Development of Agglomerated CO_2 Sorbent with Enhanced Chemical and Mechanical Stability for Hydrogen Production

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Our objective

- Improve the Sorption Enhanced Reforming (SER) process
  - Develop high performance CO_2 sorbent material
  - Minimize material production cost

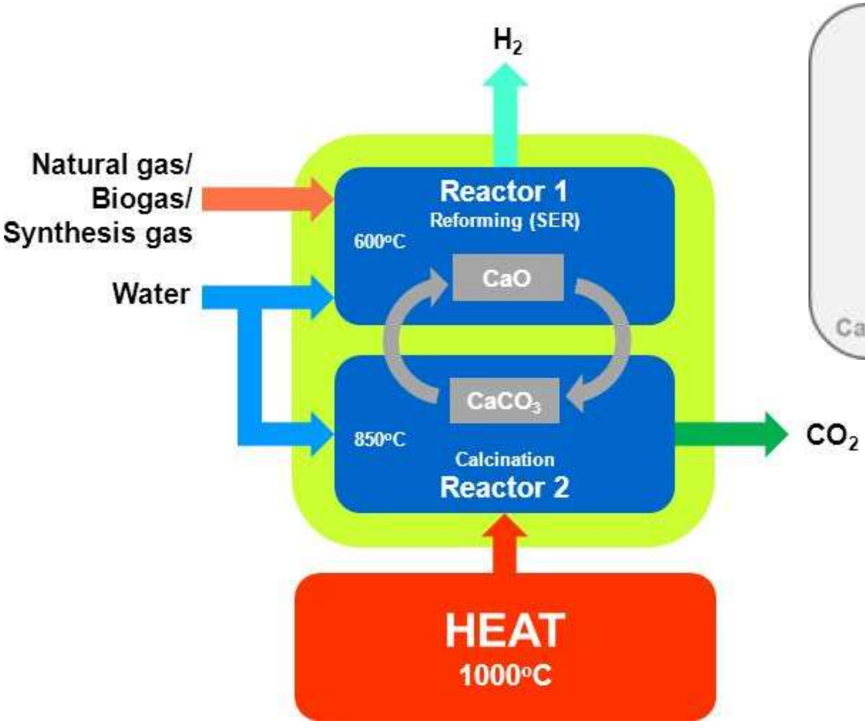
Sorption-Enhanced Reforming (SER)

- Emerging pre-combustion CO_2-capture technology
  - Reforming and high temperature CO_2 capture

- Stand-alone H_2-production with CO_2-capture
  - Industrial use
  - Transport sector

- Power production
  - H_2-production with CO_2-capture and steam boiler
    - Steam turbine cycle
  - H_2-production with CO_2-capture and CC power plant
    - Combined gas and steam turbine cycle
  - H_2-production with CO_2-capture and SOFC
    - ZEG concept – Potential for high efficiency (www.zegpower.com)

Sorption-Enhanced Reforming (SER)



Reforming

$$CH_4\,(g) + H_2O\,(g) \rightarrow CO\,(g) + 3H_2\,(g)$$

Water gas shift

$$CO\,(g) + H_2O\,(g) \rightarrow CO_2\,(g) + H_2\,(g)$$

Carbonation

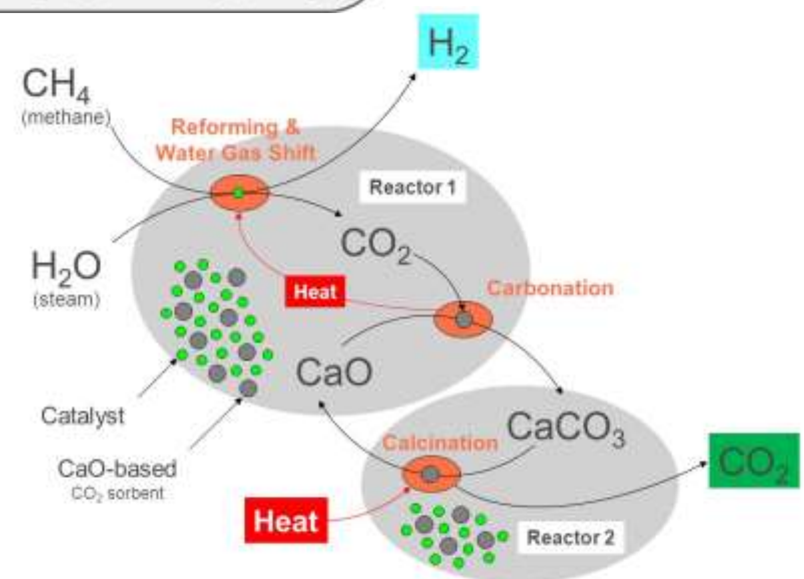
$$CaO\,(s) + CO_2\,(g) \rightarrow CaCO_3\,(s)$$

Total reaction (SER)

$$CaO\,(s) + CH_4\,(g) + 2H_2O\,(g) \rightarrow CaCO_3\,(s) + 4H_2\,(g)$$

Combination of :

- Reforming
- Water gas shift
- Carbonation



- Higher H_2-yields (95 vol% +) than in conventional SMR, in one single step, and at lower temperature (500-600°C)
- No need for shift reactors and catalysts
- Production of relatively pure CO_2
- Simplified process layout and process intensification
- Potential for lower production costs and energy savings

