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NETL 2012 Conference on Multiphase Flow Science

A Reaction Rate Model for Carbonation of a Regenerable MgO-based Sorbent

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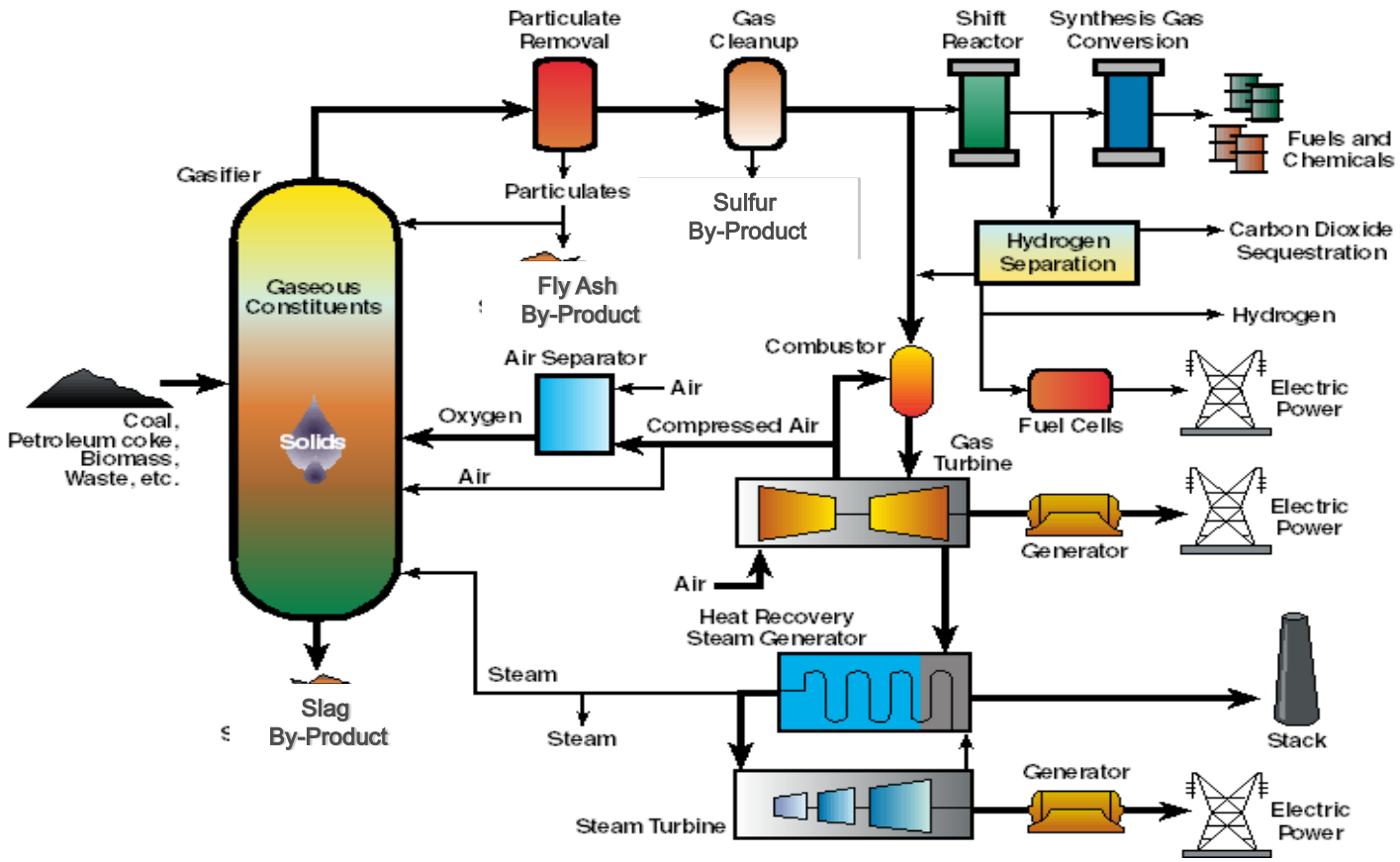
Background

Gasification-Based Energy Production Systems



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Regenerable MgO-Based Sorbent

