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Development and application of high temperature CO_2 sorbents

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Outline

- Background and principles
- Our approach:
  - Continuous lab scale reactor testing
    - Recent results using natural Ca-based sorbents
  - Search for new sorbents
    - Search based on thermo-dynamic properties
- Conclusions and further prospects.

http://www.epa.gov/climatechange/effects/

Background

- Separation of CO_2 from gas mixtures using solid sorbents at high temperature (500-900 °C) represents an alternative to processes at ambient or sub-ambient temperatures. Two important examples:
  - The carbonate looping process (CL) [1]
  - Sorption enhanced -steam methane reforming/-water-gas shift reactions (SE-SMR) [2].

1) J.C. Abanades, E.J. Anthony, J. Wang, J.E. Oakey, *Environ. Sci. Technol., 39, (2005), 2861*
2) D.P. Harrison, *Ind. Eng. Chem. Res., 47, (2008), 6486*

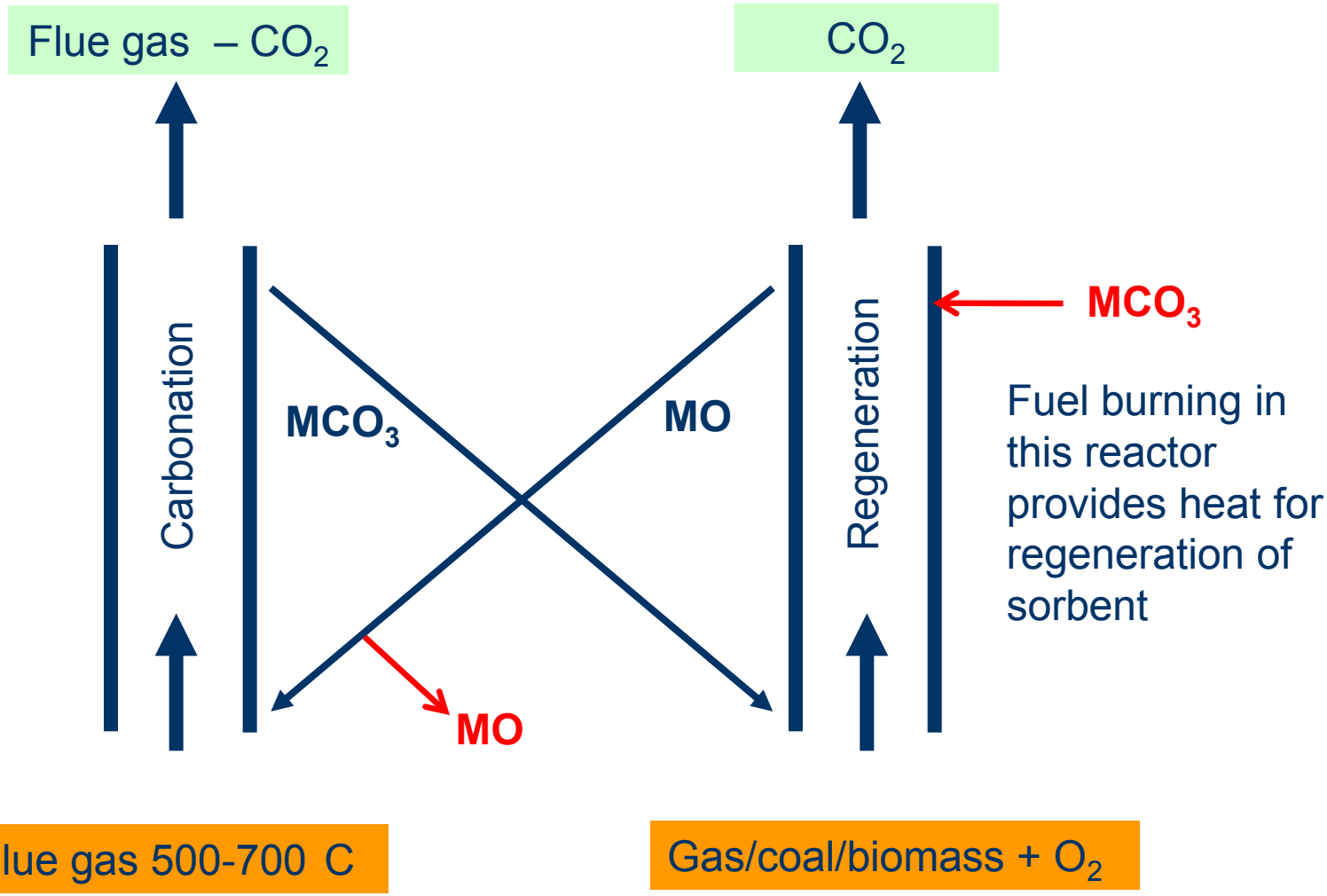
Application principles

- The sorbents are typically a metal oxide that reacts with CO_2 and form a carbonate.

