Performance of Mn-Fe-based Oxygen Carriers in Coal Combustion by *i*G-CLC and CLaOU processes.

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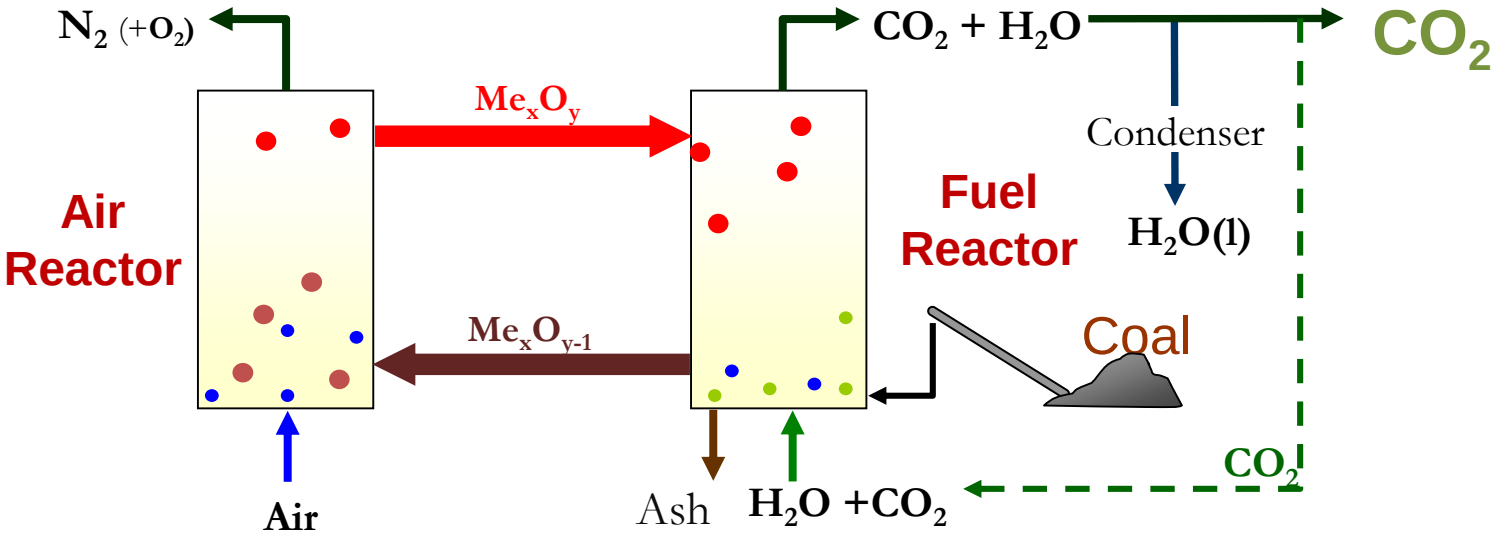
Direct coal feeding to the fuel reactor



Two options have been proposed depending on how carbon is converted

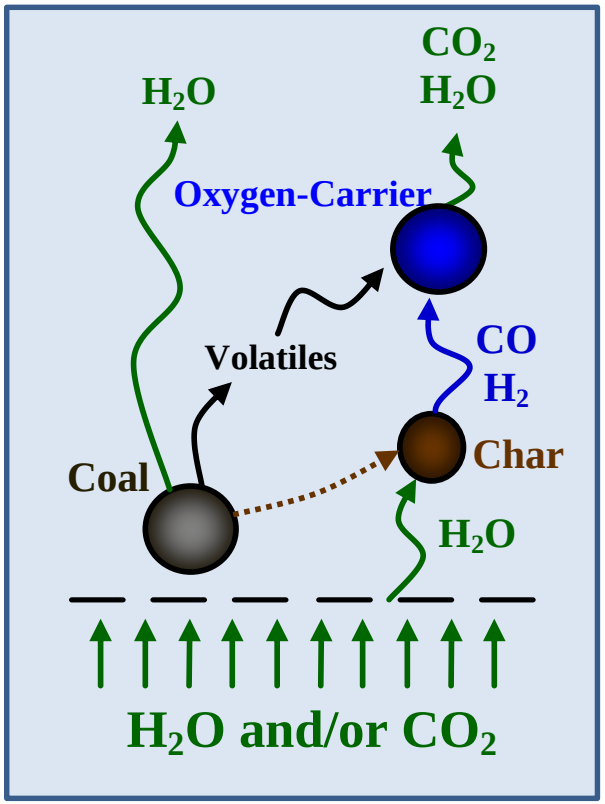
*i*G-CLC In situ Gasification Chemical Looping Combustion[1]

Solid fuel is gasified in situ by H_2O and CO_2 supplied as fluidizing gas.
OC reacts with gasification products to produce CO_2 and H_2O

CLOU Chemical Looping with Oxygen Uncoupling[2]

Solid fuel is burned with gaseous oxygen released by the oxygen carrier

In situ Gasification Chemical Looping Combustion



Coal is dried and devolatized

$$\text{Coal} \longrightarrow H_2O + \text{Volatile matter} + \text{Char}$$

Remaining solid char is gasified to give gaseous H_2 and CO

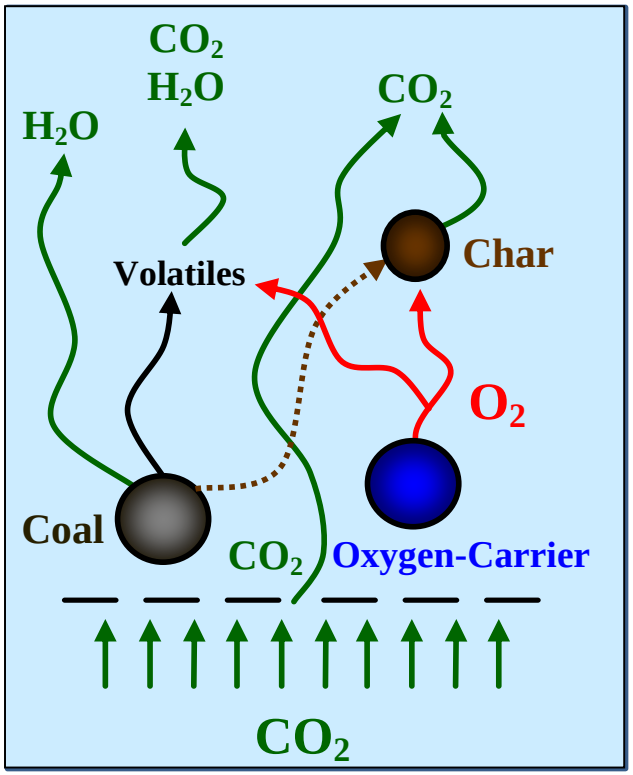
$$\text{Char} + H_2O \longrightarrow H_2 + CO$$

$$\text{Char} + CO_2 \longrightarrow 2\,CO$$

Volatiles and Gasification Products react with oxygen carrier by a gas-solid reaction

$$\begin{matrix}\text{Volatile matter} \\ H_2 + CO\end{matrix} + n\,Me_xO_y \longrightarrow CO_2 + H_2O + n\,Me_xO_{y-1}$$

