



Energy research Centre of the Netherlands

Advanced Membrane Reactors for Carbon-Free Fossil Fuel Conversion

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Contents

The project

Objectives

R&D results ECN

Reactor design

System analysis

Materials science

Catalyst testing

Conclusions

Advanced Membrane Reactors in Energy Systems

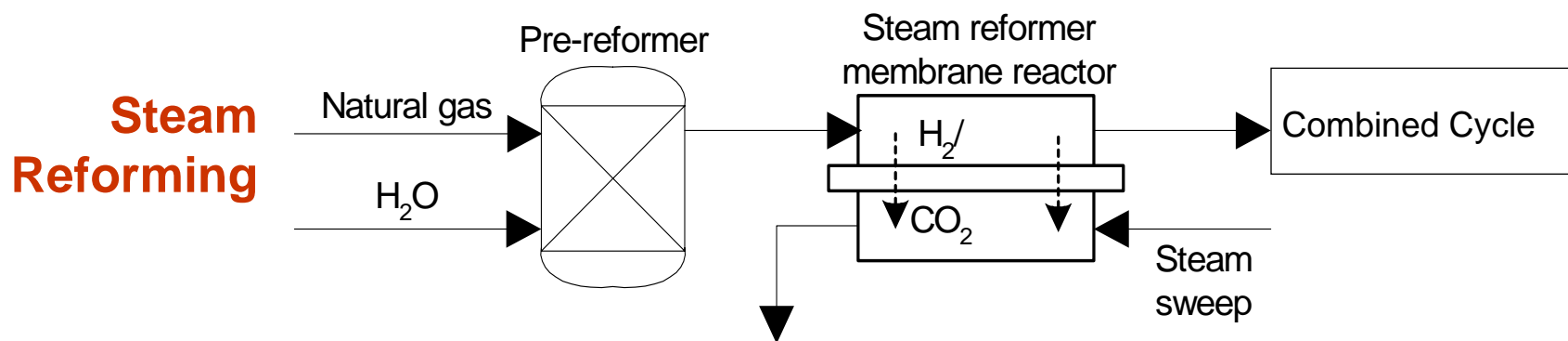
Development of novel membranes for membrane reactors.

Objective:

The purpose of this project is to develop H₂ and CO₂ membranes to allow combinations of natural gas reforming or WGS with H₂ or CO₂ separation in separation enhanced reactors, i.e. membrane reactors, for carbon-free hydrogen production or electricity generation.

Application:

NGCC with CO₂ membrane reformer reactor

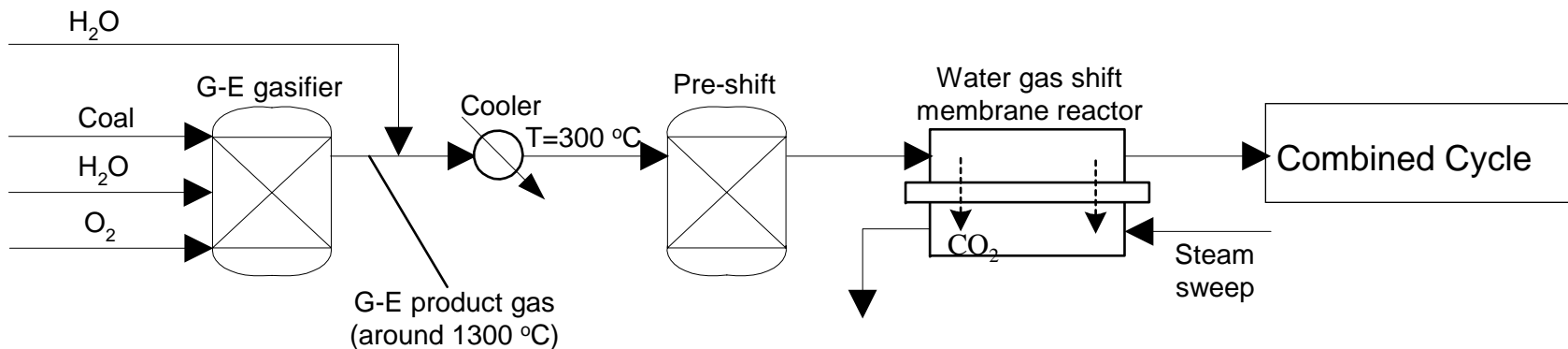


Advantages compared to H₂ membrane reformer:

- eliminating the requirement of water gas shift reactors: cost reductions
- offering higher conversion efficiencies at lower temperatures
- H₂ rich stream remains at elevated pressure and temperature
- CO inhibition of membrane not foreseen
- no need for CO₂ cleaning section

Application:

IGCC with CO₂ membrane water gas shift reactor



Advantages compared to H₂ membrane WGS reactor:

- eliminating the requirement of LT water gas shift reactor: cost reduction
- incomplete CO conversion in WGS does not reduce the IGCC efficiency but lowers CO₂ capture ratio
- H₂ rich stream remains at elevated pressure and temperature
- CO inhibition of membrane not foreseen
- no need for CO₂ cleaning section

Reactor Design/System analysis

CO₂ versus H₂ selective membranes

Main Question

Membrane application:

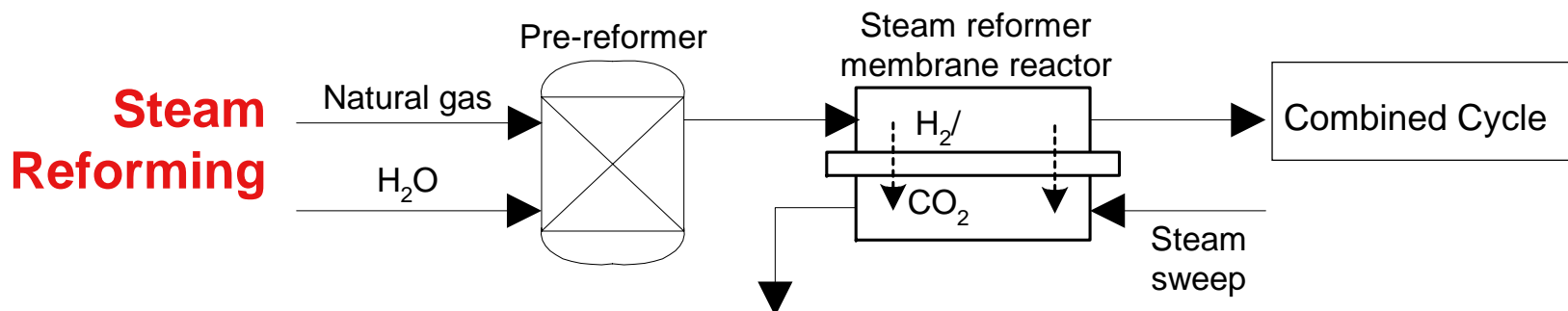
'Everybody' agrees on the fact that either H₂ or CO₂ selective membranes are viable options for carbon capture technologies

