

A model for the uptake of a gaseous compound by a
particulate sorbent: the case of carbon dioxide
sequestration with dolomite

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1 Description of the Zecomix project

2 The TSSER system

3 Particle model description

4 Results and discussion

5 Conclusions

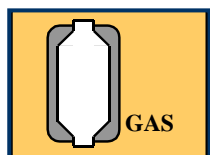
1. Description of the Zecomix concept

The ZECOMIX Project is aimed at studying an integrated process that produces both hydrogen and power from coal with high efficiency and zero emission.

This activity is developed in a larger framework of Italian Public Research Plan project as third line named: “Integrated Hydrogen and Power Production adopting Hydrogasification of Coal ”

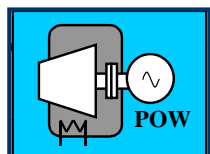


The construction of a ZECOMIX experimental facility at ENEA Casaccia Research Center, has been recently funded by Ministry of Research for developing hydrogen technology.



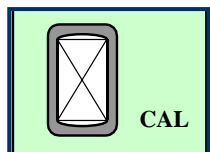
Hydrogasification of coal

Reforming, Shift and Decarbonization of Syngas by means of CaO based sorbents

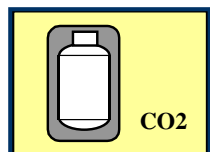


Syngas Combustion with Oxygen supplied by the ASU

Power production in Advanced Steam Cycle

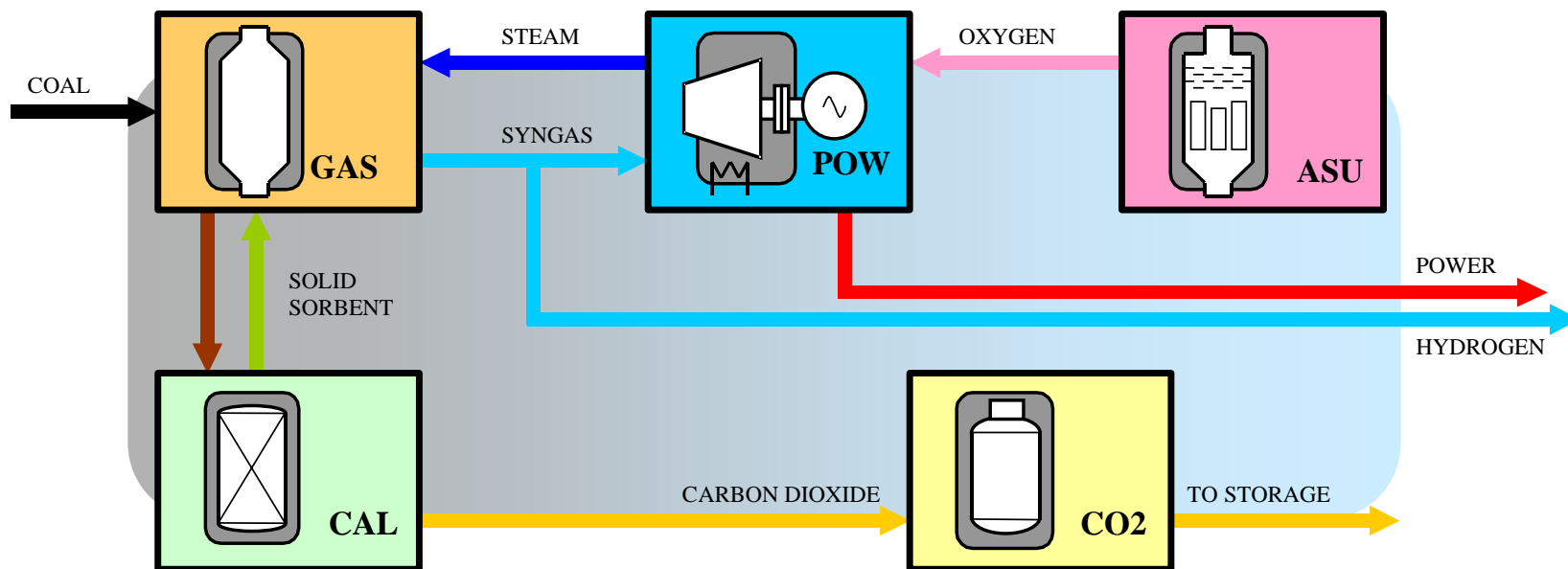


Solid sorbent Regeneration with Calcination Process



Carbon Dioxide Drying and Compression