Chemical Looping with Oxygen Uncoupling



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$$\text{Coal} \longrightarrow H_2O + \text{Volatile matter} + \text{Char}$$

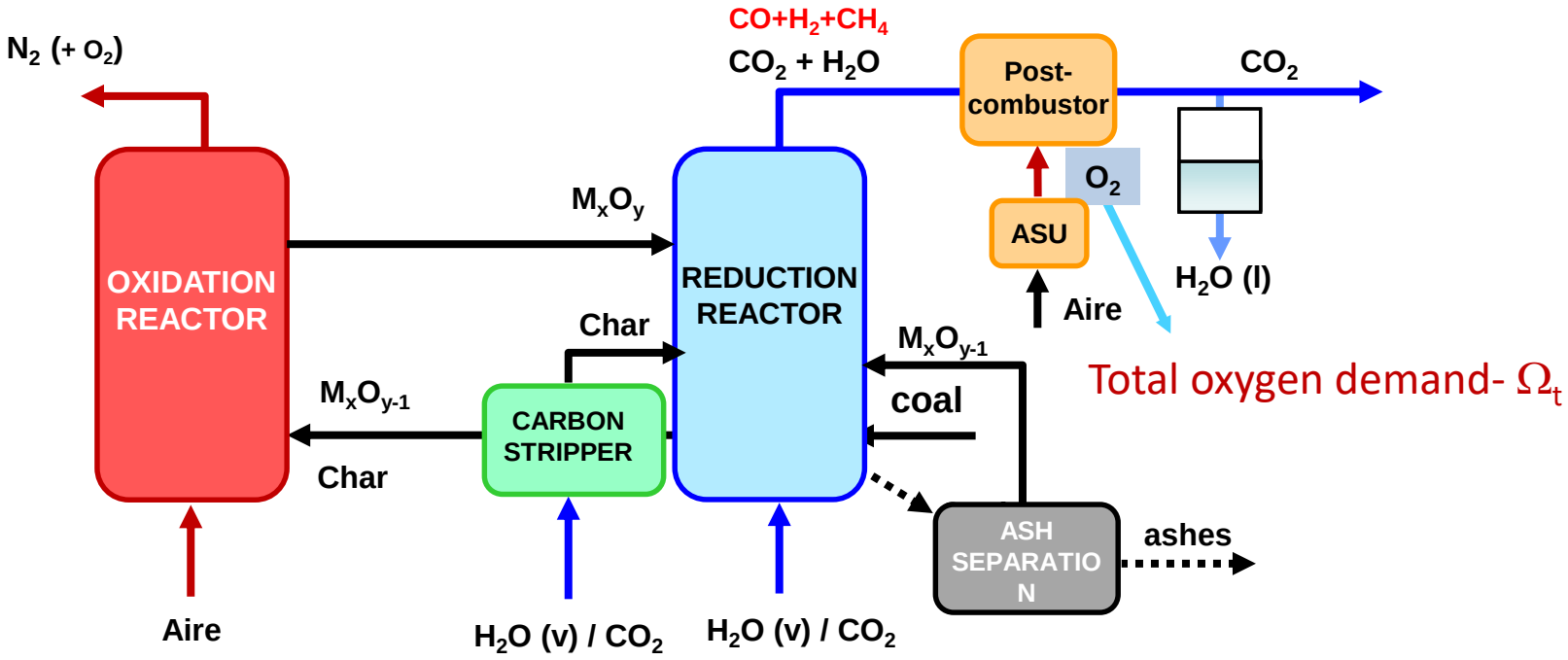
Oxygen carrier with capacity to release gaseous OXYGEN (O_2)

$$2\,Me_xO_y \longrightarrow 2\,Me_xO_{y-1} + O_2$$

Volatiles and Char react with OXYGEN (O_2) as in common combustion with air

$$\begin{matrix}\text{Volatile matter} \\ \text{Char}\end{matrix} + O_2 \longrightarrow CO_2 + H_2O$$

CLC with coal



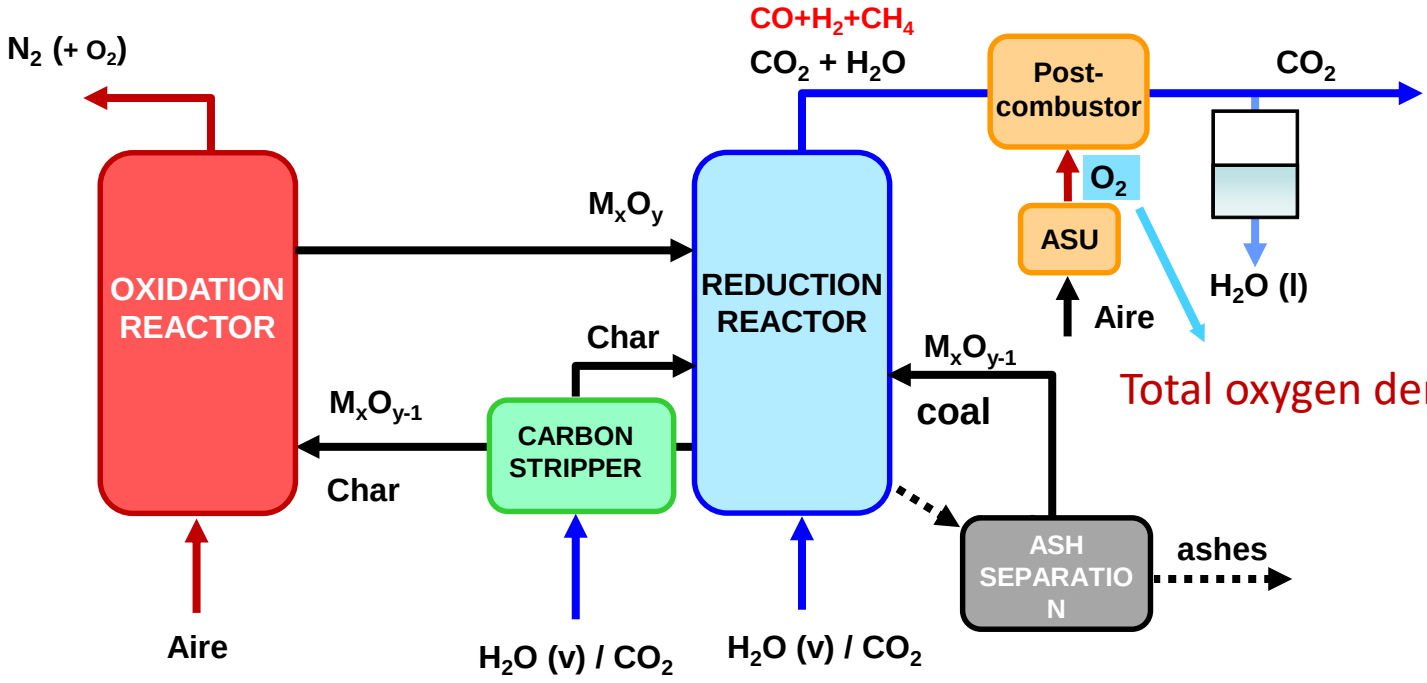
- Oxygen carrier losses with ash draining from the bed.
- Incomplete CO_2 capture. Unreacted char is transfered to the air reactor in which is burnt with air giving CO_2 emissions to the atmosphere.