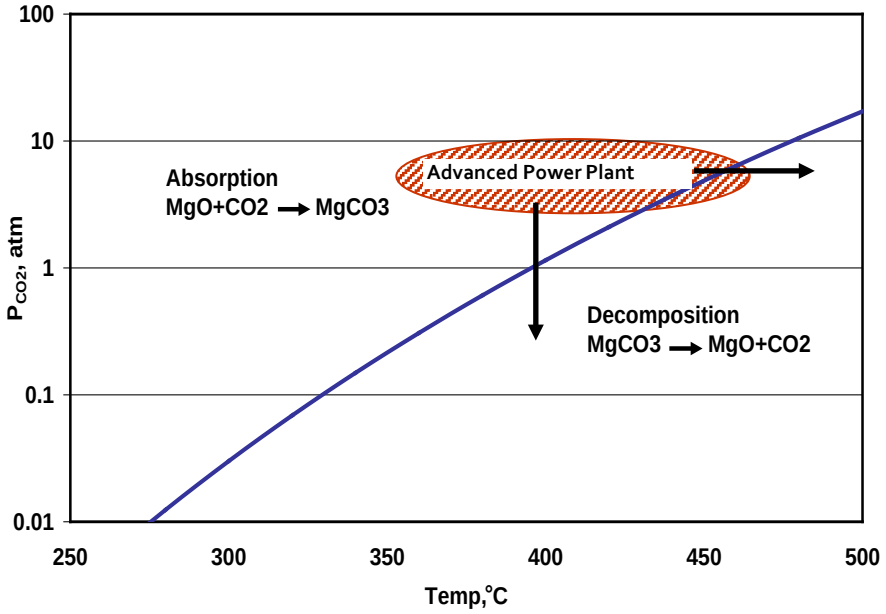
- **CO_2 Capture Reactions**

  $MgO + CO_2 \Rightarrow MgCO_3$ **Absorption**

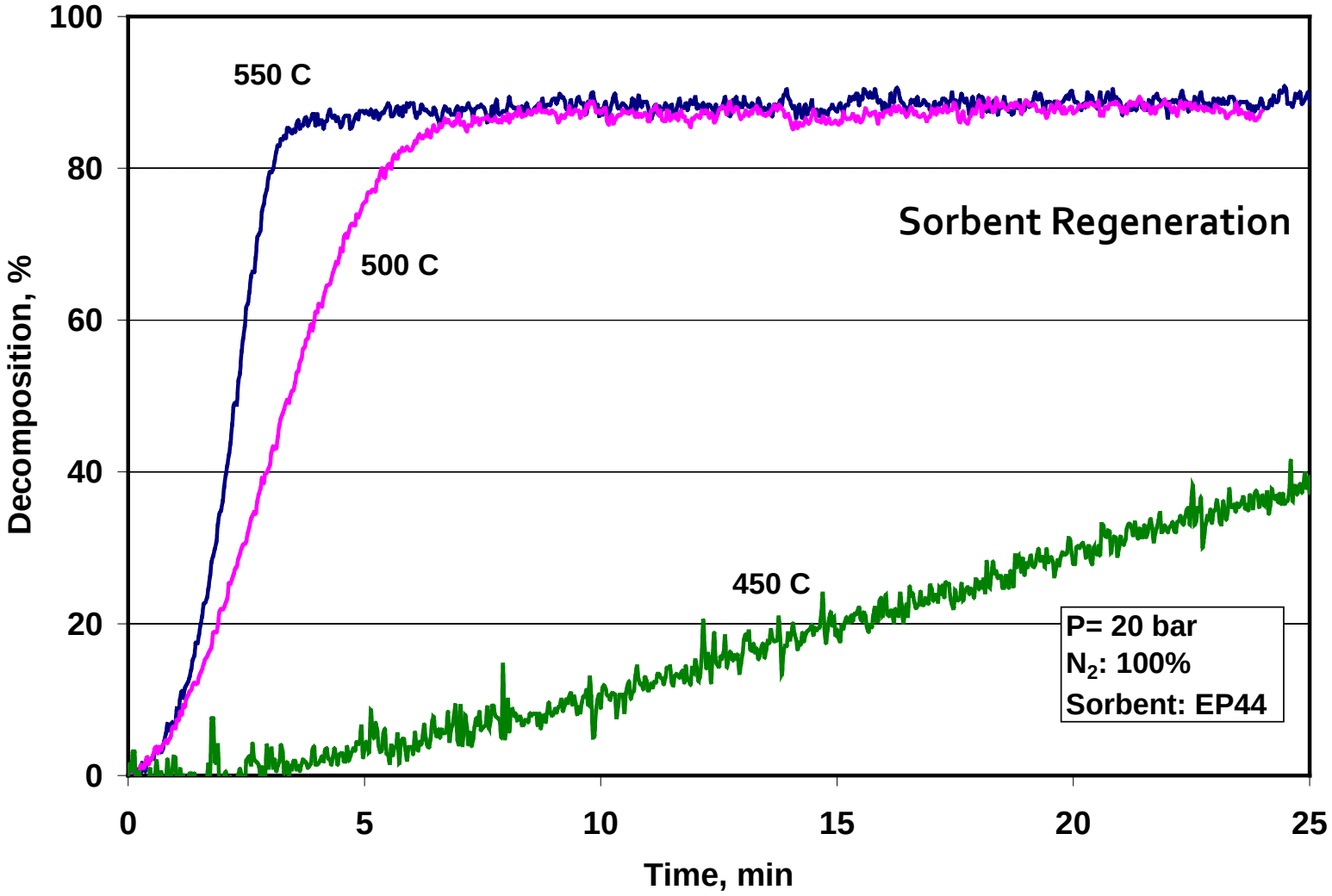
  $MgO + CO_2 \Rightarrow MgCO_3$ **Regeneration**