- A subsequent regeneration decomposes the carbonate and thus releases CO_2 as a gas. The newly reformed metal oxide is then ready for use again.

$$MO + CO_2 \underset{700\text{-}900\ C}{\overset{500\text{-}700\ C}{\rightleftharpoons}} MCO_3$$

Carbonate looping



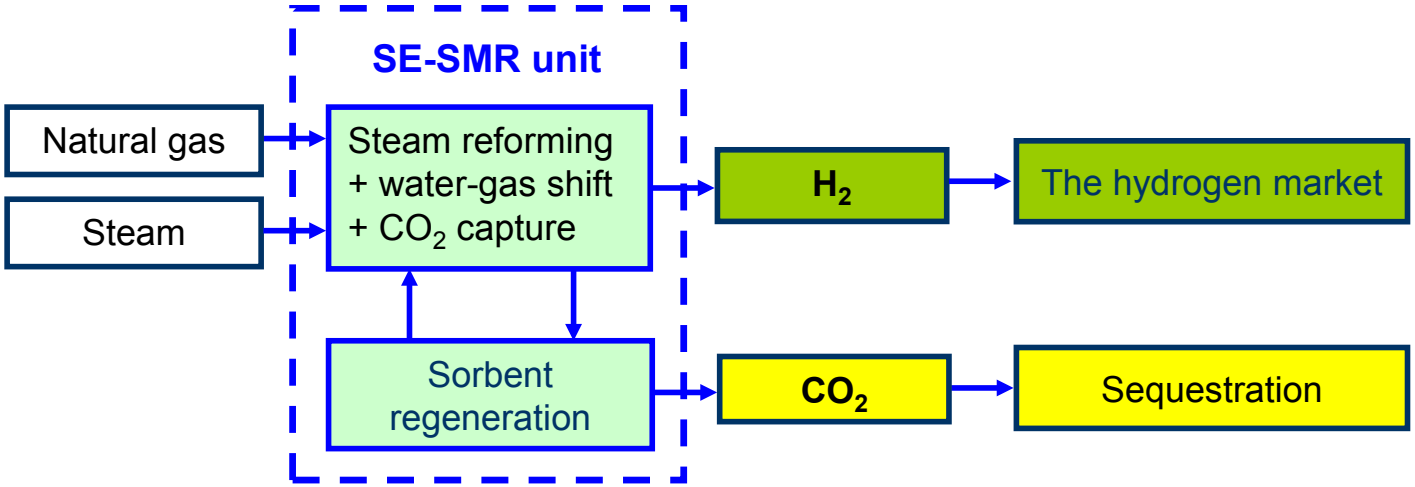
1) J.C. Abanades, E. J. Anthony, J. Wang, J. E. Oakey, *Environ. Sci. Technol.* 39 (**2005**) 2861.

Sorption-enhanced methane steam reforming

Hydrogen production from natural gas with simultaneous capture and separation of CO_2.

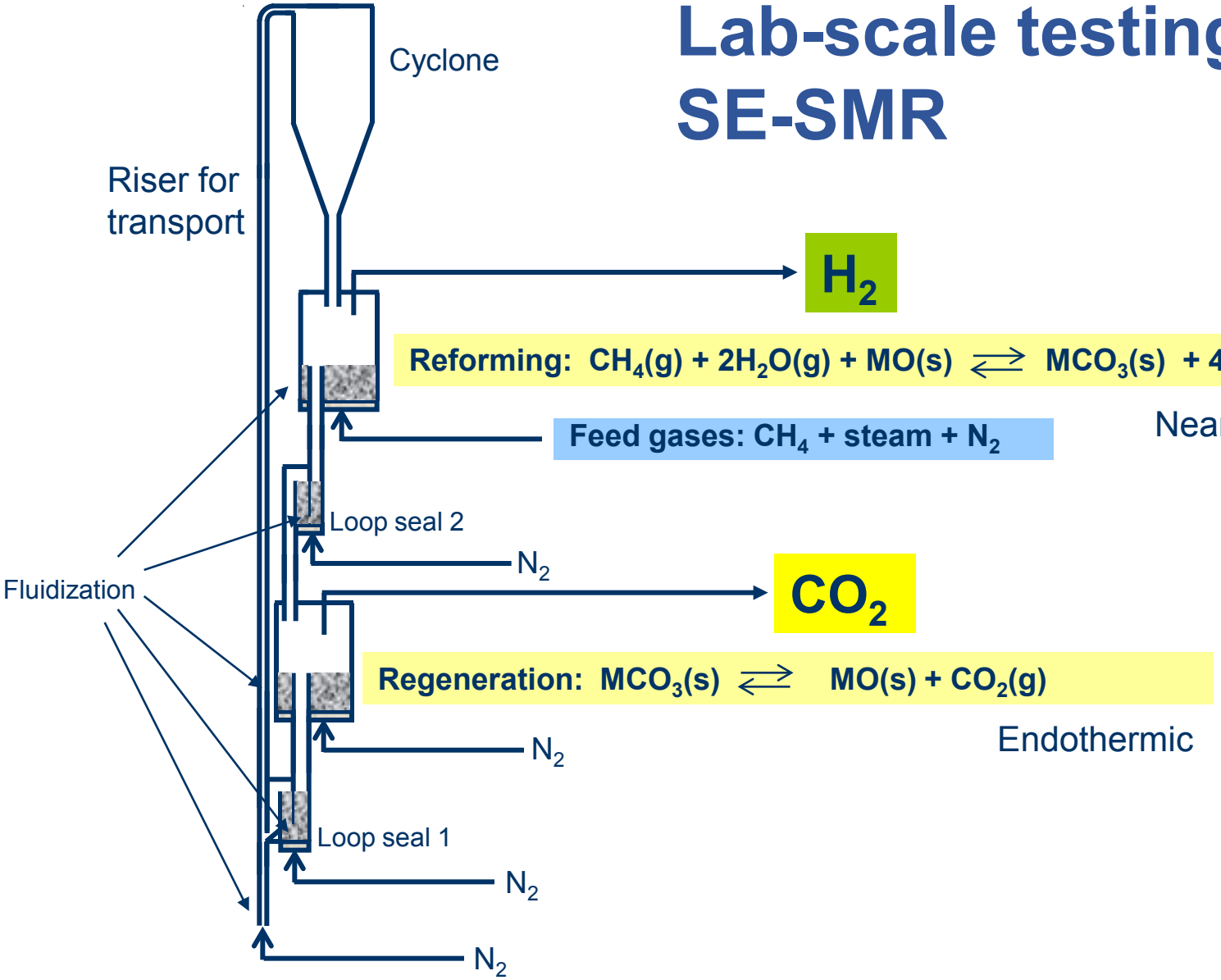
One possible concept:
Sorption enhanced methane steam reforming, SE-SMR [1].