CARBON STRIPPER

- Incomplete combustion of gases coming from FR, that force the use of one oxygen polishing step to finish the combustion to CO_2 and H_2O.

Oxygen polishing step

CLC with coal



- ***Process improvement***

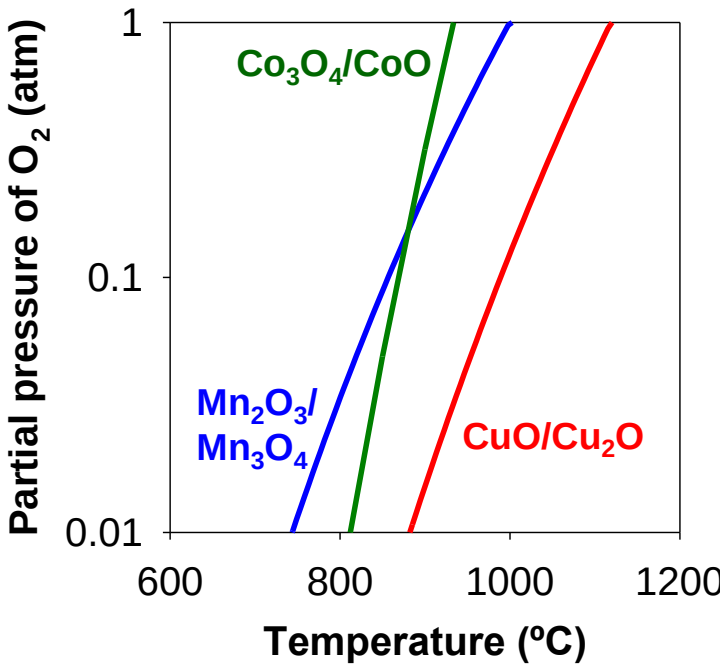
  Optimization of operating variables

  Design modifications

  Increasing the reactivity of the oxygen carrier, or using CLOU or CLaOU

CLOU oxygen carriers

- Appropriate thermodynamic for oxygen uncoupling at temperature of interest
- Cu, Mn, Co, mixed oxides.
- Mn oxides needs to use for oxidation at temperatures around 800 ºC. This gives usually low oxidation rates.
- Mn containing mixed oxides can increase the oxidation temperature
- This work focus in Mn-Fe mixed oxides. That have some CLOU conversion that can be added to CLC.

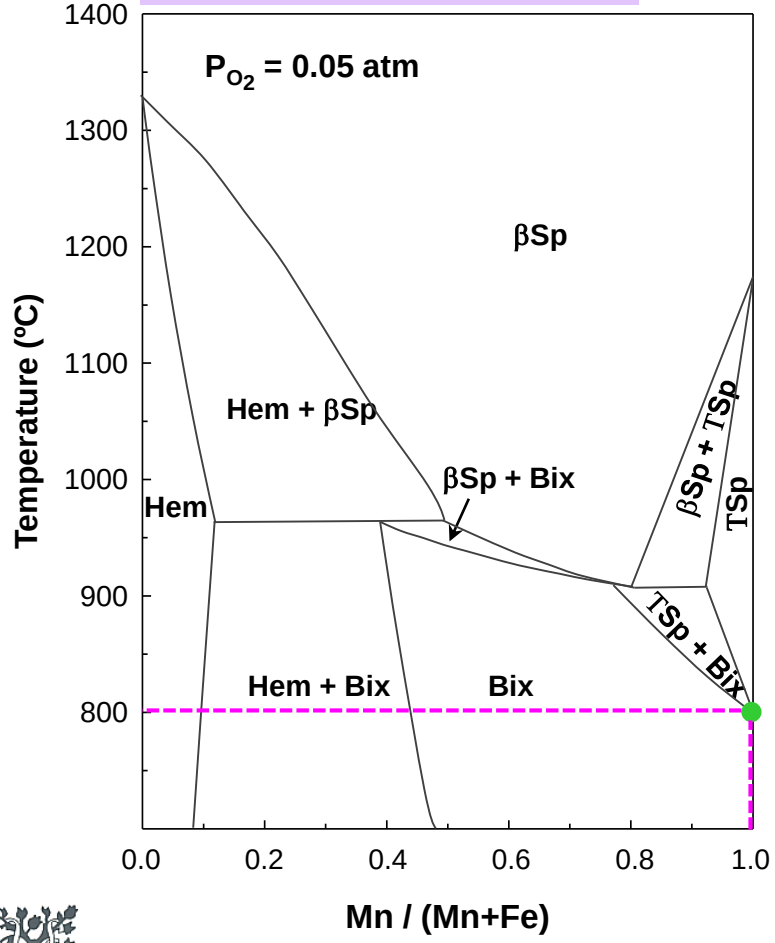


Fe – Mn mixed oxides

Increase of the oxidation reactivity in Mn-based oxygen carriers

$Mn_2O_3 + Fe_2O_3 \Rightarrow (Mn_xFe_{1-x})_2O_3$

*FactSage thermochem. software



- When all the bixbyite is Mn_2O_3:

$$6\ Mn_2O_3 \longleftrightarrow 4\ Mn_3O_4 + O_2$$

Bixbyite — Spinel

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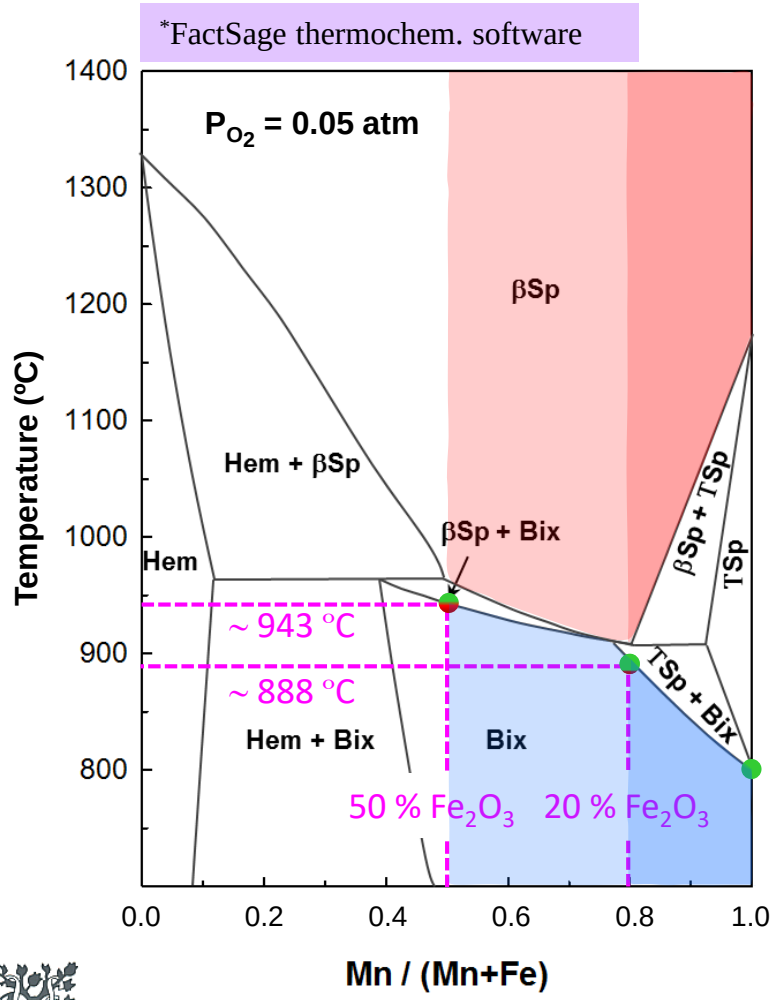

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  $6\ Mn_2O_3 \longleftrightarrow 4\ Mn_3O_4 + O_2$

  Bixbyite — Spinel

- By replacing Mn_2O_3 by Fe_2O_3 the transition temperature between the oxidized and reduced phases increases:

  $6\ (Mn_xFe_{1-x})_2O_3 \leftrightarrow 4\ (Mn_xFe_{1-x})_3O_4 + O_2$

  Bixbyite (Bix) — β-Spinel (β-Sp)

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Objective

To develop and test low cost oxygen carriers of Fe-Mn suitable for iG-CLC and CLOU processes that can be easly separable from coal ashes.

$$(Mn_x\ Fe_{1-x})_2\ O_3$$

Oxygen carrier preparation

Physical mixture + spray drying + calcination

- Mn_3O_4 (77 %) + Fe_2O_3 (24 %) — $(Mn_{0.77}Fe_{0.23})_3O_4$
- Mn_3O_4 (60 %) + Fe_2O_3 (33 %) + TiO_2 (7 %) — $(Mn_{0.66}Fe_{0.34})_2Ti_{0.15}\ O_{3.3}$

Spray drying

Calcination – 2 hours 1350 °C or 1200 °C (with Ti)

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Characterization of oxygen carriers

		Mn77Fe[SD1350]	Mn66FeTi7[SD1200]
Sintering conditions	Time (h)	4 + 2	4 + 2
	Temperature (ºC)	950 + 1350	950 + 1200
Crushing strength (N)		1.7	2.0
XRD main phases (%)	$(Mn_xFe_{1-x})_2O_3$	13.6	81.0
	$(Mn_xFe_{1-x})_3O_4$	86.4	13.4
	TiO_2	-	5.6
Amorphous (%)		20	24
Relative permeability, K_m (-)		2.5	1.6

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- TiO_2 addition to increase mechanical strenght of the oxygen carrier

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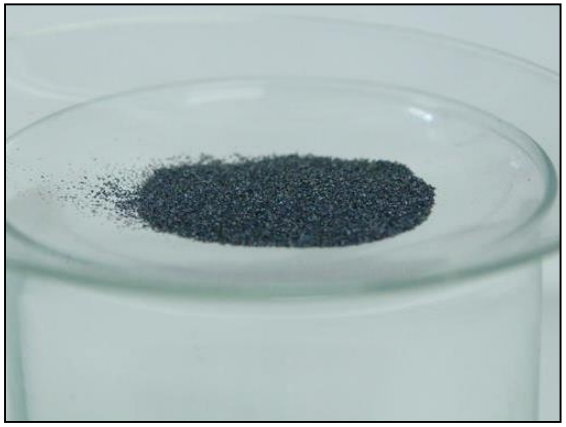
Mn66FeTi7 (SD1200)