1. Integration of Main Areas



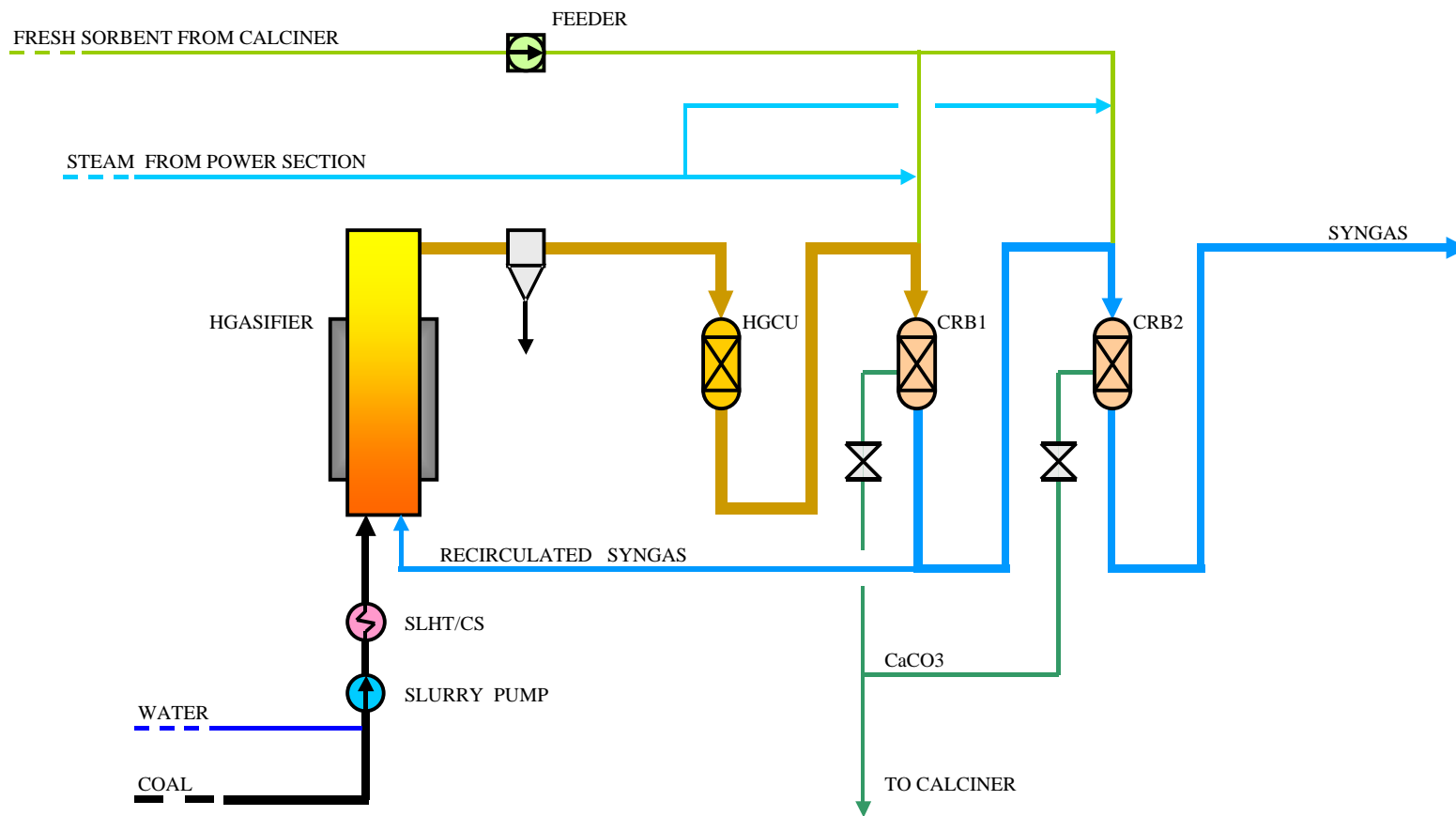
Main areas : **GASIFICATION**

POWER PRODUCTION

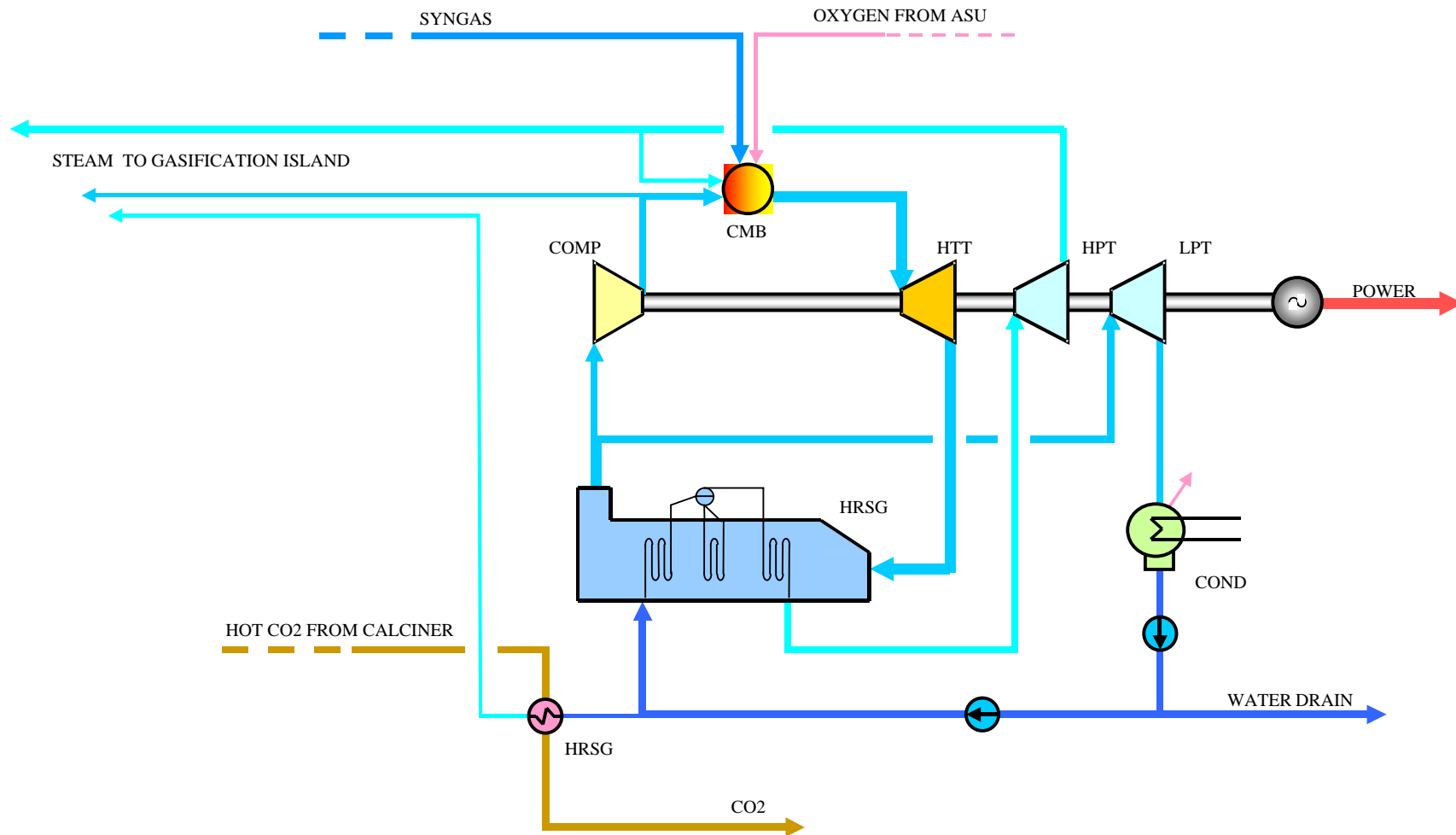
SORBENT CALCINATION

CO2 DRYING & COMPRESSION + Air Separation Unit

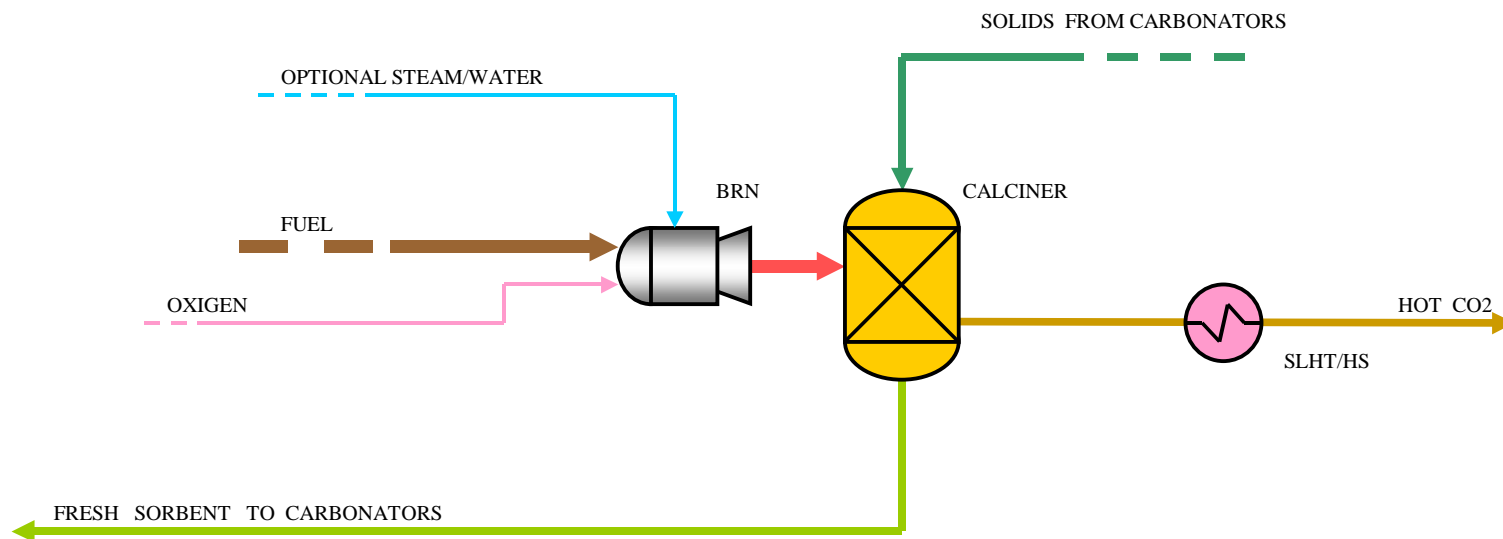
1. Gasification/decarbonization island



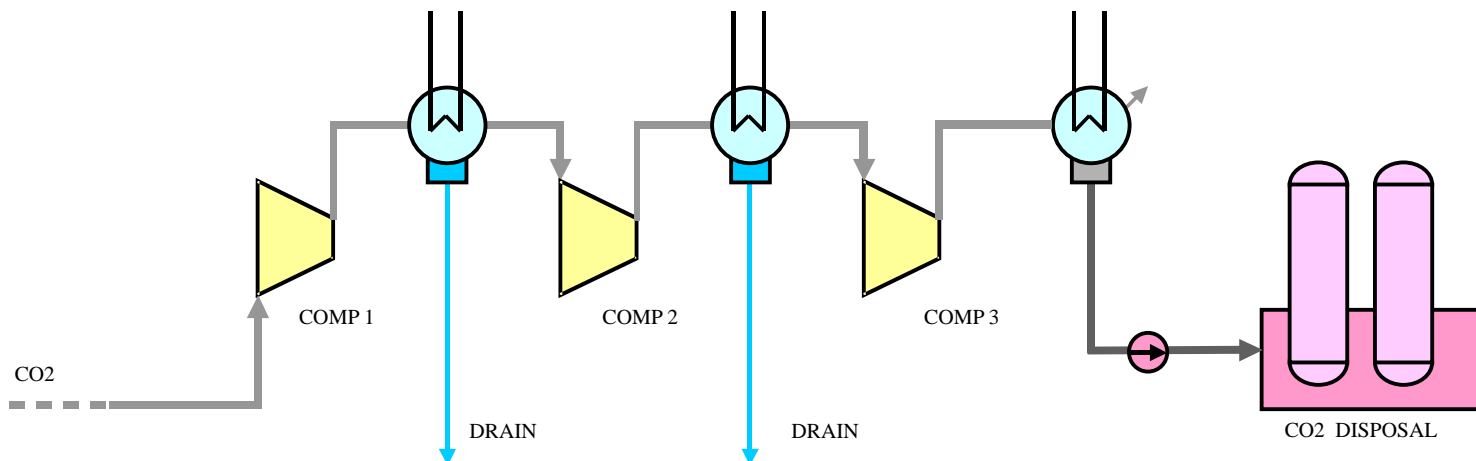
1. Power Section



1. Calcination Unit



1. Carbon Dioxide Drying and Compression



1 Description of the Zecomix concept

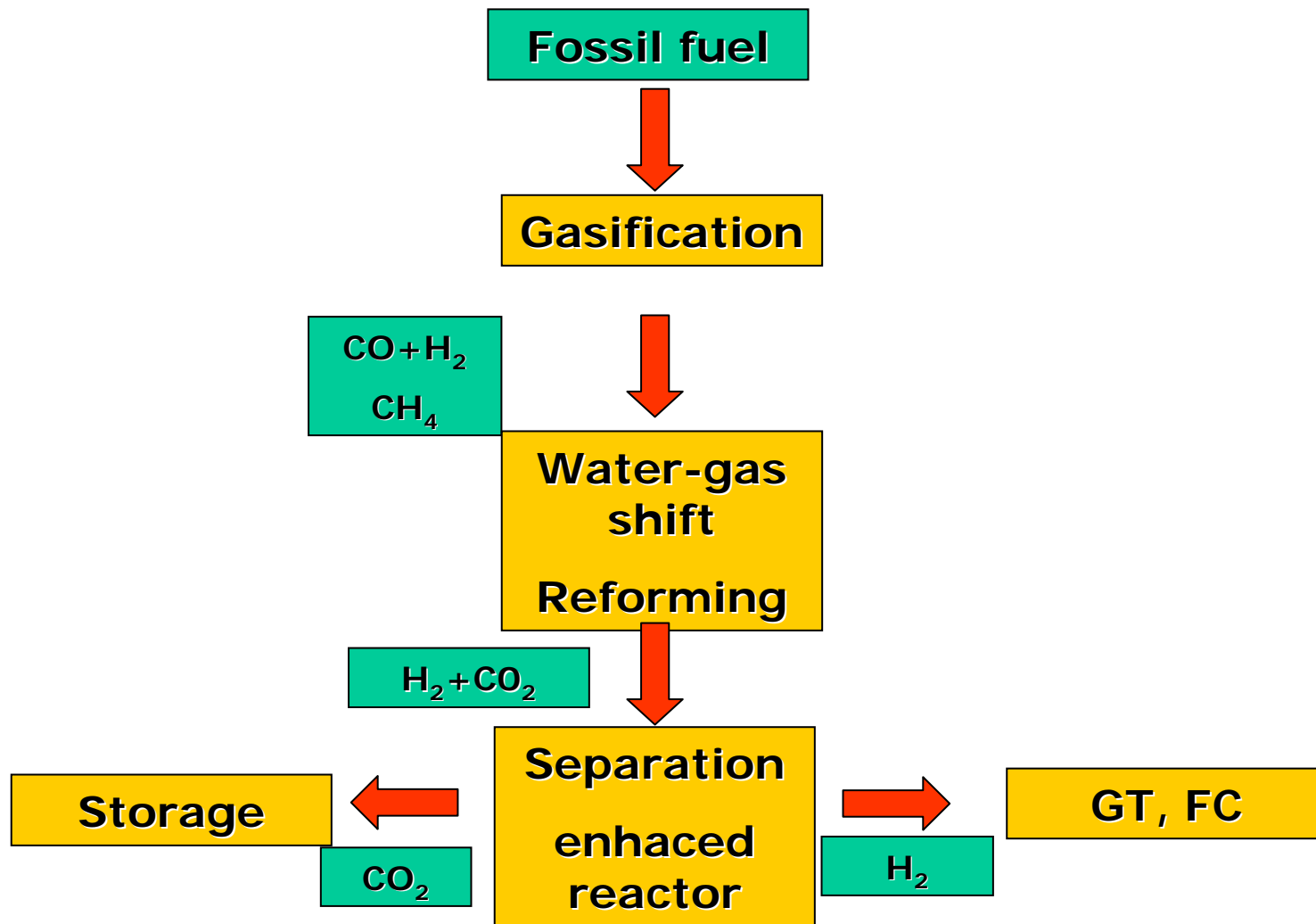
2 The TSSER system

3 Particle model description

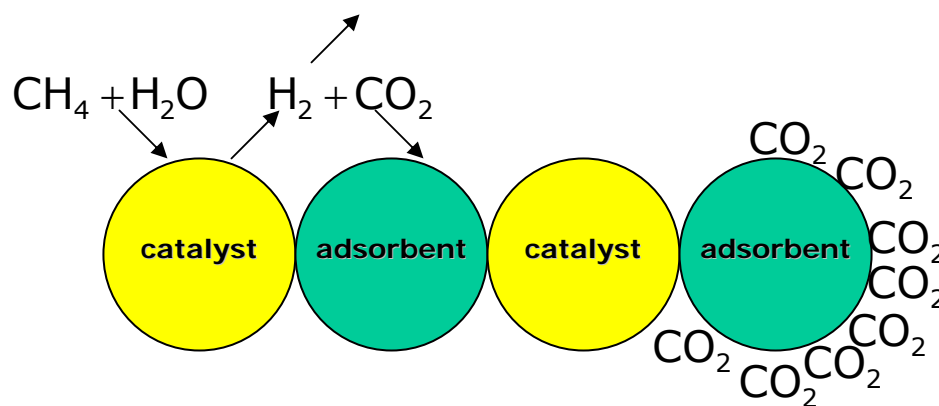
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2. Pre-combustion decarbonisation



