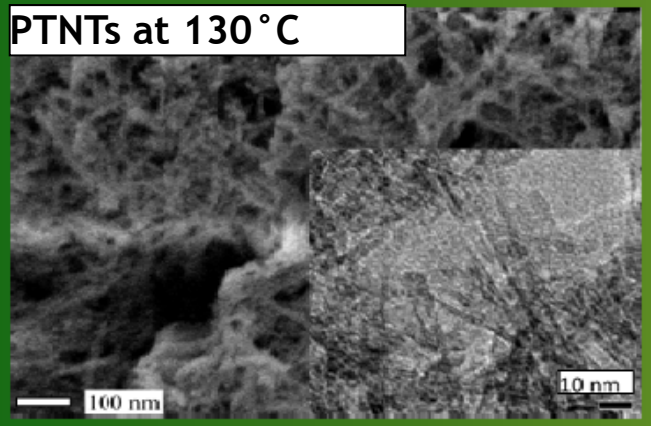
- The diameter of the pipe is 1.5m
- Approximately 2 million grids were used
  - There are 5 times finer grids in the porous domain than the two other regions



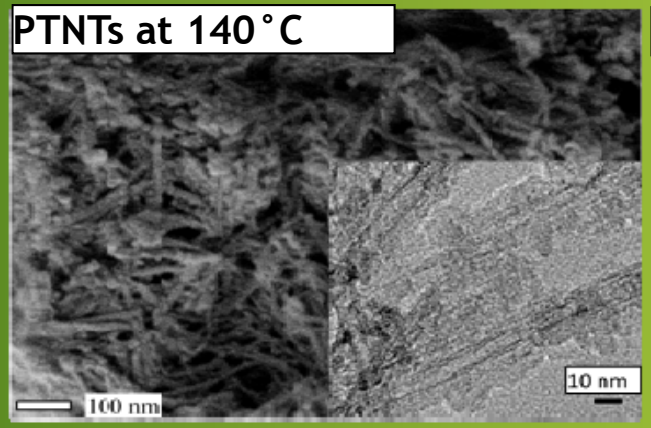


SEM-TEM Results

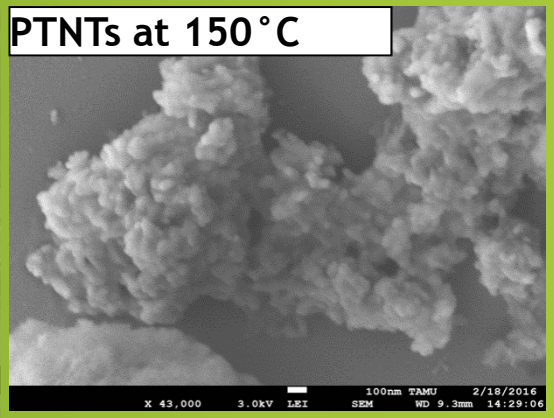
PTNTs at 130˚C



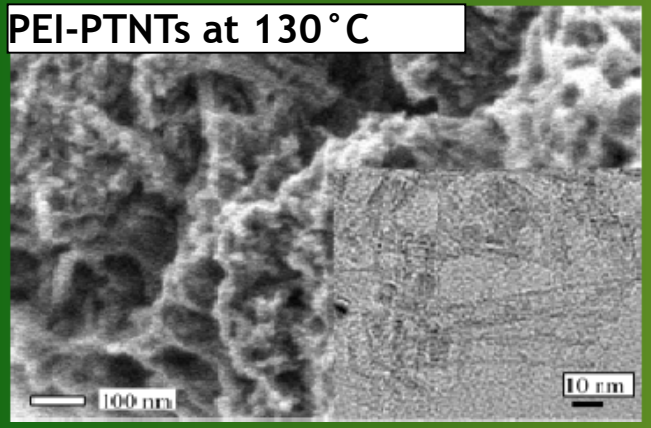
PTNTs at 140˚C



