Evidence for Nucleation and Growth Mechanisms for CO_2 Capture with Impregnated PEI Sorbents

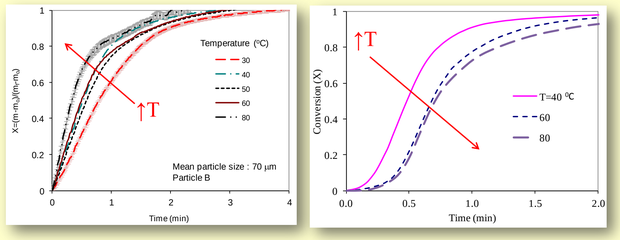
Larry Shadle - U.S. Department of Energy, National Energy Technology Laboratory

the ENERGY lab

Website: www.netl.doe.gov
Customer Service: 1-800-553-7681

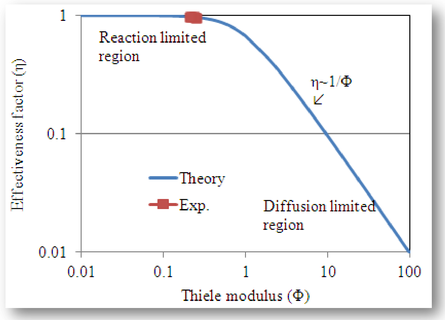
Temperature Dependence on Rate

DEA *PEI*



- **Clay impregnated with diethanolamine (DEA) demonstrates typical temperature dependence**
- **PEI has negative temperature dependence**
  - DEA: Rate increases with T
  - PEI: Rate Decreases with T

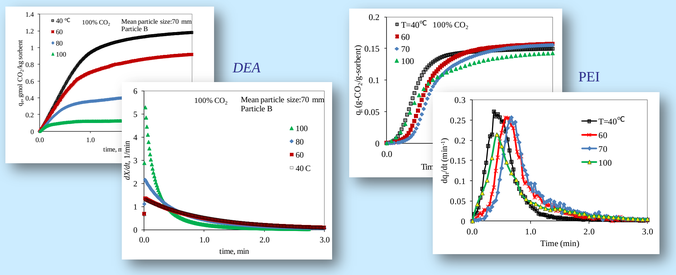
Theile Modulus Analysis



General Theile Modulus is the ratio of the kinetic rate to the diffusion rate

$$\emptyset = \frac{d_p}{6}\left[\frac{(n+1)\,k^n\,RT}{2D_A^{eff}}P_{A,i}^{n-1}\right]^{1/2}$$

Kinetic Data Type



- **Clay impregnated with diethanolamine (DEA)demonstrates typical decreasing rate…Maximum rate at time=0s**
- **PEI has maximum rate at time>0s**
  - DEA: Max Rate at initial time (classical Arrhenius 1st order kinetics)
  - PEI: Max Rate at later time (S-shape, diffusion controlled kinetics)

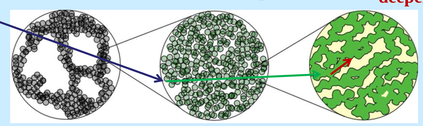
Monazam et al. (2010) *AIChE Journal*, 57(11) p. 3153-3159.

Monazam, et al. (2012)…Absorption Kinetics…by Solid Supported Amine Sorbent, AIChE Journal.

Diffusion to PEI surface - FAST

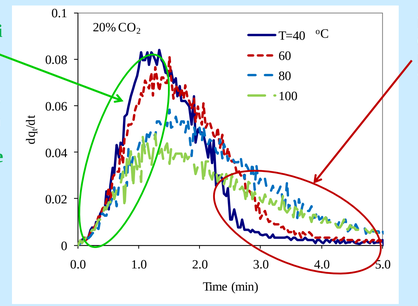
Adsorption kinetics– rate controlling for PEI for surface at the mouth of mesopores

Transport of CO_2 to deeper PEI multi-layers

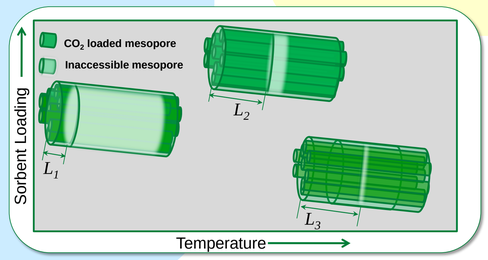


Adapted from Mebane et al. (2011) International Pittsburgh Coal Conference, Pittsburgh, PA, Sept. 12-14.