Calcination (regeneration)

$$CaCO_3\,(s) \rightarrow CaO(s) + CO_2\,(g)$$

Hydrogen production in one single step

Material requirements

High CO_2- sorption capacity

Low production and recirculation costs

Fast capture and regeneration kinetics

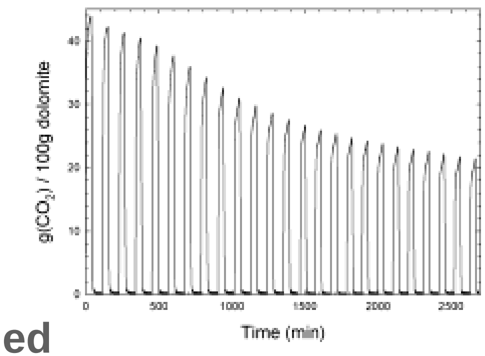
Mechanical and thermal stability

Stable in high/low steam/CO_2 partial pressure

Compatible with Ni catalyst

Natural CaO-based sorbents: calcite and dolomite

- Good availability and low cost
- Large absorption capacity and satisfactory reaction kinetics
- Proven SER hydrogen yields up to 95+ vol%



- Loss of sorption capacity during cycling
- Not optimal mechanical stability

For pre-combustion applications:

- Sulphur removal from raw material is often needed
- Do not match catalyst lifetime

Use of an inert porous solid support to reduce sintering of CaO particles and increase the chemical and mechanical stability of the material

Al_2O_3, $MgAl_2O_4$, $Ca_{12}Al_{14}O_{33}$, SiO_2, CuO, $CaTiO_3$, ZrO_2 etc…

Mayenite is the material chosen for this study

Synthesis of the CaO-based sorbent material with mayenite support

Hydrothermal synthesis

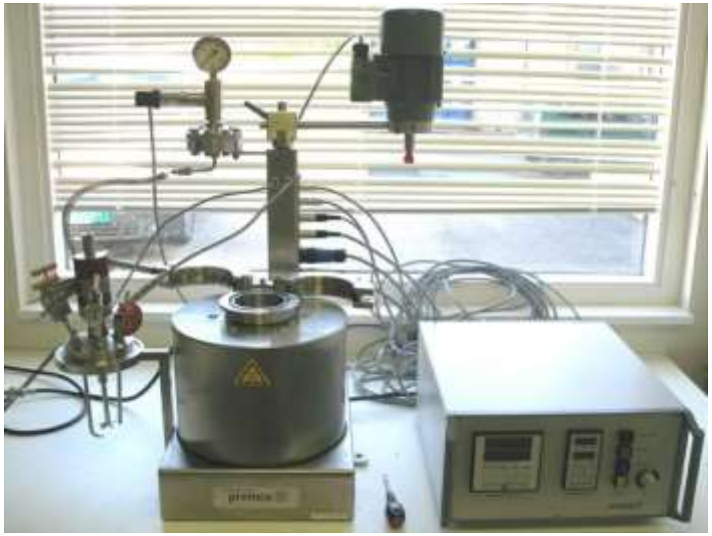
- Hydroxide precursors solutions mixed in an autoclave
- Heating of the reactants to 150°C accompanied by pressure increase to 3-4 bar. Water works both as pressure transmitting medium and as a solvent.
- Cooling, filtration and drying
- Calcination

Advantages of hydrothermal synthesis

- Low cost precursor materials ($Ca(OH)_2$ and $Al(OH)_3$)
- Quite low temperature
- Products are homogeneous in composition
- Easy to control the purity, composition and size of particles
- Easy to up-scale
- Cost effective

Hydrothermal synthesis equipments

Autoclaves (50 mL) with pressure, temperature and flow control
~10 g material can be prepared



Pressurized reactor (600 mL) with pressure, temperature and flow control with optional gas bubbling
~100 g material can be prepared

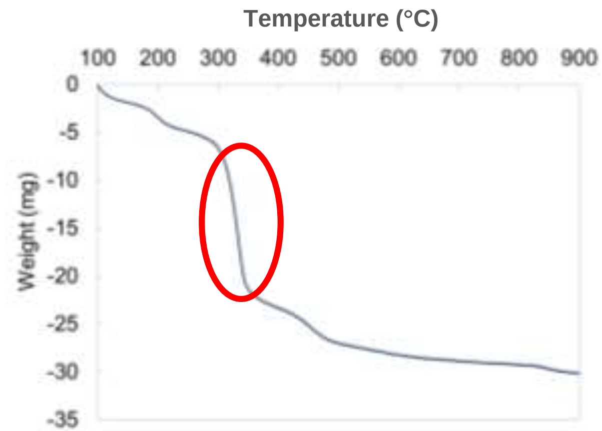
Hydrothermal synthesis of synthetic sorbents