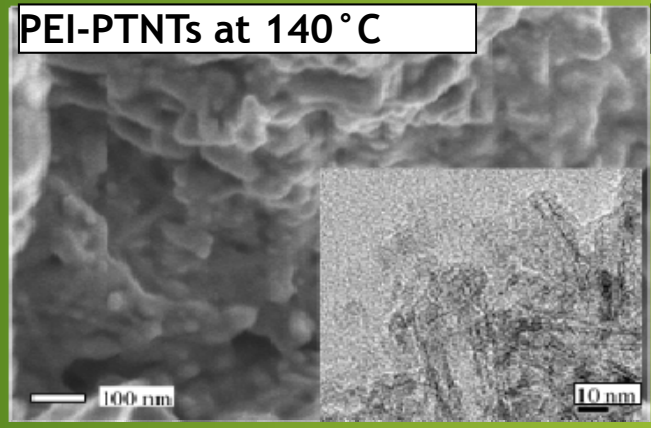
PTNTs at 150˚C



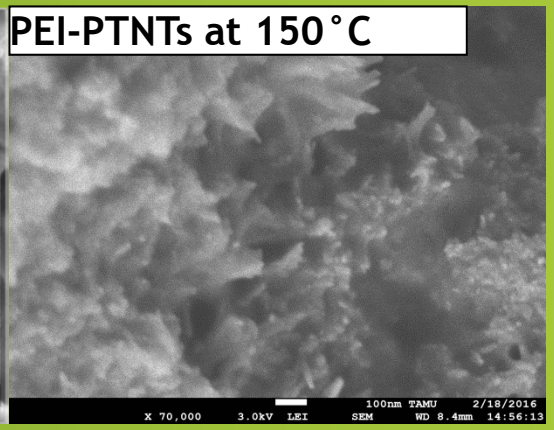
PEI-PTNTs at 130˚C



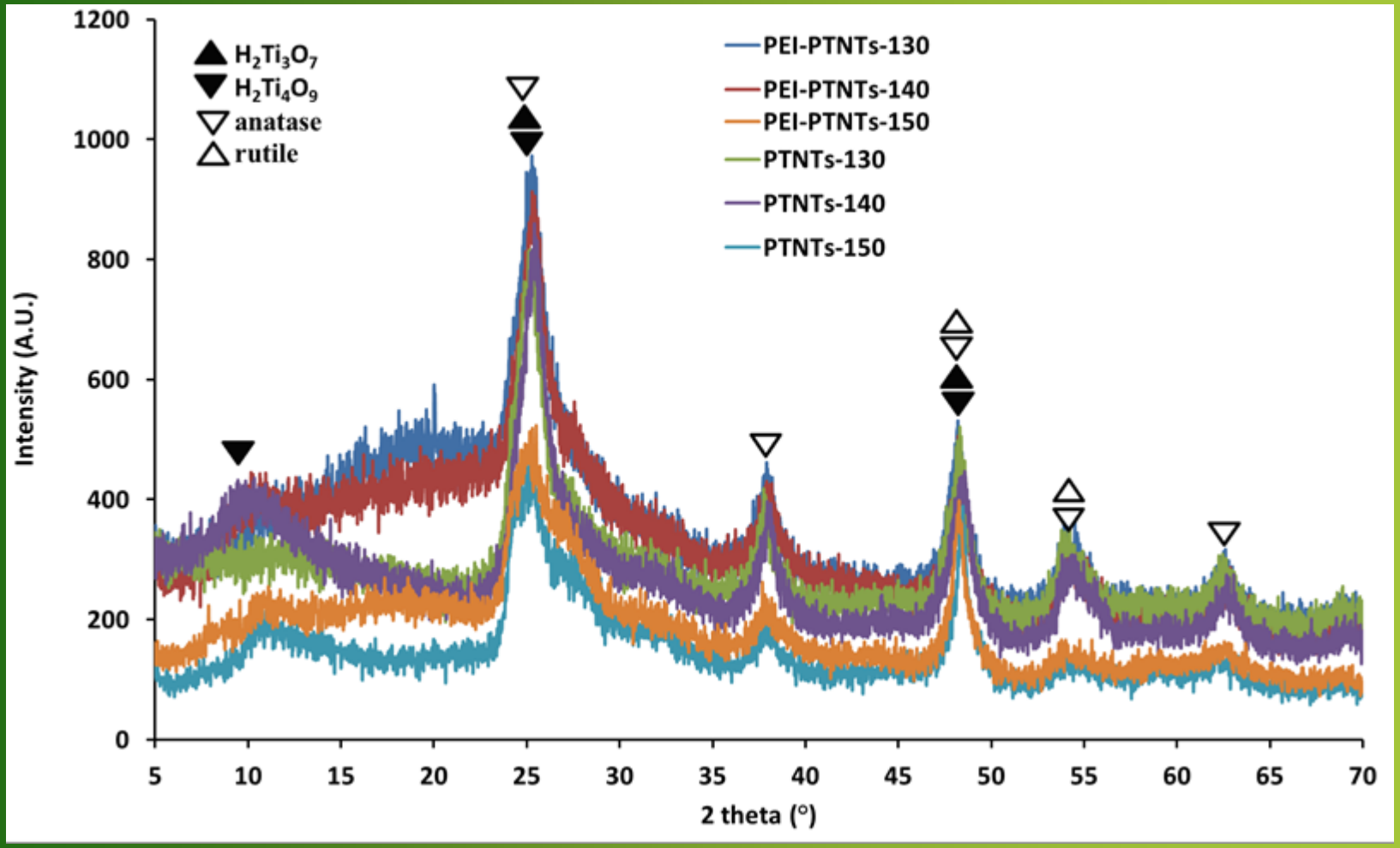
PEI-PTNTs at 140˚C



