MATERIALS SELECTION FOR THE CHEERS PROJECT ON CHEMICAL LOOPING COMBUSTION

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EERA European Energy Research Alliance

AMPEA Advanced Materials and Processes for Energy Applications

EERA AMPEA virtual workshop on "*Carbon Capture Utilisation and Storage*" March 10-11, 2021

IFP Energies nouvelles

CHEERS 中欧污染物减排技术研究

CHEERS PROJECT

H2020 *LCE-29-2017: CCS in Industry, including BioCCS*

CHEERS: CHinese-**E**uropean **E**mission-**R**educing **Solutions**

Demonstration at 3 MWth scale with petcoke as feedstock (China) and integrated assessment for industrial scale-up.

TRL4

Pilot unit at IFPEN

10 kWth

CHEERS

中欧污染物减排技术研究

5 years (2017 ⇨ 2022)

9 partners including:

- SINTEF (Coordination + Oxygen carrier)
- IFPEN (Design, techno-economic study)
- TOTAL (Engineering / procurement)
- TSINGHUA Univ., DONGFANG Boiler (Design / Construction and operation)

~20 M€ (UE + China)

EU funding: 9.7 M€

Cold mock-up

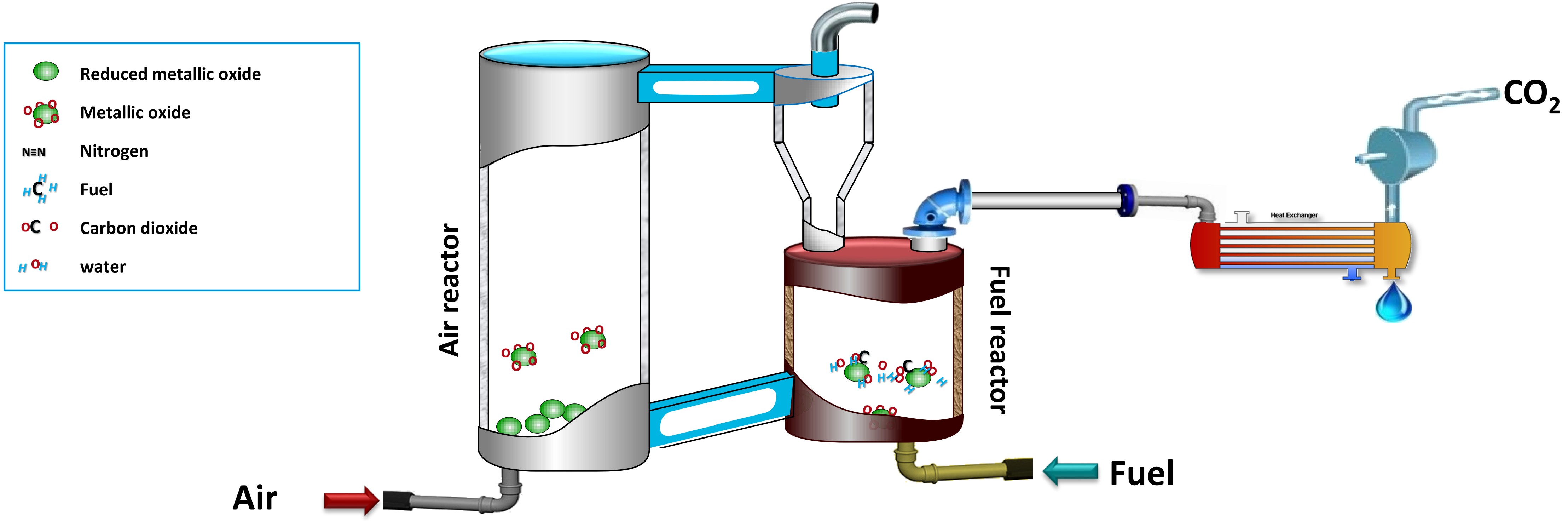
1MWth eq.

TRL7

Demo unit

3 MWth

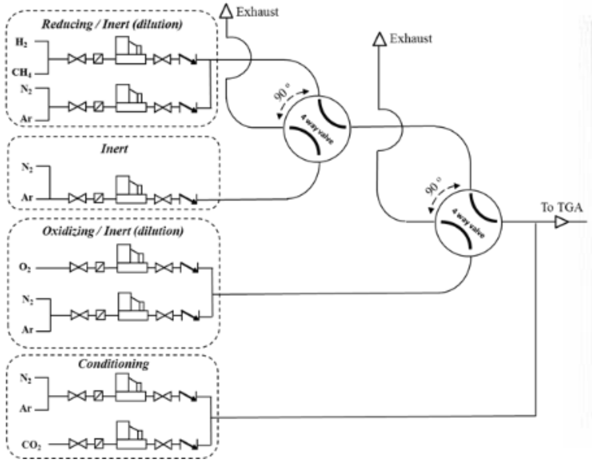
CLC PRINCIPLE



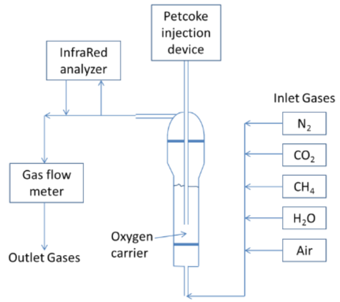
- Intrinsic oxygen separation ⇨ No energy penalty except for CO2 compression
- Appropriate technology for Gas, Liquid and Solid fuels combustion
- Valuable co-products : N_2 , H_2O

WP3 : Oxygen Carriers and Characterization of Fuel Conversion Phenomena

- TGA screening (SINTEF)
  - Sample weight <1 g
  - Oxygen transfer capacity measurement
  - Reaction kinetics
  - Stability (SEM analysis)



- Batch fluidized bed testing (IFPEN) of TGA selected materials
  - 100 g < Sample weight < 200g
  - Petcoke reactivity testing
  - Agglomeration and stability



- Circulating fluidized bed (IFPEN)
  - ~50 kg required

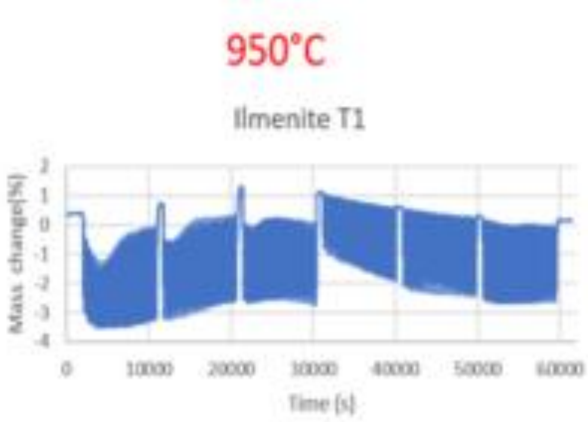
Select 2 oxygen carriers for use in demo unit

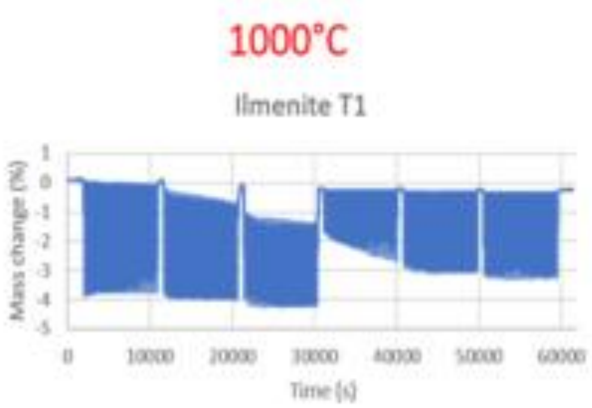
SCREENED MATERIALS

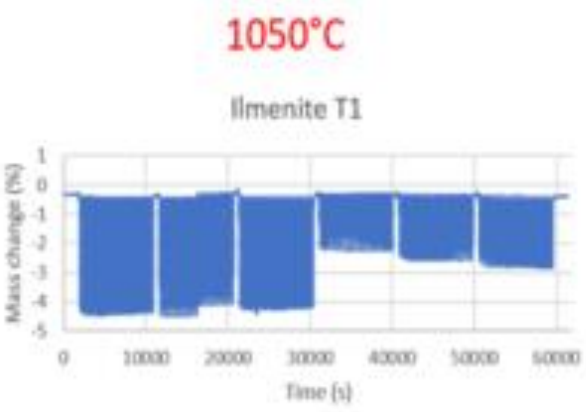
Materials	Origin	Form
Ilmenite-No	Norway	Mineral
Ilmenite-Vet.	Vietnam	Mineral
Ilmenite-Moz.	Mozambique	Mineral
Fe-rich ores	Guangxi, China	Mineral
$MnSi_{0.25}$ syn.	Lab, SINTEF	Synthetic
$MnSi_{0.4}$ syn.	Lab, SINTEF	Synthetic
CMTF8440	Lab, SINTEF	Synthetic
CMTF8341	Lab, SINTEF	Synthetic
CMTF8332	Lab, SINTEF	Synthetic
CMTF8431	Lab, SINTEF	Synthetic
FeMnTi(Mg) syn.	Lab, SINTEF	Synthetic
GT Mn ore	China	Mineral
MG Mn ore	China	Mineral
LY Mn ore	China	Mineral