- **Water-Gas-Shift Reaction**

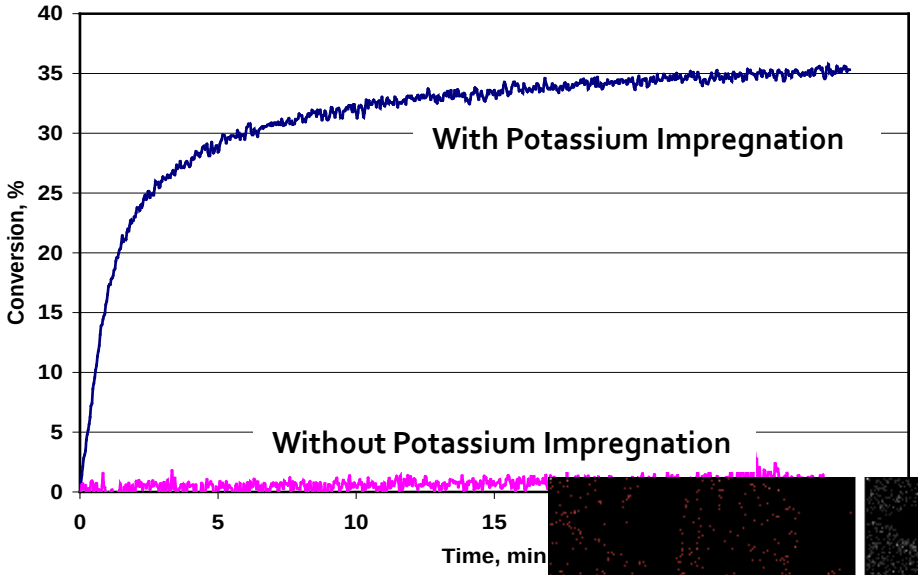
  $CO + H_2O \Rightarrow CO_2 + H_2$

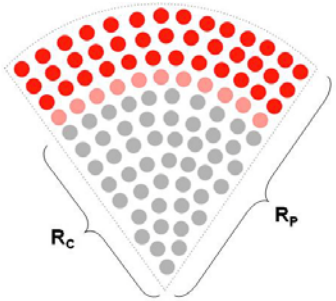


Experiments:CO2 Capture & Sorbent Regeneration

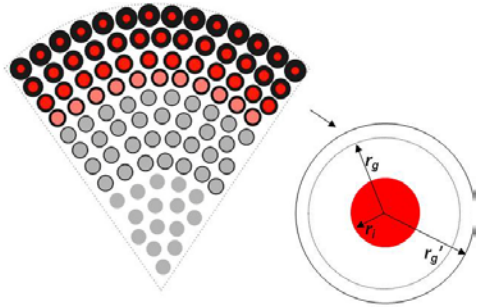


Two-Zone Expanding Grain Reaction Rate





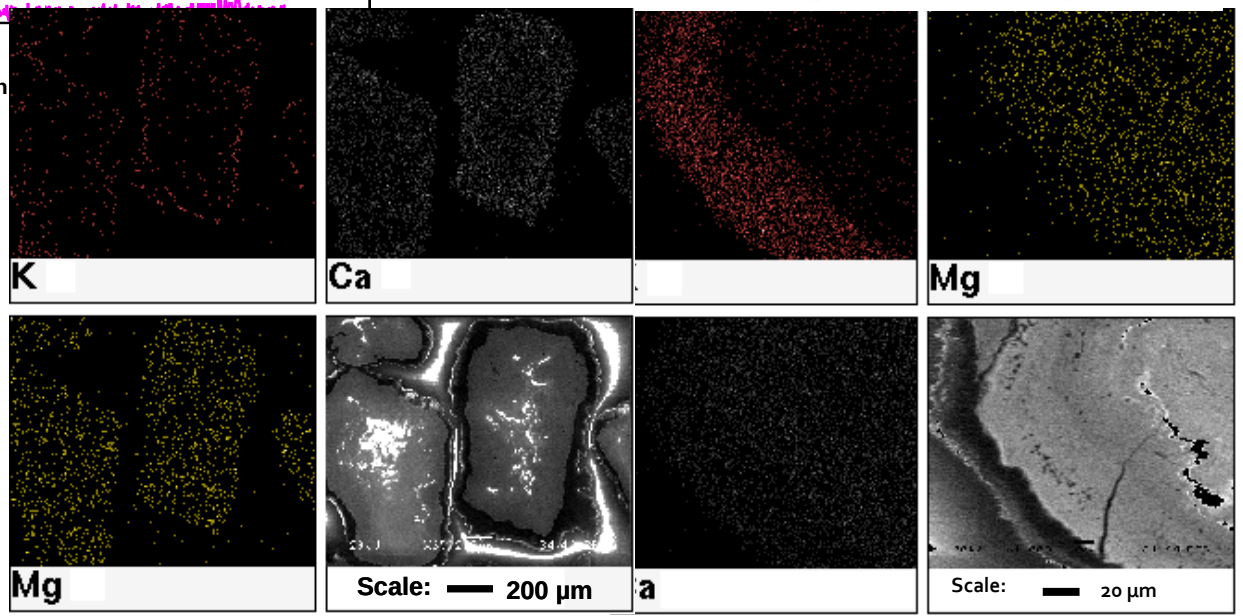
a: Non-Reacted Particle



b: Reacted Particle

R_P: Radius of Particle
R_C: Radius of Inner Layer

r_i : The radius of the unreacted core of the grain
r_g: Initial radius of the grains
r_g': The radius of the expanded grain



Governing Equations

- **Mass balance around the particle for reactant gas (i.e. CO_2)**

$$\frac{1}{R^2}\frac{\partial}{\partial R}\left(D_e R^2 \frac{\partial C_R}{\partial R}\right) - 3(1-\varepsilon)\frac{r_i^{\,2}}{r_g^{\,3}} k\left(C_i - C_e\right)^n = 0$$

B.C.: (a) $\frac{\partial C_R}{\partial R} = 0$ @ $R = o$ (b) $C_g = C_R$ @ $R = R_p$

- **Mass balance around the grain for reactant gas (i.e. CO_2)**

$$D_g\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_g}{\partial r}\right)\right] = 0$$

B.C.: (a) $C_g = C_R$ @ $r=r_g'$ (b) $D_g\left(\frac{\partial C_g}{\partial r}\right) = k.\left(C_g - C_e\right)^n$ @ $r=r_i$

- **Radius at Reaction interface**

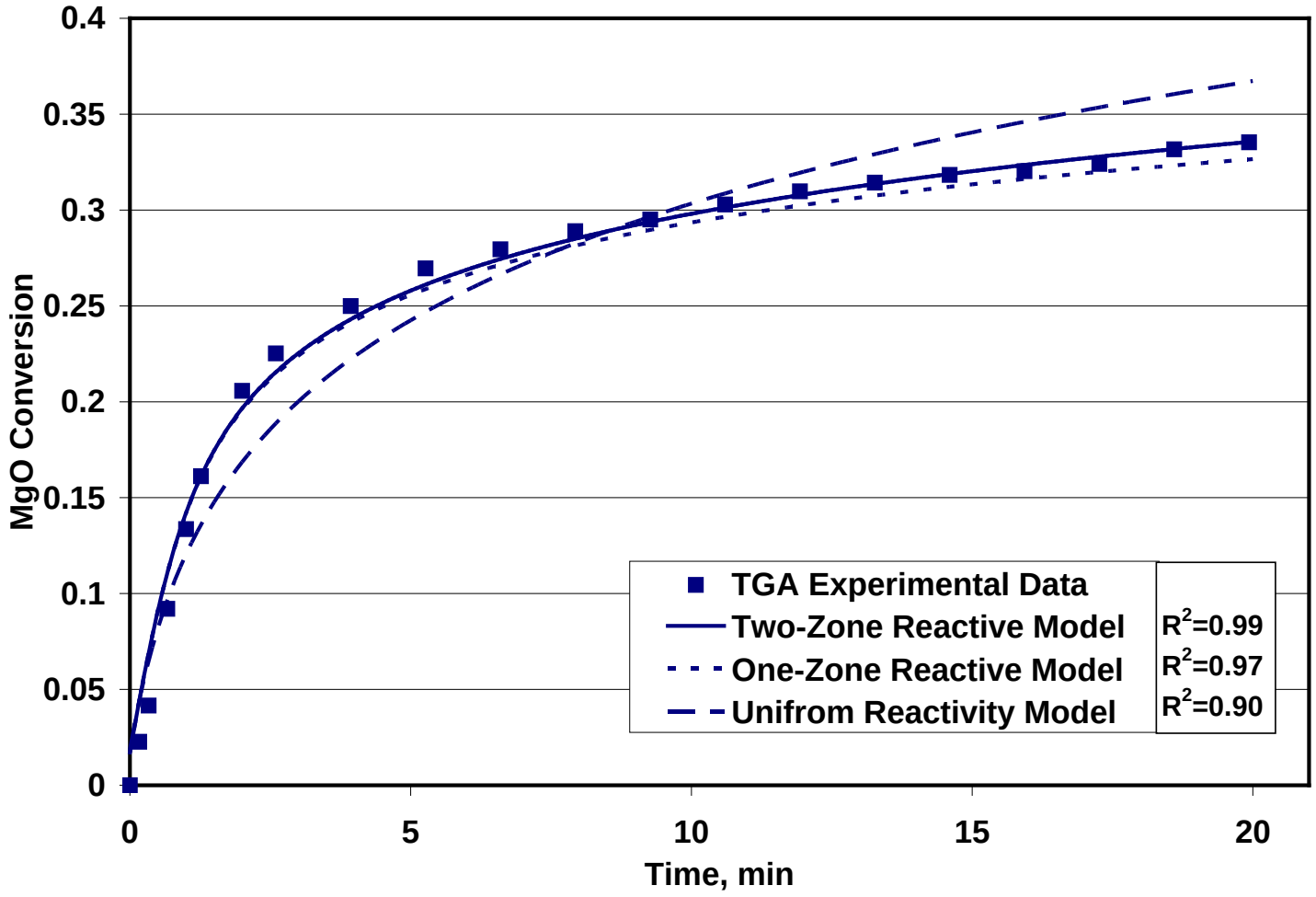
$$\frac{dr_i}{dt} = -\frac{k}{\rho_{MgO}}\left(C_g - C_e\right)$$

I.C.: $r_i = r_g$ @ $t=o$

- **Overall Conversion of the particle**

$$X_{overall} = \frac{3}{R_0^3}\int_0^{R_0} R^2.\left(1 - r_i^3 / r_g^3\right)dR$$