PEI-PTNTs at 150˚C

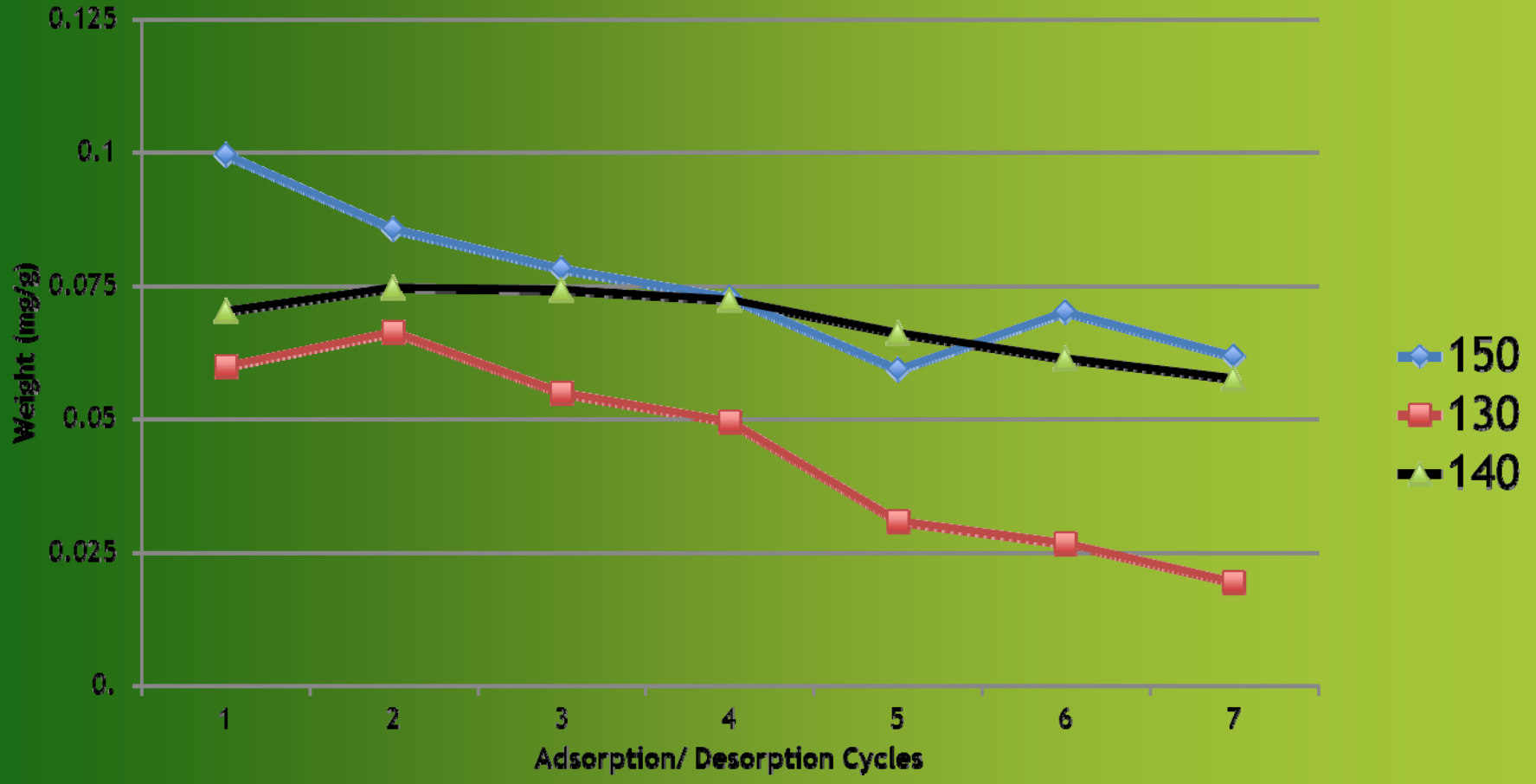


XRD Results



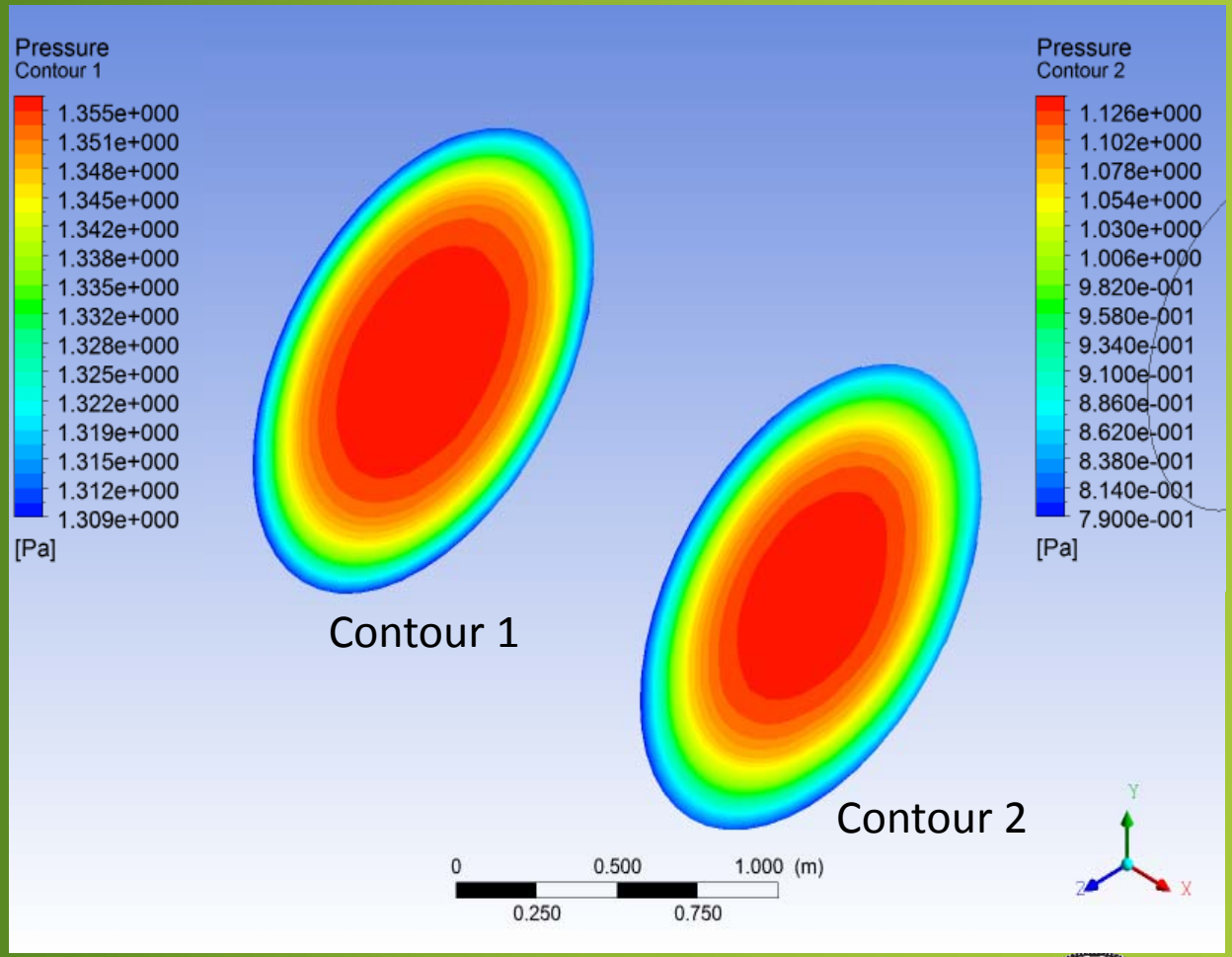
Their typical series of peaks occurs at 2θ = 9.6, 25.2, 38.0, 48.2, 62.0 degrees, representing various types of nanotubes $H_2Ti_3O_7$, $H_2Ti_4O_9$, anatase and rutile developed after hydrothermal treatment.

PEI-PTNTs (130°C,140°C and 150°C) Adsorption Capacity (mg/g)