In aqueous solution, 150 °C, 1-5h, Solid/Liquid= 3

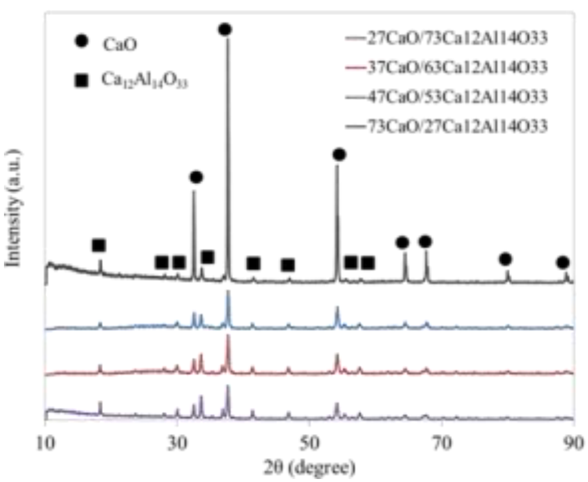
$3Ca(OH)_2 + 2Al(OH)_3 \rightarrow Ca_3Al_2[(OH)_4]_3$
(Hydrogarnet)

Hydrogarnet decomposition T > 350 °C

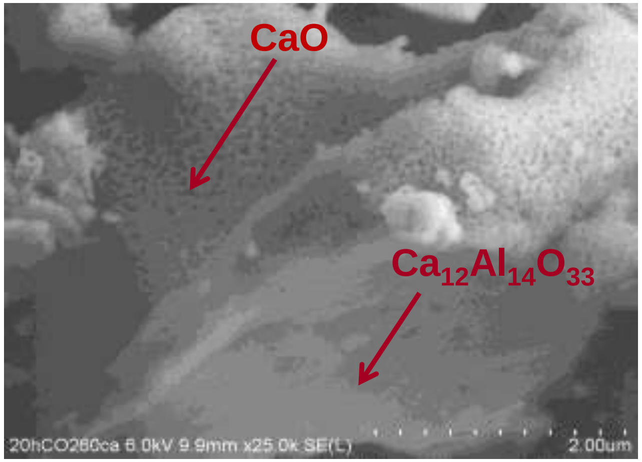
$7Ca_3Al_2[(OH)_4]_3 \rightarrow 9CaO + Ca_{12}Al_{14}O_{33} + 42H_2O$
(Mayenite)



Decomposition curve of the hydrogarnet



Calcined at 1000°C, 1h



High micro-porosity

Agglomeration of hydrothermal sorbent powders

- The synthesized micro-powders are too fine to be handled in a process using either packed or fluidized bed reactors

→ The powder must be agglomerated to form granules

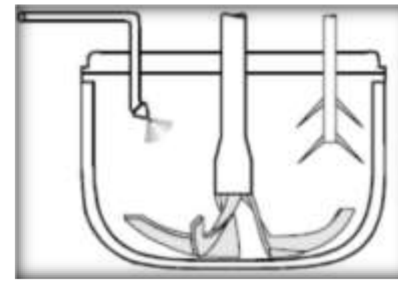
Requirements

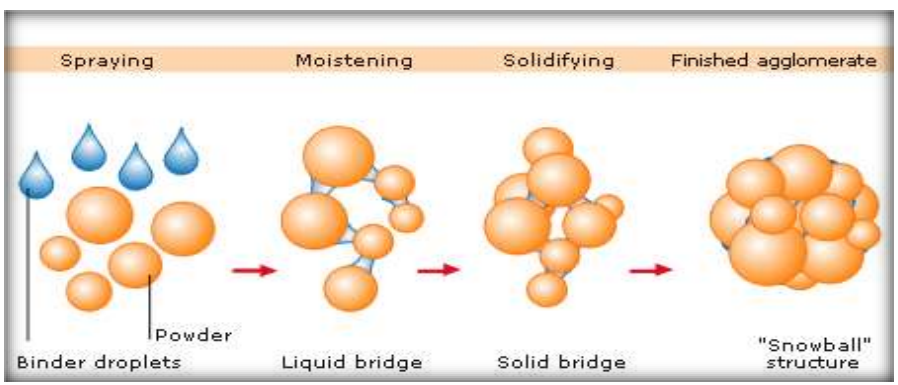
- Produce uniform granule mixtures
- Generate specific size, shape, porosity and density
- Obtain good mechanical strength

Agglomeration technique: High shear agglomeration

High energy mixing and granulation

- Aqueous binder (5% PEG) is used (wet granulation)
- Binder is dispersed by a rotating blade which provides shear forces in the powder mass
- Inter-particle bonds strengthen and powder particles stick together to form larger granules