Model Fit to Experimental Data



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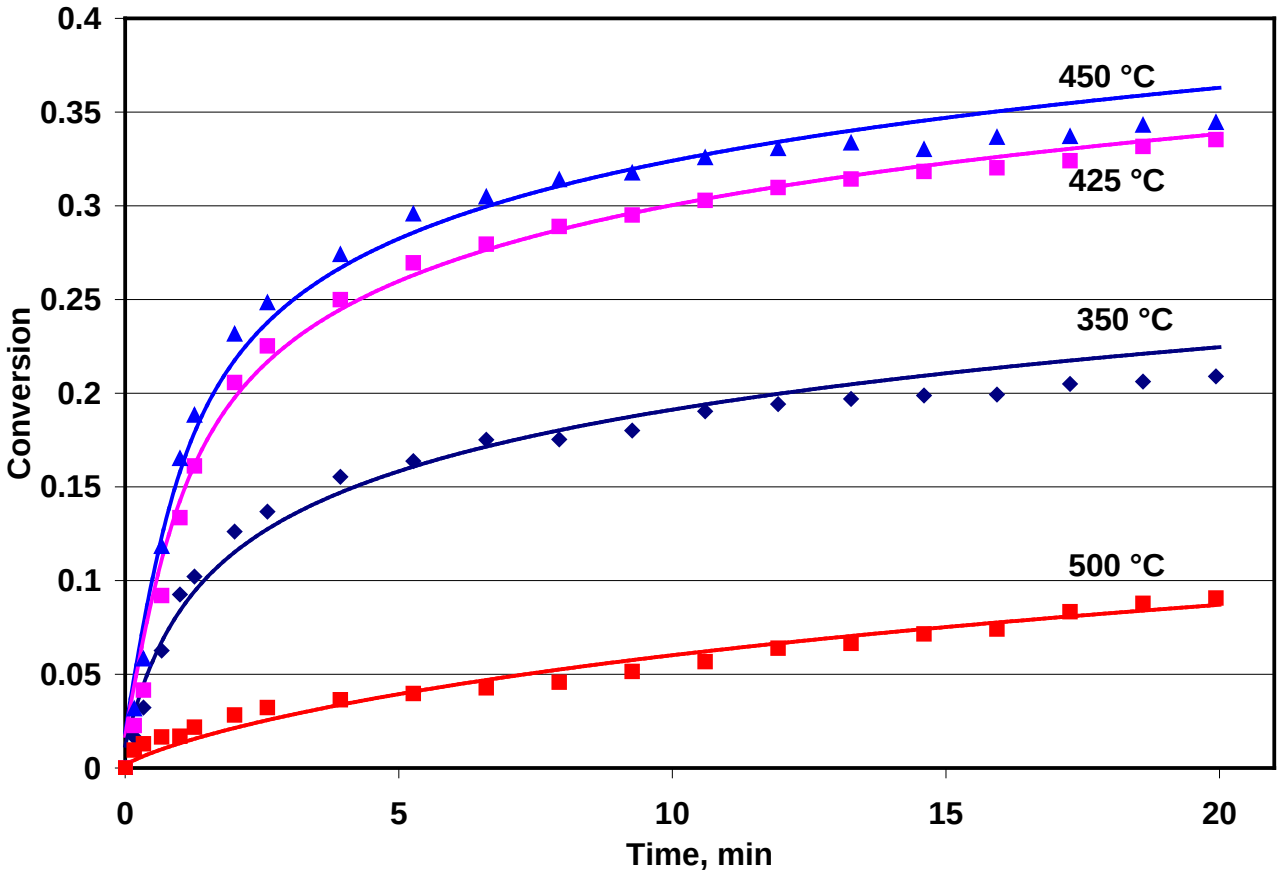
Model Fit to Experimental Data



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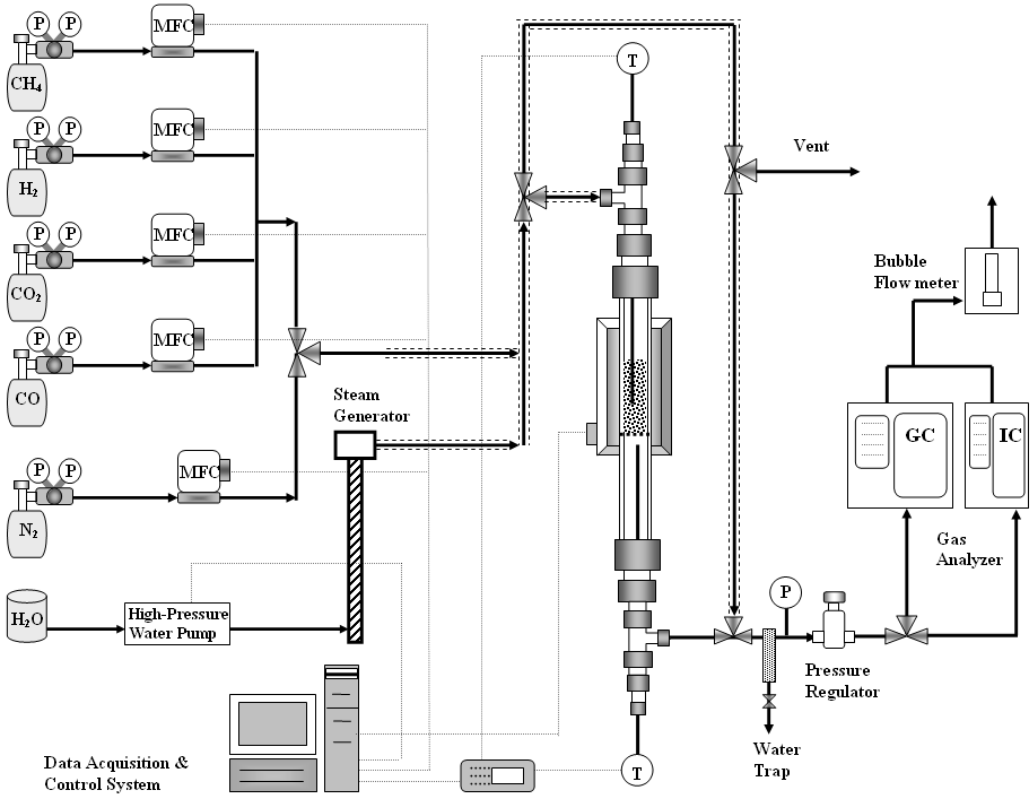
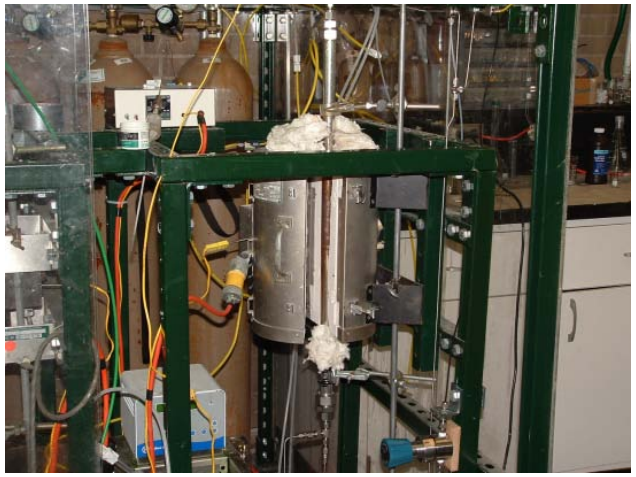
Packed-Bed Tests