Product nuclei formation thermo-dynamically favored at low T - adsorption kinetic controlled rate

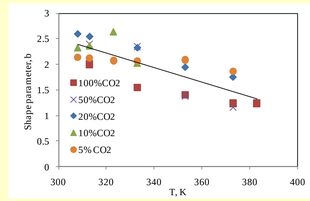


Nuclei growth – CO_2 transport to PEI multi-layers increases with T

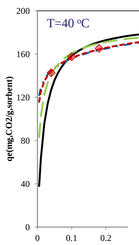


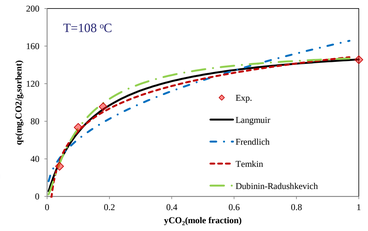
Diffusion Controlled Growth Rate

- **Product Nuclei formation was reduced at higher T**
  - Increased reverse reaction rates
  - Heterogeneous sites tend towards homogeneous
- **Nuclei growth increased with increased T**
  - **Diffusion controlled growth theory:**
  - b = 1.5 for zero nucleation rate
  - b = 1.5 to 2.5 for decreasing nucleation rate
  - b > 2.5 for increasing nucleation rate
- **Overall Nucleation and Growth Rate:** $\frac{dX}{dt} = 0.42e^{\frac{662}{T}} y_{CO_2}^{0.693}(1-X)\sqrt{-\ln(1-X)}$



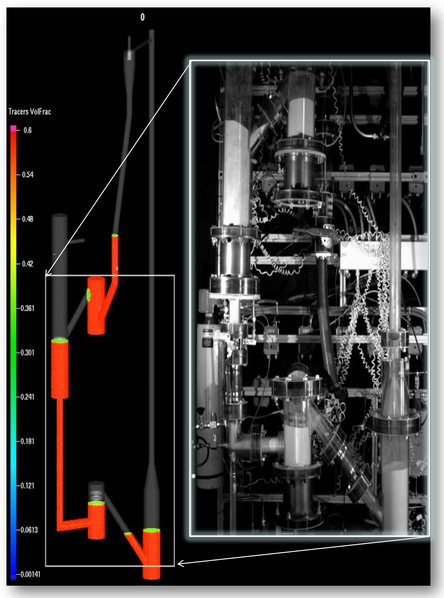
Absorption Isotherms

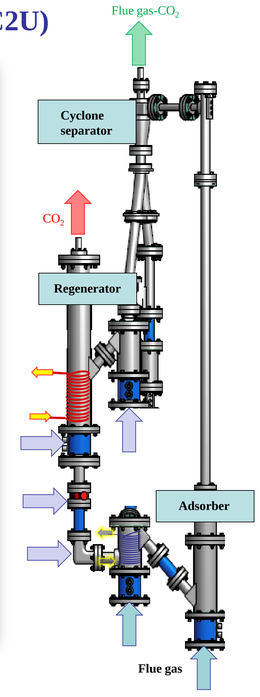




- **Temkin isotherm fits best overall**
- **Langmuir isotherm fits only at highest T**

Carbon Capture Unit (C2U)





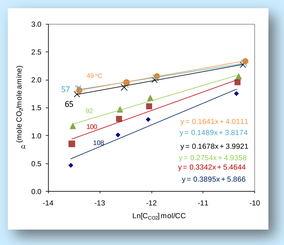
Adsorption Isotherms Show Change in Mechanism

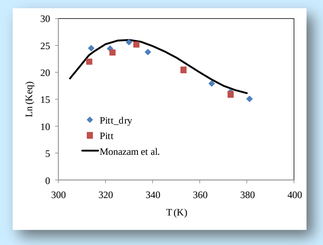
$$\alpha_e = \frac{RT}{-\Delta H}\ln(K_{eq}C_{CO_2}) = B\ln(K_{eq}C_{CO_2})$$

$$\alpha_e = B\ln(K_{eq}) + B\ln(C_{CO_2})$$

$$\ln(K_{eq}) = B\ln(K_{eq})/B$$

Temkin's isotherm model is based upon heterogeneous surface:
The heat of adsorption of all molecules in the layer decreases linearly with coverage.





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