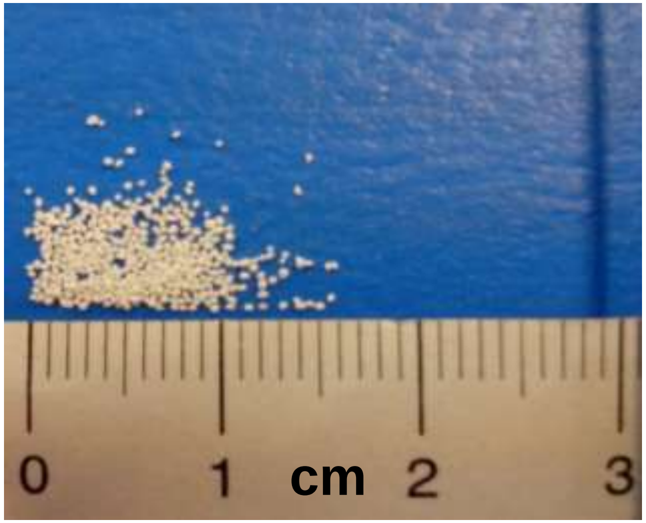




Agglomerated hydrothermal sorbent

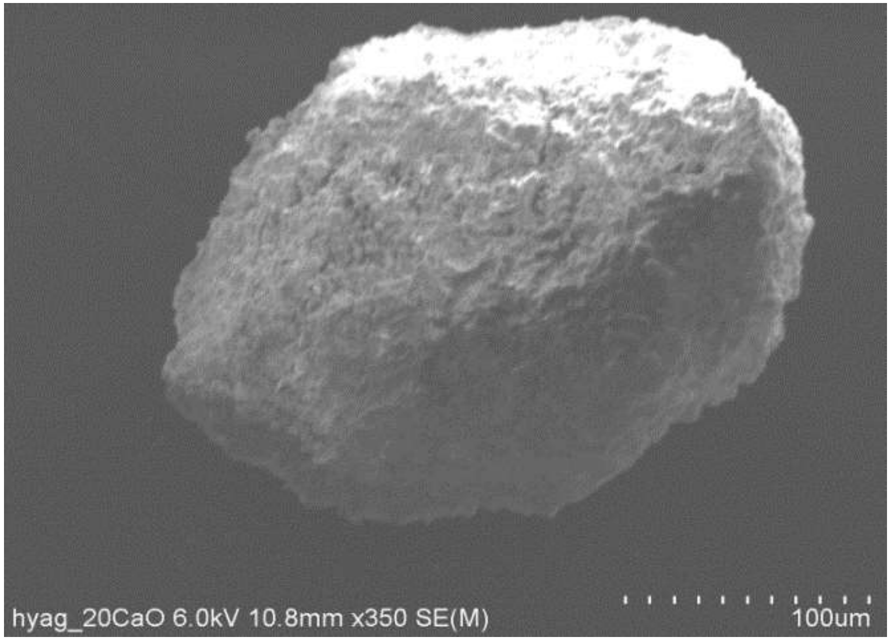
Sorbent : **Hydrothermal dried powder**

Agglomeration conditions:
Impeller speed: 1000 rpm
Chopper speed: 3600 rpm
Binding agent: 5 % polyethylene glycol (PEG 4000) in water

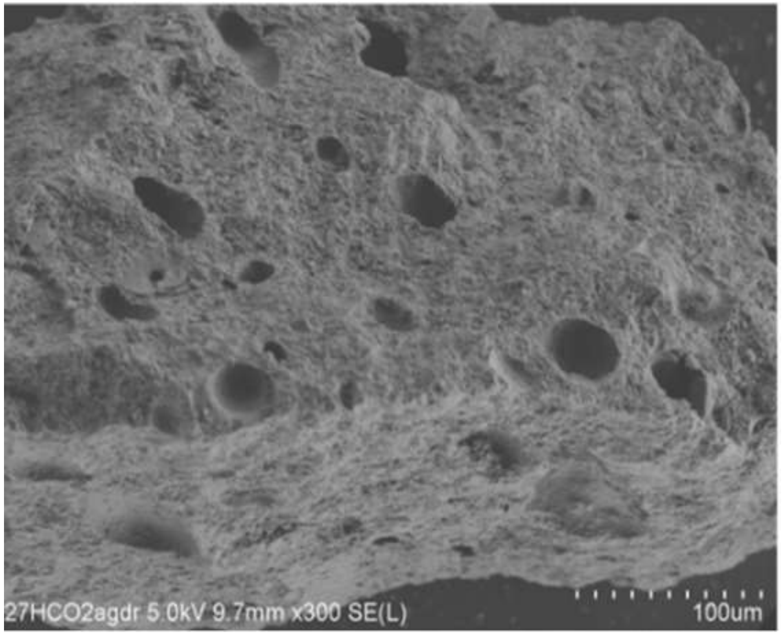


SEM pictures of agglomerated hydrothermal sorbent

High shear agglomeration



Near to spherical granules



Macro-porous granules

Mechanical properties of agglomerated sorbent

Digital Force Gauge
SHIMPO FGV-10X

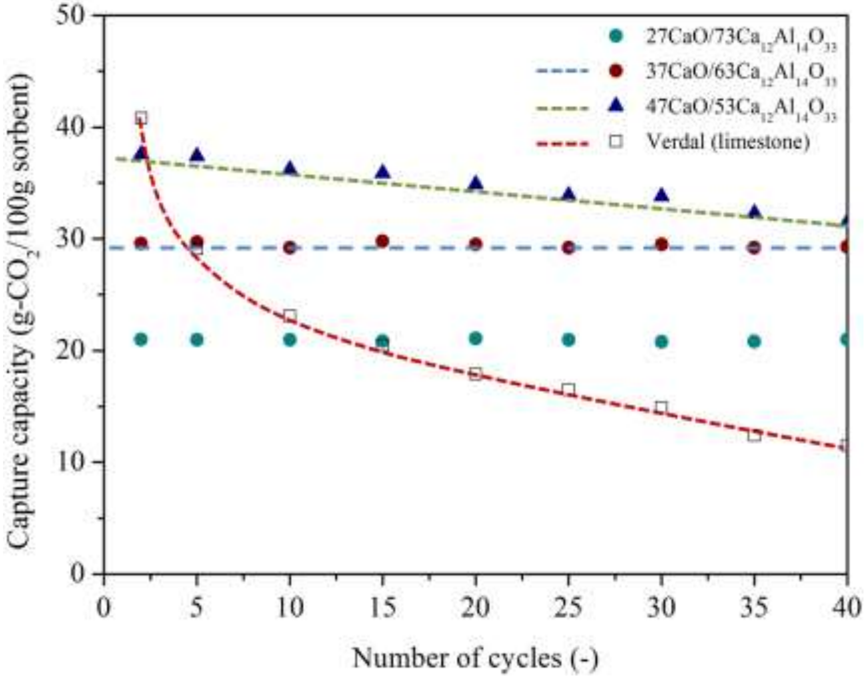
Measurements of crushing strength

Sorbent	Median crushing strength (N)
Limestone (Verdal)_uncalcined	7.0
Limestone (Verdal)_calcined	1.6
Hydrothermal _agglom	11.4
Sol-gel _agglom	13.4