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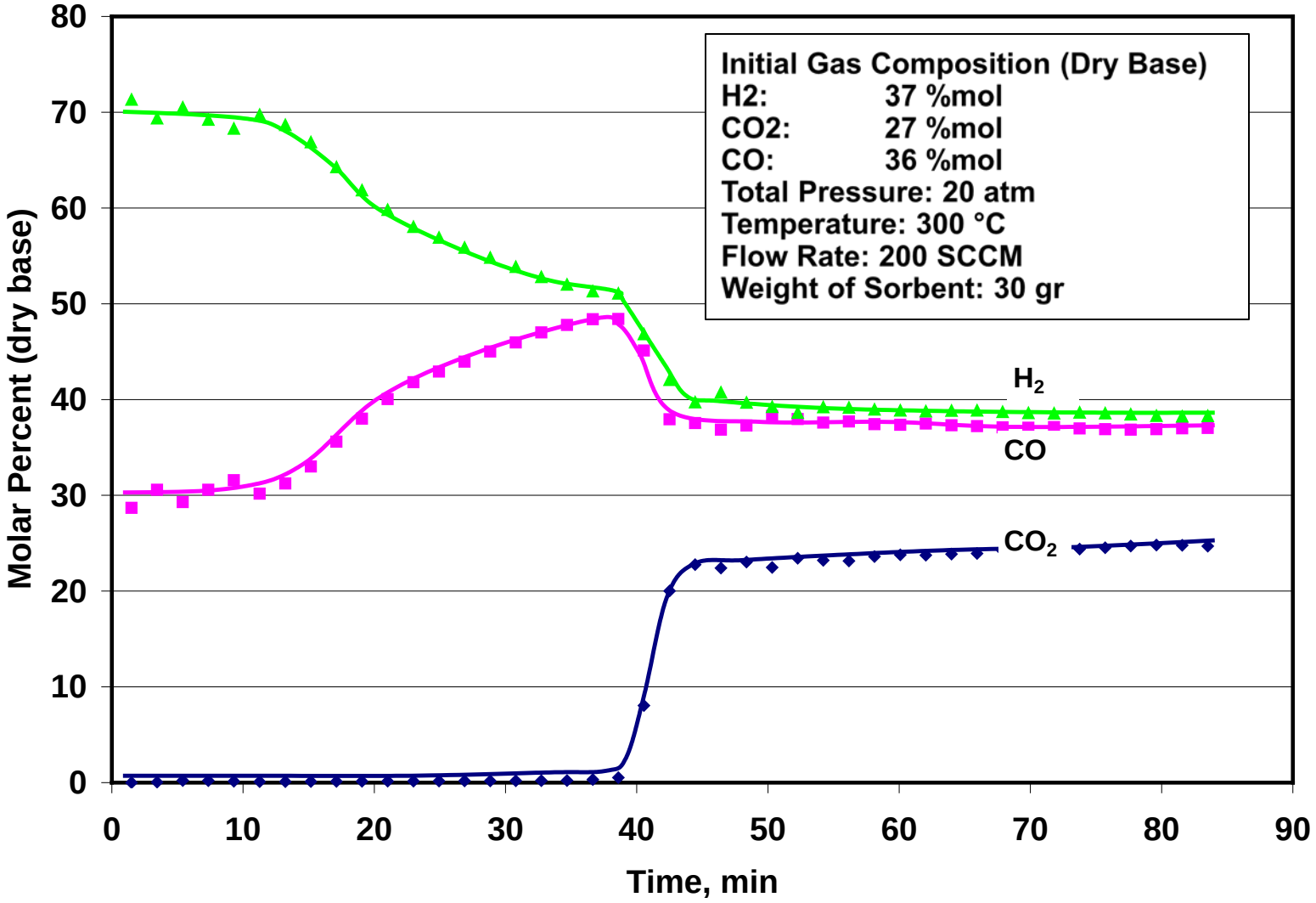
Packed-Bed Results



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Numerical Modeling

Species Conservation Equations

- For heterogeneous reactive systems: Conservation of species in each phase

$$\frac{\partial}{\partial t}(\varepsilon_g \rho_g y_i) + \nabla.(\varepsilon_g \rho_g v_g y_i) = R_j$$

- R_j is the heterogeneous reaction rate

- An Ideal reaction model for CFD applications should:
  - Capture the real physics
  - Not increase the CPU time significantly
  - Be easy to implement in CFD codes

- Grain Model:
  - Captures the real physics
  - Is an implicit model (needs 2 additional equations)
  - Increases CPU time
  - Is not easy to implement in commercial CFD codes

Governing Equations

- **Mass balance around the particle for reactant gas (i.e. CO_2)**

$$\frac{1}{R^2}\frac{\partial}{\partial R}\left(D_e R^2 \frac{\partial C_R}{\partial R}\right) - 3(1-\varepsilon)\frac{r_i^{\,2}}{r_g^{\,3}} k\left(C_i - C_e\right)^n = 0$$

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- **Radius at Reaction interface**

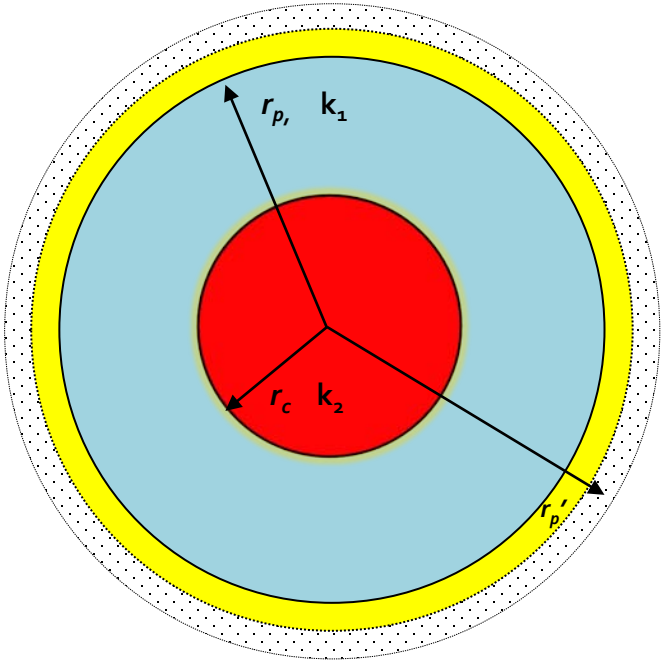
$$\frac{dr_i}{dt} = -\frac{k}{\rho_{MgO}}\left(C_g - C_e\right)$$