But.....:

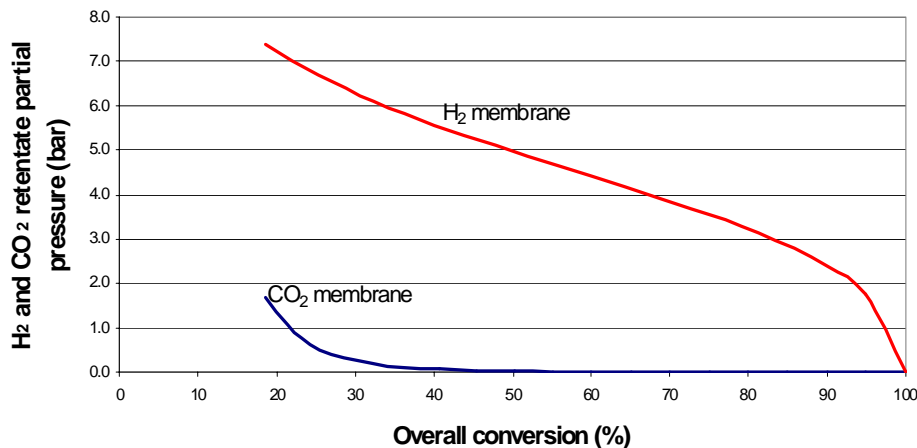
*'Nobody' cares or dares to look into the process boundary conditions:
Are both membranes equally fit to operate in a certain process??*

Reactor Design/System analysis

CO₂ versus H₂ selective membranes: Reforming



Membrane reformer: Residual partial pressure of permeating component in retentate as a function of conversion.



@ 600 °C, 40 bar, S/C = 3, Sweep: steam 5 bar, 600 °C, Sweep flow/Feed flow = 0.11 (mole/mole)

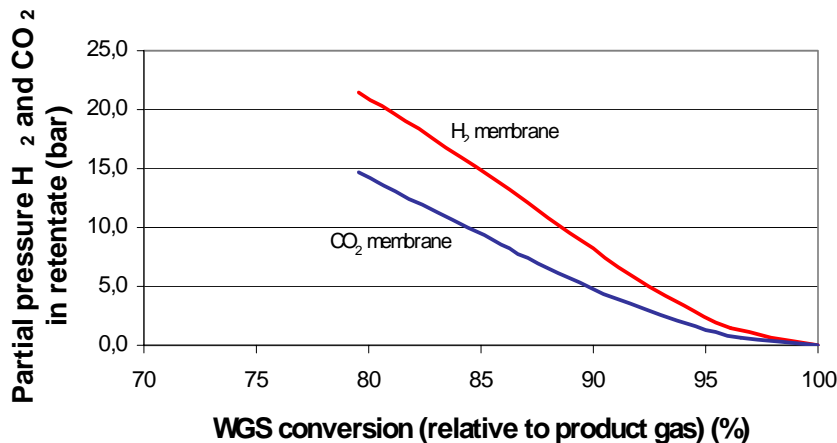
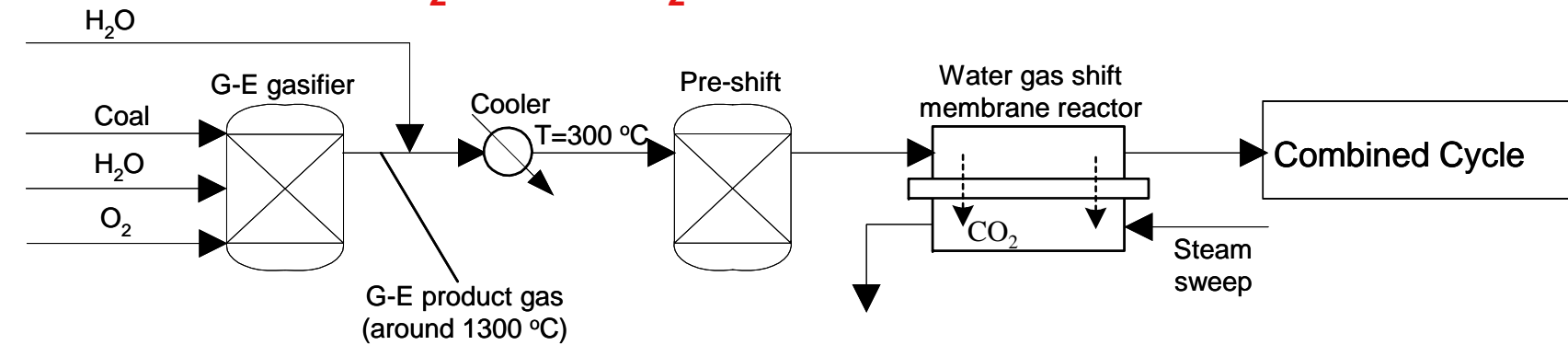
➤ Conversion relatively easy enhanced by separation of H₂ → favourable kinetics

➤ CO₂ selective membranes show a too low conversion and are therefore not suitable, as opposed to H₂ selective membranes

