STEAM METANE REFORMING WITH CO$_2$ CAPTURE
Modeling and experimental study on sorbent and catalyst materials

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1. Context

University of L’Aquila is a partner in the European research project ASCENT (Advanced Solid Cycles for Efficient Novel Technologies)[1]

In this framework, the Chemical Reactors and Industrial Chemistry laboratory is involved in:

- synthesis and experimental study of materials for Sorption Enhanced Steam Methane Reforming (SE-SMR) in cooperation with University of Strasbourg – ICPEES
- mathematical modeling of the behaviour of these materials

2. Intro: SE-SMR

**SORPTION ENHANCED – STEAM METHANE REFORMING (SE-SMR)**

(T = 650 °C ; P = 1 atm)

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>ΔH&lt;sup&gt;0&lt;/sup&gt;&lt;sub&gt;298 K&lt;/sub&gt; (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Methane Reforming (SMR)</td>
<td>CH&lt;sub&gt;4&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;O → CO + 3H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>+206.2</td>
</tr>
<tr>
<td>Water Gas Shift (WGS)</td>
<td>CO + H&lt;sub&gt;2&lt;/sub&gt;O ⇌ CO&lt;sub&gt;2&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-41.2</td>
</tr>
<tr>
<td>Carbonation (CBN)</td>
<td>CaO&lt;sub&gt;(s)&lt;/sub&gt; + CO&lt;sub&gt;2&lt;/sub&gt; → CaCO&lt;sub&gt;3(s)&lt;/sub&gt;</td>
<td>-178.2</td>
</tr>
</tbody>
</table>

**Regeneration**

(T = 800 - 900 °C ; P = 1 atm)

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>ΔH&lt;sup&gt;0&lt;/sup&gt;&lt;sub&gt;298 K&lt;/sub&gt; (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination</td>
<td>CaCO&lt;sub&gt;3(s)&lt;/sub&gt; → CaO&lt;sub&gt;(s)&lt;/sub&gt; + CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>+178.2</td>
</tr>
</tbody>
</table>

2. Intro: CSCM

**Bi-functional CSCM** avoids mass transfer inter-particle resistances and allows a more intimate connection between endothermic and exothermic reaction processes.

System analysis studies\(^5\) evaluated advantages of industrial applications of SE-SMR calcium looping cycle, by means of solid circulation in a **couple of fluidized bed reactors**.
2. Intro: CSCM synthesis

1) WET MIXING
Mayenite or CaO-Mayenite

Calcination of Ca(CH₃COO)₂ to CaO (4h ; 750 °C)

CaO + Al(NO₃)₃·9H₂O
Stirring in distilled water (70 °C ; 1h)

Drying (12h ; 120 °C)

Thermal treatment 1 (4h ; 750 °C)

Hydratation + Drying (12h ; 120 °C)

Thermal treatment 2 (1.5h ; 900 °C)

2) WET IMPREGNATION
Ni-Mayenite or Ni-CaO-Mayenite

Mayenite or CaO/Mayenite + Ni(CH₃COO)₂·4H₂O or Ni(NO₃)₂·6H₂O
Stirring in distilled water (70 °C ; 1h)

Drying (12h ; 120 °C)

Thermal treatment (4h ; 900 °C)

CSCM synthesis: X-Ray Diffraction (XRD)
Wet Mixing is effective in synthesizing CaO-Mayenite sorbent
Wet Impregnation with both Ni-Acetate and Ni-Nitrate succeed in adding Nickel
3. CO$_2$ capture: experimental

50 cycles of CO$_2$-sorption/desorption in TGA:

- 100 mg of material
- 38 µm $< d_p < 106$ µm

![Diagram showing the experimental setup for CO$_2$ capture.]
CO$_2$ capture: experimental

Stabilization in sorption capacity occurs.
Reduction with Ni impregnation due to: (I) Loss of CaO in the impregnation; (II) Ni shadowing effect; (III) CaO sintering due to additional thermal treatment.
CaCO$_3$ layer grows on sorbent grains, increasing resistance for CO$_2$ penetration towards CaO core surface, where carbonation reaction occurs.
3. CO\textsubscript{2} capture: PGM