SE-SMR has been proposed to be an economical competitive alternative to conventional steam methane reforming with CO_2 capture [2].



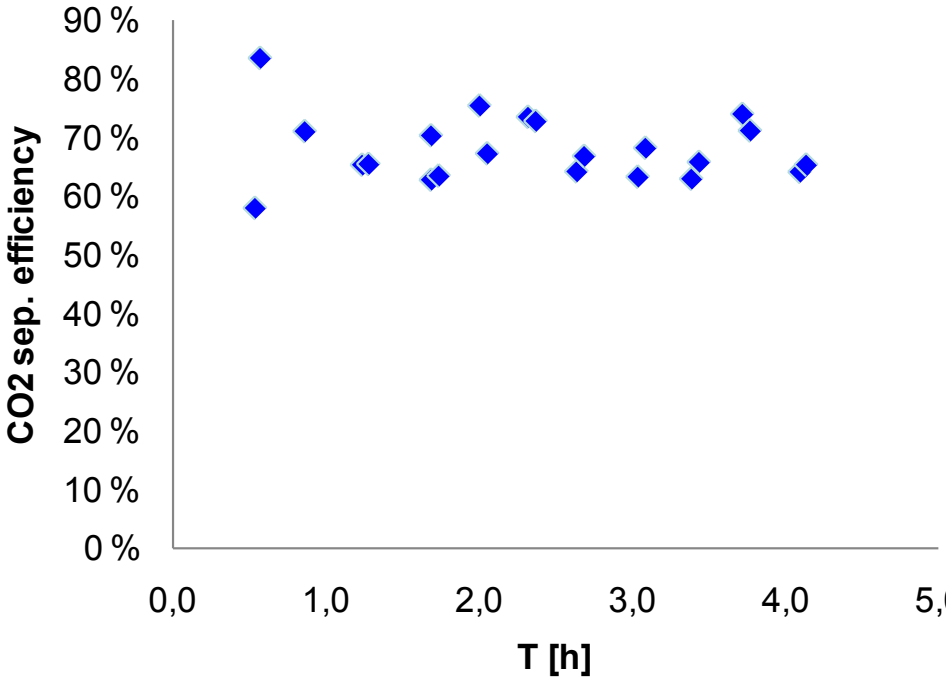
1) D.P.Harrison, *Ind. Eng. Chem. Res.* 47 (**2008**) 6486.
2) E. Ochoa-Fernandez, G. Haugen, T. Zhao, M. Rønning, I. Aartun, B. Børresen, E. Rytter, M. Rønnekleiv, D. Chen, *Green Chem.* 9 (**2007**) 1.

Lab-scale testing of SE-SMR

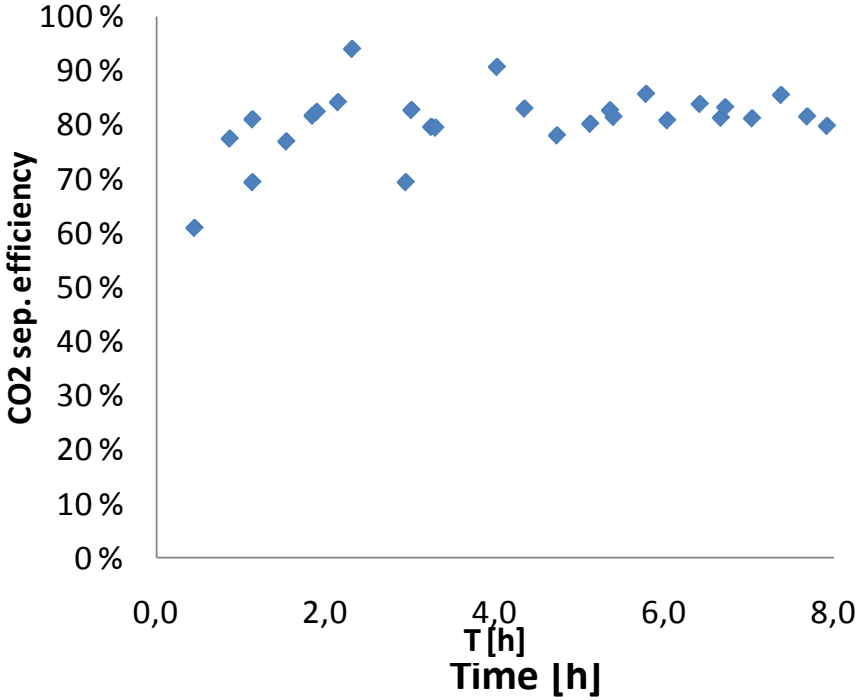


SE-SMR (feed reformer: 50 ml/min CH_4, 200 ml/min H_2O, 1860 ml/min N_2 diluent)

- Effect of catalyst/sorbent ratio:



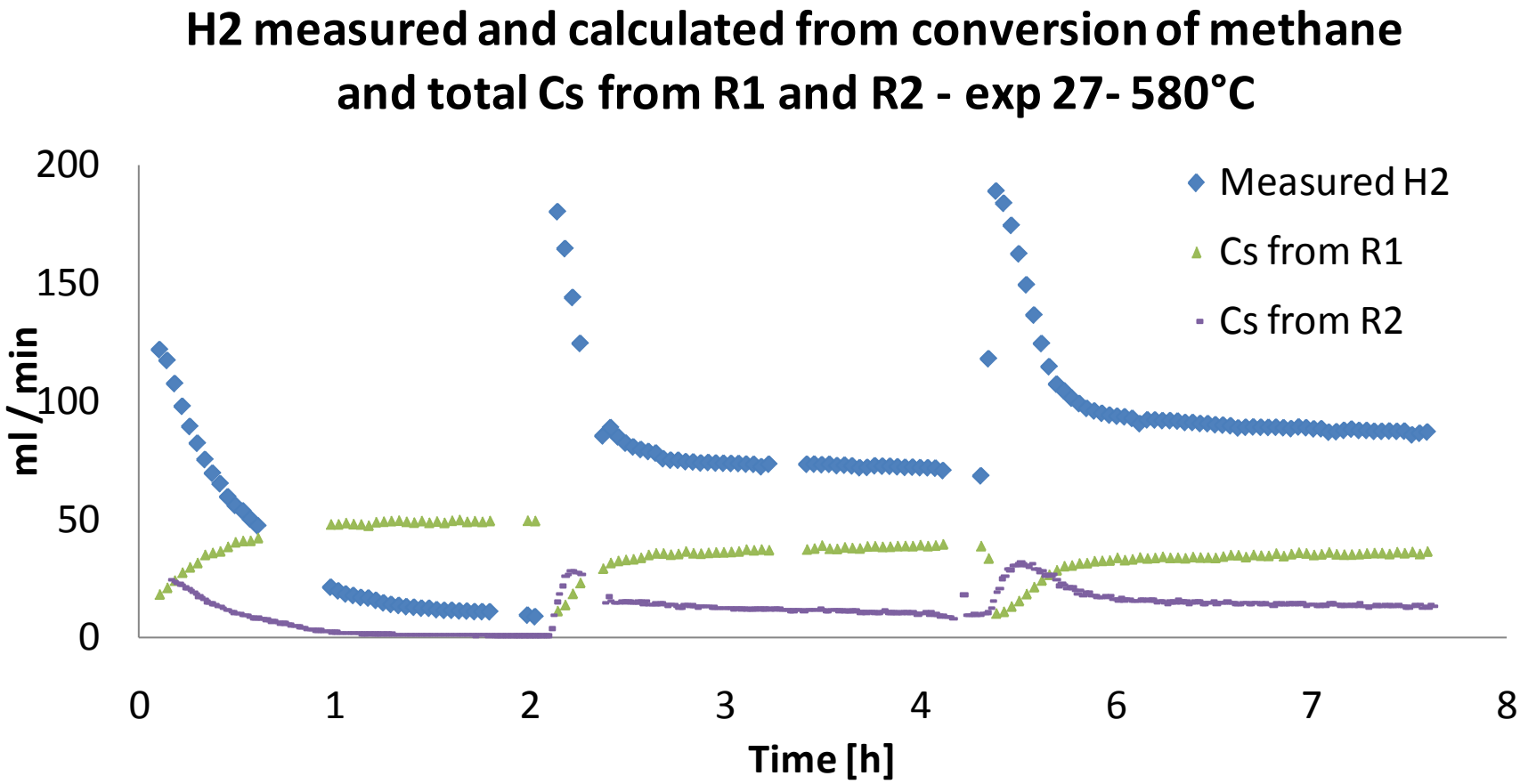
Catalyst/sorbent= 20/80



Catalyst/sorbent= 50/50

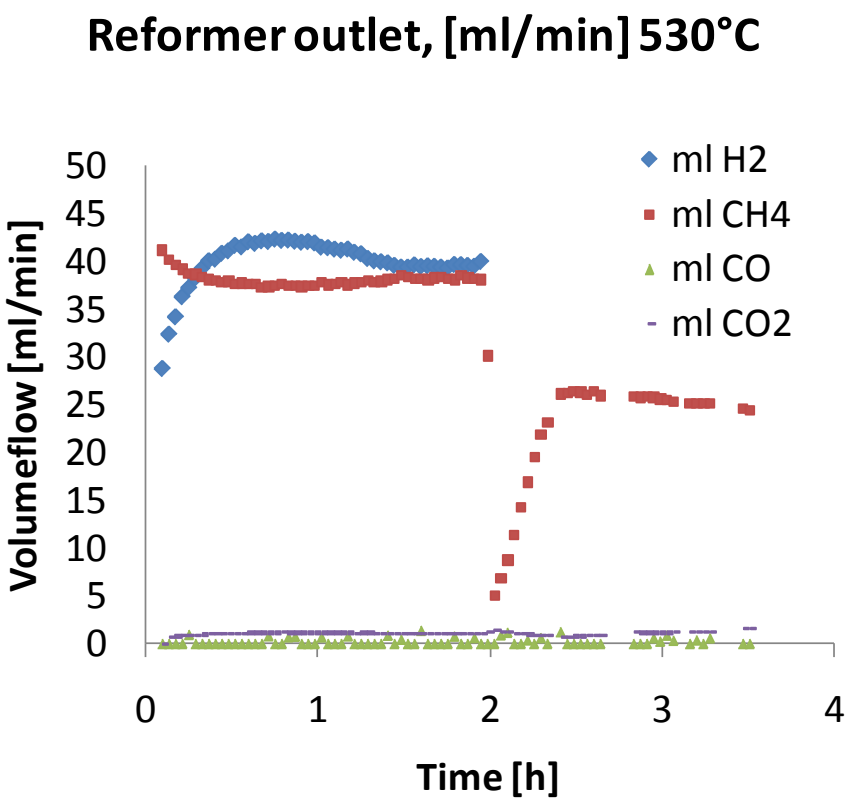
SE-SMR (feed reformer: 50 ml/min CH_4, 200 ml/min H_2O, 1860 ml/min N_2 diluent, initial catalyst/sorbent= 20/80, used and regenerated powder mixture)