See poster

Reactor Design/System analysis

CO₂ versus H₂ selective membranes: IGCC



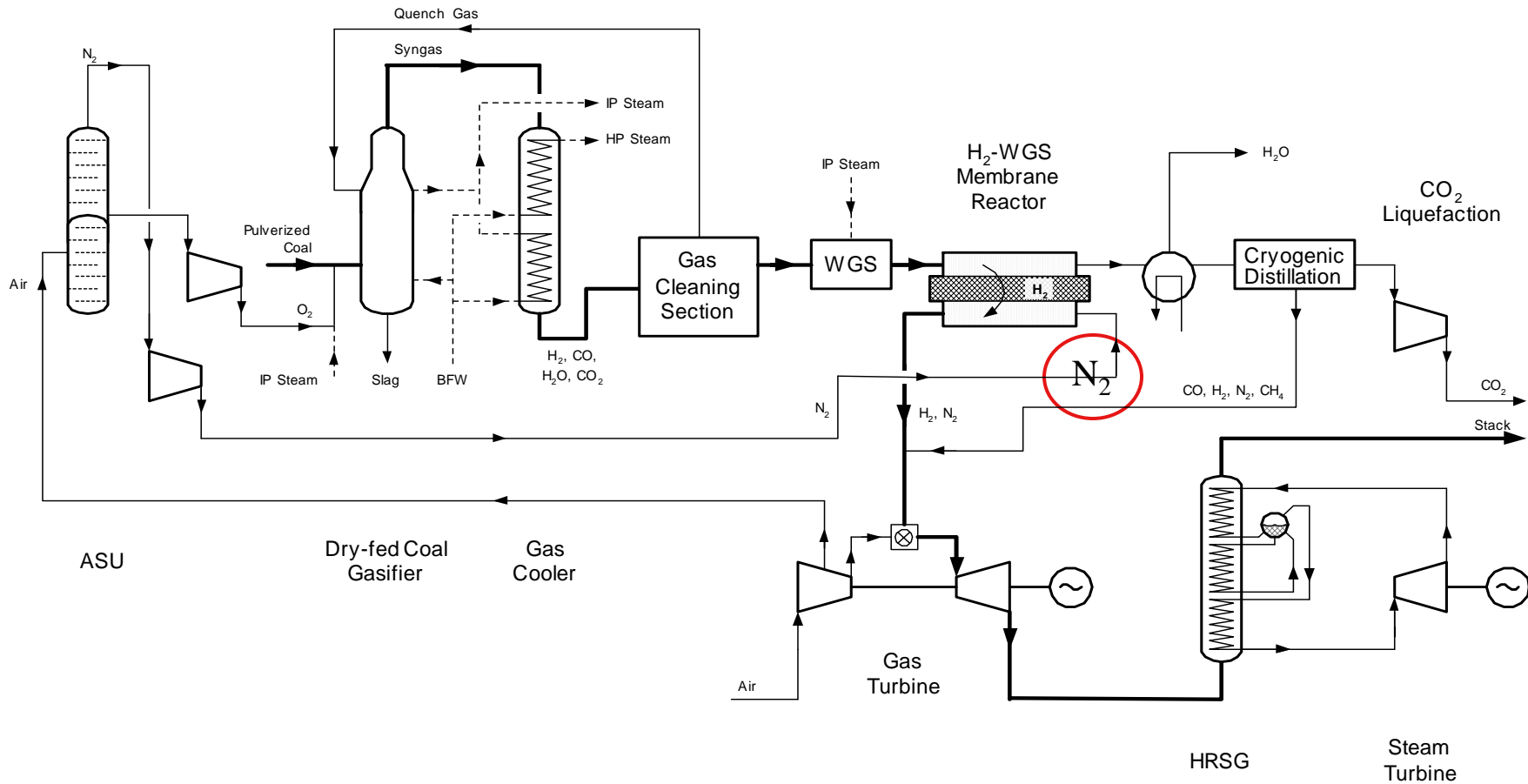
- *H₂ permeation results in better CO₂ recovery and CO conversion but CO₂ permeation does not perform much worse*
- **Complete system and exergy analysis needed to really determine all pros and cons**

@300 °C, 42.2 bar, S/C just enough to complete water gas shift, excess catalyst, Sweep: steam 17 bar, 300°C