- Natural ores
  - ☺ Cheap and abundant
  - ☺ Reactivity
  - ☹ Quick degradation leading to short lifetime
- Synthetic materials
  - ☺ Mechanical resistance
  - ☺ Reactivity
  - ☹ Manufacturing cost

TGA SCREENING RESULTS

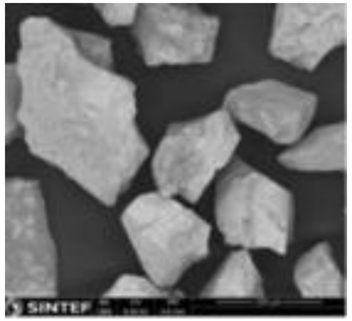




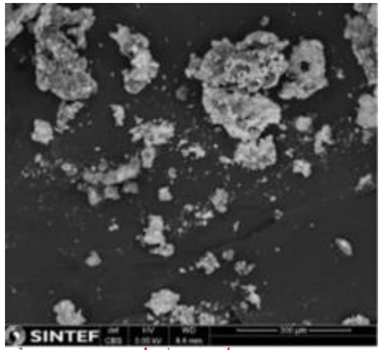


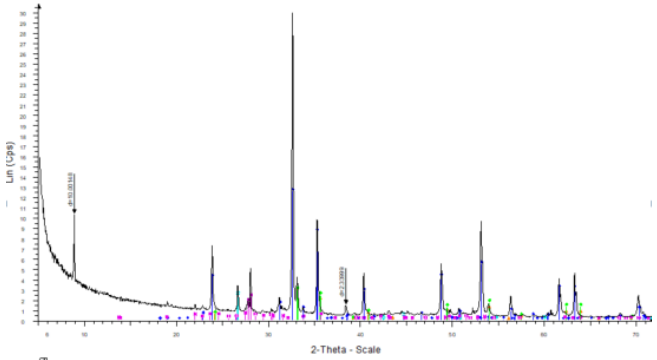
- Oxygen transfer capacity
- Reaction rates

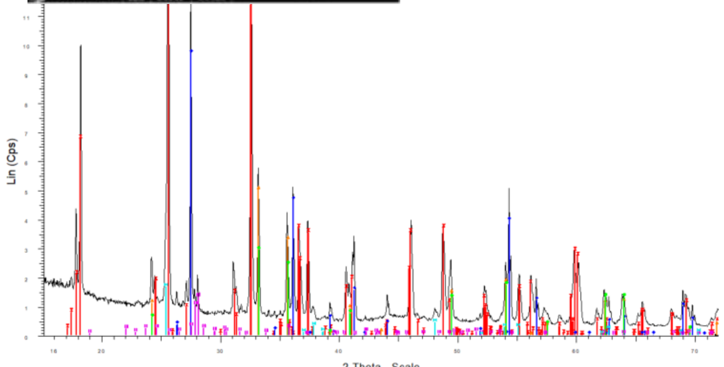
Before



After







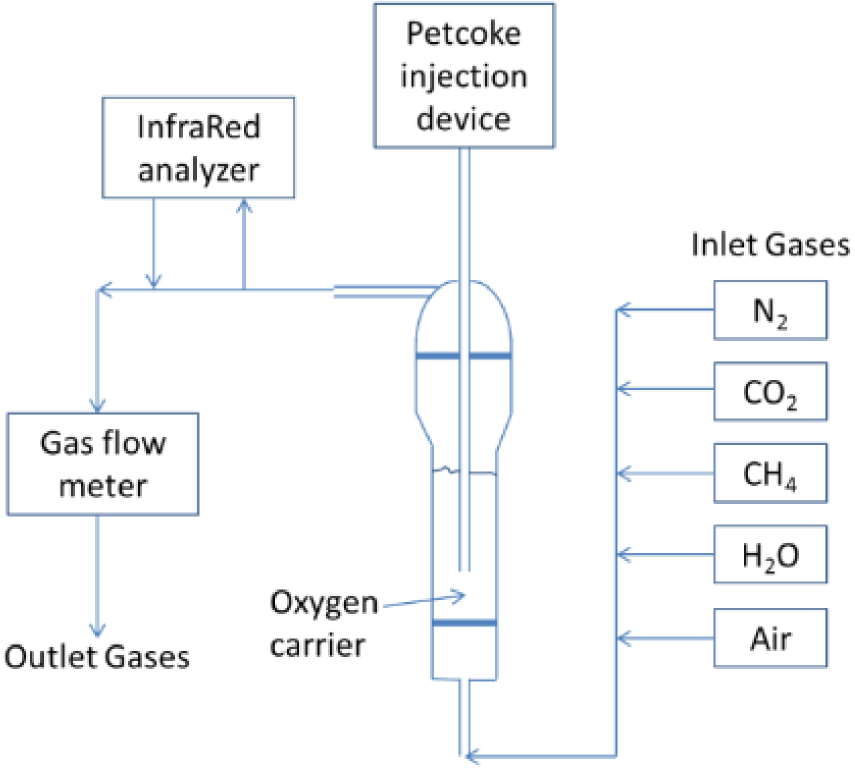
- Morphological and phase changes

TGA SCREENING

	Ilmenite-No	Ilmenite-Viet	LY Mn ore	CMTF8341	CMTF8431
O_2 Capacity	++	+	+	++	+++
Phase stability	-	-	-	+++	+
Particle shape stability	+	+	+	+++	++
Porosity formation	high	high	high	low	medium
XRD	Decomposition	Decomposition	Multi phases	Stable	Some precipitation
Reduction kinetics	Medium	medium	fast	medium	very fast

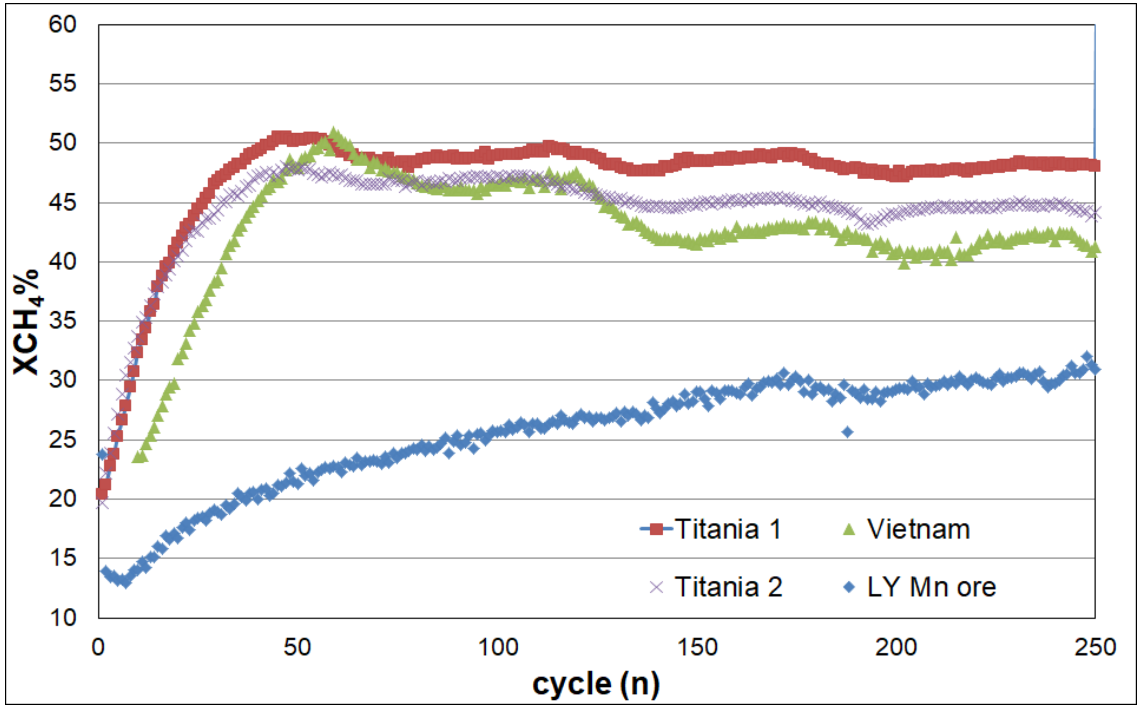
- Ilmenites from Norway and Vietnam and a Mn ore from China were chosen for further testing in batch fluidized bed
- CMTF8341 and CMTF8431 synthesis were scaled up for further testing in batch fluidised bed