Separation reactor

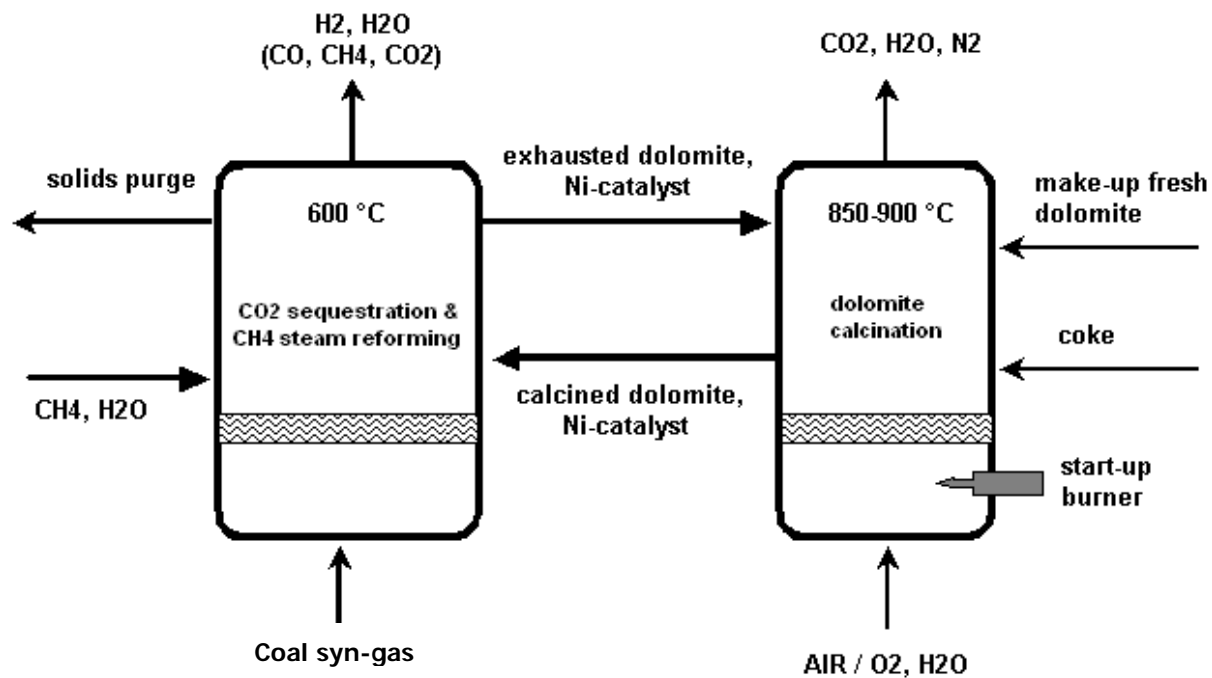


Steam reforming: $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{CO}$

Water-gas shift: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$

$\text{CH}_4 + 2\text{H}_2\text{O} \rightleftharpoons 4\text{H}_2 + \text{CO}_2$

2. Thermal swing sorption enhanced reforming concept



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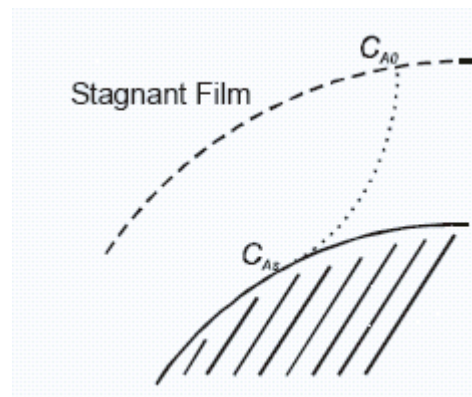
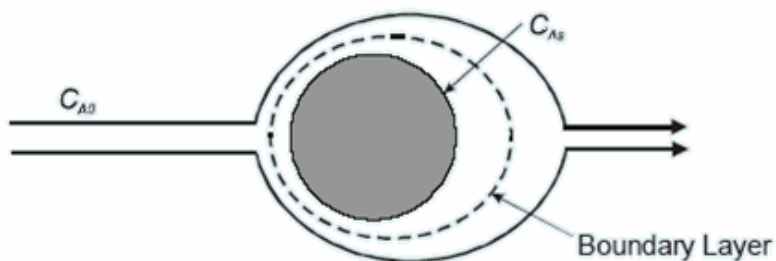
3 Particle model description

4 Results and discussion

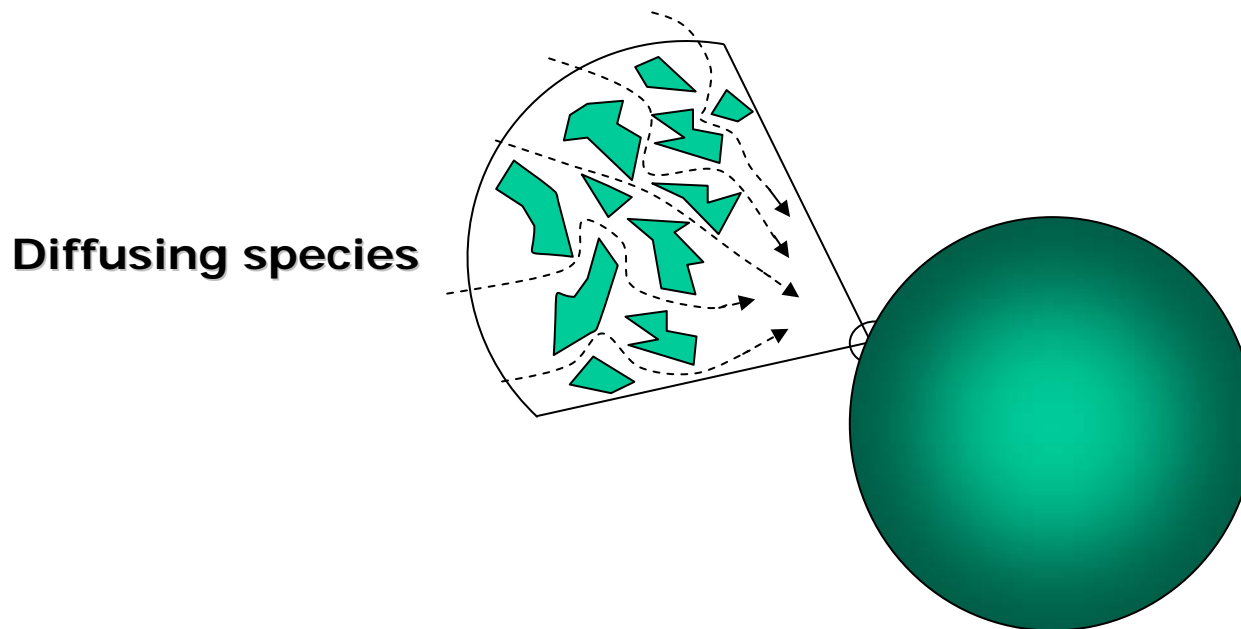
5 Conclusions

3. External resistance to mass transfer

Consider flow past a single spherical porous pellet



- Hydrodynamics boundary layer
- Fluid velocity varies with position around pellet