Particle Grain Model (PGM) applied to TGA tests contains:

• **Mole balance** on sorbent phase (CaO)
• **Mole balance on CO\textsubscript{2} and inert gas** in the internal particle voidage
• **Dynamic particle void volume evolution** due to carbonation
• **Initial conditions:**
  • sorbent completely calcined
  • no CO\textsubscript{2} in surrounding atmosphere and in pores
• **Boundary conditions:**
  • radial symmetry in concentration gradients
  • no CO\textsubscript{2} accumulation at particle external borders

3. CO$_2$ capture: CaO balance

\[
\frac{\partial X}{\partial t} = \frac{\sigma_{\text{CaO}}^0 k_s (1 - X)^{2/3} (C_{\text{CO}_2} - C_{\text{CO}_2, eq})}{1 + \frac{N_{\text{CaO}}^0 k_s}{2D_{\text{PL}}} \delta_{\text{CaO}}^0 \sqrt[3]{1 - X} \left( 1 - \sqrt[3]{\frac{1 - X}{1 - X + X \left( \frac{V_{\text{CaCO}_3}}{V_{\text{CaO}}} \right)}} \right)}
\]

Effect of CaCO$_3$ layer formation due to $X$

\[
D_{\text{PL}} = D_{\text{PL}0} \exp(-ax^b)
\]

is the Product Layer diffusion coefficient with exponential decay as a function of $X$\[8\]

---

**CO₂ capture: PGM [-] vs. experimental [◊]**

For a good fitting, only \( \delta^{0}_{CaO} \) must be progressively increased, in accordance with physical sintering phenomena.
CO$_2$ capture: PGM parameters

$D_{PL,0}$, $a$ and $b$ are kept constant for each Ni-impregnated material and its parent sorbent. $\delta_{CaO}^0$ of each Ni-impregnated material is higher than $\delta_{CaO}^0$ in its parent sorbent (sintering and/or shadowing effect due to Ni impregnation).

<table>
<thead>
<tr>
<th></th>
<th>CaO30</th>
<th>CaO30Ni(Ac)3</th>
<th>CaO54</th>
<th>CaO54Ni(N)3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate constant$^7$, $k_s$ [m$^4$ kmol$^{-1}$ s$^{-1}$]</td>
<td></td>
<td></td>
<td></td>
<td>5.95 10$^{-7}$</td>
</tr>
<tr>
<td>$\alpha$ [-]</td>
<td></td>
<td></td>
<td></td>
<td>1.65</td>
</tr>
<tr>
<td>Initial CaO grain diameter, $\delta_{CaO}^0$ [nm]</td>
<td>90</td>
<td>140</td>
<td>100</td>
<td>150</td>
</tr>
<tr>
<td>Initial value of CO$<em>2$ solid diffusion coefficient, $D</em>{PL,0}$ [m$^2$/s]</td>
<td>2.0 10$^{-5}$</td>
<td>1.5 10$^{-5}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$ [-]</td>
<td>23.5</td>
<td>23.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b$ [-]</td>
<td>0.06</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**CO$_2$ capture: PGM grain size evolution**

Grain size evolution corresponds to experimental evidences on the stabilization of CO$_2$ sorption capacity in synthetic materials. Dolomite does not have this stabilization.
4. SE-SMR: experimental

**PRE-REDUCTION:**
- 10 °C/min until 900 °C
- 900 °C for 1 h
- 10.2 Nml/min Ar
- 2 Nml/min N₂
- 2.8 Nml/min H₂

**SMR and SE-SMR:**
- 650 °C °C
- Steam/C molar = 3
- 10 Nml/min Ar
- 2 Nml/min N₂
- 2 Nml/min CH₄

**Active packed bed**
- ID = 7 mm ; m = 500 mg
- \( d_p = 100 – 125 \mu m \)
- \( P = 1 \text{ atm} \)
SE-SMR: experimental
CSCM with 10 %\textsubscript{w} of Ni performed SE-SMR and, after sorbent saturation, stably catalyzed SMR
4. SE-SMR: ADPFR model

PGM is integrated with a catalytic activity law for SMR on nickel\textsuperscript{[9]} in the configuration of Axial Dispersion Plug Flow Reactor (ADPFR), in order to simulate SE-SMR packed bed micro-reactor tests.