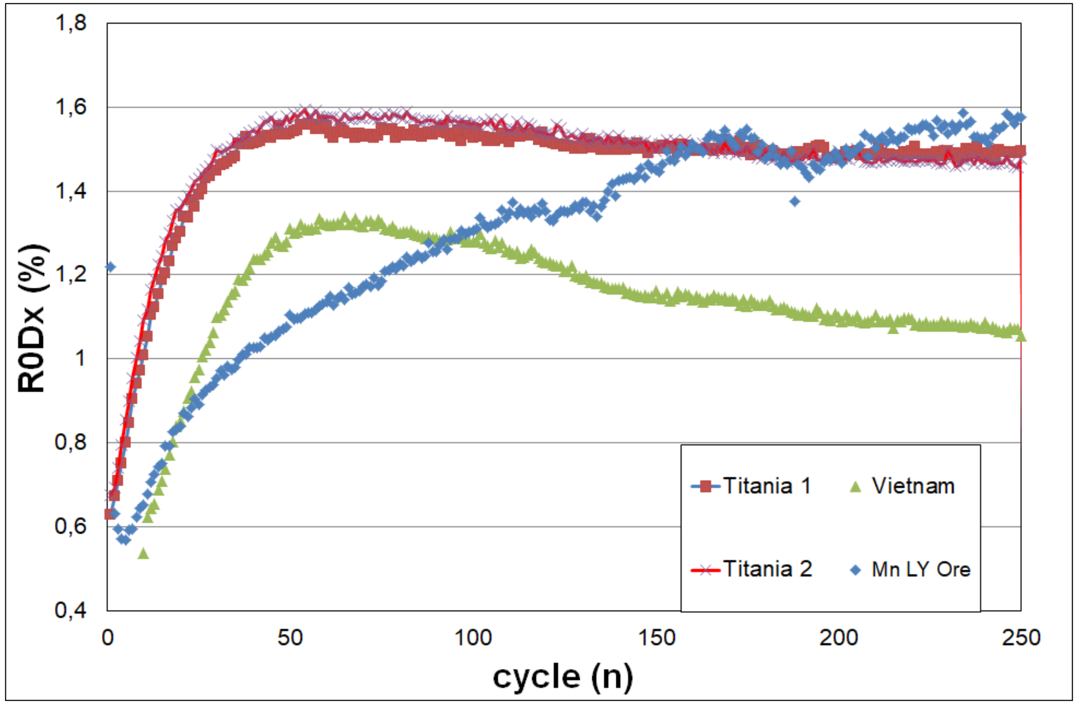
BATCH FLUIDISED BED UNIT



BATCH FLUIDISED BED AGEING

- Ageing at 900°C, using CH_4/CO_2 mix for reduction, air for oxidation

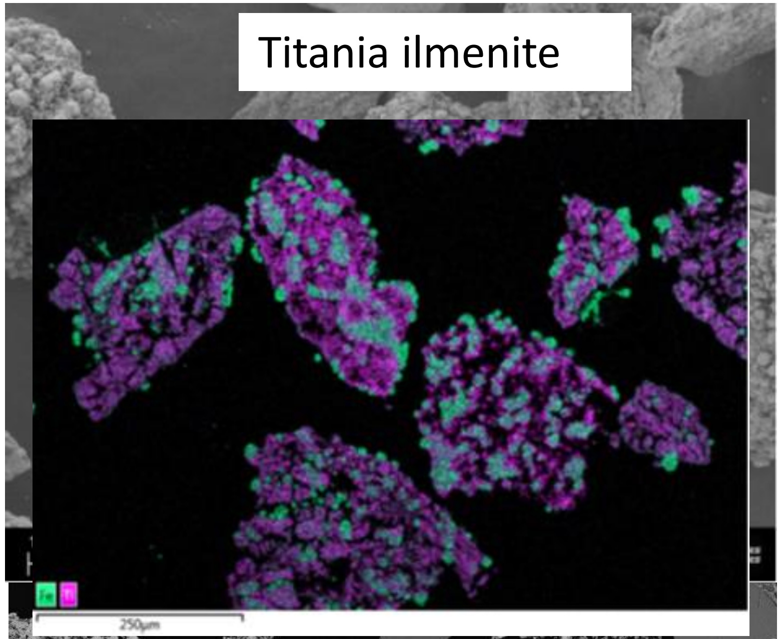


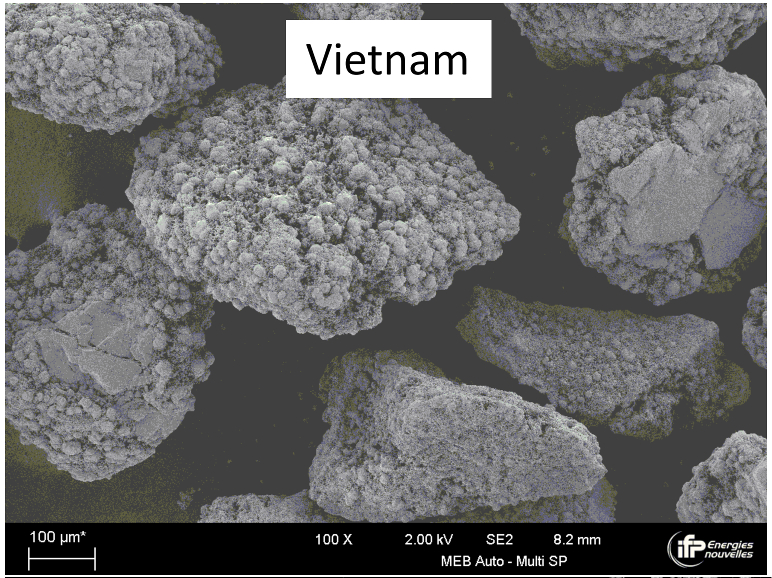


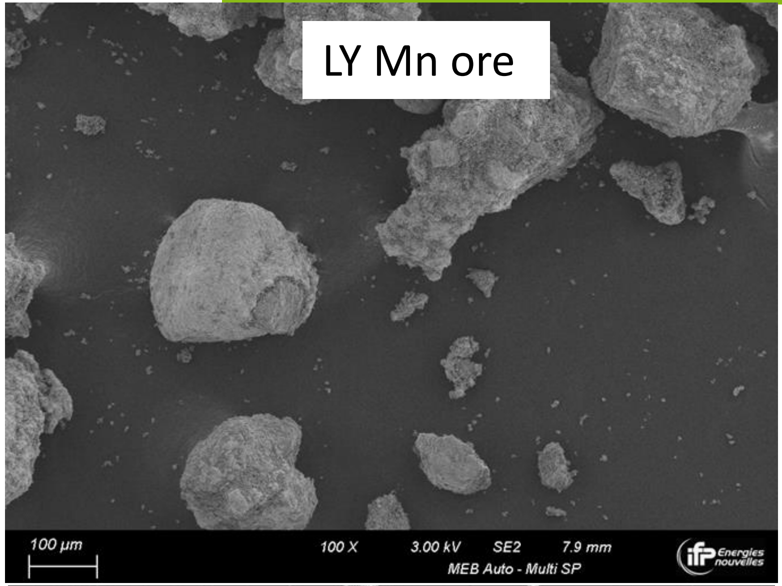
- Ilmenites require ~50 cycles activation
- Titania more reactive than Vietnamese ilmenite
- Some agglomeration occured with Titania batches