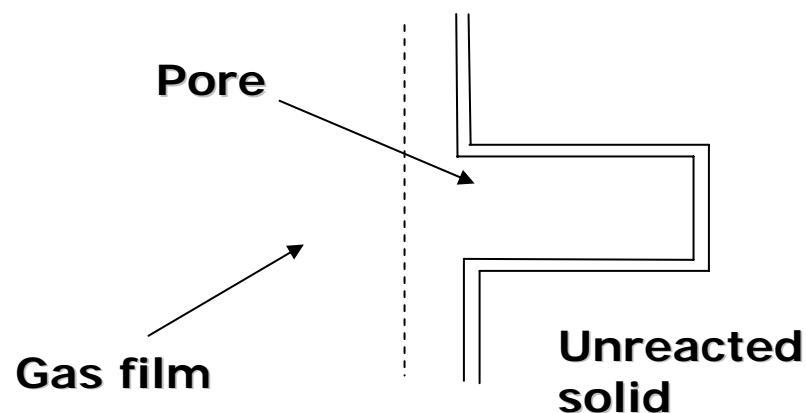
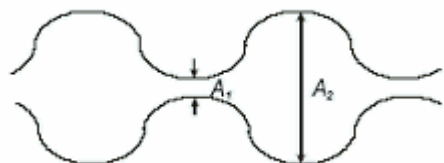


The effective diffusivity accounts for:

- Not all area available for diffusion**
- Paths are tortuous**
- Pores varying cross-sectional area**

Effective diffusivity

$$D_e = \frac{D\varepsilon\sigma}{\tau}$$



$$\beta = \frac{A_1}{A_2}$$

$$\varepsilon_p = \text{pellet porosity} = \frac{\text{void volume}}{\text{total volume}}$$

$$\tau = \text{tortuosity} = \frac{\text{actual distance}}{\text{shortest distance}}$$

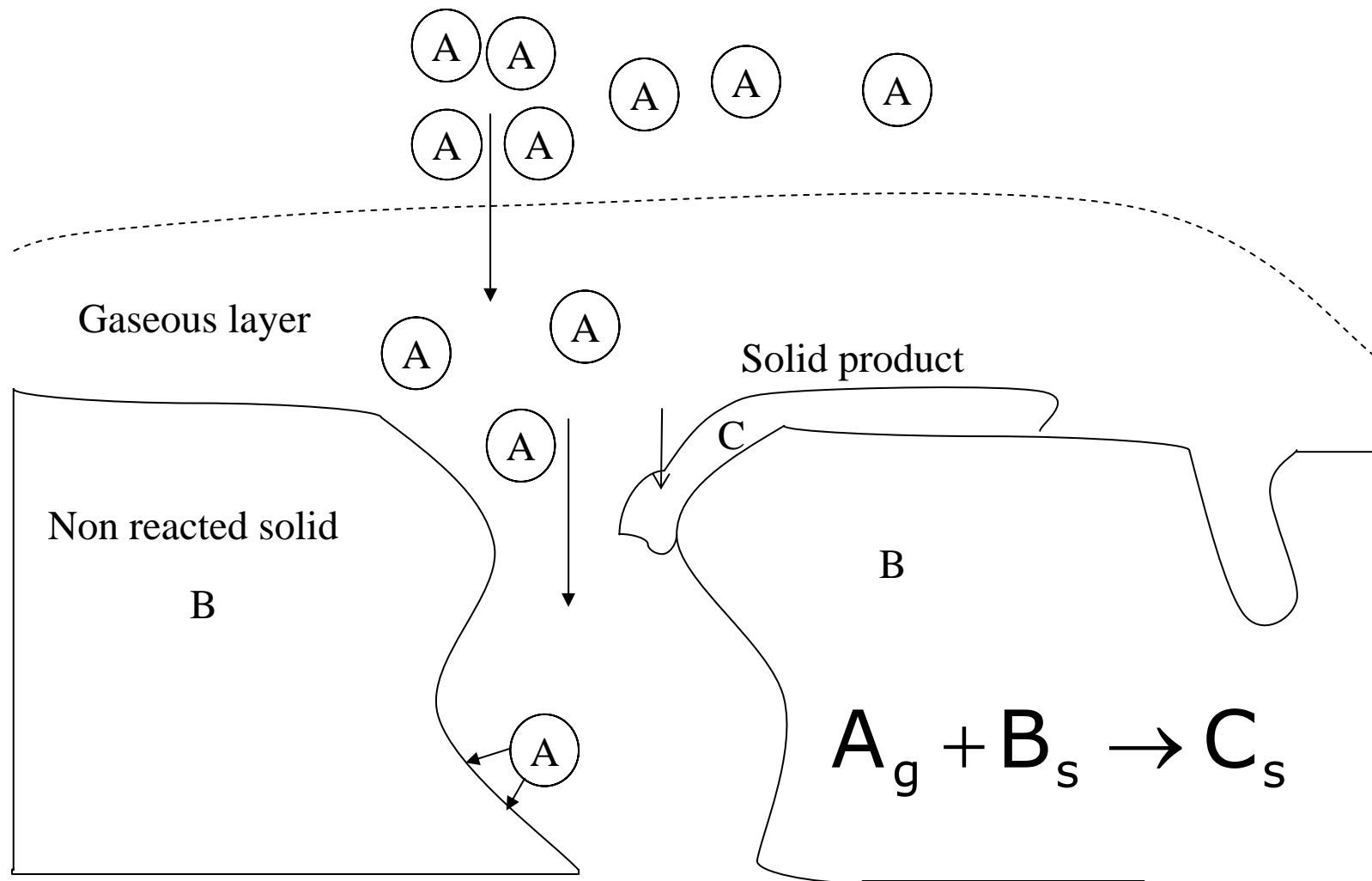
$$\sigma = \text{constrictor factor} = f(\beta)$$