See poster

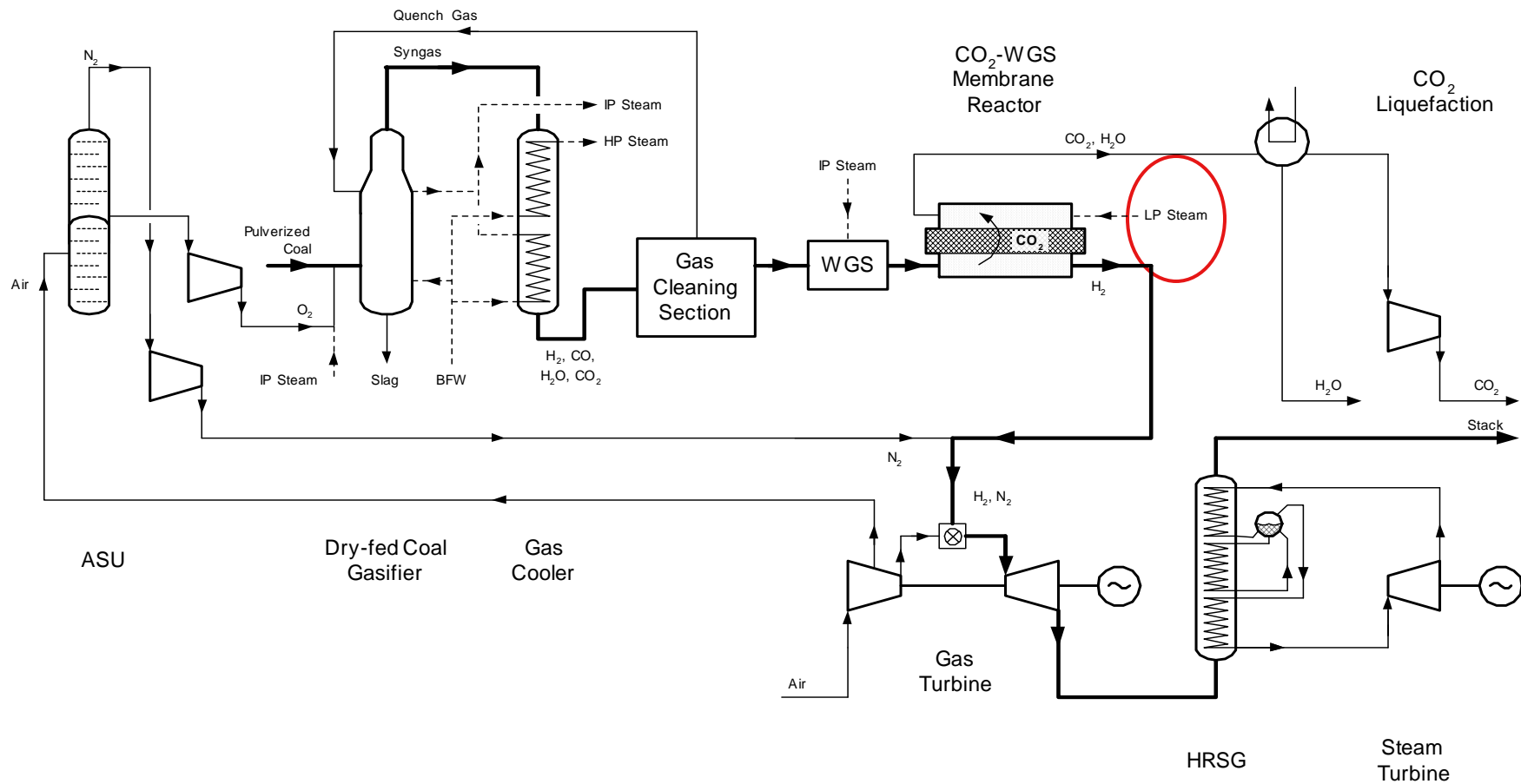
Reactor Design/System analysis

IGCC with H₂ WGS Membrane Reactor



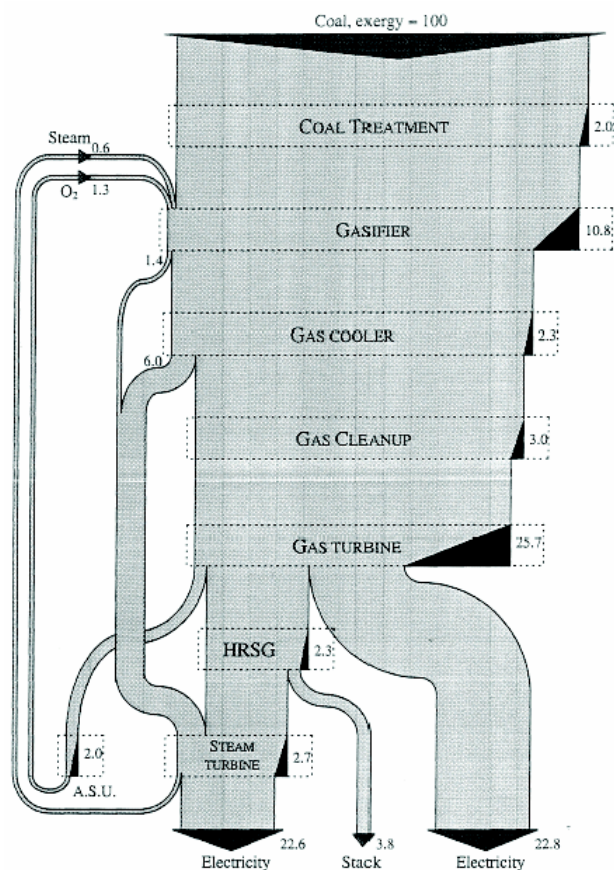
Reactor Design/System analysis

IGCC with CO₂ WGS Membrane Reactor

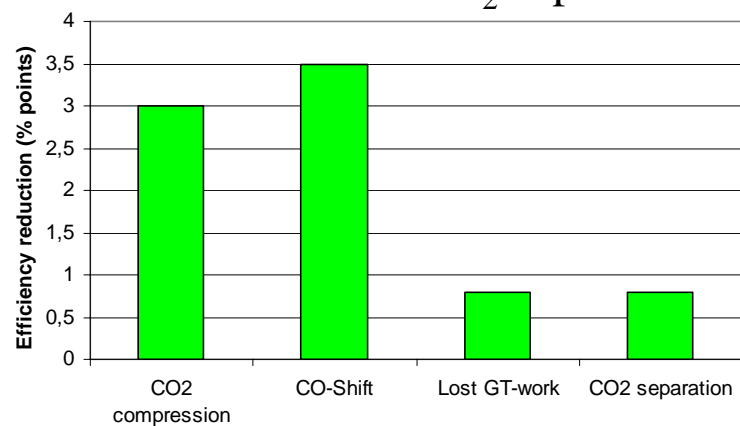


Reactor Design/System analysis

CO₂ versus H₂ selective membranes: Exergy analysis IGCC



Losses due to CO₂ capture



Case	Output [MW _e]	Efficiency [-]	Carbon Capture [-]	Membrane Area [m ²]	Sweep Steam [kg/s]
IGCC Base Case	500	47.9	-	-	-
IGCC Selexol (HT- & LT-WGS)	417	39.9	91.7	-	-
IGCC H ₂ -selective WGS-MR	425	40.7	84.8	15000	-
IGCC CO ₂ -selective WGS-MR	398	38.1	85.5	22500	55.6