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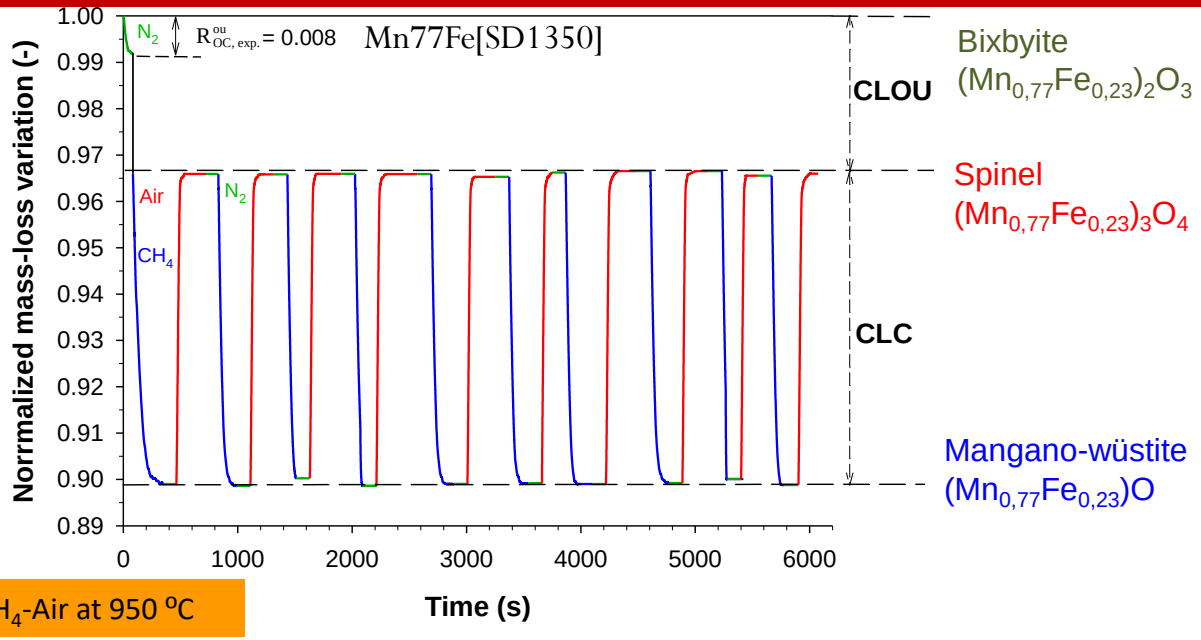
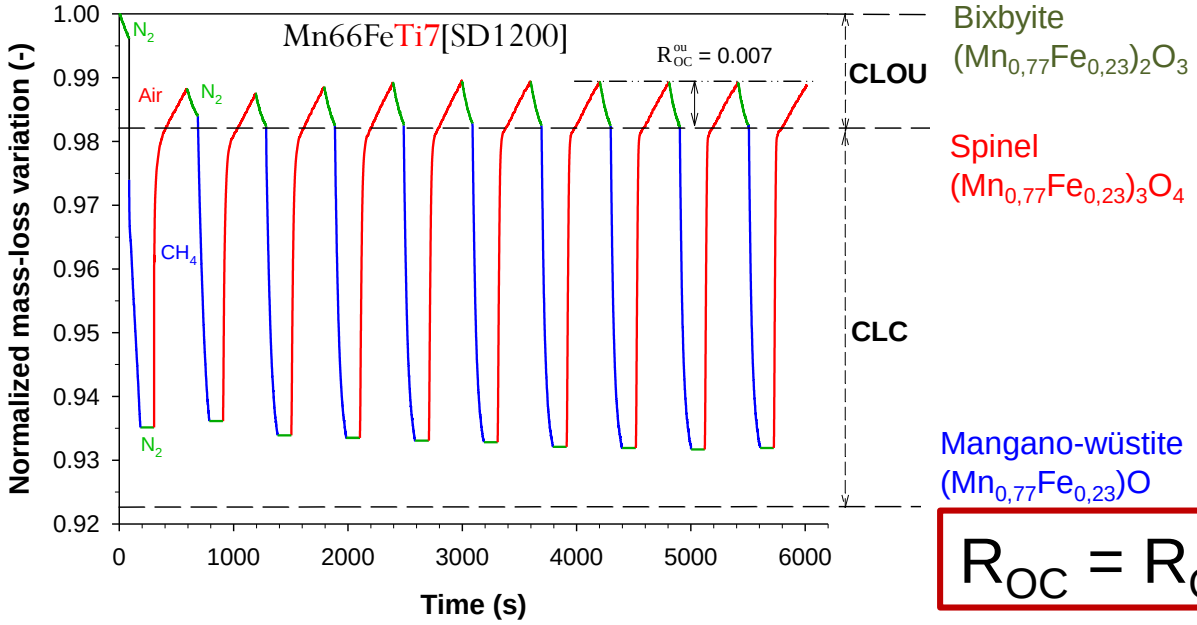
Reactivity by TGA