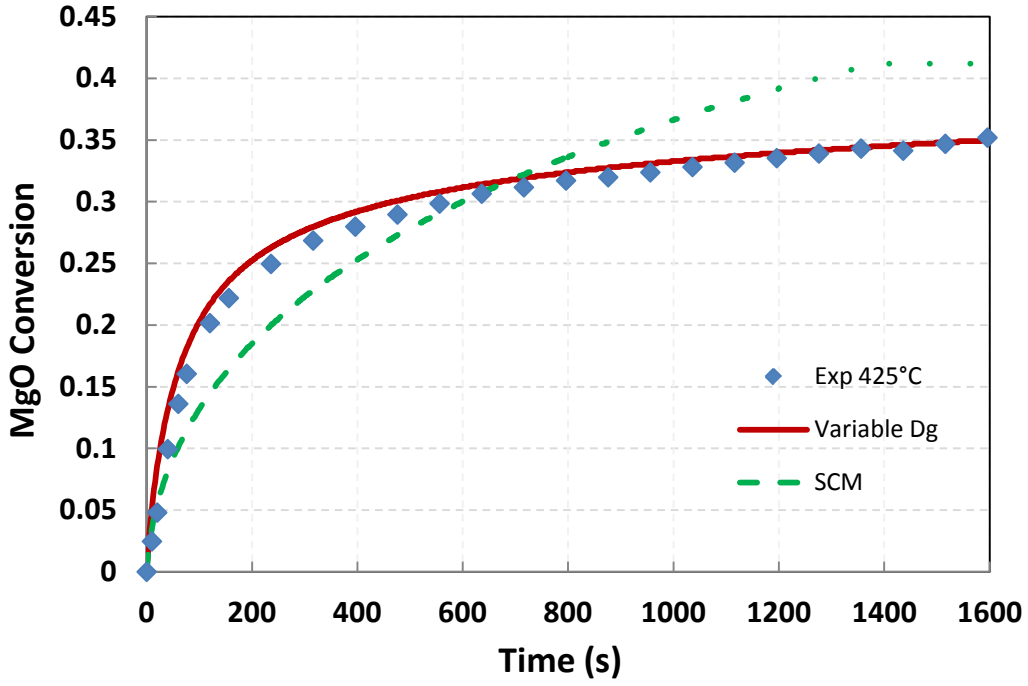
I.C.: $r_i = r_g$ @ $t=o$

- **Overall Conversion of the particle**

$$X_{overall} = \frac{3}{R_0^3}\int_0^{R_0} R^2.\left(1 - r_i^3 / r_g^3\right)dR$$

Two-Zone Variable Diffusivity Shrinking Core Model with Expanding Product Layer





r_c : Radius of the low reactive zone (k_2)
r_p : Initial radius of the particles
r_p': Radius of the expanded particle

Gas Film
Product Layer
Highly Reactive Zone (k_1)
Low Reactive Zone (k_2)

** Abbasi et al., Fuel , 2012*

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Key Assumptions

1- There are two distinct reactive zones inside the particles

2- Process is controlled by both surface reaction and product layer diffusion

3- There is an Expanding product layer $r_p = r'_p \sqrt[3]{(1-X)+ZX}$

4- Effective product layer diffusivity is a function of conversion due to expansion (and increased tortuosity)

$$D_g = D_{g0}(-\alpha X^{\beta})$$

5- Intrinsic reaction rate is Arrhenius type $k_s = k_{s0}\exp(-\frac{E}{RT})$

Governing Equations

$$-\frac{dr_i}{dt}=\frac{(C_b-C_e)/N^o_{MgO}}{\underbrace{\frac{r_i^{\,2}}{r_p k_g}}_{\text{film}}+\underbrace{\frac{(r_p-r_i)r_i}{r_p D_g}}_{\text{Product Layer}}+\underbrace{\frac{1}{k_s}}_{\text{Reaction}}}$$

$$\Longrightarrow \quad \frac{dr_i}{dt}=-\frac{k_s}{N^o_{MgO}}\left[\frac{(C_b-C_e)}{1+\frac{k_s}{D_g}r_i\left(1-\frac{r_i}{r_p'}\right)}\right]$$

$$X=1-\left(\frac{r_i}{r_p}\right)^3 \quad \Longrightarrow \quad dr_i=-\frac{r_p}{3}(1-X)^{-\frac{2}{3}}dX$$

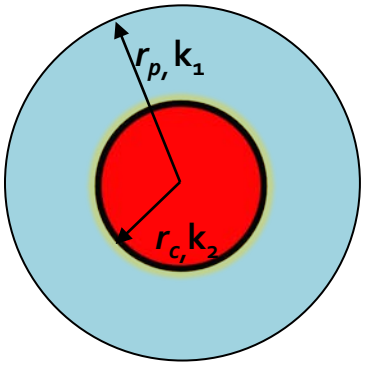
$$r_p=r_p'\sqrt[3]{(1-X)+ZX}$$

$$Z=\frac{\rho_{product}\cdot M_{react}}{\rho_{react}\cdot M_{product}}$$

$$D_g=D_{g0}(-\alpha X^{\beta})$$

$$\frac{dX}{dt}=-\frac{\frac{3}{r_p}\frac{k_s}{N^o_{MgO}}(C_b-C_e)(1-X)^{\frac{2}{3}}}{1+\frac{k_s}{D_g}r_p(1-X)^{\frac{1}{3}}\left(1-\sqrt[3]{\frac{1-X}{1-X+XZ}}\right)}$$

$$k_s=\begin{cases}k_1 & for\ \ r\geq r_c\\ k_2 & for\ \ r<r_c\end{cases}$$



Validity of Shrinking Core Model

Thiele Modulus

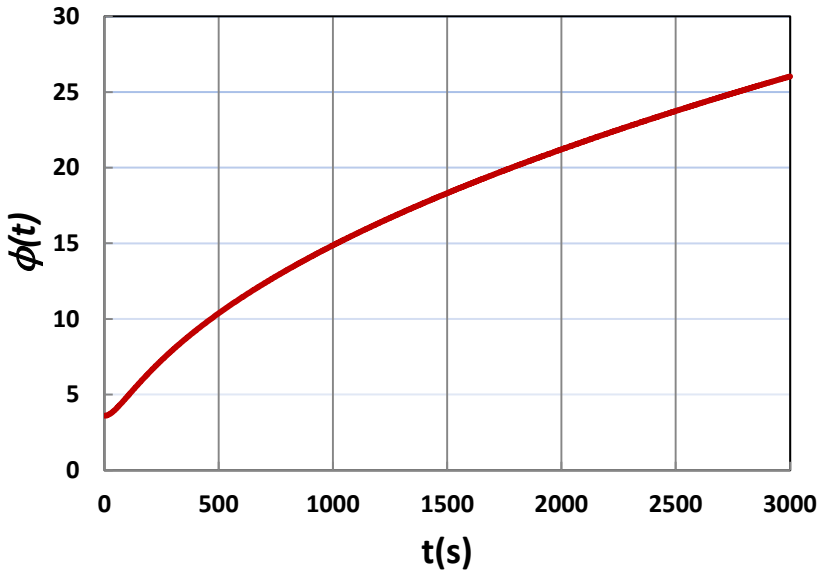
$$\Phi = \sqrt{\frac{Ka^2}{D}} \quad \frac{reaction}{diffusion}$$