BATCH FLUIDISED BED AGEING

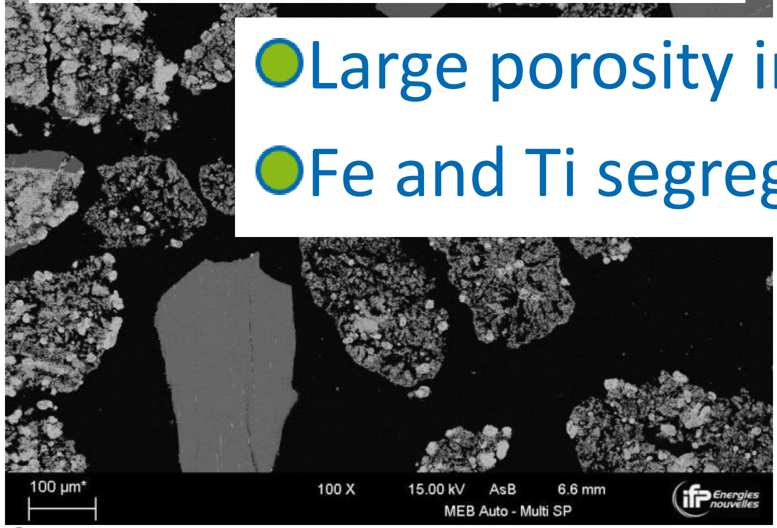
NEW ENERGIES

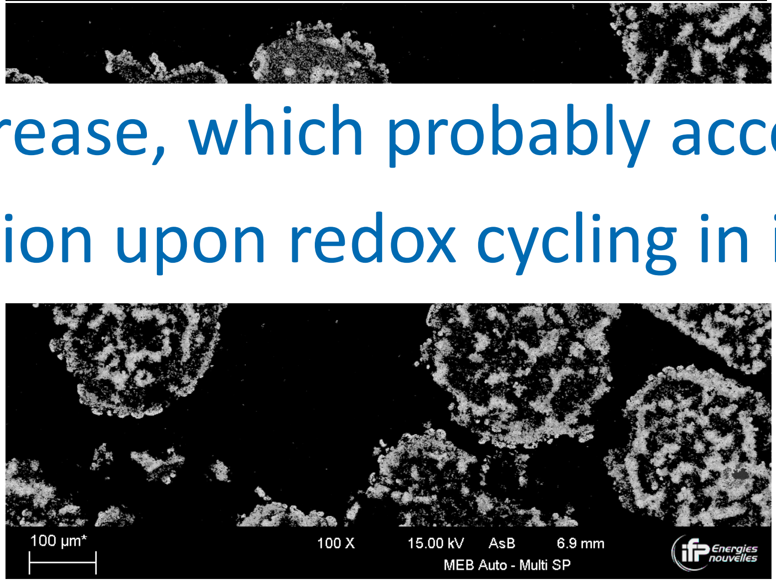


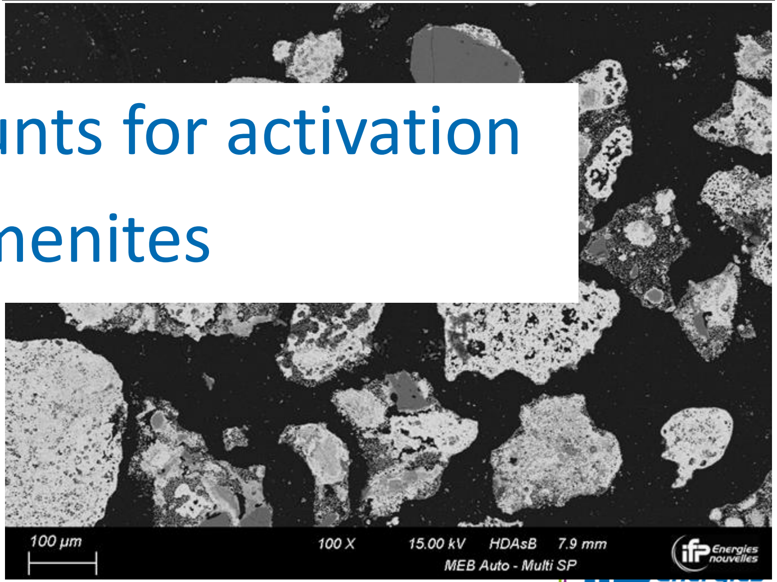




- Large porosity increase, which probably accounts for activation
- Fe and Ti segregation upon redox cycling in ilmenites

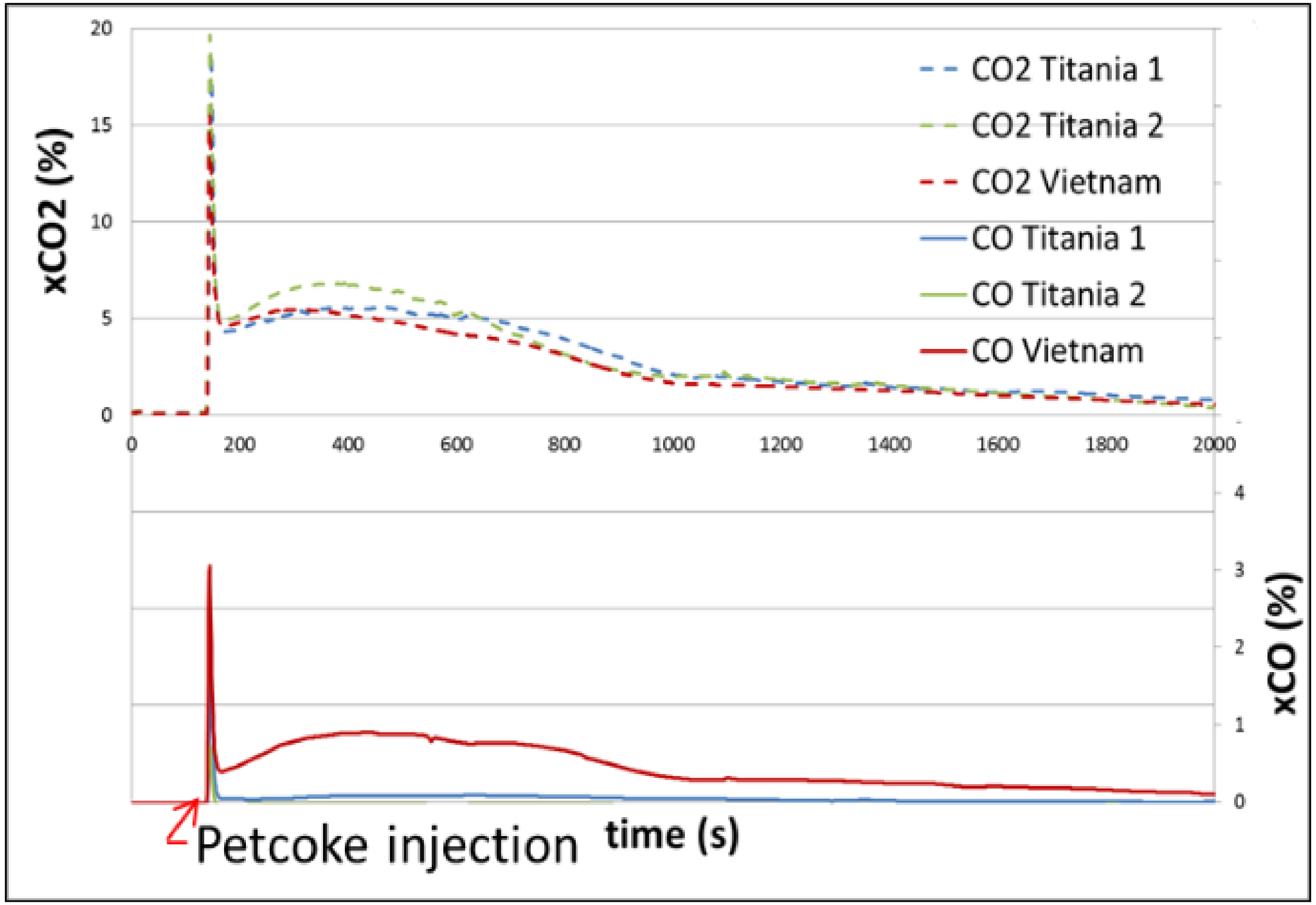






BATCH FLUIDISED BED : PETCOKE COMBUSTION

- Particles were activated with CH_4/CO_2 for 50 cycles at 900°C, then petcoke was injected