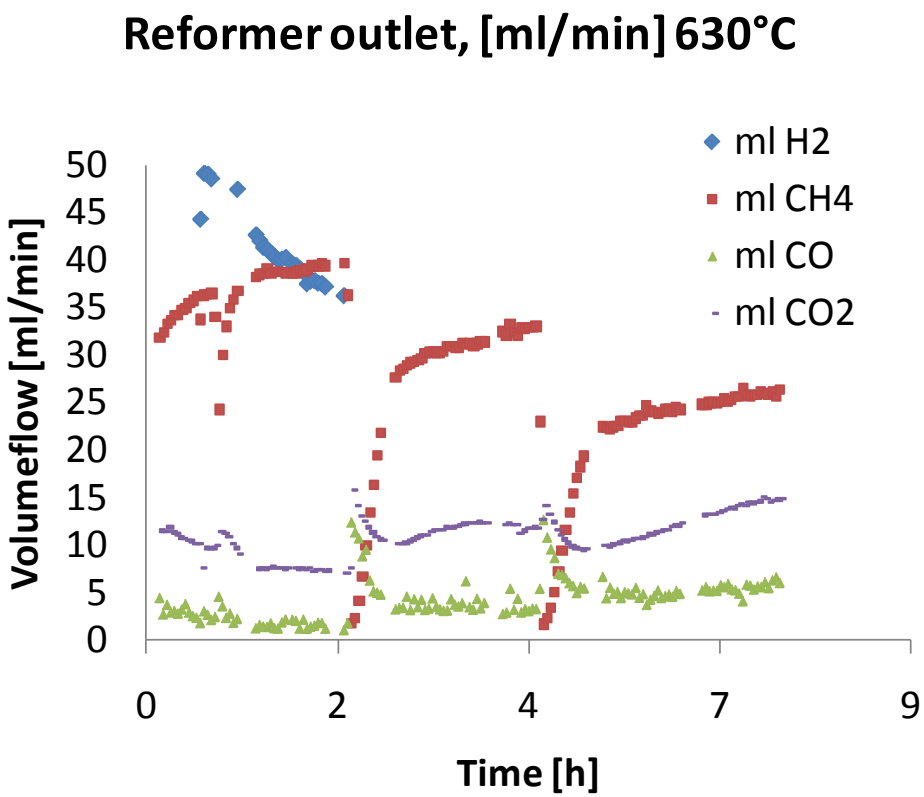
- Effect of catalyst addition during experiment:



SE-SMR (feed reformer: 50 ml/min CH_4, 200 ml/min H_2O, 1860 ml/min N_2 diluent, initial catalyst/sorbent= 20/80, used and regenerated powder mixture)

- Effect of reformer temperature:





Sorbent development

The objectives of this WP is to develop solid sorbents for CO_2 capture processes at elevated temperatures (500-900 °C) and pressures (20-30 bar) suitable for industrial use.

Our long term goal is to identify a production method for new sorbent material, for a large demonstration unit, based on cheap raw materials.

$$MO + CO_2 \underset{700\text{-}900\ C}{\overset{500\text{-}700\ C}{\rightleftharpoons}} MCO_3$$