Sensitivity analysis on CO₂ permeation: see poster

Reactor Design/System analysis: Conclusions

Reactor modeling

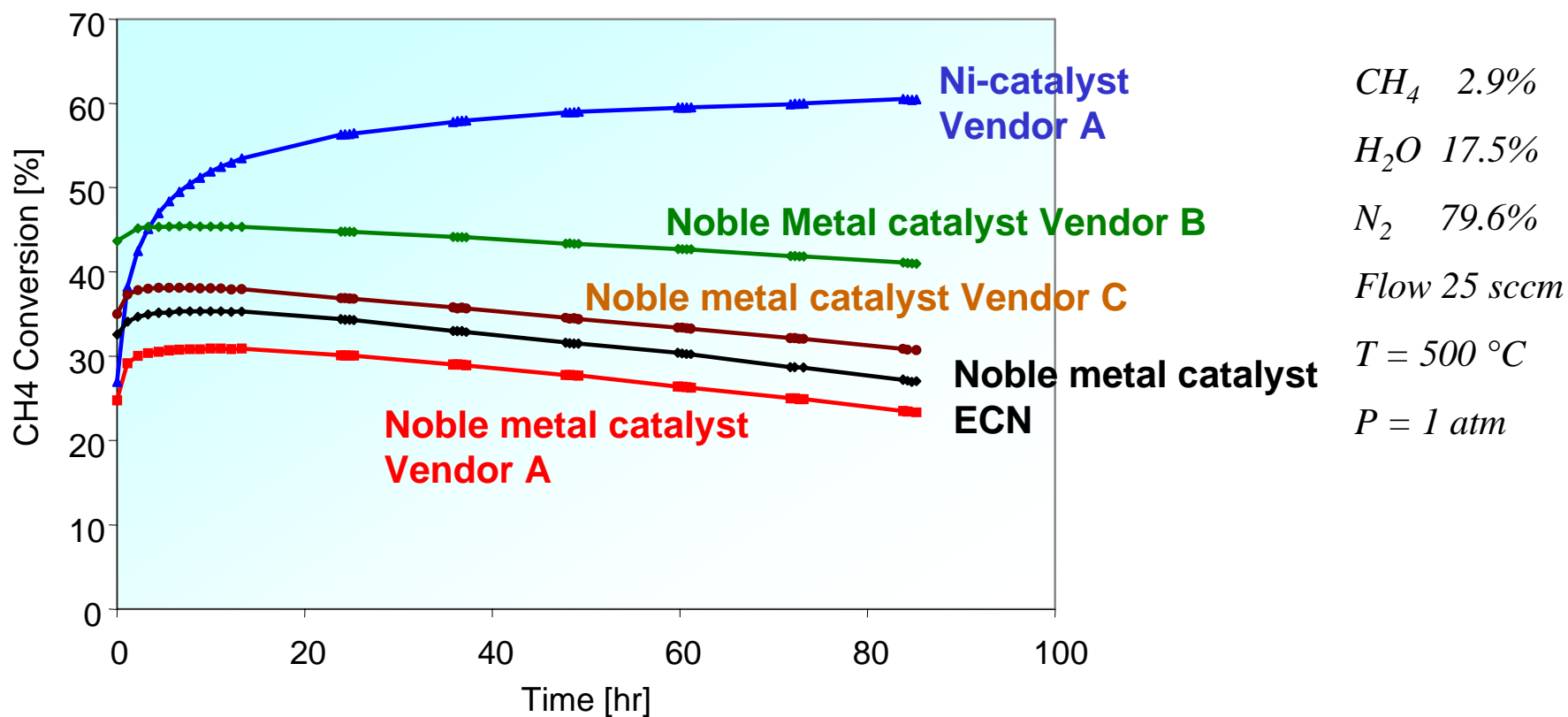
- Membrane reformer for CO₂ capture in NGCC
 - CO₂ selective membranes show a too low CH₄ conversion and are therefore not suitable for CO₂ capture in NGCC power plants
- Water gas shift membrane reactor for CO₂ capture in IGCC
 - CO₂ selective membranes give CO conversions in IGCC comparable to H₂ separating membranes and offer therefore a viable alternative

System analysis IGCC

- Coal gasifiers always produce H₂/CO₂-ratios higher than unity, resulting in a higher H₂ partial pressure, which is beneficial in membrane permeation
- The steam sweep flow applied in CO₂-selective WGS-MR results in higher efficiency penalty for CO₂ capture compared to H₂-selective WGS-MR

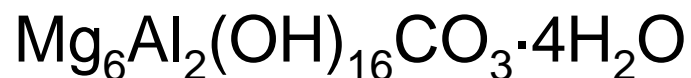
Materials Science-Catalysis

Stability test of commercial catalyst



Materials Science-assumption

Hydrotalcite general formula:



Mg/Al

OH⁻

H₂O

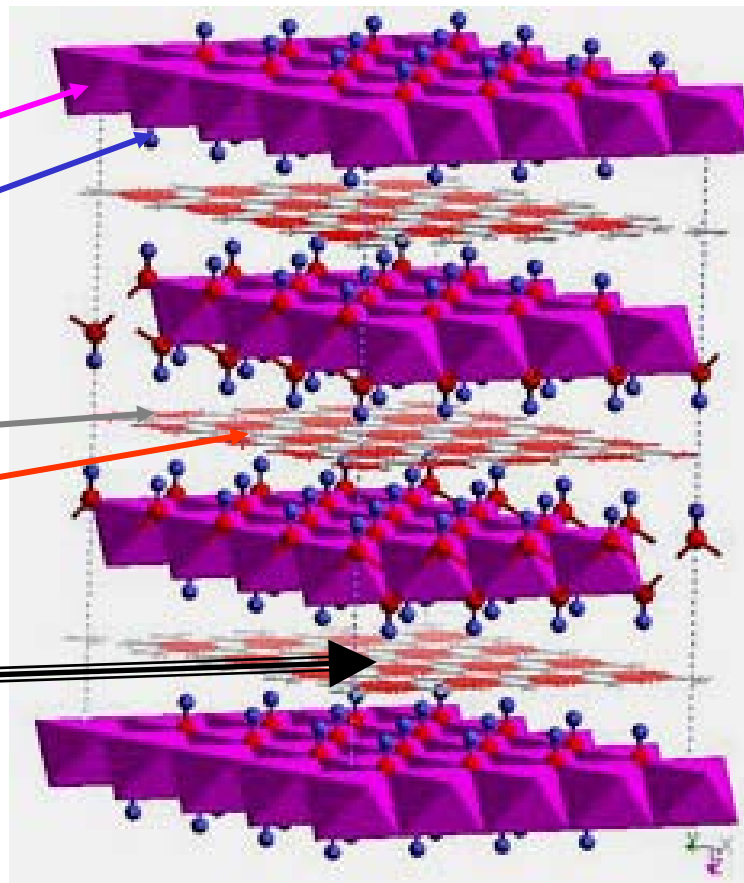
CO₃²⁻

CO₂ transport channel??