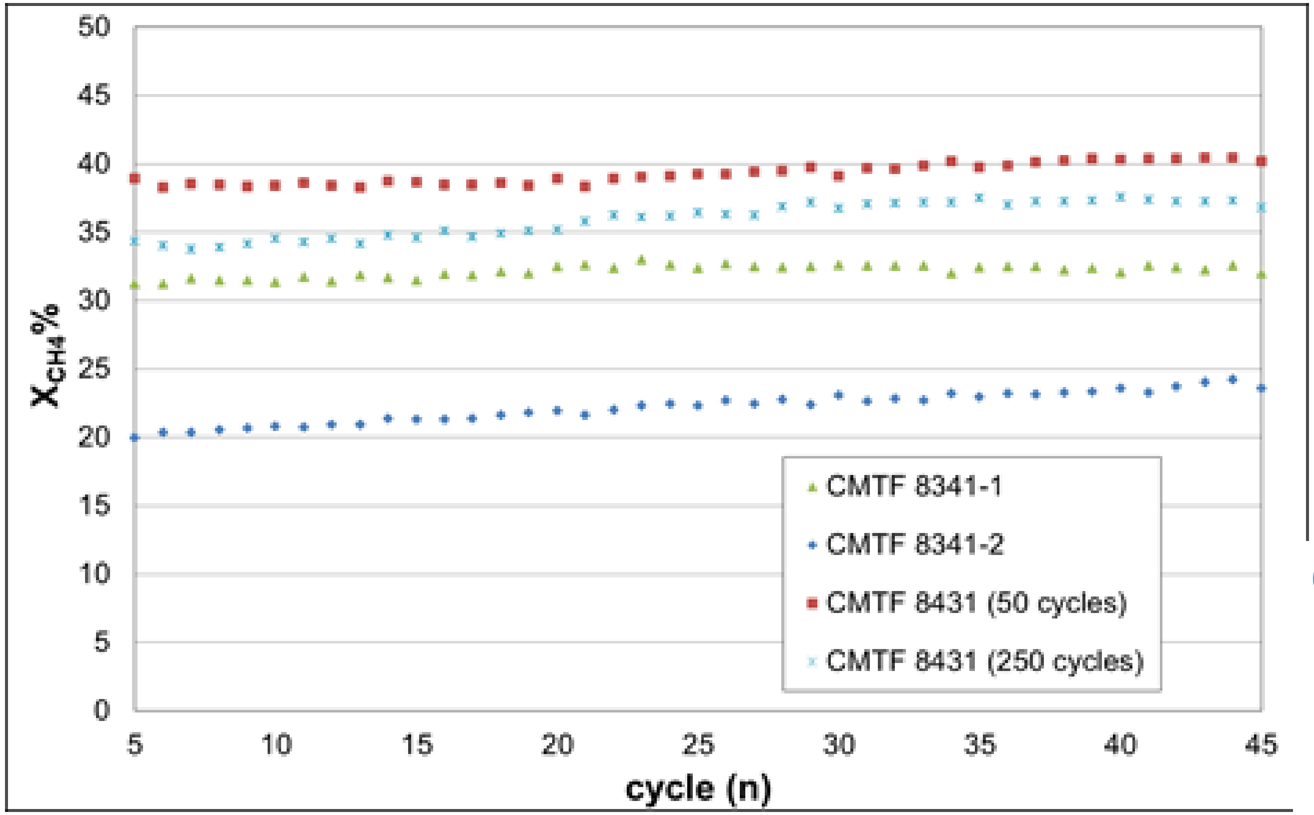


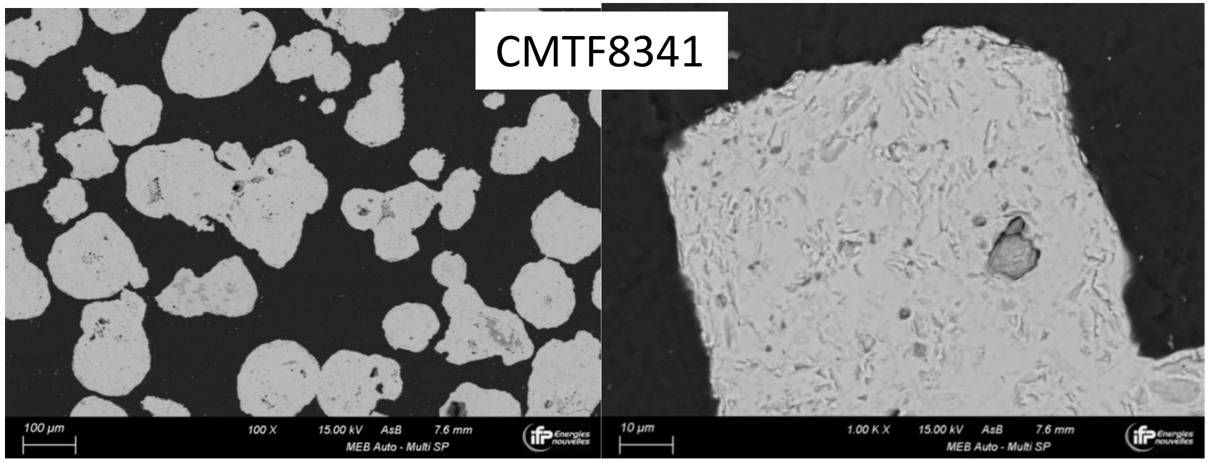
with 33 or 50% steam in fluidizing gas,

at 900 or 940°C

- Volatiles are instantly burnt
- Afterwards, petcoke gasification is the limiting step
- Vietnamese ilmenite not as reactive with CO as Titania batches