CH_4-Air at 950 °C



No CLOU

Suitable for *i*G-CLC

$R_{OC} = R_{OC}^{g} = 6.7$ wt %

Partial CLOU

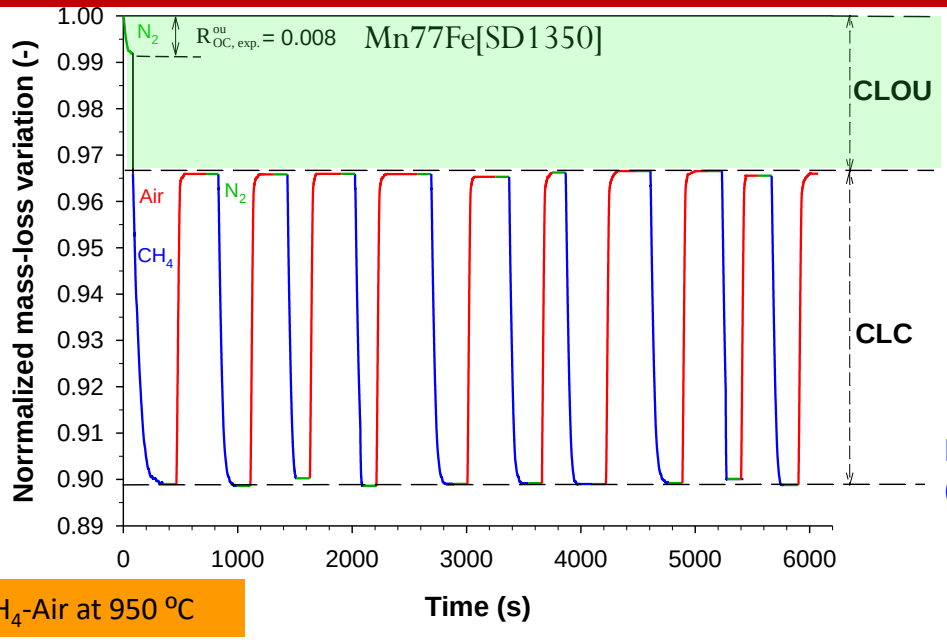
+

Suitable for iG-CLC

CLaOU

$R_{OC} = R_{OC}^{g} = R_{OC}^{g} = 5.8$ wt %

Reactivity by TGA



Bixbyite $(Mn_{0,77}Fe_{0,23})_2O_3$

Spinel $(Mn_{0,77}Fe_{0,23})_3O_4$

Mangano-wüstite $(Mn_{0,77}Fe_{0,23})O$

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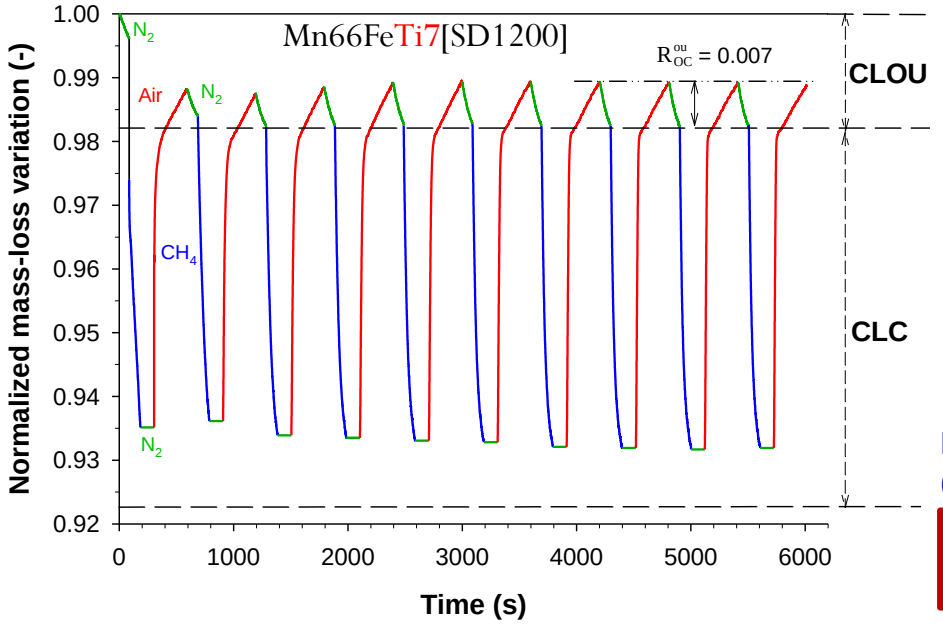

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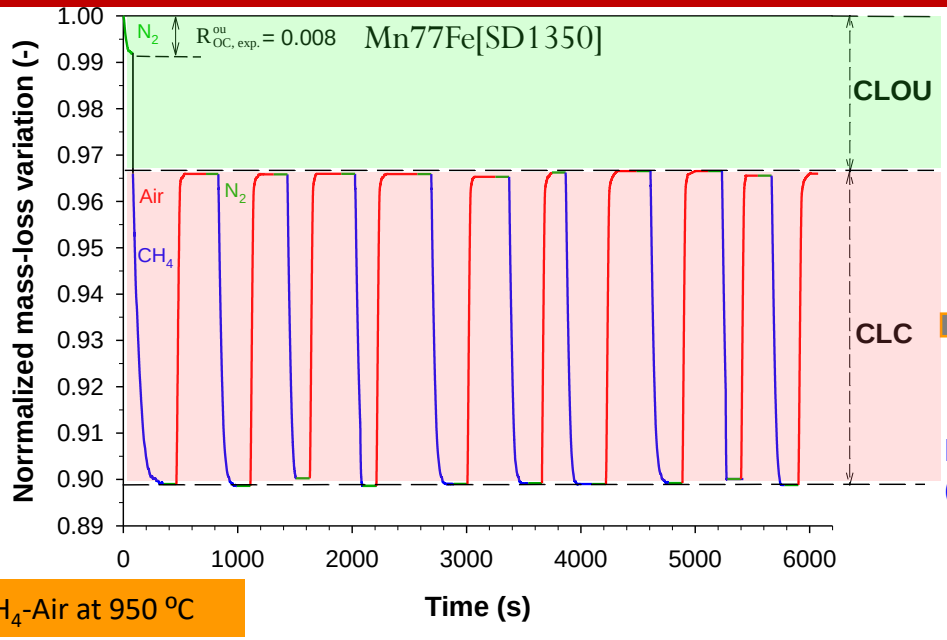

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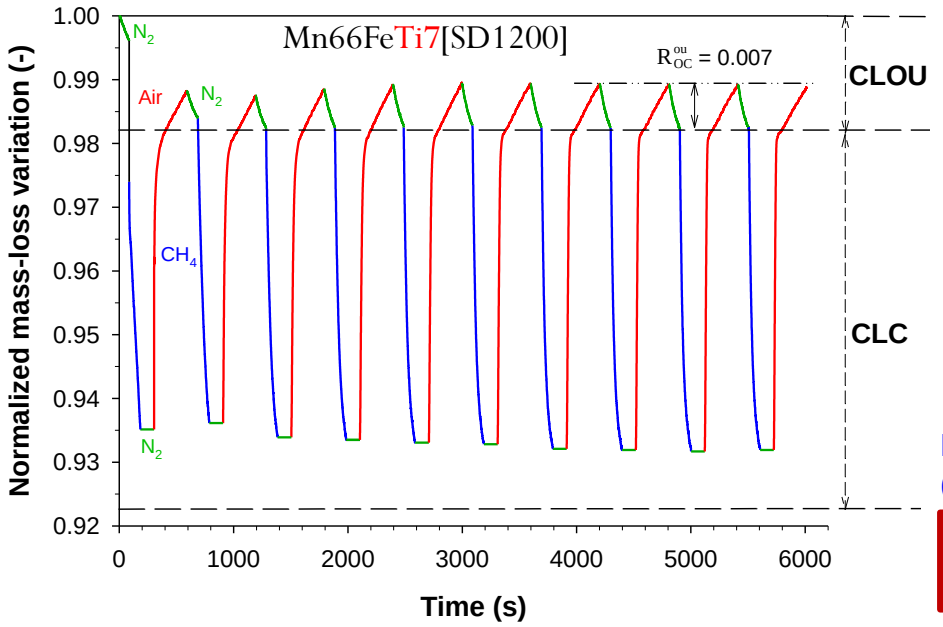