Rhombohedral system:

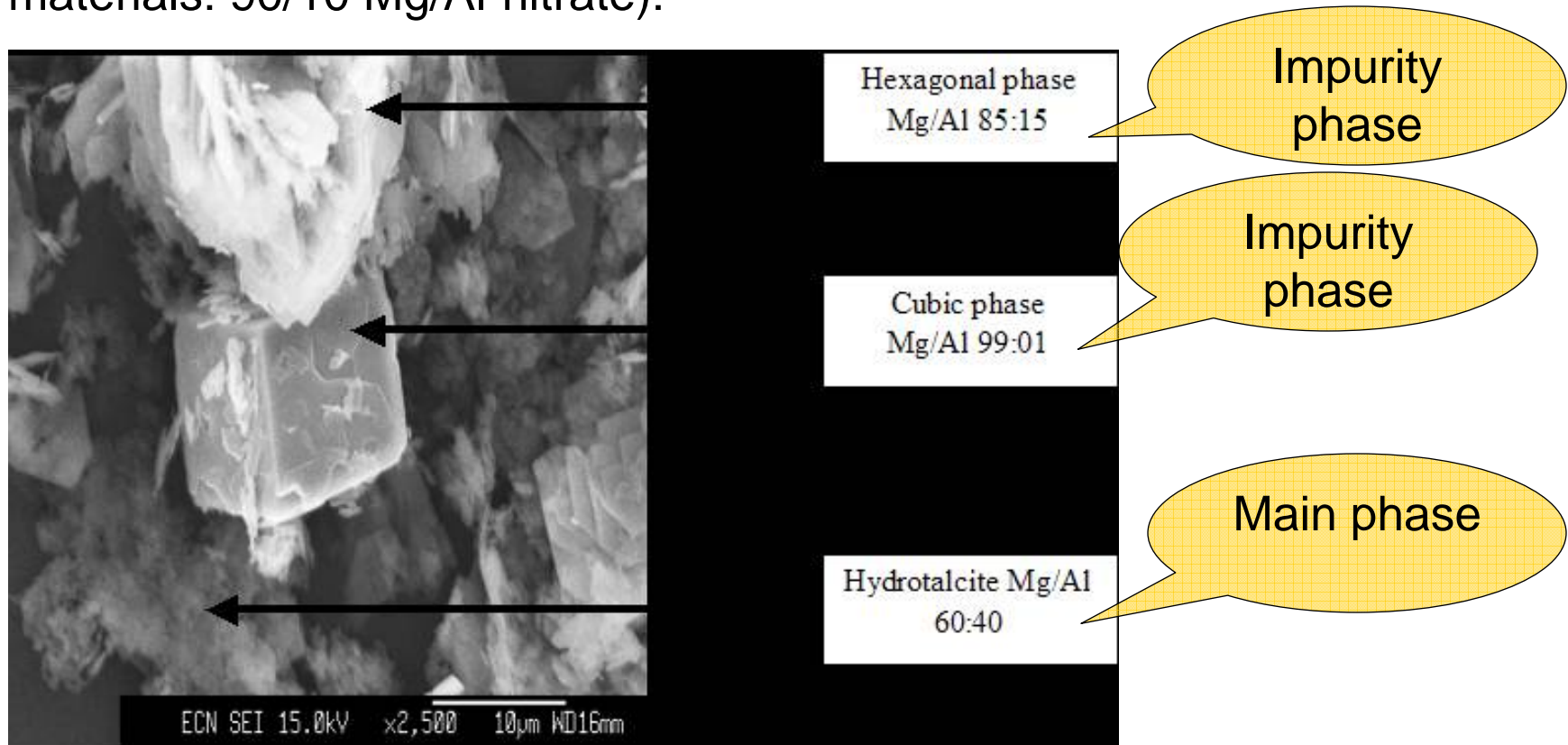
$R\bar{3}m$

$a=b \approx 3\text{\AA}$ $c \approx 23\text{\AA}$

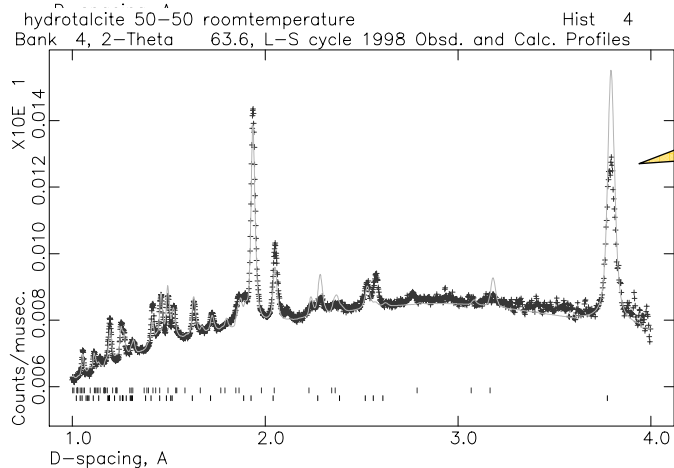
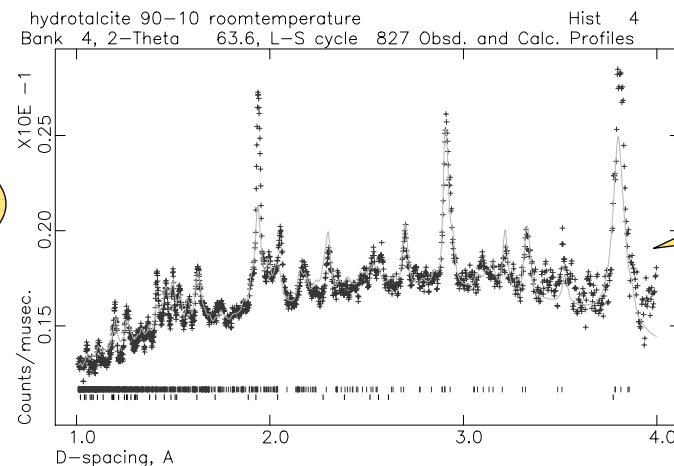
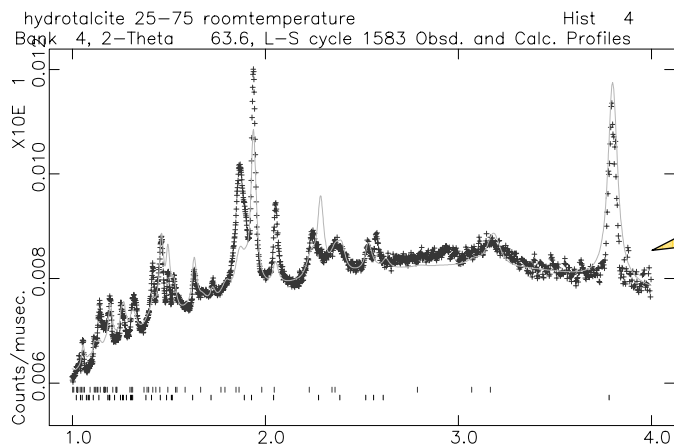