BATCH FLUIDISED BED AGEING



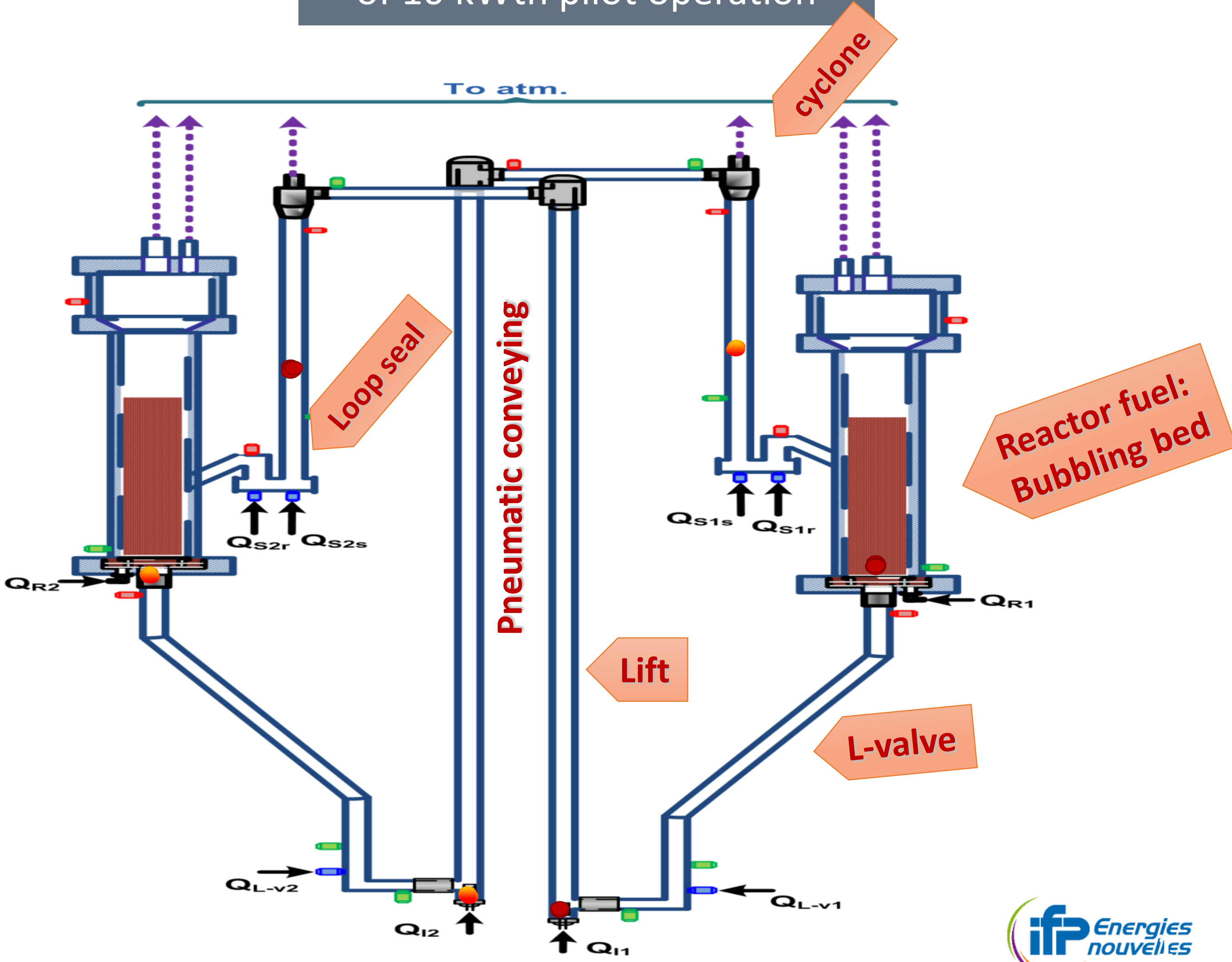


- Very stable perovskite reactivity towards CH_4
- Reactivity depends on fabrication method
- Could hardly detect any differences by XRD, SEM and Hg porosimetry
- ☹ After petcoke testing, strong S poisoning was observed

10 KWth PILOT DESCRIPTION

- Pilot is composed of:
  - 3 bubbling fluidized reactors
    - 1 fuel reactor and 2 air reactors
  - L-valves
    - Control of the solid flowrates
- It is fully automatized to:
  - Control each reactor solid level independently
  - Control independently gas and solid residence times
- Continuous petcoke injection

Example with only 1 air reactor of 10 kWth pilot operation



TESTING PROCEDURE

OC circulation

- Loading: ~30 kg of oxygen carrier
- Establish desired temperatures in reactors (FR: 900°C, AR: 850°C)
- Achieve stable operating conditions

→

OC activation

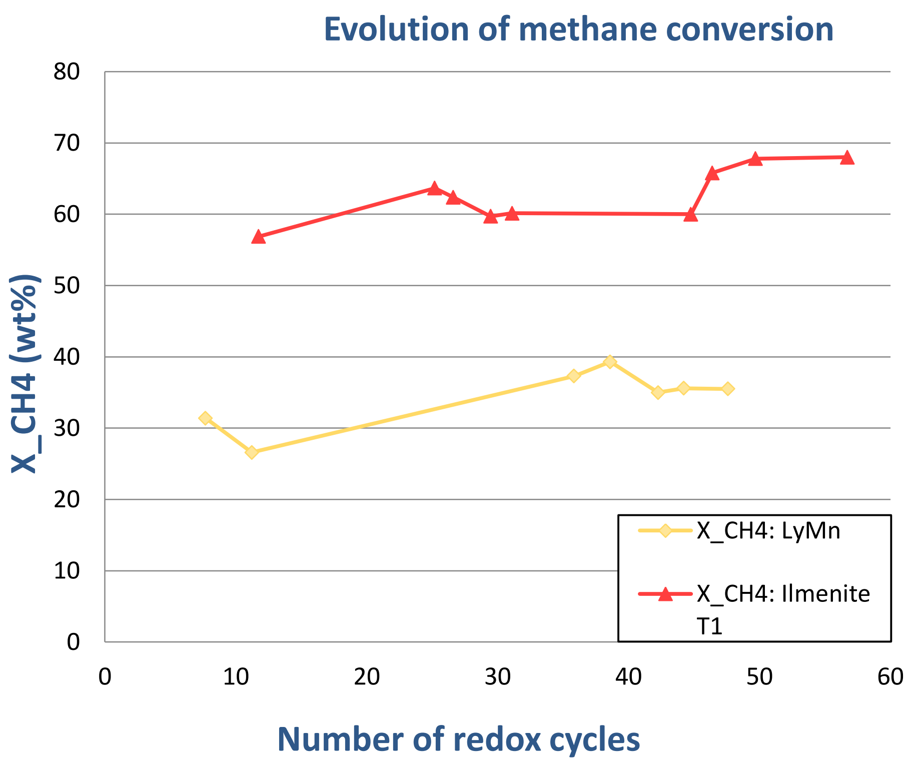
- Injection of methane (10% CH4, 90% N2) until stable CH4 conversion

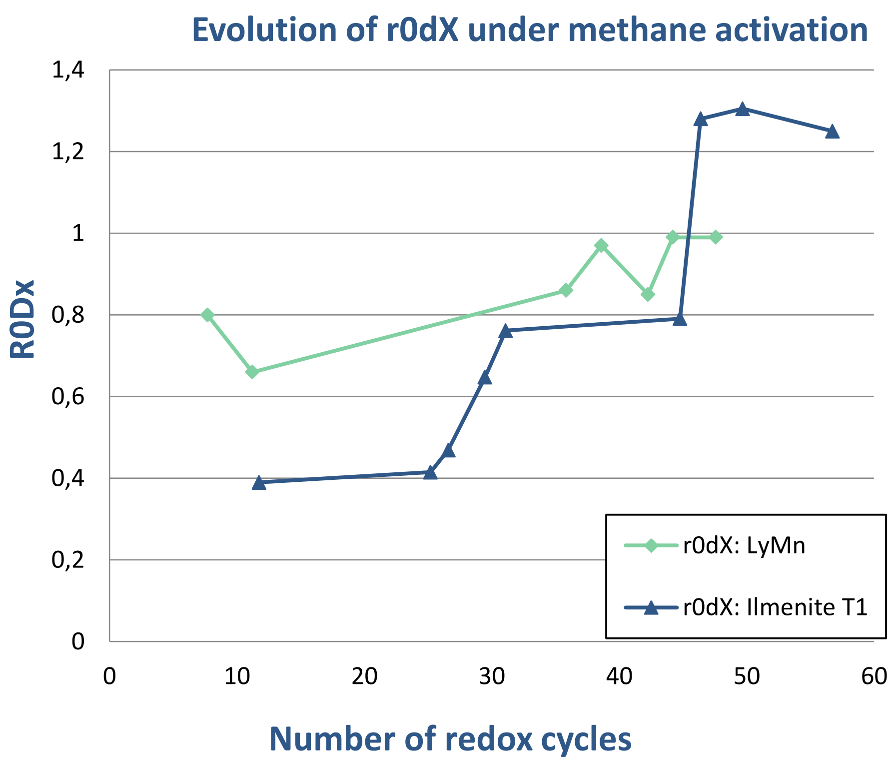
→

Petcoke injection

- Performance testing at varying operating conditions
- $\dot{m}_{PC} = 120\ \frac{g}{h}$,
- $\dot{m}_{OC} = 20\ \frac{kg}{h}$
- $X_{H2O} = 0{,}5\ w/w$