$\Phi \simeq 0.01$ *Reaction is controlling*

$\Phi \simeq 100$ *Diffusion is controlling*

Shrinking core model is applicable in an intermediate regime

Thiele Modulus in our study



Onischak and Gidaspow, "Separation of Gaseous Mixtures by Regenerative sorption on Porous Solids. Part II: Regenerative separation of CO_2", Recent Developments in Separation Science, ed. N. Li, 1972

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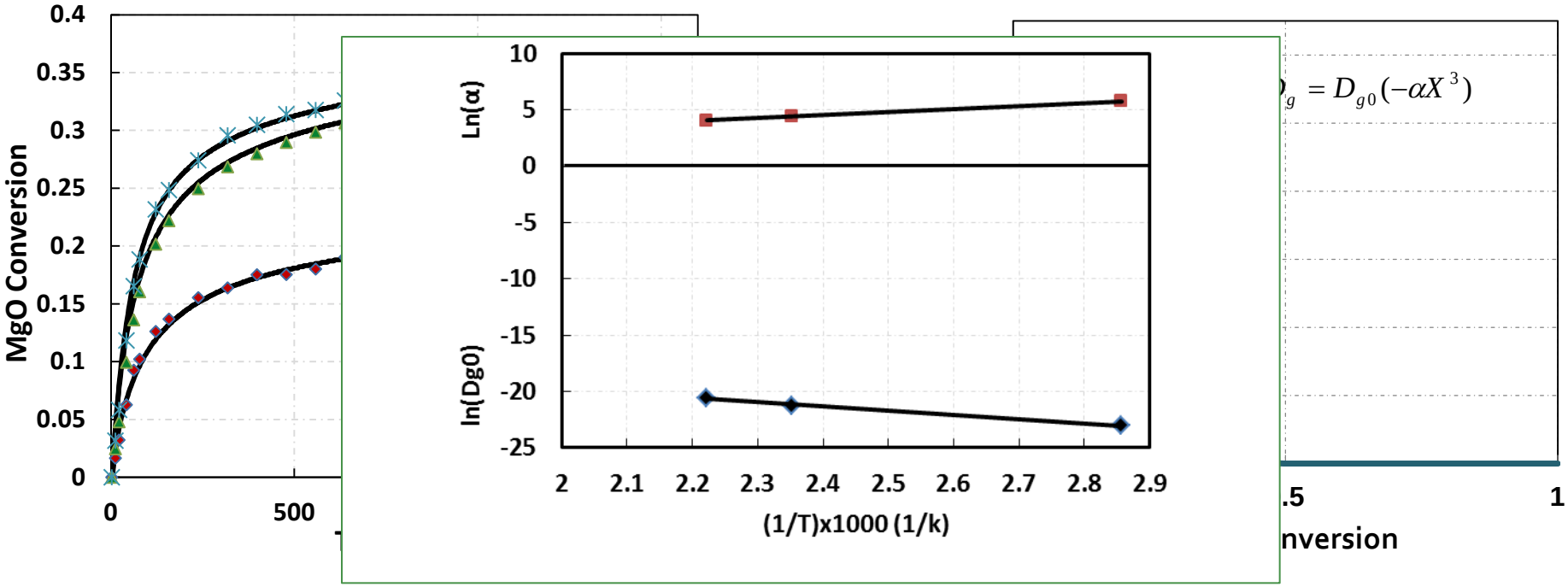
Reaction Model vs TGA Experimental Date



Model Parameter	Without Steam			With Steam
	350 °C	425 °C	450 °C	425 °C
D_{g0}	1.1E-10	6.0E-10	1.2E-9	2.1E-9
α	3.5E+2	8.1E+1	5.7E+1	4.6E+1
β	3	3	3	3

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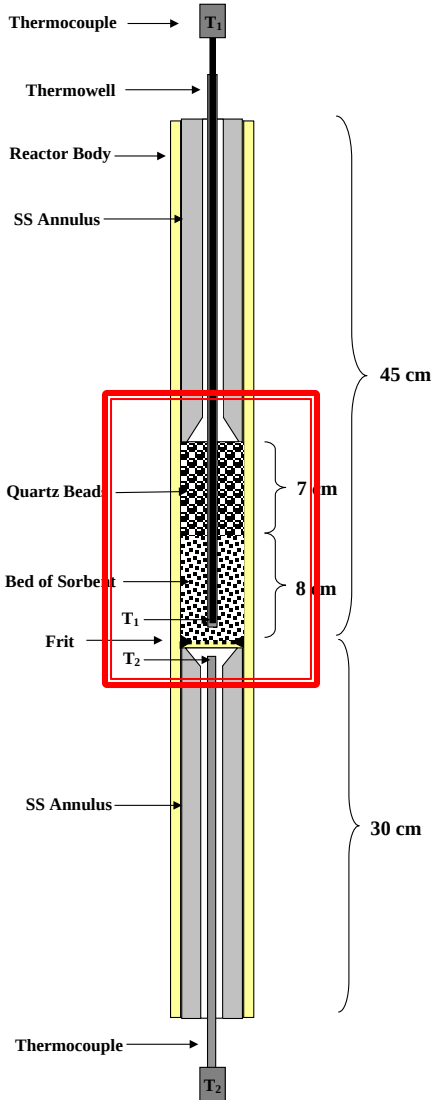
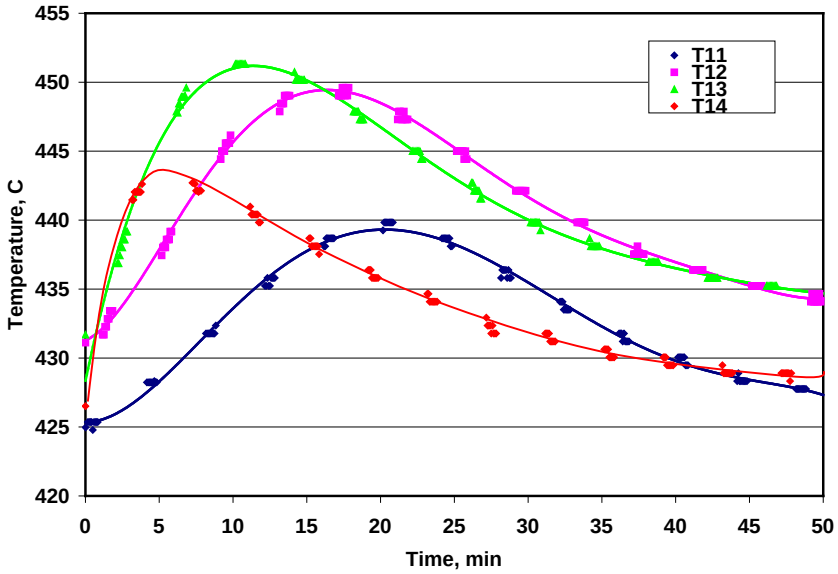
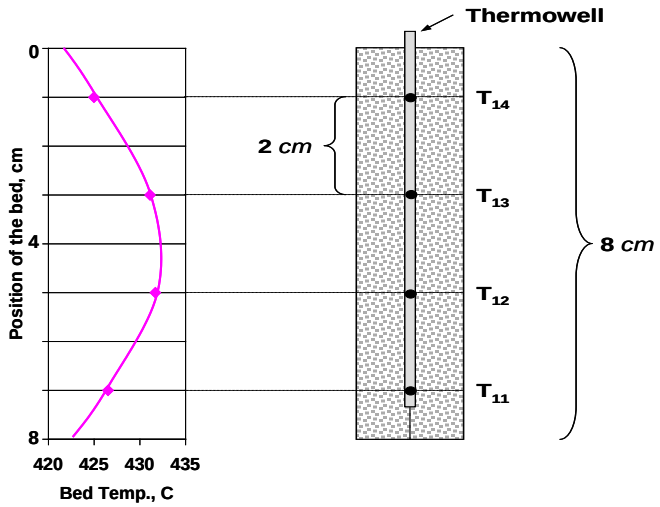
Packed-Bed Model