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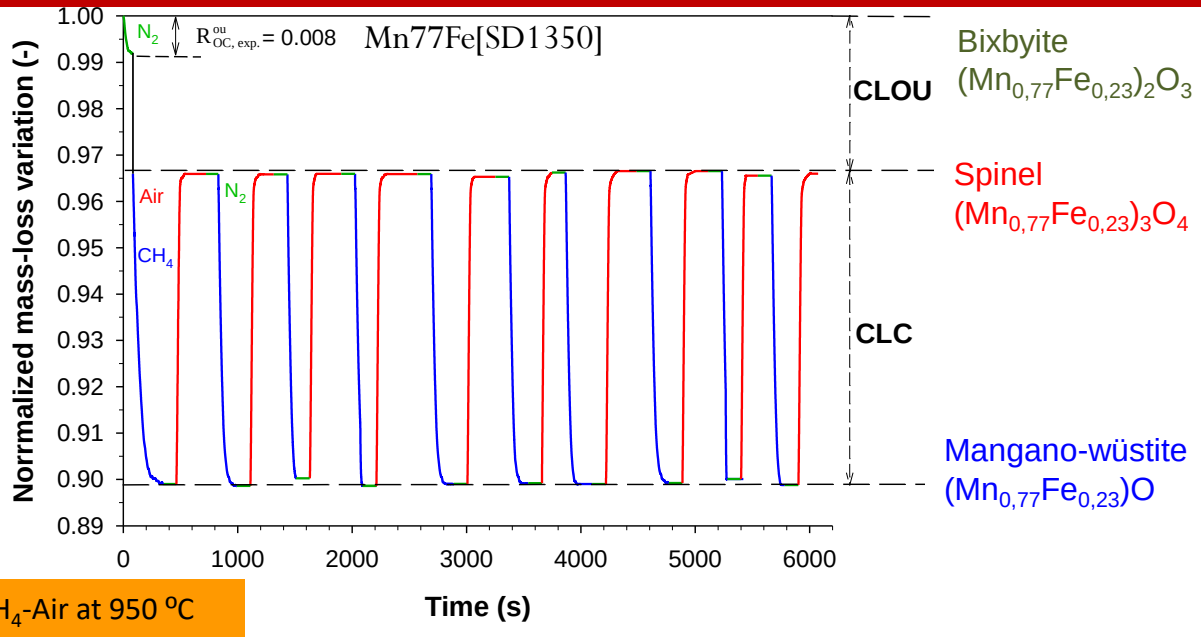

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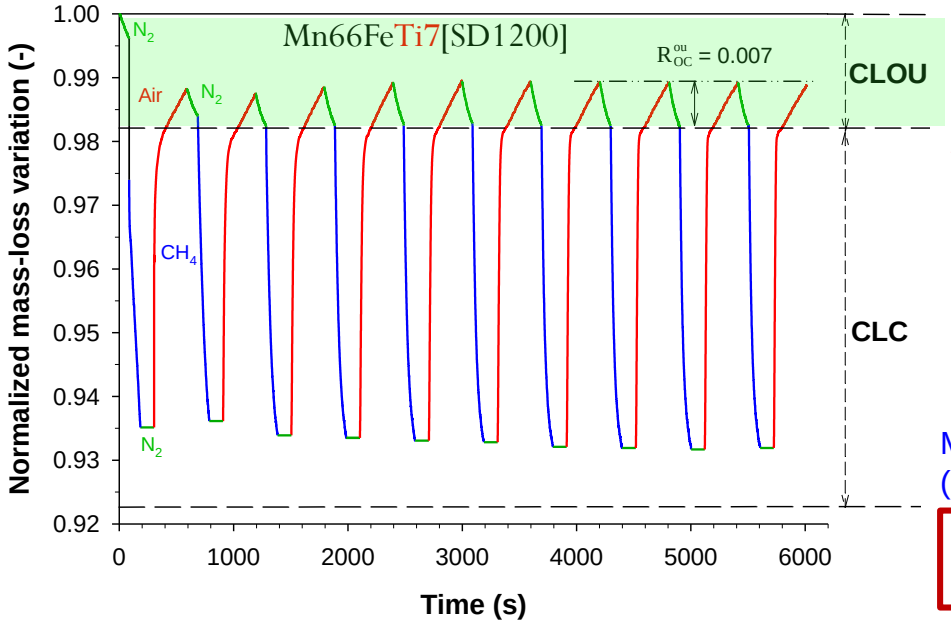

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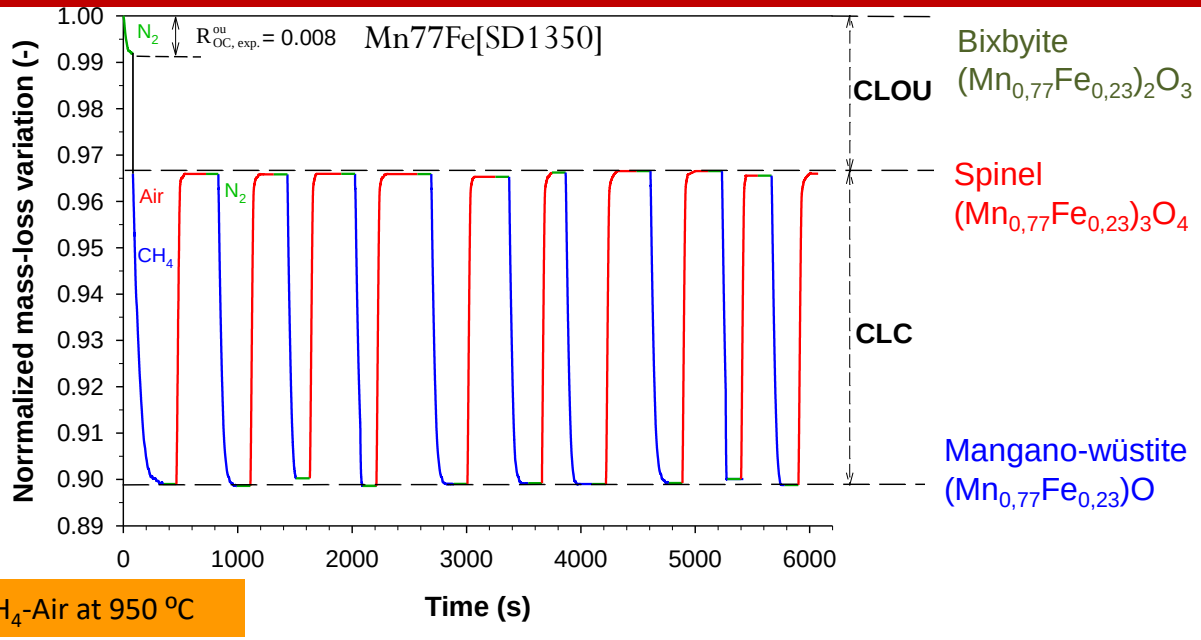