Materials Science-composition

SEM-EDX result hydrothermally synthesized sample (starting materials: 90/10 Mg/Al-nitrate):



Materials Science-composition



ND very suitable to see

- a) Light elements C, O, H
- b) Difference between Mg and Al

Diffraction experiment on GEM at
ISIS, UK

Materials Science-composition

Materials:

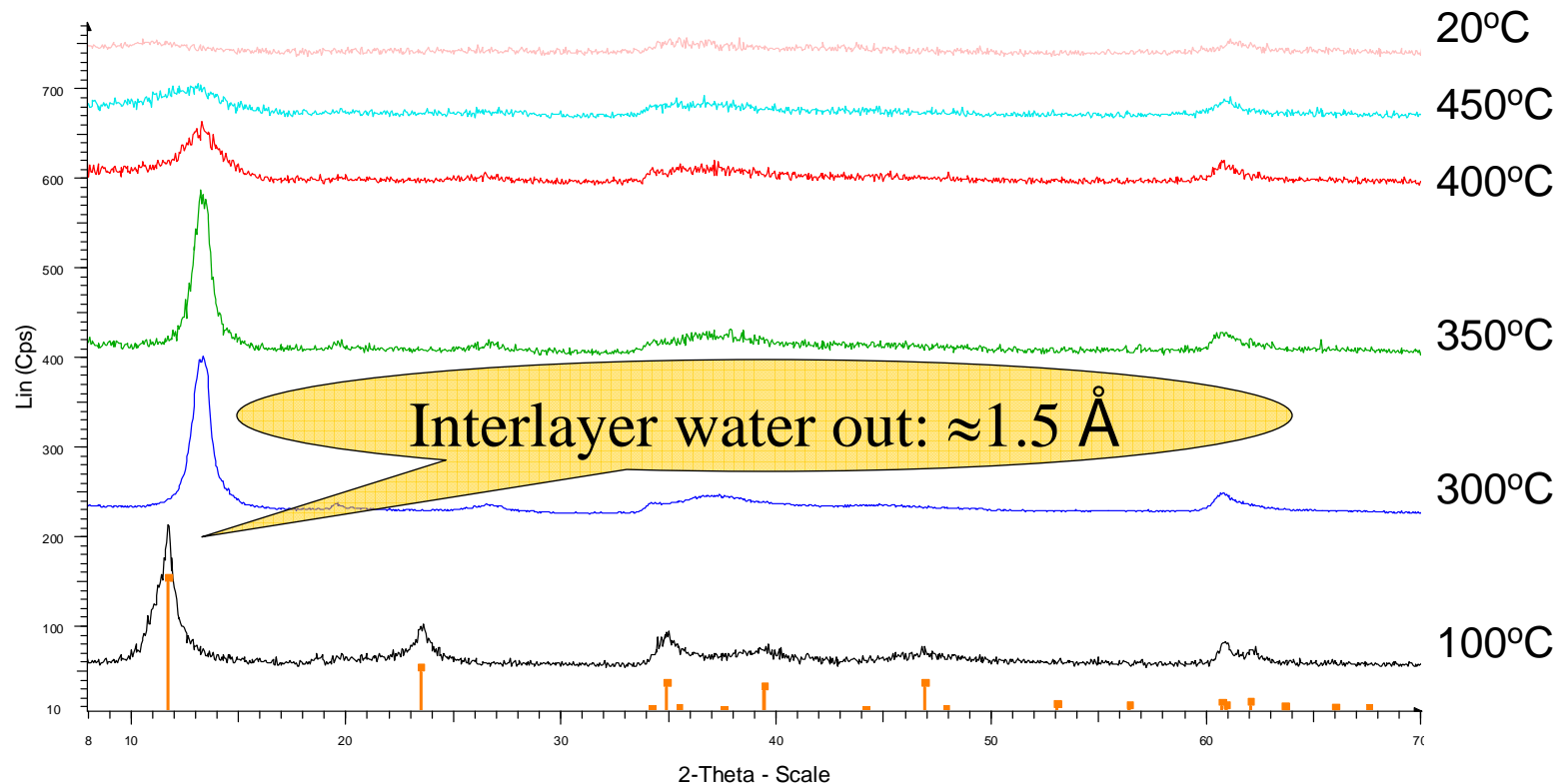
- Rather poor crystallinity, esp. impurities
- 50/50 sample relatively pure: refinable (GSAS)

Results:

- Composition $\text{Mg}_{0.64}\text{Al}_{0.36}(\text{OH})_2(\text{CO}_3)_{0.18} \cdot 1.0\text{H}_2\text{O}$
- $\text{Mg} < 0.64$: Boehmite impurity (Al rich)
- $\text{Mg} > 0.64$: Hydromagnesite impurity (Mg rich)