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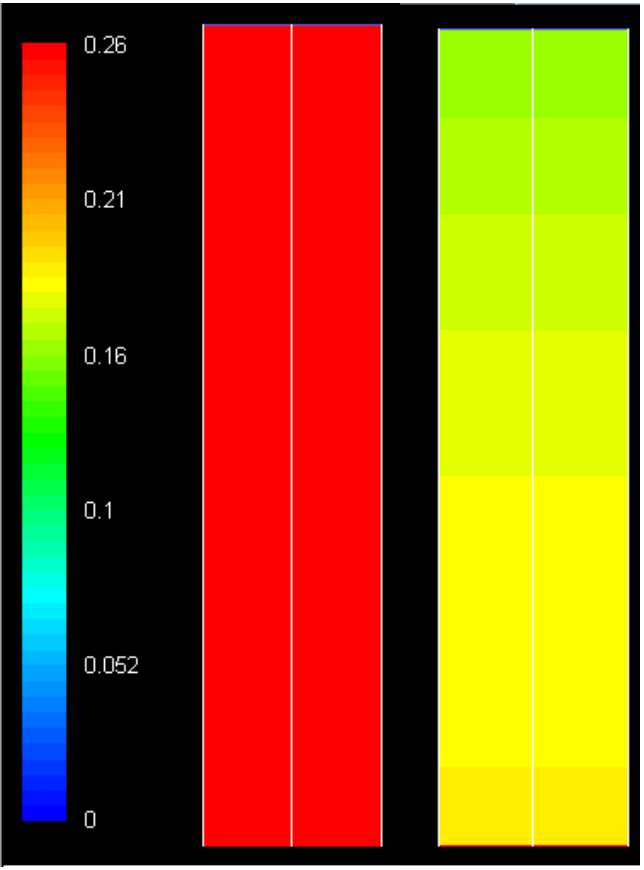
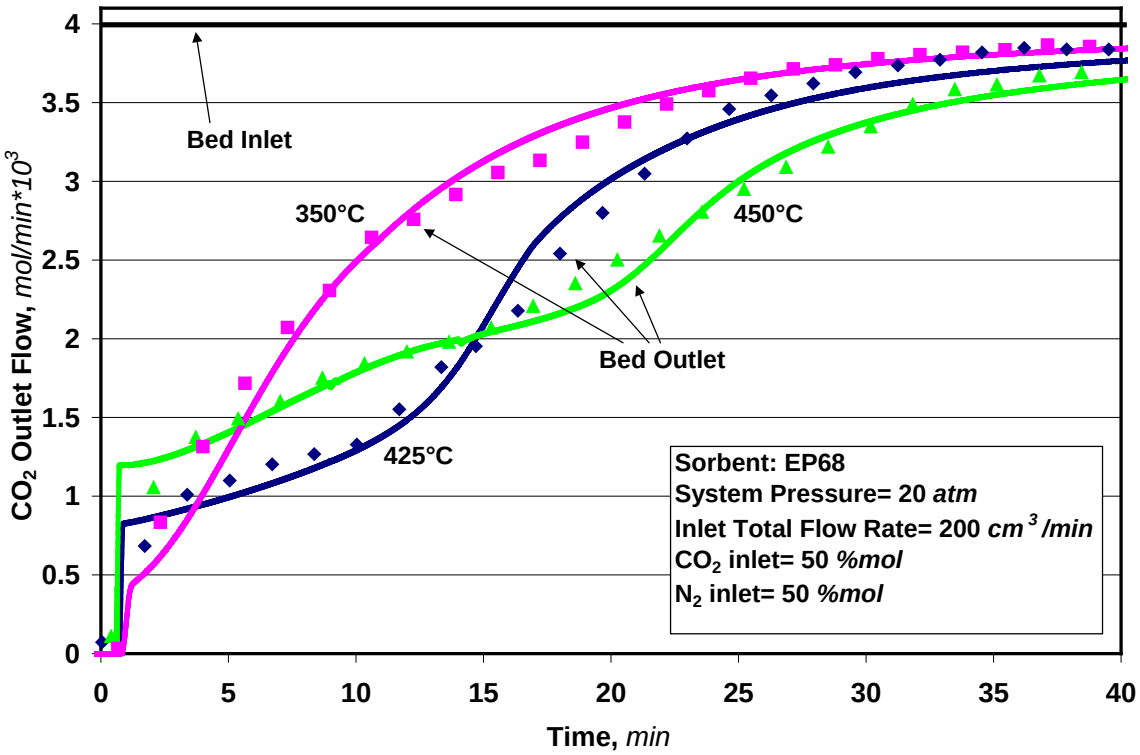
MgO Mass Fraction in the Packed-Bed

@ 425°C start 50 min





CO_2 Absorption Breakthrough Curve at Different Operating Temperatures

Summary

- An explicit reaction rate model has been developed which is able to describe the reaction rate data obtained in TGA.
- The reaction model is suitable for CFD applications due to its explicit formulation.
- The reaction model was validated vs the experimental data obtained in pack-bed.
- Future work includes:
  - Application of the CFD and reaction models in simulations of a bubbling bed and circulating fluidized bed reactors.
  - Modeling of Regeneration reaction
  - Modeling of the process

Acknowledgement

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