D_K = Knudsen diffusivity

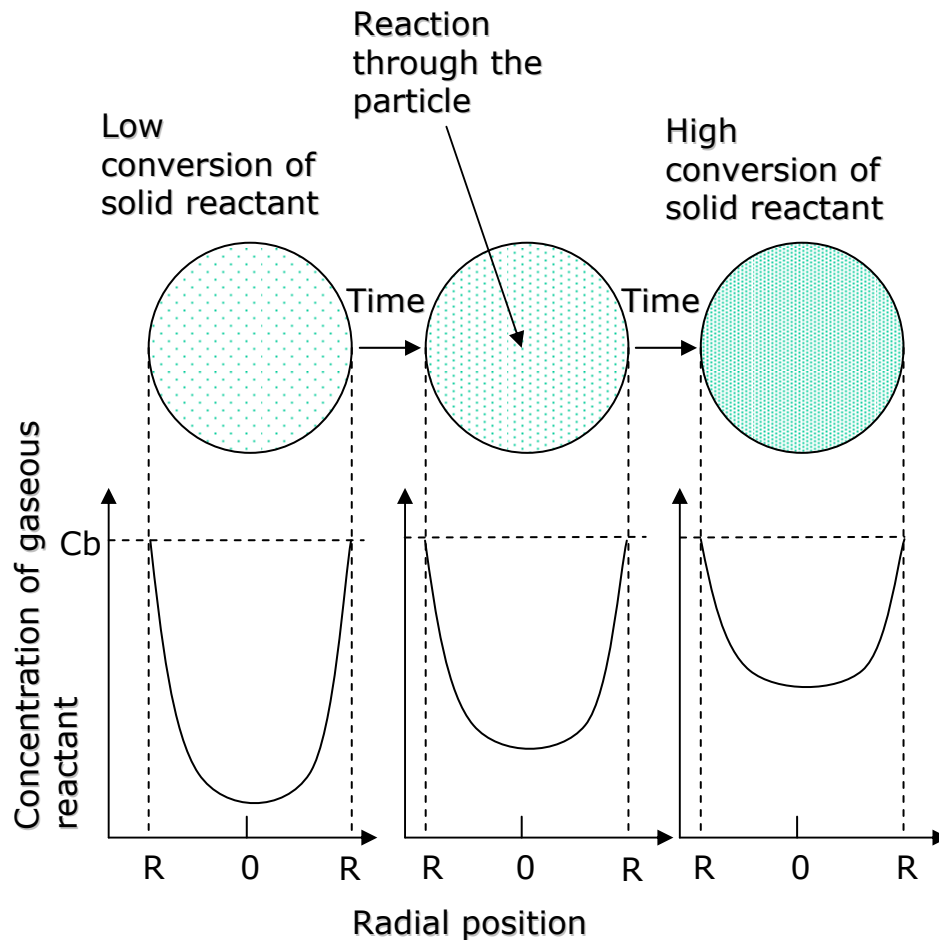
D_{AB} = Bulk diffusivity

$$D = \frac{1}{(1 - \gamma_A)/D_{AB} + 1/D_K}$$

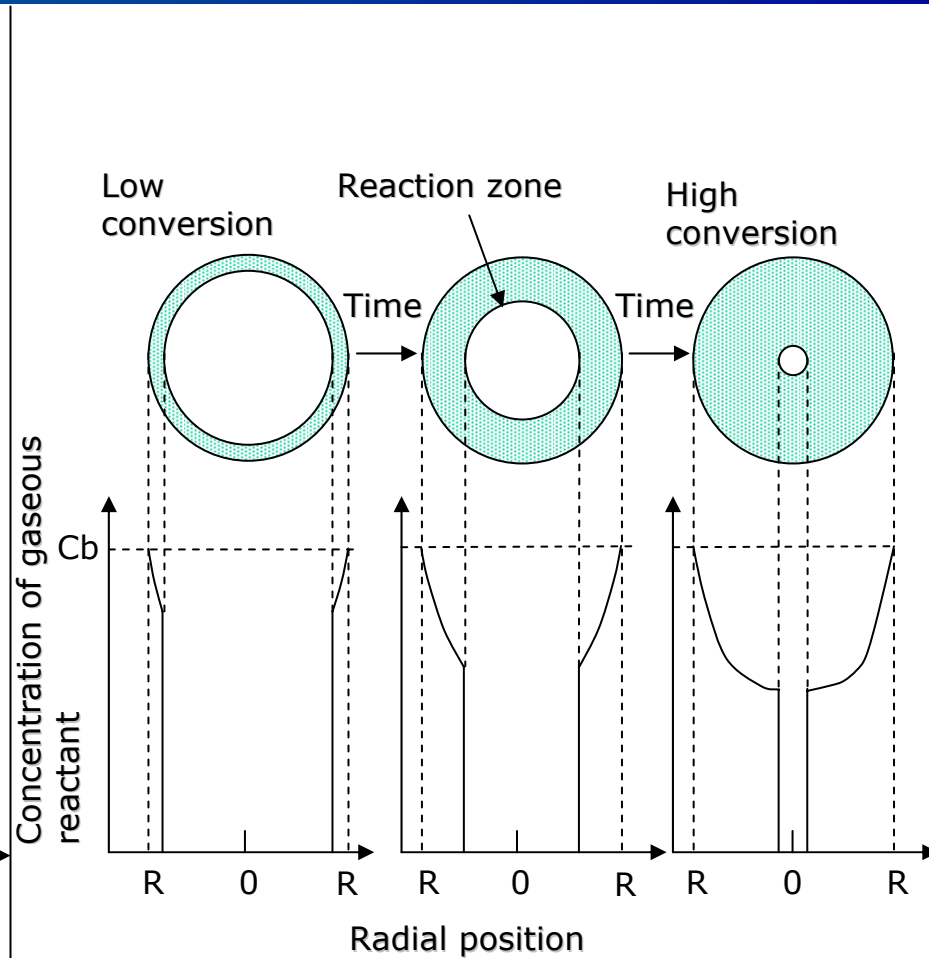
3. Schematic representation of gas – solid reactions



3. Kinetic models for the conversion of solids

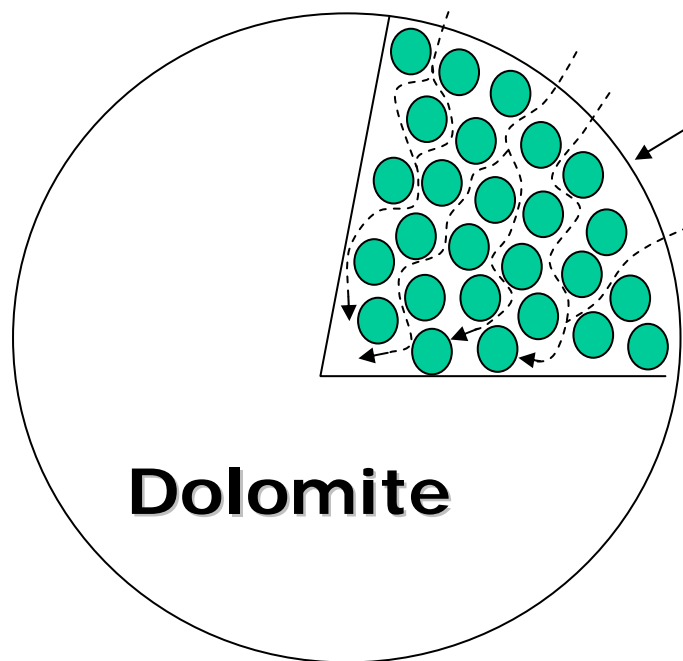


Uniform-reaction model



Shrinking-core model

3. Spherical grain model 1/3



Grains

$$\sigma = \sigma_{\text{CaO}} + \sigma_{\text{MgO}} = \left[N_{0\text{Ca}} V_{\text{CaO}} \frac{6}{\delta_{\text{CaO}}} (1 - X)^{2/3} + N_{0\text{Mg}} V_{\text{MgO}} \frac{6}{\delta_{\text{MgO}}} \right]$$

$$r_A = k_0 (C_A - C_{Ae}) = k \sigma_{\text{CaO}} (C_A - C_{Ae})$$

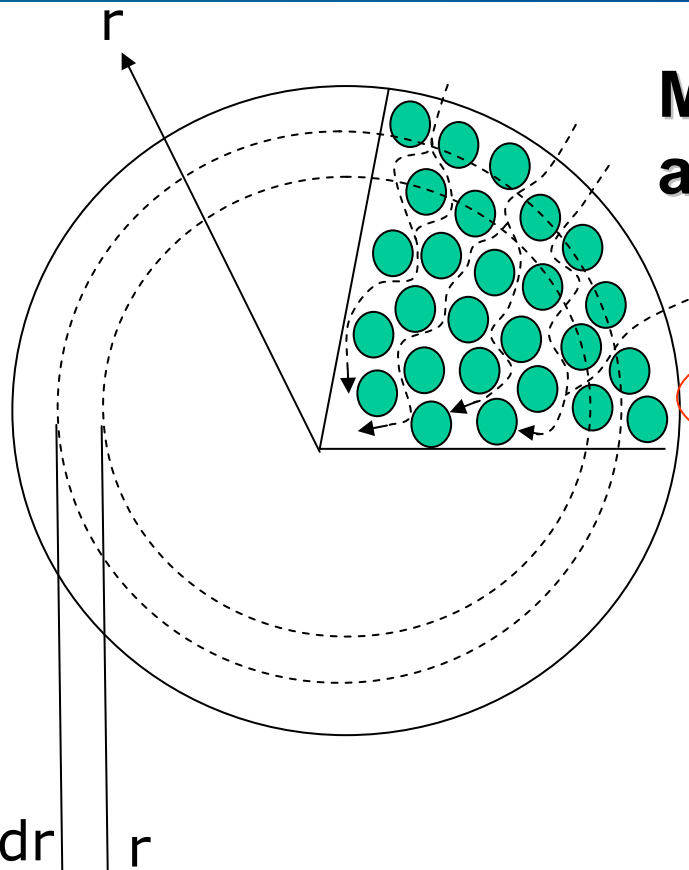
$N_{0\text{Ca}}, N_{0\text{Mg}}$ = moles of calcium and magnesium carbonate per unit volume of dolomite particle