Materials Science-composition

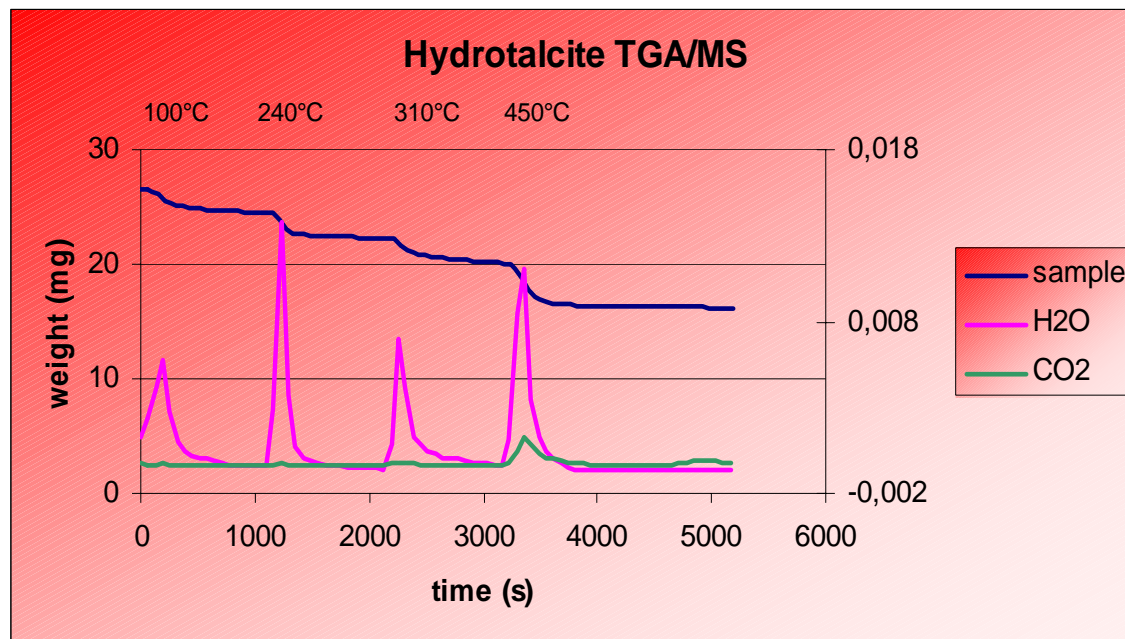
In-Situ
XRD under
N₂/CO₂/H₂O



File: MG 50 pellet 100 N2 CO2.raw - Start: 5.000 ° - End: 80.000 ° - Step: 0.050 ° - Step time: 2. s
 File: MG 50 pellet 300 N2 H2O.raw - Start: 5.000 ° - End: 80.000 ° - Step: 0.050 ° - Step time: 38. s
 File: MG 50 pellet 350 N2 H2O.raw - Start: 5.000 ° - End: 80.000 ° - Step: 0.050 ° - Step time: 2. s
 File: MG 50 pellet 400 N2 H2O.raw - Start: 5.000 ° - End: 80.000 ° - Step: 0.050 ° - Step time: 2. s
 File: MG 50 pellet 450 N2 H2O.raw - Start: 5.000 ° - End: 80.000 ° - Step: 0.050 ° - Step time: 2. s
 File: MG 50 pellet RT N2 after heattreatments.raw - Start: 5.000 ° - End: 80.000 ° - Step: 0.050 ° - Step time: 4. s
 01-089-0460 (C) - Hydrotalcite, syn - (Mg_{0.667}Al_{0.333})(OH)₂(CO₃)_{0.167}(H₂O)_{0.5} - Rhombo.H.axes - a 3.04600 - b 3.04600 - c 22.77200 - alpha 90.000 - beta 90.000 - gamma 120.000 - Primitive - R-3m (166)

➤ There is no structural memory effect!!!

Materials Science-material stability



1. Adsorbed water @100°C
 $H_2O(ad) \leftrightarrow H_2O(g)$
2. Interlayer water @240°C
 $H_2O(abs) \leftrightarrow H_2O(g)$
3. Hydroxides @310°C
 $Mg(OH)_2 \leftrightarrow MgO + H_2O(g)$
4. Carbonates @450°C
 $Mg(OH)_2 + MgCO_3 \leftrightarrow 2MgO + CO_2(g) + H_2O(g)$

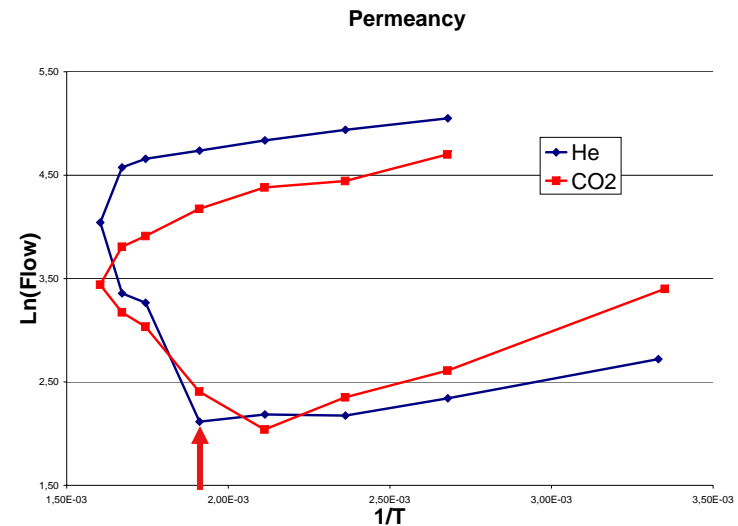
First tentative working hypothesis

Materials Science-CO₂ transport

Dense membrane produced using cold isostatic pressing under 2000 bar sliced to about 2,4 mm thick discs.

- Rest porosity about 15%
- Permeancy measured of CO₂ and He

- No significant difference between He and CO₂ (Knudsen-like)
- At 250°C the material deteriorates and permeancy goes up



Materials Science-Conclusions

Hydrotalcites

- Hydrotalcites exist in a small compositional window around $\text{Mg/Al}=0.64/0.36=1.8$
- Hydrotalcites are not stable above 200°C
 - dense HTC membranes are not feasible in the T,p window of the applications
 - porous HTC membranes not first choice
 - search for alternative hydroxidic materials or porous supports impregnated with hydroxides

Catalyst

- Four (pre)commercial pre-reforming catalysts have been tested.
- Cheap Ni-catalyst is promising and could do the job in reformers with CO_2 selective membranes.

Summary

Reactor Design/System analysis

- CO₂ selective membranes show a too low CH₄ conversion
 - driving force for CO₂ permeation too low to enhance reform reaction
- CO₂ selective membranes for WGS give CO conversions comparable to H₂ separating membranes and offer therefore a viable alternative
 - from efficiency point of view steam sweep should be as low as possible

Materials Science

- Hydrotalcites are not stable above 200°C
 - Dense HTC membranes are not feasible in the T,p window of the foreseen applications
 - porous HTC membranes not first choice
 - search for alternative hydroxidic materials or porous supports impregnated with hydroxides

Questions?



Questions?



Posters