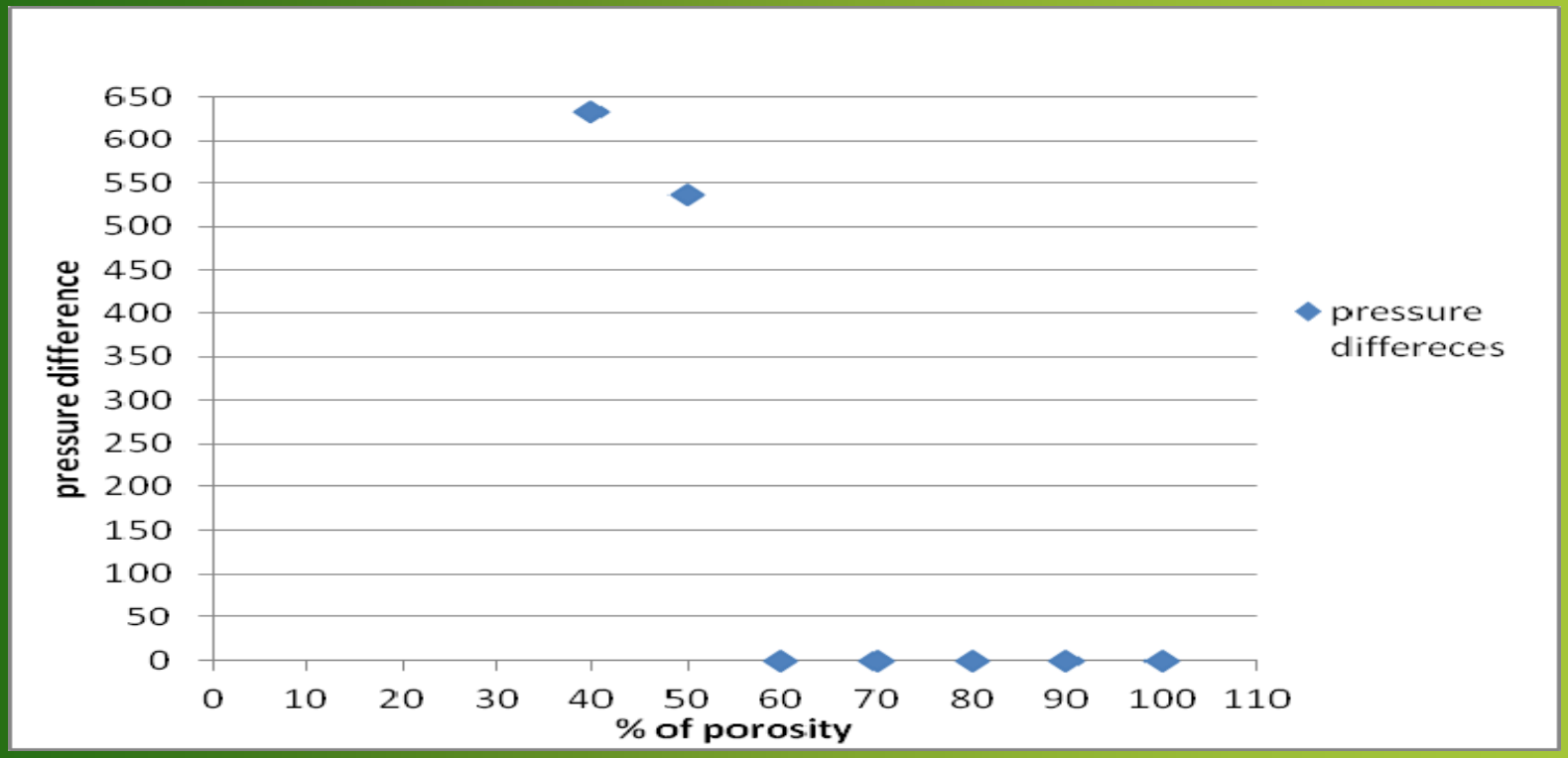


Pressure Contours

- The pressure contour is for a case of 50% porosity
- Contour 1&2 represents before entering and after exiting the porous region
- Pressure drops at the exit of the porous region



Average Pressure Difference between Contours at different porosities



- Pressure difference increases as the porosity decreases
- Up to 60% porosity, the pressure drop is negligible
- Pressure drop is increased sharply below 60% porosity

Conclusions

- SEM and TEM characterized scattered and overlapped PTNTs and PEI-PTNTs as tubular nanostructures for 130°C and 140°C
- Both ends of the nanotubes are open. The outside diameter of nanotubes were observed to be between 6-8 nanometers (nm) with length of 200-400 nanometers (nm) as confirmed through FE-SEM and TEM
- The XRD characterizations discovered that no remarkable peak shift happened before and after PEI impregnation
- Steady CO_2 adsorption is observed with the PEI-PTNTS samples
- Pressure contour has been expressed for solid porous materials used in CO_2 capture

Future Studies

- Optimize PTNTs from the hydrothermal process
- Develop other PEI varied adsorbents using different molecular weights of PEI
- Porosity measurements will be taken of samples
- Pressure drop within the carbon capture device will be calculated with further decrease in porosity and with grid refinement

Acknowledgements

- This work is supported by the Department of Energy, National Energy Technology Laboratory Grant, DE-FE0023040 and partially by
- Some of the personnel are supported through The National Science Foundation (NSF) through the Center for Energy and Environmental Sustainability (CEES) a NSF CREST Center, Award #1036593
- The Investigators would like to thank
  - Texas A&M Imaging Center
  - Dr. Hylton McWhinney and Mr. Tony Grady; Department of Chemistry, Prairie View A&M University

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Questions?