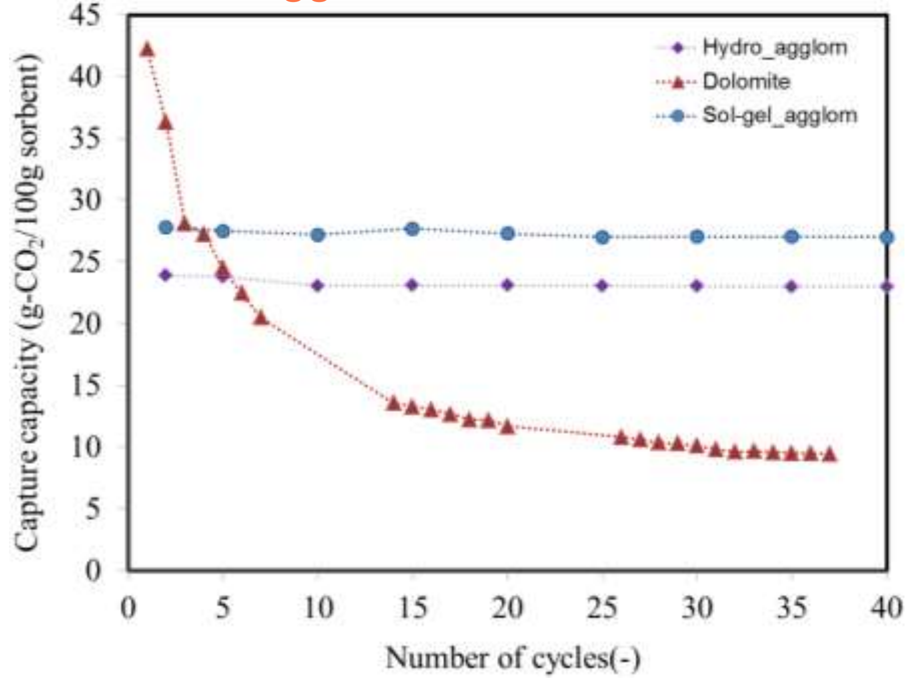
Better crushing strength than raw limestone

TGA multi-cycling of hydrothermal sorbents

Hydrothermal sorbents (pelletized)