**Hypothesis:** negligible composition gradients around each particle and inside particle pores

**Unique concentration value at a given position and time instant for each gaseous component**

In addition to PGM equations and conditions, there are:

- **Mole balances in gas flowing around particles and inside their pores**
- **Initial conditions** in the packed-bed:
  - Completely calcined packed-bed
  - No other species than inert within the packed-bed
- **Boundary conditions** due to axial dispersion in packed-bed:
  - Molar inlet flowrates corrected by backwards axial dispersion flow at packed-bed entrance
  - No concentration gradients at packed-bed exit

4. SE-SMR: gas phase balance

\[ \frac{\partial \epsilon_p}{\partial t} = \left( 1 - \frac{V_{CaCO_3}}{V_{CaO}} \right) f_{CaO}^0 \frac{\partial X}{\partial t_i} \]

Dynamic particle void evolution

\[ \frac{\partial [\epsilon_p(1 - \epsilon) + \epsilon] \cdot C_i}{\partial t} = D_R \frac{\partial^2 C_i}{\partial z^2} - \frac{1}{S} \frac{\partial F_i}{\partial z} + r_i(1 - \epsilon) \]

Overall reaction rate\[^6,^9\] for specie \( i \)

\[ r_i = (v_{i,SMR} \cdot r_{i,SMR} + v_{i,WGS} \cdot r_{i,WGS}) \cdot \rho_p^0 \cdot \frac{\%_{Ni,eff}}{\%_{Ni,ref}} + v_{i,CBN} \cdot r_{i,CBN} \]

Molar flow rates

\[ F_i = y_i F_{tot} = C_i \frac{RT}{P} F_{tot} \]

Axial dispersion coefficient
**SE-SMR: ADPFR [-] vs. experimental [◊]**

ADPFR simulations are in good agreement with experiments, both for the initial SE-SMR phase (guessing the breakthrough time) and for the following SMR.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packed-bed voidage, $\epsilon$ [-]</td>
<td>0.5</td>
</tr>
<tr>
<td>Reactor axial dispersion coefficient, $D_R$ [m$^2$/s] $^{[10,11]}$</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td>CaO grain initial diameter, $\delta_{\text{CaO}}$ [nm]</td>
<td>140</td>
</tr>
</tbody>
</table>

CaO conversion ($X$) from ADPFR simulation, as a function of dimensionless bed height ($z^*$) and time ($t$), shows that the initial part of packed bed (flow direction as reference) never operates carbonation in the explored time range.
5. Conclusions

- **Wet mixing** and **wet impregnation methods** are suitable for the production of Combined Sorbent Catalyst Materials (CSCM) for Sorption Enhanced – Steam Methane Reforming (SE-SMR)

- **CSCM** with different amounts of free CaO and Ni **were synthesized and tested experimentally** for TGA multicycle CO₂ sorption/desorption and for SE-SMR in a packed-bed microreactor
  - During TGA tests, a stabilization of CO₂ sorption capacity occurs for CSCM and their parent sorbent, with acceptable final values
  - CSCM can operate stably SE-SMR and SMR (after sorbent saturation)
5. Conclusions

A Particle Grain Model (PGM) was developed and used to simulate TGA multicycle CO$_2$ sorption/desorption tests:

- For a given material, only one parameter must be varied with the cycle number to get a good fitting between PGM results and experimental data: CaO grain initial diameter
- For a given family of CSCM and their parent sorbent, all other PGM parameters assume same values respectively
- PGM also confirms the tendency of CO$_2$ sorption capacity to be stabilized in synthetic materials with the number of cycles, by the evolution of CaO grain initial diameter value
5. Conclusions

- PGM is integrated with a *catalytic activity law of SMR* in the *Axial Dispersion Plug Flow Reactor (ADPFR) configuration*, for simulating SE-SMR microreactor tests:
  - The breakthrough (transition from SE-SMR and SMR) is described in agreement with experimental data for all the CSCM tested, which differ according to their free CaO fraction
  - The CaO grain diameter value, chosen in order to have a good fitting of TGA experimental data by PGM, is suitable for SE-SMR simulation too