ACTIVATION OF TITANIA1 AND LY Mn ORE



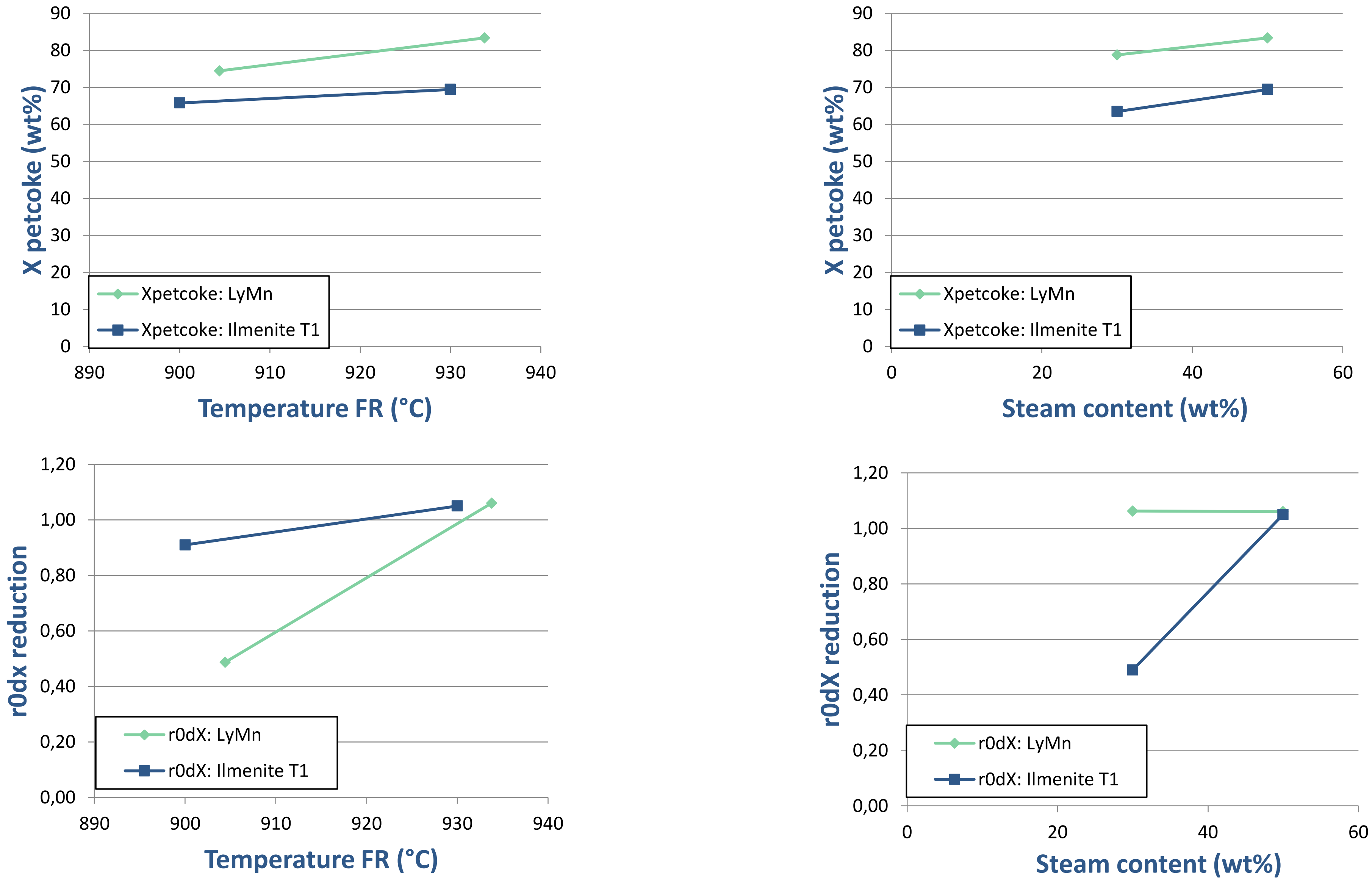


- LY Mn ore achieves lower methane conversion and $R_0\Delta X$ than Titania1

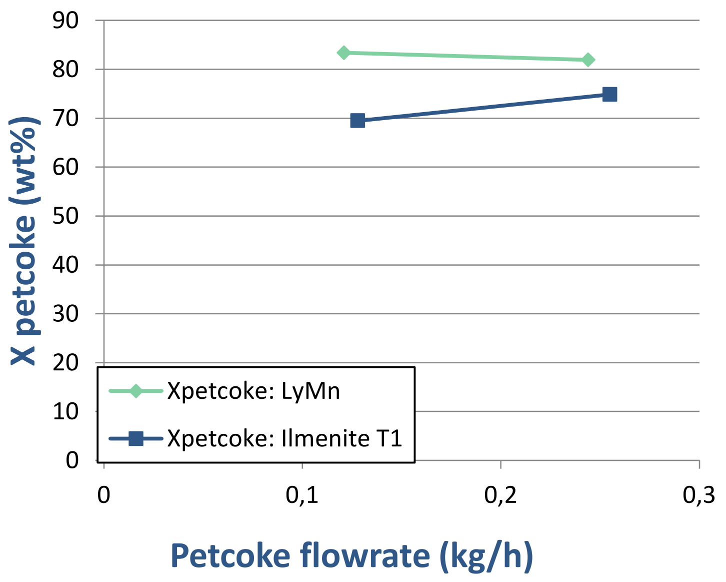
PETCOKE COMBUSTION WITH ILMENITE AND LY Mn ORE

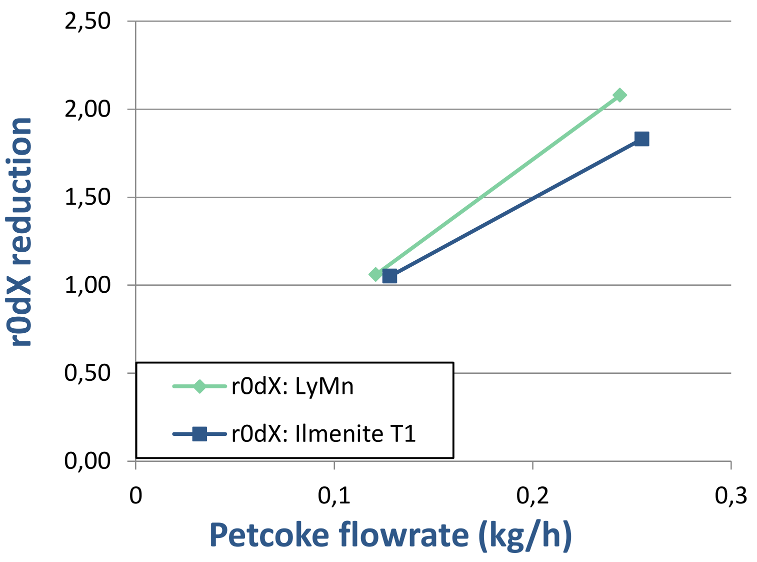
Test type	Steam content (%)	Petcoke flowrate (g/h)	Temp. (°C)	OC flowrate (kg/h)
Ilmenite				
ref	49	118	927	20
Temp.	50	110	904	21
Temp.	50	120	898	21
Petcoke flowrate	50	258	928	21
Steam content	31	115	929	21
OC flowrate	50	119	922	10
LY Mn Ore				
Ref	50	120	930	20
Petcoke flowrate	50	**240**	930	20
Steam content	**30**	120	930	20
OC flowrate	50	120	930	**30**
Temp.	50	120	**900**	20