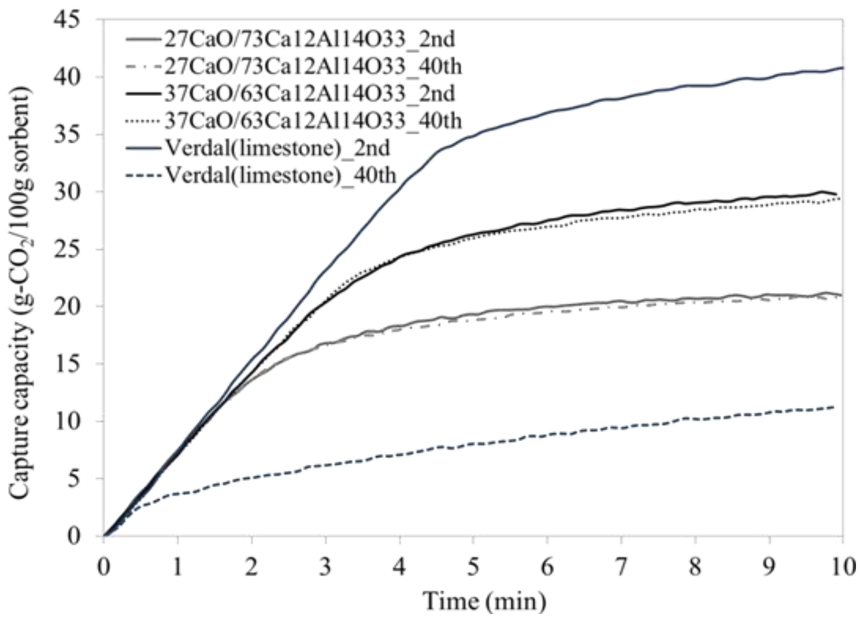
Agglomerated sorbents

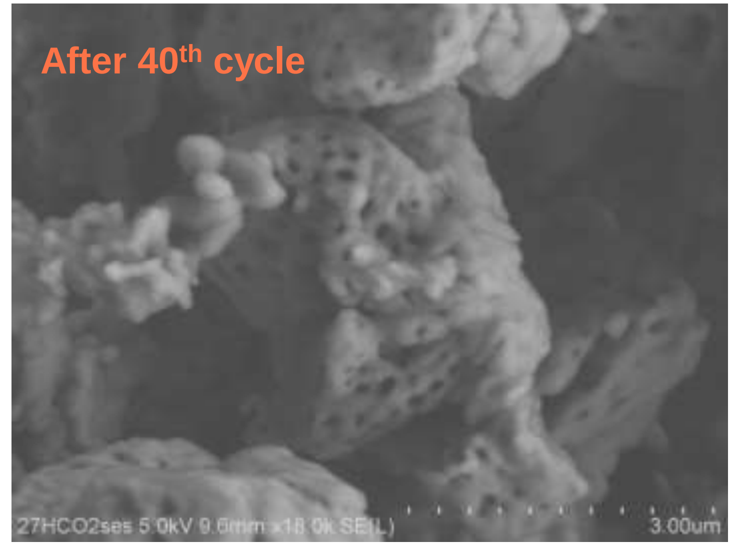


Carbonation: 600 °C for 10 min; 15 vol % CO_2, 47 vol % H_2O balanced in N_2
Regeneration: 850 °C for 3 min; 21 vol % CO_2, 77 vol % H_2O, balanced in N_2

- High chemical stability for sorbents with more than 60 wt% mayenite
- CO_2 uptake around 30g CO_2/100g calcined sorbent
- About 4 times the CO_2 uptake of limestone after 40 cycles

Long-term chemical stability of hydrothermal sorbent



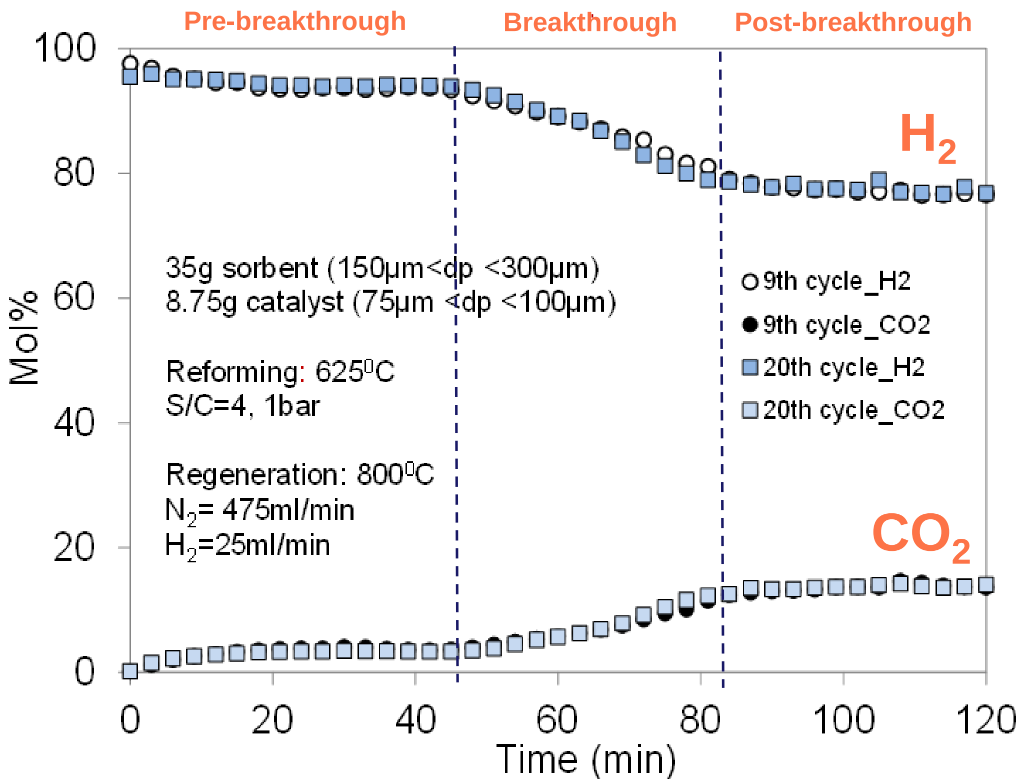


Micro-porosity conserved

Carbonation: 600 °C for 10 min; 15 vol % CO_2, 47 vol % H_2O balanced in N_2
Regeneration: 850 °C for 3 min; 21 vol % CO_2, 77 vol % H_2O, balanced in N_2

- No loss of reaction kinetics with increasing number of cycle
- >95% conversion of available CaO
- Micro-porous structure of the material is conserved