- The successful validation of the PGM model will allow to predict the behavior of SE-SMR pilot scale reactors, when their hydrodynamics is properly described.
Thanks for your attention

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Numaguchi and Kikuchi model

Kinetics of catalytic SMR and WGS reactions are described by Numaguchi and Kikuchi model\(^9\) (NK model):

\[
r_{SMR} = \frac{k_{SMR}^0 \cdot \exp\left(-\frac{E_{SMR}}{RT}\right) \left(p_{CH_4}p_{H_2O} - \frac{p_{CO}p_{H_2}^3}{K_{SMR}}\right)}{p_{H_2O}^{1.596}} \quad \left[\frac{kmol}{kg \cdot s}\right]
\]

\[
r_{WGS} = \frac{k_{WGS}^0 \cdot \exp\left(-\frac{E_{WGS}}{RT}\right) \left(p_{CO}p_{H_2O} - \frac{p_{CO_2}p_{H_2}}{K_{WGS}}\right)}{p_{H_2O}} \quad \left[\frac{kmol}{kg \cdot s}\right]
\]

Values of kinetic parameters and equilibrium constants are reported in Aloisi et al.\(^6\)

In simulations, \(k_{SMR}\) and \(k_{WGS}\) are multiplied by the ratio between the actual Ni content and that in the NK catalyst (10% wt).

PGM for solo-sorption tests (1)

\[
\frac{\partial X}{\partial t} = \frac{\sigma_{Ca0}^0 k_s (1 - X)^{2/3} (C_{CO_2} - C_{CO_2,eq})}{1 + \frac{N_{Ca0}^0 k_s}{2D_{PL}} \delta_{Ca0}^0 \sqrt[3]{1 - X} \left(1 - \frac{1 - X}{\sqrt[3]{1 - X + X\zeta}}\right)} = \frac{r_{CBN}}{N_{Ca0}^0}
\]

\[
\frac{\partial (\varepsilon_p \cdot C_{CO_2})}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_{CO_2,eff} r^2 \frac{\partial C_{CO_2}}{\partial r}\right) - r_{CBN}
\]

\[
C_{inert} = \frac{P}{RT} - C_{CO_2}
\]

\[
\frac{\partial \varepsilon_p}{\partial t} = (1 - \zeta) f_{Ca0}^0 \frac{\partial X}{\partial t}
\]

where:

\[
X = X(r, t); \quad C_{CO_2} = C_{CO_2}(r, t); \quad \varepsilon_p = \varepsilon_p(r, t)
\]

\[
D_{CO_2,eff} = D_{CO_2} \varepsilon_p^\alpha = \frac{1}{(1 - y_{CO_2})/D_{CO_2,N_2} + 1/D_{knu,CO_2}} \varepsilon_p^\alpha
\]

\[
D_{PL} = D_{PL,0} \exp(-aX^b)
\]

A simplified version of PGM to simulate TGA sorption tests.
**PGM for solo-sorption tests (2)**

**Initial conditions:**

\[
X(0 \leq r \leq R, \ t = 0) = 0
\]  \hspace{1cm} (8)

\[
C_{\text{inert}} (0 \leq r \leq R, \ t = 0) = \frac{P}{RT}
\]  \hspace{1cm} (9)

**Boundary conditions:**

\[
\frac{\partial C_{CO_2}}{\partial r} = 0 \hspace{1cm} \text{at } r = 0 \text{ and } t > 0
\]  \hspace{1cm} (10)

\[
D_{CO_2,\text{eff}} \cdot \frac{\partial C_{CO_2}}{\partial r} = h_{CO_2} \cdot (C_{CO_2,\text{bulk}} - C_{CO_2}) \hspace{1cm} \text{at } r = R \text{ and } t > 0
\]  \hspace{1cm} (11)

The above conservation equations, congruence, boundary and initial conditions are made dimensionless by introducing the following variables:

\[
y_{CO_2} = C_{CO_2} \frac{RT}{P}, \hspace{0.5cm} r^* = \frac{r}{R}, \hspace{0.5cm} t^* = \frac{t}{\tau} \hspace{1cm} \text{where} \hspace{0.5cm} \tau = \frac{1}{k_s \cdot N_{CaO}^0 \cdot \sigma_{CaO}^0}
\]  \hspace{1cm} (12)

The dimensionless system of equations are integrated numerically by the MATLAB® PDEPE algorithm (finite difference method).