PERFORMANCE COMPARISON



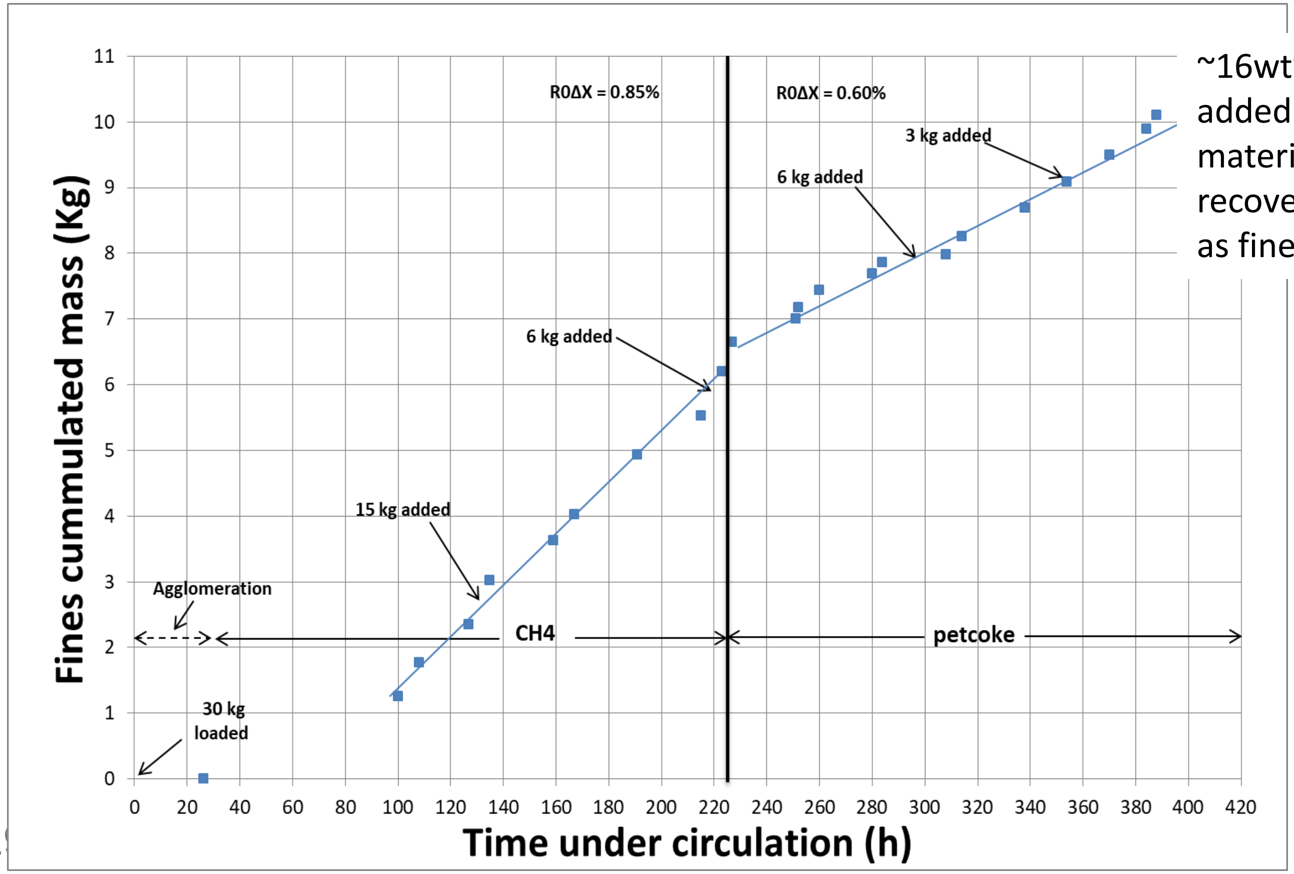
PERFORMANCE COMPARISON



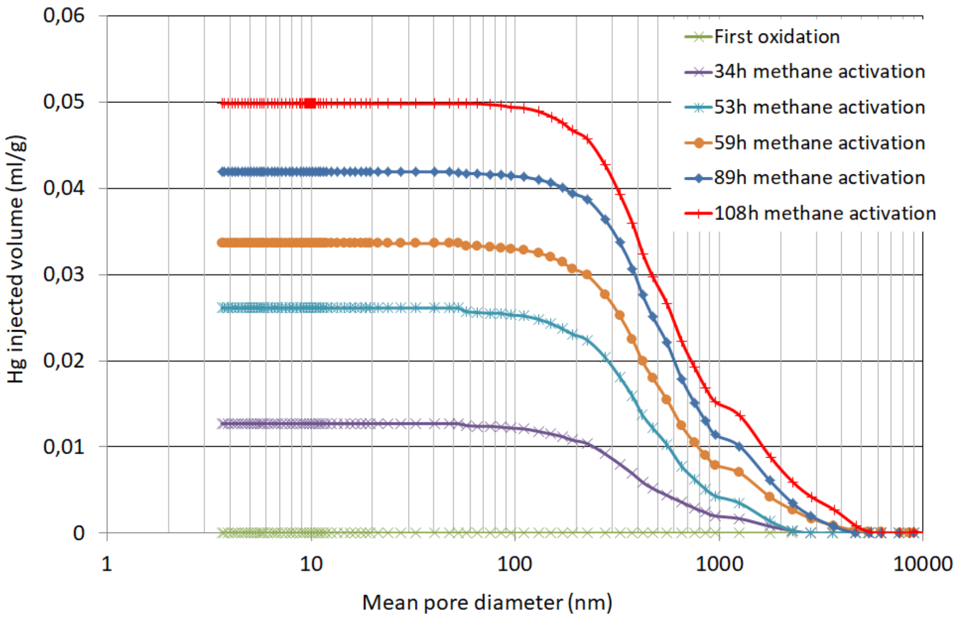


PRACTICLE CONSIDERATIONS

- Ilmenite:
  - Many agglomeration troubles occured, particularly upon heating up the unit with ilmenite
  - Porosity increase and formation of an iron oxide layer around the particles



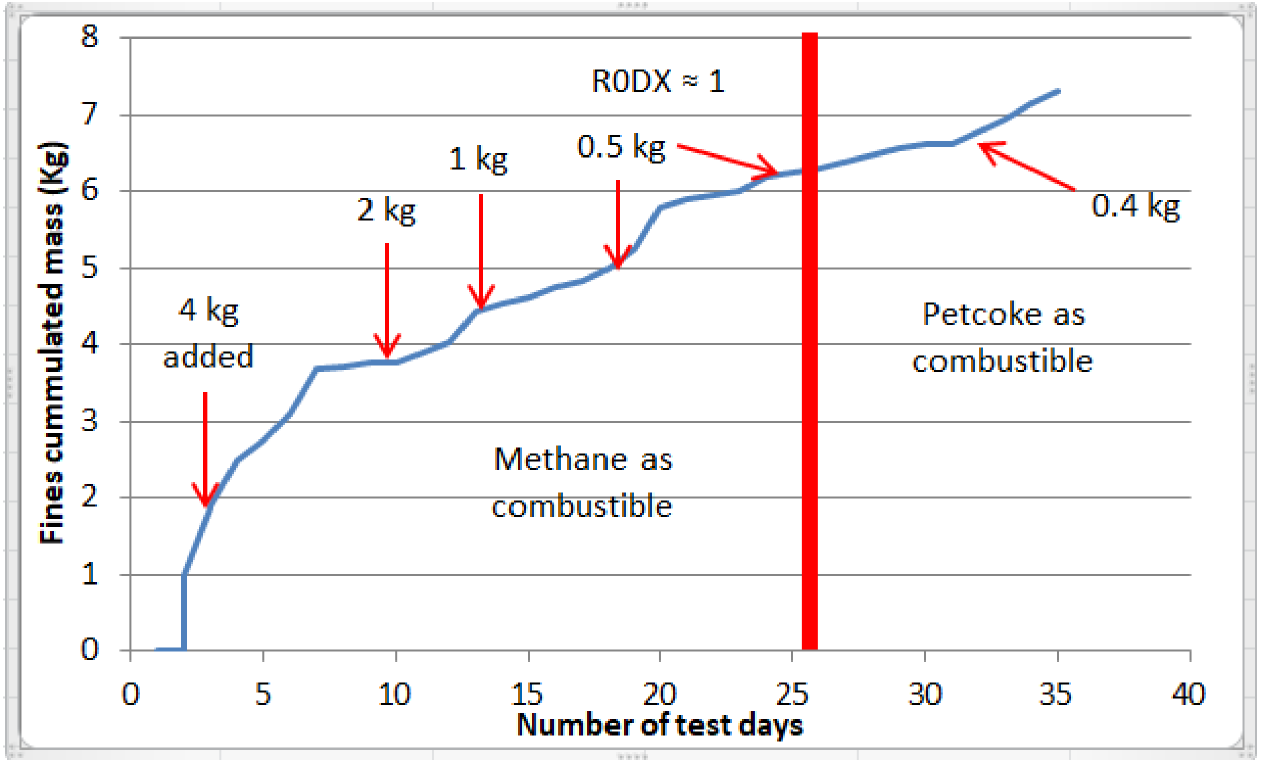
~16wt% of added material recovered as fines



Under CH_4 ($R_0\Delta X$~0,85), 0,13wt%/h fine formation -> 770h lifetime
With petcoke ($R_0\Delta X$~0,6), 1430h lifetime

PRACTICLE CONSIDERATIONS

- LY Mn ore :
  - No agglomeration troubles during the test, but agglomerates were found in the 2nd air reactor's L-valve and at the outlet of the three reactors
  - A significant amount of fines was collected during the test (7kg, i.e. 18,5% of added material)
  - Analysis of aged particles is underway



CONCLUSIONS

- CMTF perovskites
  - Promising stability and reactivity
  - Cannot be used with sulfur rich fuel

- Norwegian ilmenite and an Fe-poor Mn ore have been tested in IFPEN's 10 kW_{th} pilot :
  - High petcoke conversion achieved with both materials
  - Lifetime at low levels of transferred oxygen ($R_0\Delta X \leq 1$) is not very high
  - Circulation seems easier with the Mn ore but agglomeration issues observed in both cases (can be managed thanks to appropriate design and operating procedures)

- Conclusion: Cost of production and material availability will ultimately determine the choice of first oxygen carrier

Thank you for your attention!

CHEERS

中欧污染物减排技术研究

Project No: **764697**
Project acronym: **CHEERS**
Project full title:
Chinese-European Emission-Reducing Solutions

项 目 号：**764697/ 2017YFE0112500**
项目缩写：**CHEERS**
项目名称：中欧污染物减排技术研究

Type of Action: **RIA**

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