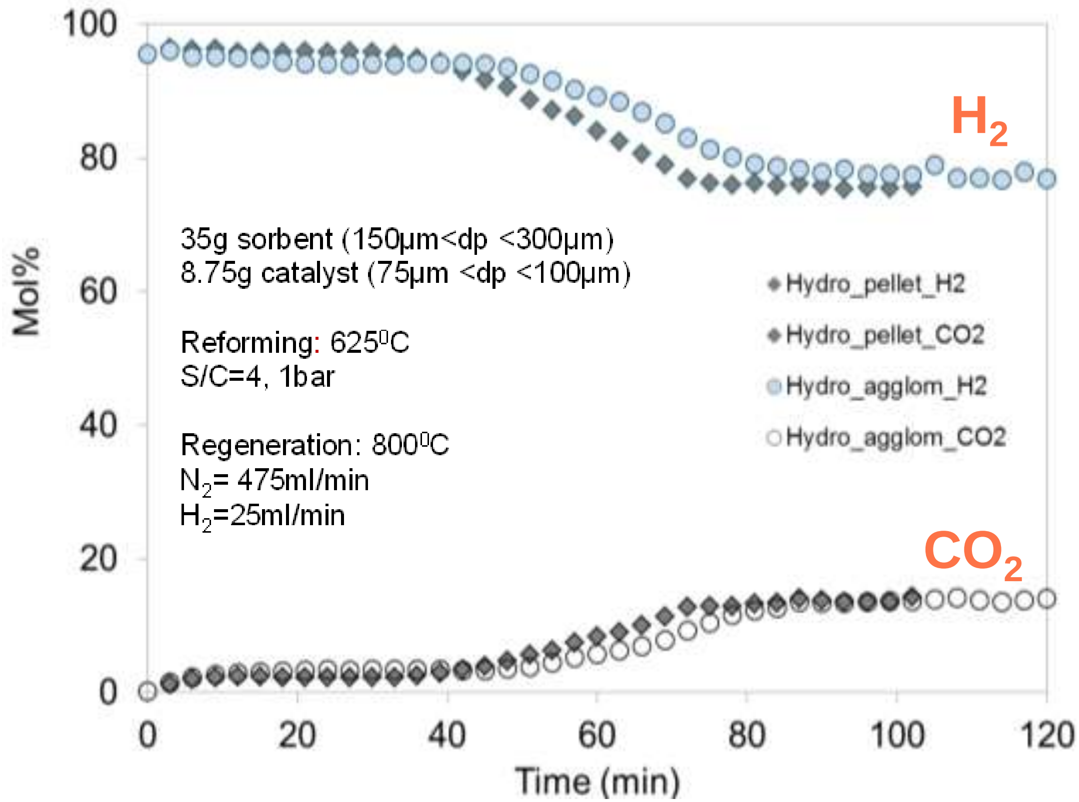
H_2 production by SER in fixed bed reactor using agglomerated hydrothermal sorbent



- Multi-cycle tests show stable enhanced H_2 production
- >95 mol% H_2 is produced in each cycle

- **Commercial reforming catalyst**
- **Sorbent/catalyst = 4 w/w; Feed flow = 600 ml_N/ min; WHSV = 0.647 h^{-1}**
- **Little H_2 added during regeneration to prevent oxidation of catalyst**

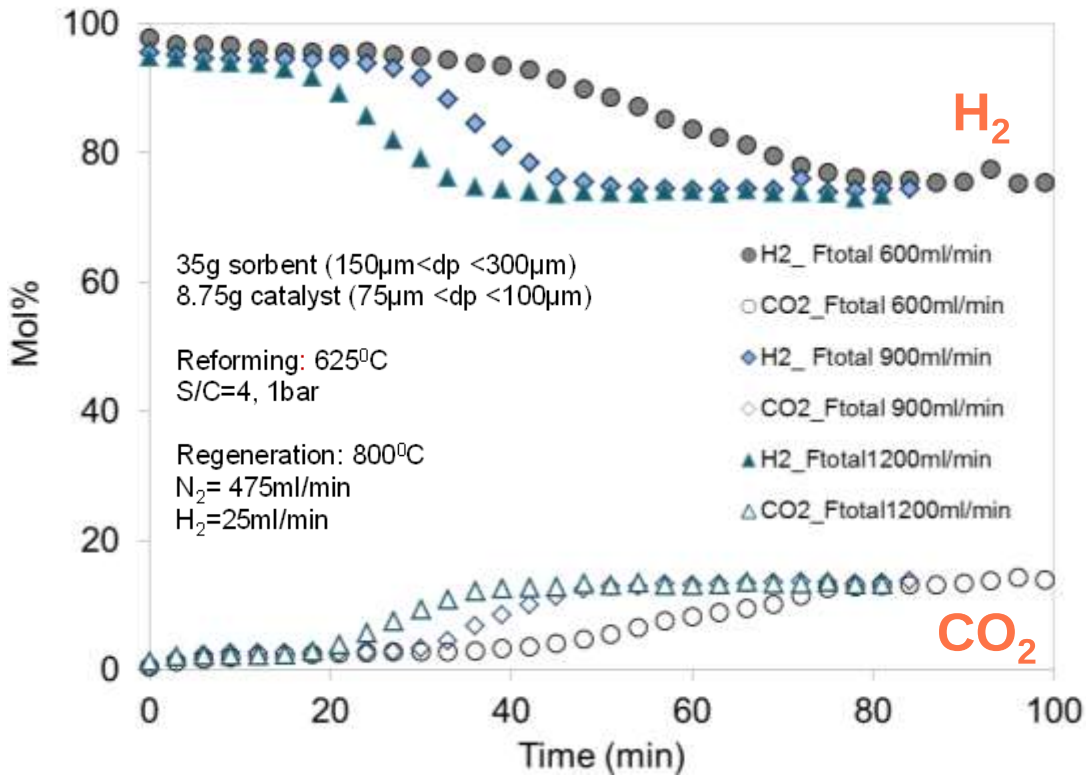
Agglomerated vs pelletized sorbent in SER reaction, fixed bed reactor



- Production time is slightly improved for the agglomerated sorbent compared to pelletized (50MPa) sorbent
- Better micro-porosity contributes to a better sorbent conversion and a longer production time for agglomerated sorbent

- **Commercial reforming catalyst**
- **Sorbent/catalyst = 4 w/w; Feed flow = 600 ml_N/ min; WHSV = 0.647 h^{-1}**
- **Little H_2 added during regeneration to prevent oxidation of catalyst**