A simplified version of PGM to simulate TGA sorption tests.
TGA multicycle calculations

CaO conversion \((X)\) at each time \((t)\) of a given carbonation cycle \((i)\)

\[
X(t, i) = \frac{\Delta m(t, i)}{\Delta m(\infty)^*} \cdot \theta
\]

*: referred to completely calcined, fresh sample

\(\theta = \text{fresh sample initial mass utilized in the long term test divided by that adopted in the cyclic carbonation tests.}\)
CSCM deriving from CaO30 show a slight decrease in sorption capacity (SC) in comparison to their parent sorbent, bigger with Ni-acetate. SC reaches a remarkable stability as a function of the cycle number.
TGA multicycles result (2)

CSCM deriving from CaO54 show a substantial decrease in sorption capacity in comparison to their parent sorbent although a remarkable stability at increasing cycle number is reached also in this case.
**Values for TGA multicycle simulations**

*Reduction of capture capacity with Ni impregnation* can be ascribed to: (I) Loss of CaO in the impregnation process; (II) Shadowing effect of Ni; (III) CaO sintering due to thermal treatments.

<table>
<thead>
<tr>
<th></th>
<th>CaO30</th>
<th>CaO30Ni(Ac)3</th>
<th>CaO54</th>
<th>CaO54Ni(N)3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature, T [°C]</strong></td>
<td></td>
<td></td>
<td>650</td>
<td></td>
</tr>
<tr>
<td><strong>Pressure, P [atm]</strong></td>
<td></td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td><strong>CO2 partial pressure in the gaseous bulk, (p_{CO_2} ) [atm]</strong></td>
<td></td>
<td></td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td><strong>Particle diameter, (d_p ) [μm]</strong></td>
<td></td>
<td></td>
<td>38-106</td>
<td></td>
</tr>
<tr>
<td><strong>Molar volume ratio, (\zeta = \frac{V_{CaCO_3}}{V_{CaO}} ) [-]</strong></td>
<td></td>
<td></td>
<td>2.18</td>
<td></td>
</tr>
<tr>
<td><strong>Initial particle density, (\rho_{p,0} ) [kg/m3]</strong></td>
<td>2102</td>
<td>2288</td>
<td>1853</td>
<td>1875</td>
</tr>
<tr>
<td><strong>Initial particle voidage, (\varepsilon_{p,0} ) [-]</strong></td>
<td>0.30</td>
<td>0.25</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td><strong>Effective (long term) capture capacity, (\frac{g(CO_2)}{100g(sorbent)} )</strong></td>
<td>27.3</td>
<td>19.2</td>
<td>41.3</td>
<td>36.1</td>
</tr>
</tbody>
</table>

*calculated
**CO₂ capture: PGM [-] vs. experimental [◊]**

For a good fitting, only $\delta_{\text{CaO}}^0$ must be progressively increased, in accordance with physical sintering phenomena.
\[
\frac{\delta_{\text{CaO}}^0(N + 1)}{\delta_{\text{CaO}}^0(N)} = \frac{1 + \gamma N^2 + \varphi N}{1 + \gamma (N - 1)^2 + \varphi (N - 1)}
\]

<table>
<thead>
<tr>
<th>Material</th>
<th>(\gamma)</th>
<th>(\varphi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO30</td>
<td>(-2.90 \cdot 10^{-4})</td>
<td>(2.97 \cdot 10^{-2})</td>
</tr>
<tr>
<td>CaO30Ni(Ac)3</td>
<td>(-8.34 \cdot 10^{-6})</td>
<td>(8.48 \cdot 10^{-3})</td>
</tr>
<tr>
<td>CaO54</td>
<td>(-5.24 \cdot 10^{-4})</td>
<td>(4.44 \cdot 10^{-2})</td>
</tr>
<tr>
<td>CaO54Ni(N)3</td>
<td>(-1.47 \cdot 10^{-3})</td>
<td>(1.27 \cdot 10^{-1})</td>
</tr>
</tbody>
</table>