δ_{CaO} = diameter of calcium oxide grain

X = conversion level

k_0 = effective reaction rate constant

k = rate constant for surface reaction



Mole balance of solid product in a spherical grain particle

$$N_{0Ca} \frac{\partial X}{\partial t} = \frac{k_0 (1-X)^{2/3} (C_A - C_{Ae})}{1 + \beta(X)}$$

s.t.:

$$X = 0 \text{ at } r \leq R \text{ and } t = 0$$

$$\beta(X) = \frac{k}{D_{pl}} \cdot \frac{1}{2} \delta_{CaO}^3 \sqrt[3]{1-X} \left[1 - \sqrt[3]{\frac{1-X}{1+X(Z-1)}} \right]$$

$$k_0 = k N_{0Ca} V_{CaO} \frac{6}{\delta_{CaO}}$$

Mole balance of gaseous reactant for diffusion in a spherical grain particle

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left[D_e r^2 \frac{\partial C_A}{\partial r} \right] - \frac{k_0 (1-X)^{2/3} (C_A - C_{Ae})}{1 + \beta(X)} = \frac{\partial(\epsilon C_A)}{\partial t}$$

s.t.:

$$\frac{\partial C_A}{\partial r} = 0 \quad \text{at } r = 0 \text{ and } t \geq 0$$

$$-D_e \frac{\partial C_A}{\partial r} = k_m (C_A - C_b) \quad \text{at } r = R \text{ and } t \geq 0$$

$$C_A = 0 \quad \text{at } t = 0 \text{ and } r \leq R$$

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$$\lambda = \frac{r}{R_0}; \quad \tau^* = k_0 t; \quad C_A^* = \frac{C_A}{C_{A0}}$$

4. Orthogonal collocation technique and Method of lines

$$1) \quad \varepsilon_j \Phi^2 \frac{\partial C_{A,j}^*}{\partial \tau^*} = D_{ej}^* \sum_{i=1}^{N+1} B_{j,i} \cdot C_i^* + \left(\sum_{i=1}^{N+1} A_{j,i} \cdot D_{ei}^* \right) \cdot \left(\sum_{i=1}^{N+1} A_{j,i} \cdot C_i^* \right) +$$

$$- \Phi^2 \frac{(1 - X_j)^{2/3} (C_{A,j}^* - C_{Ae}^*)}{1 + \beta(X_j)} [1 - C_{A0} V_{CaO} C_{A,j}^* (Z - 1)]$$

$$2) \quad \Gamma \frac{\partial X_j}{\partial \tau^*} = \frac{(1 - X_j)^{2/3} (C_{A,j}^* - C_{Ae}^*)}{1 + \beta(X_j)}$$

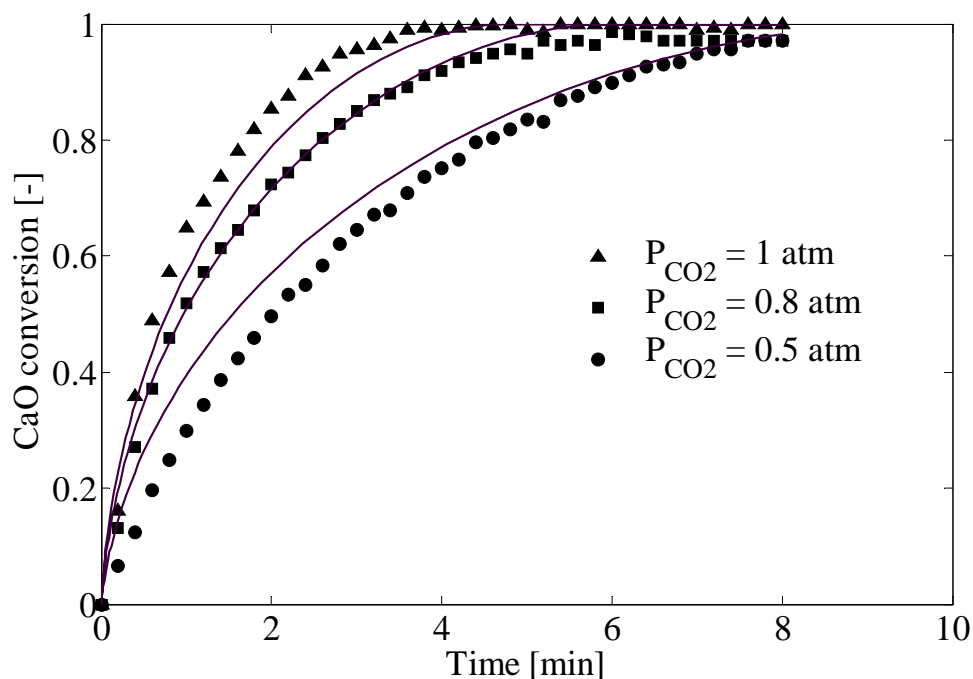
$$3) \quad \sum_{i=1}^{N+1} A_{N+1,i} \cdot C_i^* = Sh_e \frac{1 - C_{N+1}^*}{D_{eN+1}^*}$$

$$\tilde{X}(\tau^*) = 3 \int_0^1 X(\tau^*, \lambda) \cdot \lambda^2 d\lambda$$

with

$$Z = V_{CaCO_3} / V_{CaO}; \quad \varepsilon_j = \varepsilon_0 - N_{0Ca} V_{CaO} (Z - 1) X_j; \quad D_{ej}^* = D_j^* \varepsilon_j^2 \quad \text{and } j = 1, 2, \dots, N.$$