Effect of space velocity on SER performances, fixed bed reactor

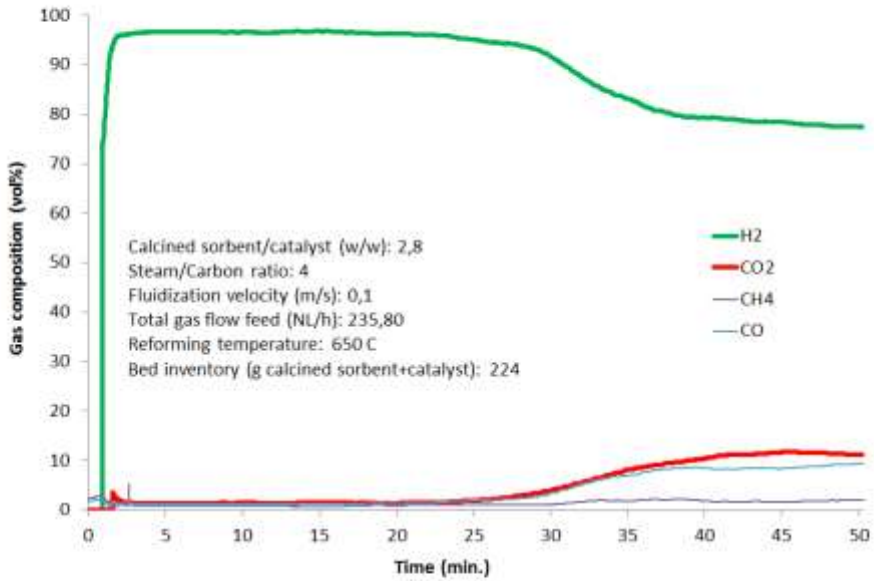


- Sharper breakthrough is obtained when increasing gas velocity
- Good SER performances even at higher gas velocity
- Less than 2 mol% CO_2 is released with >95mol% H_2 production

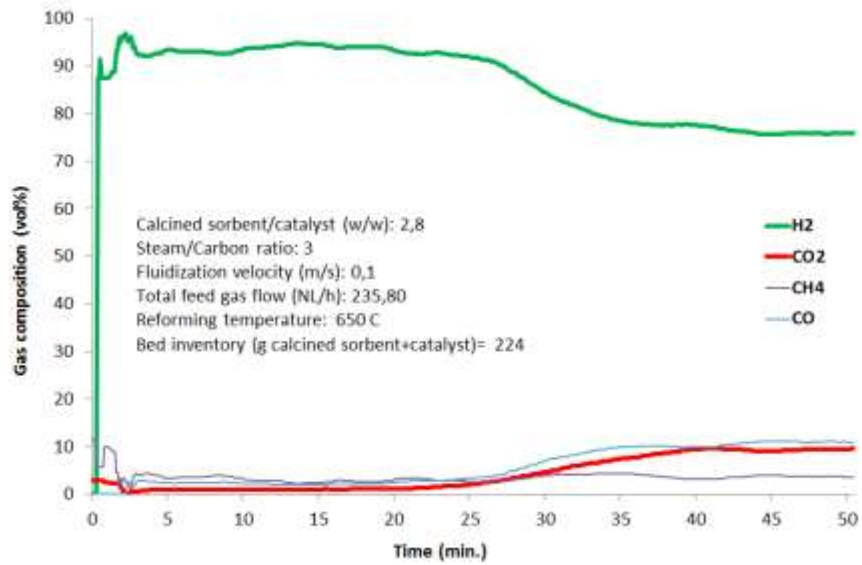
- **Commercial reforming catalyst**
- **Sorbent/catalyst = 4 w/w; Feed flow = 600-1200 ml$_N$/ min; WHSV = 0.647-1.294 h^{-1}**
- **Little H_2 added during regeneration to prevent oxidation of catalyst**

H_2 production by SER in <u>fluidized bed reactor</u> using agglomerated hydrothermal sorbent

S/C ratio = 4



S/C ratio = 3



- **Commercial reforming catalyst**
- **Sorbent/catalyst = 2.8 w/w; 0.1 m/s fluidization velocity**

- Good SER performance also in fluidized bed conditions
- 95+ vol% H_2 was produced for S/C ratios 3 and 4

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Conclusions and further work

- IFE developed a new simple and low-cost synthesis method for production of CaO-based CO_2 sorbent with high chemical stability
  - 4 times the CO_2 uptake of limestone after 40 cycles

- An agglomeration process using shear agglomeration has been developed for granule production with enhanced mechanical properties
  - 7 times the crushing strength of calcined limestone

- Agglomerated sorbent granules were successfully tested in both fixed and fluidized bed reactors for H_2 production by SER

- Multi-cycle operation confirmed the excellent stability of the sorbent, more than 95 mol% H_2 was produced in a single reaction step

Further work

- Test the agglomerated sorbent in SER multi-cycle with steam in the regeneration
- Development of combined sorbent-catalyst granules for reduced CAPEX/OPEX
- Up-scaling of production methods
- Test of the sorbent material in relevant SER process conditions (SER fluidized bed pilot plant at HyNor Lillestrøm, Norway)

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  www.ife.no/depts/envtech

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Thank you for your attention!!