\(\delta_{\text{CaO}}^0\) as a function of cycle number

**Functional relationship between CaO grain diameter and cycle number** to simulate the dynamic sorption behavior for both sorbents and sorbent-catalyst materials.
ADPFR dynamic model (1)

Gas phase molar balances

\[
\frac{\partial \left[ \varepsilon + (1 - \varepsilon) \varepsilon_p \right] \cdot C_i}{\partial t} = D_R \frac{\partial^2 C_i}{\partial z^2} - \frac{1}{S} \frac{\partial F_i}{\partial z} + r_i (1 - \varepsilon) \tag{13}
\]

\[
F_i = y_i F_{\text{tot}} = C_i \frac{RT}{P} F_{\text{tot}} \tag{14}
\]

Sorbet dynamic conversion

\[
\frac{\partial X}{\partial t} = \frac{\sigma_{CaO}^0 k_s (1 - X)^{2/3} \left( C_{CO_2} - C_{CO_2,eq} \right)}{1 + \frac{N_{CaO}^0 k_s}{2D_{pl}} \delta_{CaO}^0 3^{1/3} \sqrt{1 - X} \left( 1 - \frac{1 - X}{\sqrt{1 - X + X \zeta}} \right)} = \frac{r_{CBN}}{N_{CaO}^0} \tag{15}
\]

\[
r_i = \left( \nu_{SMR,i} \cdot r_{SMR} + \nu_{WGS,i} \cdot r_{WGS} \right) \cdot \rho_p,0 \cdot \frac{w_{Ni}^{\text{eff}}}{w_{Ni}^{\text{ref}}} + \nu_{CBN,i} \cdot r_{CBN} \tag{16}
\]

\(\nu_{SMR,i}, \nu_{WGS,i}, \nu_{CBN,i}\) are the stoichiometric coefficients of component \(i\), negative for reactants and positive for products
ADPFR dynamic model (2)

**Boundary conditions:**

\[ F_{i,in} = S \left( u \cdot C_i(0, t) - D_R \frac{\partial C_i}{\partial z} \bigg|_{z=0} \right) ; \quad \frac{\partial C_i}{\partial z} \bigg|_{z=L} = 0 \]  (17)

**Initial conditions:**

\[ X(t = 0) = 0 ; \quad C_{inert}(0 \leq z \leq L, t = 0) = \frac{P}{RT} \]  (18)
**Micro-reactor SMR tests: experimental**

The **Nickel-based Weight Hourly Space Velocity (Ni-WHSV)** is referred to the mass of Ni in the reactor and methane inlet flow rate.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ni-WHSV</th>
<th>Ni</th>
<th>$\chi_{CH4, SMR1}$</th>
<th>$\chi_{CH4, SMR2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_{I_{CH4}} h^{-1} g_{Ni}^{-1}$</td>
<td>%$_w$</td>
<td>850 °C</td>
<td>750 °C</td>
</tr>
<tr>
<td>CaO0Ni(N)10</td>
<td>2.45</td>
<td>10</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>CaO0Ni(N)6</td>
<td>4.00</td>
<td>6</td>
<td>100</td>
<td>99.6</td>
</tr>
<tr>
<td>CaO0Ni(N)4.5</td>
<td>5.31</td>
<td>4.5</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>CaO0Ni(N)3</td>
<td>7.97</td>
<td>3</td>
<td>100</td>
<td>99.5</td>
</tr>
<tr>
<td>CaO0Ni(N)3</td>
<td>18.17</td>
<td>3</td>
<td>100</td>
<td>99.0</td>
</tr>
</tbody>
</table>
Micro-reactor SMR tests: simulations

$H_2$ and $CH_4$ measured concentrations are always well predicted by the model, while CO is to some extent over estimated and $CO_2$ under predicted in the kinetic regime.