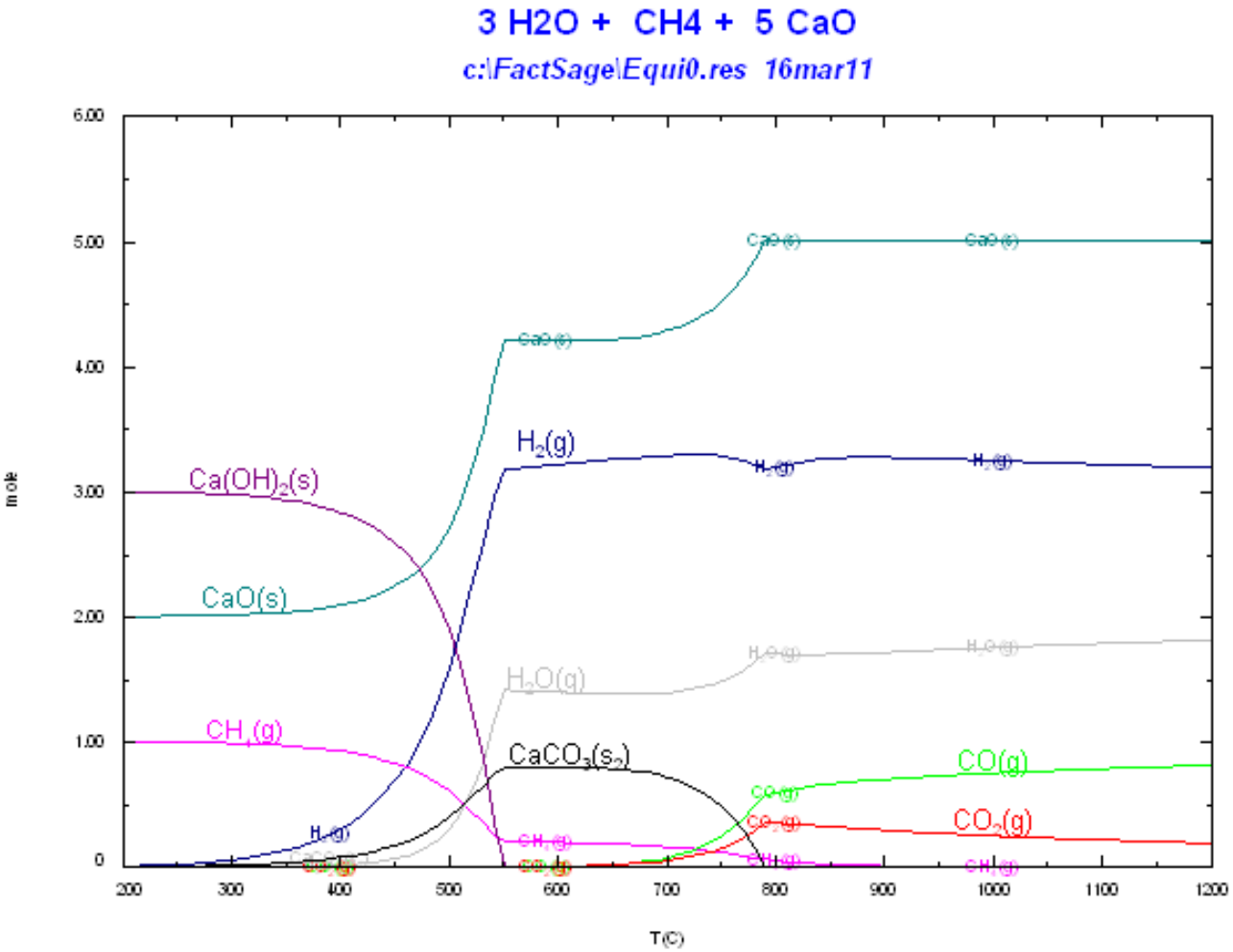
State of the art (2009) high temperature CO_2 sorbents are usually based on Ca-oxides or Li/Na-silicates/zirconates.

- **Li-based:**
  - Li_2ZrO_3
  - Li_4SiO_4
- **Ca-based:**
  - CaO **(lime)**
  - $Mg_{0.5}Ca_{0.5}O$ **(from dolomite)**
  - CaO/support **("synthetic")**

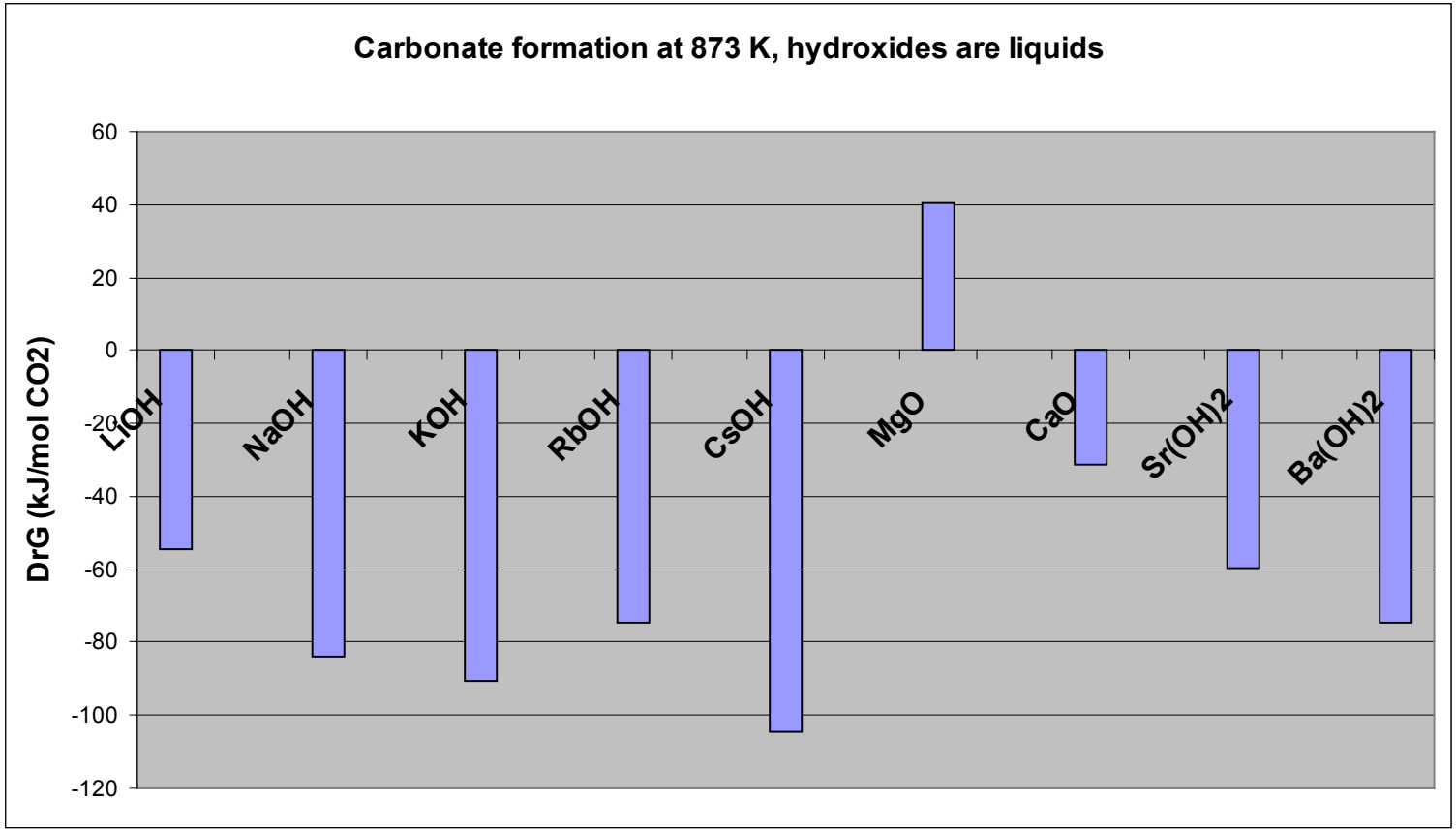
Thermodynamic search for potential novel solid sorbents:

- using FactSage 6.1
- Use thermodynamic calculations to evaluate various oxides, both simple and mixed oxides for carbonate formation at realistic process conditions (SE-SMR: 44% H_2O, 35% H_2, 11% CH_4, 7% CO_2, 2% CO, 5 bar tot).
- Sulphur tolerance has been studied:
  - Do sulphide species (as H_2S) react with the sorbent and if, does it form sulphides (S^{2-}) or sulphates (SO_4^{2-})?
  - How do such species influence CO_2 capacities and how must these sorbents be regenerated?

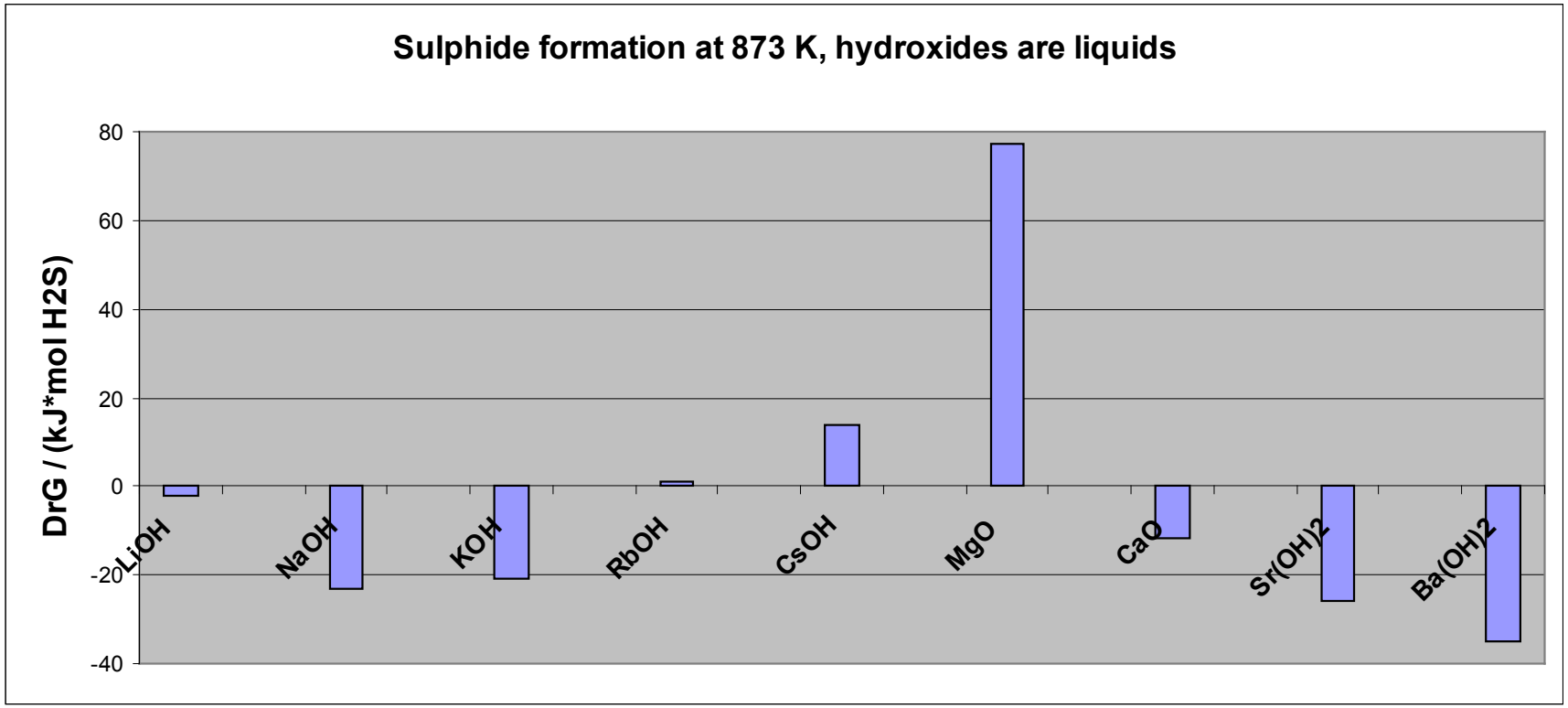
The CaO example:



Thermodynamic evaluation, example of data:



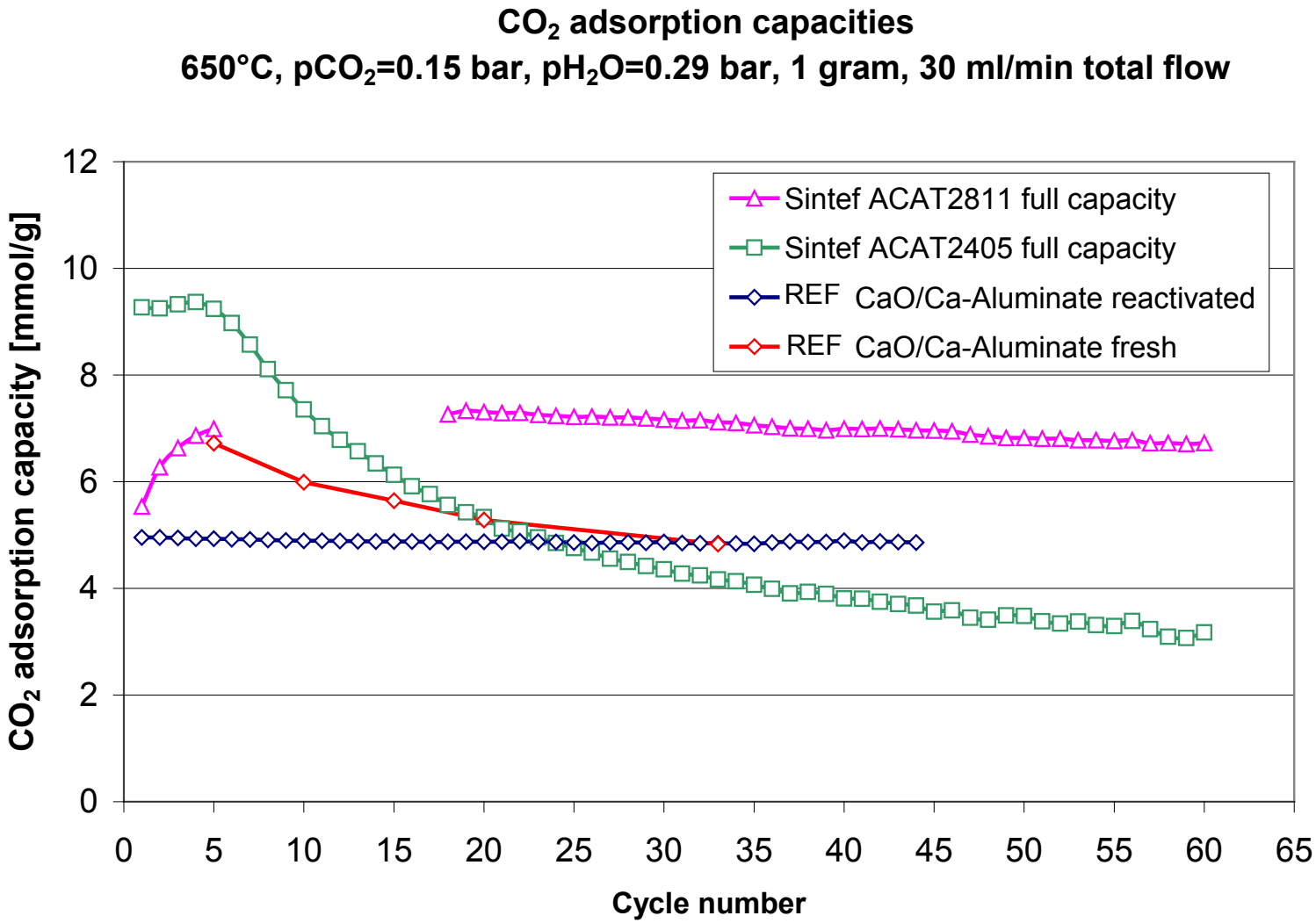
Gibbs free energy of carbonate formation at 873 K for selected hydroxides and oxides



Gibbs free energy of sulphide formation at 873 K for selected hydroxides and oxides

Summary thermodynamics

- For single component sorbents based on alkali and alkaline earth oxides/hydroxides the main trends are:
  - Most of the selected oxides/hydroxides have so high CO_2 affinity that thermal regeneration is challenging, and the incorporation of elements with less CO_2 affinity in the sorbent material may be necessary to facilitate a higher CO_2 equilibrium pressure.
  - The alkaline earth metals have a stronger tendency to form both carbonates and sulphides than the alkali metals. The alkali metals are more selective towards carbonate formation.
  - The regeneration should be performed in low O_2 concentration an at a rather high temperature to avoid sulphate formation
- Rb, seem to have interesting properties with high CO_2 affinity and very low tendency for sulphide and sulphate formation.
- The modified alkaline earth metals are better suited as CO_2 sorbents in a sweet (H_2S free) feed gas.
- Bulk CaO have good thermodynamic properties for cyclic temperature swing sorption-desorption without modification/incorporation of new elements in the sorbent material.


CO2 adsorption capacities
650°C, pCO2=0.15 bar, pH2O=0.29 bar, 1 gram, 30 ml/min total flow
CO2 adsorption capacity [mmol/g]
Cycle number
Sintef ACAT2811 full capacity
Sintef ACAT2405 full capacity
REF CaO/Ca-Aluminate reactivated
REF CaO/Ca-Aluminate fresh
0
2
4
6
8
10
12
0
5
10
15
20
25
30
35
40
45
50
55
60
65

Summary

- Finally, a lab scale CFB reactor system is working well for SE-SMR using calcined dolomite as sorbent and $NiO/NiAl_2O_4$ as catalyst
  - which can be used to evaluate novel sorbents (and catalysts) at a relatively small scale (approx 200 ml powder)

- Identification of novel sorbent compositions by the use of thermodynamic calculations using relevant process conditions are in progress.
  - CaO has good thermodynamic properties (no surprise!)
  - Some new leads will be tested.

Acknowledgement

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Thank you for your kind attention