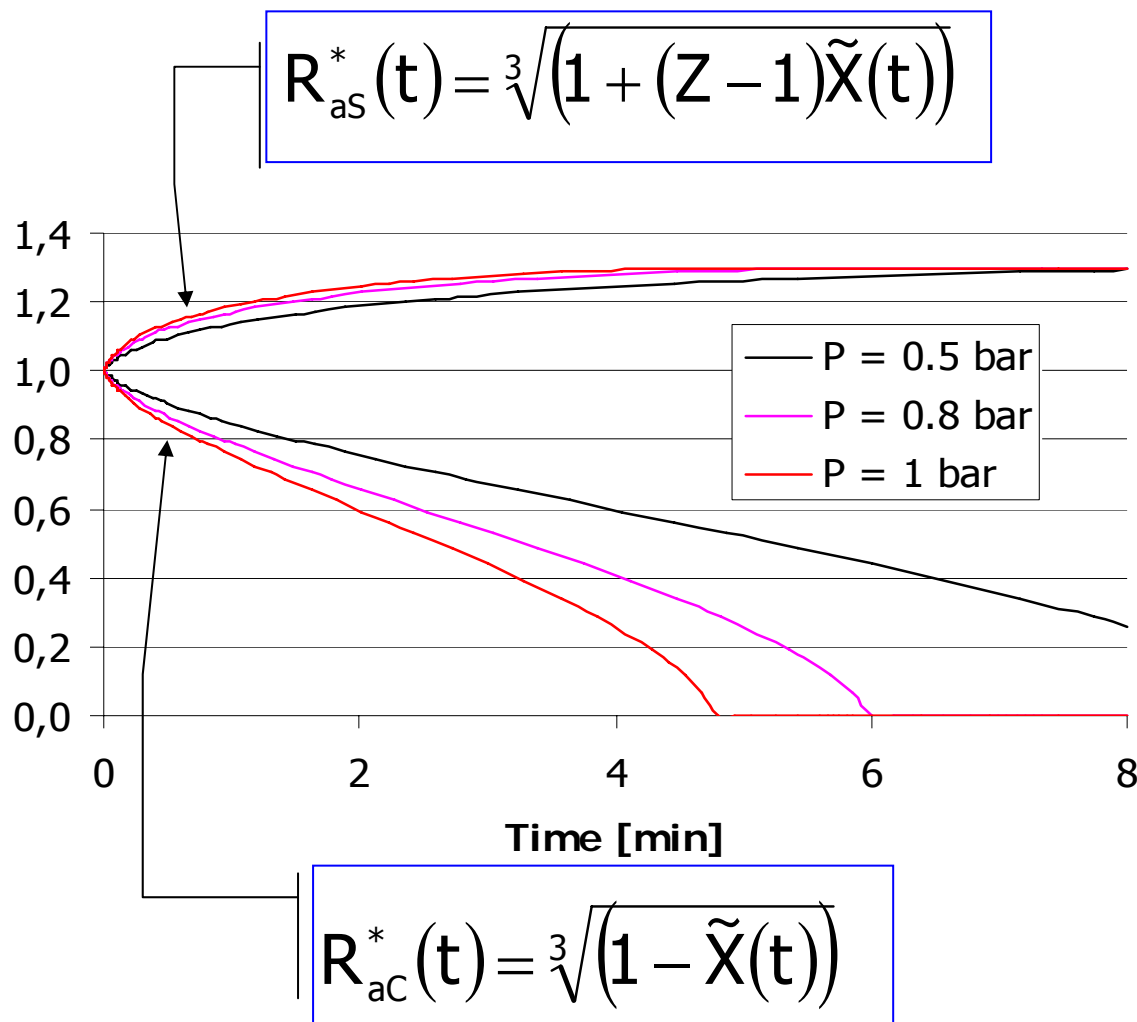
$$D_j = \left[(1 - y_{A,j}) / D_{AB} + 1 / D_{kn,j} \right]^{-1}; \quad D_j^* = D_j / D_{e0}; \quad \Gamma = \frac{N_{0Ca}}{C_{A0}}; \quad \Phi = R_0 \sqrt{\frac{k_0}{D_{e0}}}$$



Johnsen K, Grace JR, Elnashaie SSEH, Kolbeinsen L, Eriksen D.
Modelling of sorption-enhanced steam reforming in a dual fluidized bubbling bed reactor. Ind. Eng. Chem. Res. 2006

Value of parameters used	
Parameters	Value
N_{0Ca} [mol/cm ³]	8.8×10^{-3}
N_{0Mg} [mol/cm ³]	8.4×10^{-3}
δ_{CaO} [nm]	166
ϵ_0 [-]	0.46
Sh [-]	2.34
R_0 [μm]	125
T_0 [°C]	550
k_S [cm ⁴ /(mol s)]	5.95×10^{-2}
k [cm/s]	5.23×10^{-4}
k_0 [1/s]	28.14
D_{pl} [cm ² /s]	2.6×10^{-10}

4. The core and outer radius of the grain



$$R_{aC}^*(t) = \frac{R_{aC}(t)}{(1/2)\delta_{CaO}}$$

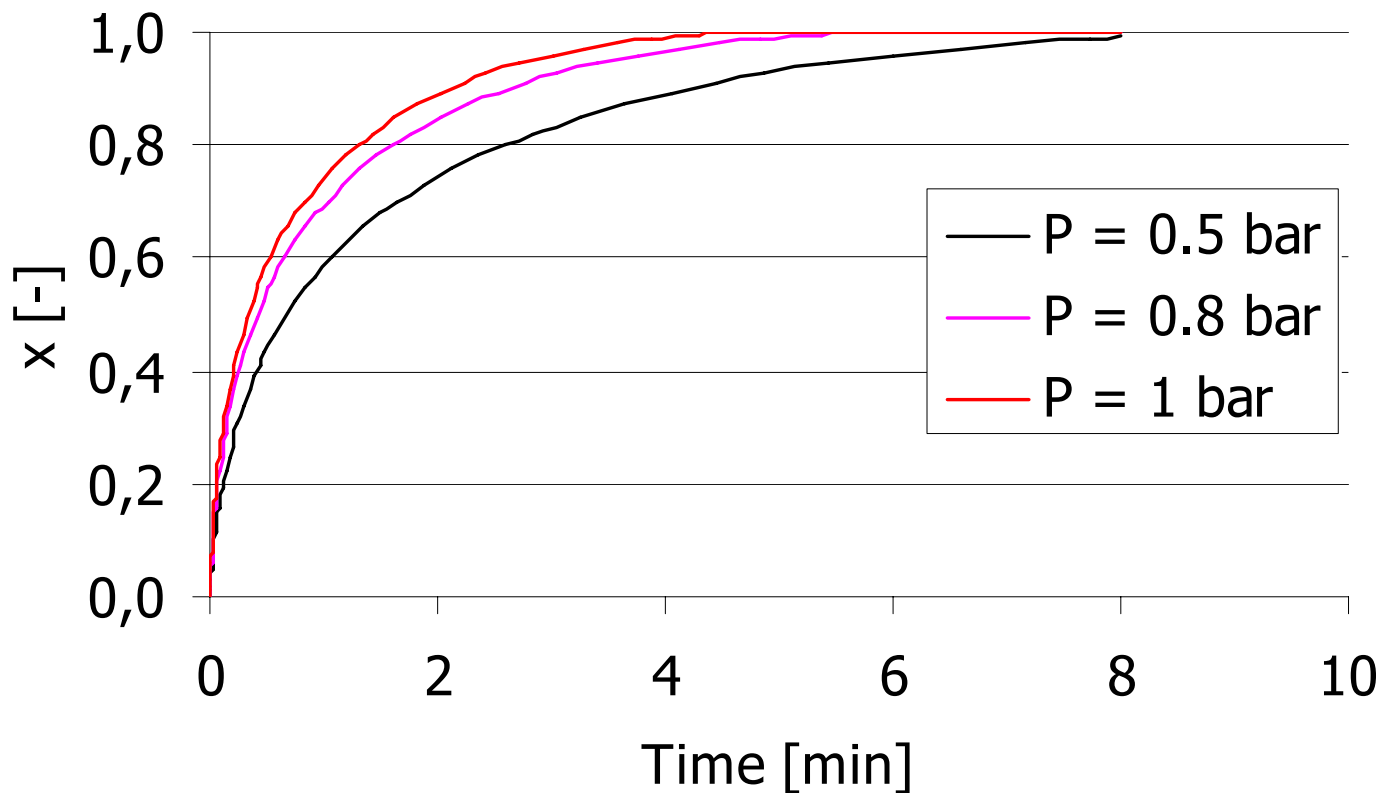
$$R_{aS}^*(t) = \frac{R_S(t)}{(1/2)\delta_{CaO}}$$

$$R_{aS,final}^* = \sqrt[3]{Z}$$

$$R_{aS,final}^* = 1.29$$

4. The volumetric conversion of the grain

$$x(t) = 1 - \frac{R_{aC}^3(t)}{R_{aS}^3(t)} = \frac{Z\tilde{X}(t)}{1 + (Z-1)\tilde{X}(t)}$$



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- Mathematical modeling of Simultaneous Reaction and Diffusion (SRD) process;
- Orthogonal collocation technique and method of lines in order to solve a parabolic partial differential equation;
- Changing grain model with $\delta_{\text{CaO}}=166\mu\text{m}$ and $D_{\text{pl}}=2.6\cdot 10^{-10}\text{ cm}^2/\text{s}$

Thank you