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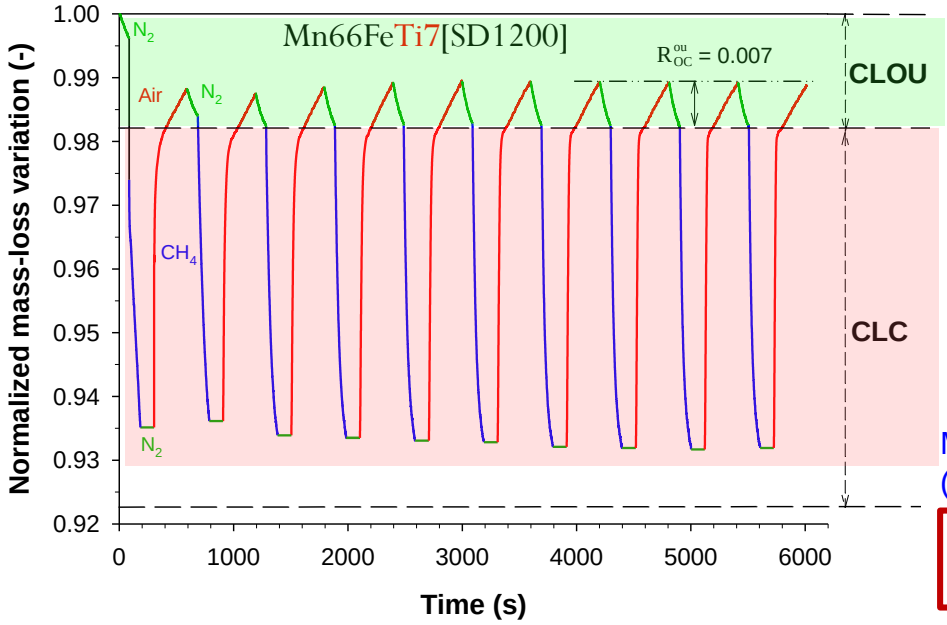

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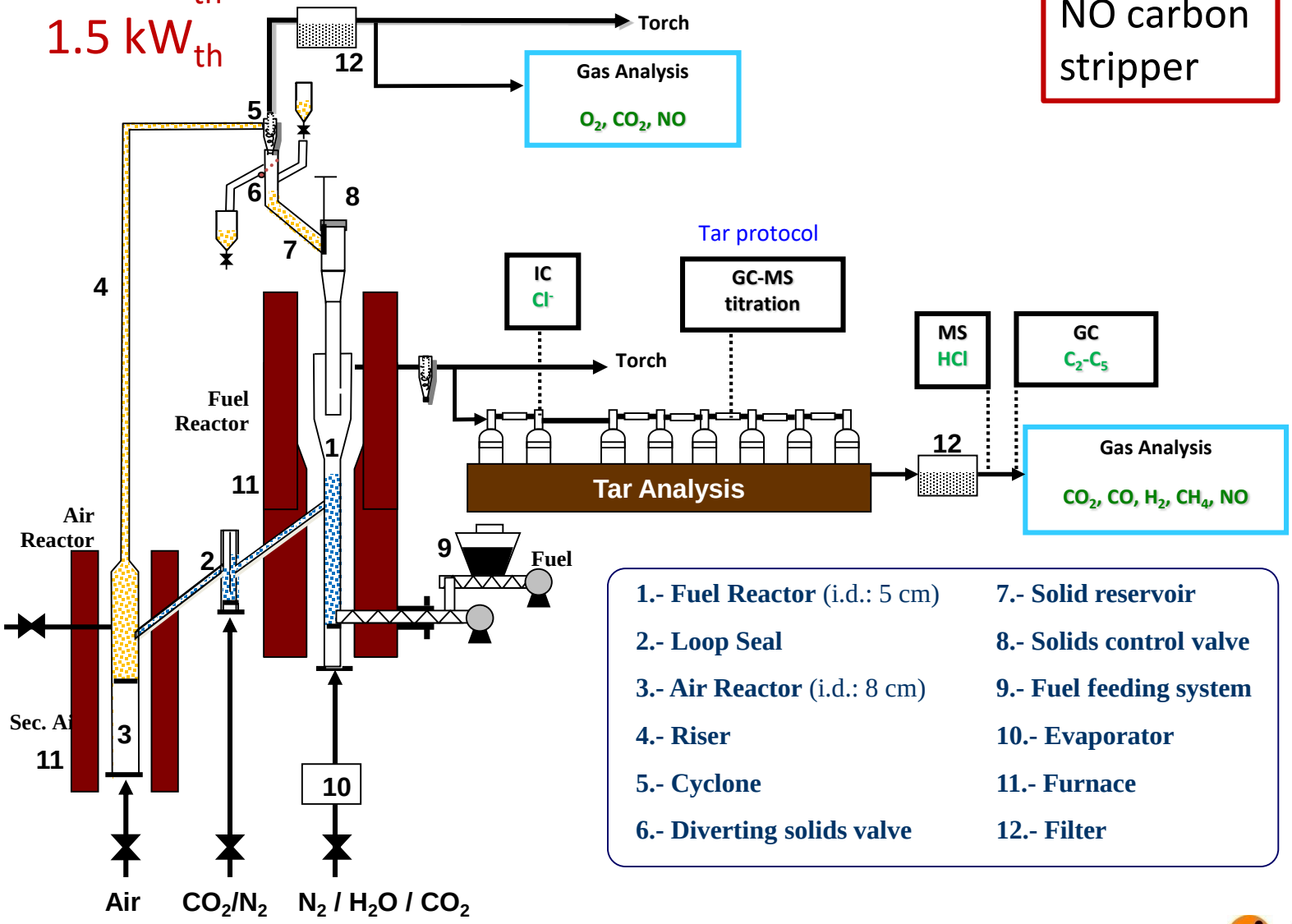
Continuous unit for solid fuel CLC

iG-CLC 500 W_{th}

CLOU 1.5 kW_{th}

NO carbon stripper



1.- **Fuel Reactor** (i.d.: 5 cm)
2.- **Loop Seal**
3.- **Air Reactor** (i.d.: 8 cm)
4.- **Riser**
5.- **Cyclone**
6.- **Diverting solids valve**
7.- **Solid reservoir**
8.- **Solids control valve**
9.- **Fuel feeding system**
10.- **Evaporator**
11.- **Furnace**
12.- **Filter**

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Data evaluation

- All the volatiles exit through the FR and are captured
- All the ungasified char is fully burnt in the AR

Total oxygen demand

$$\Omega_T = \frac{\text{Ox. required combustion of unburnt products}}{\text{Ox. Required for complete combustion of biomass}}$$

CO_2 capture efficiency

$$\eta_{CC} = \frac{\text{Carbon converted to gas in the FR}}{\text{Carbon introduced in the FR}}$$

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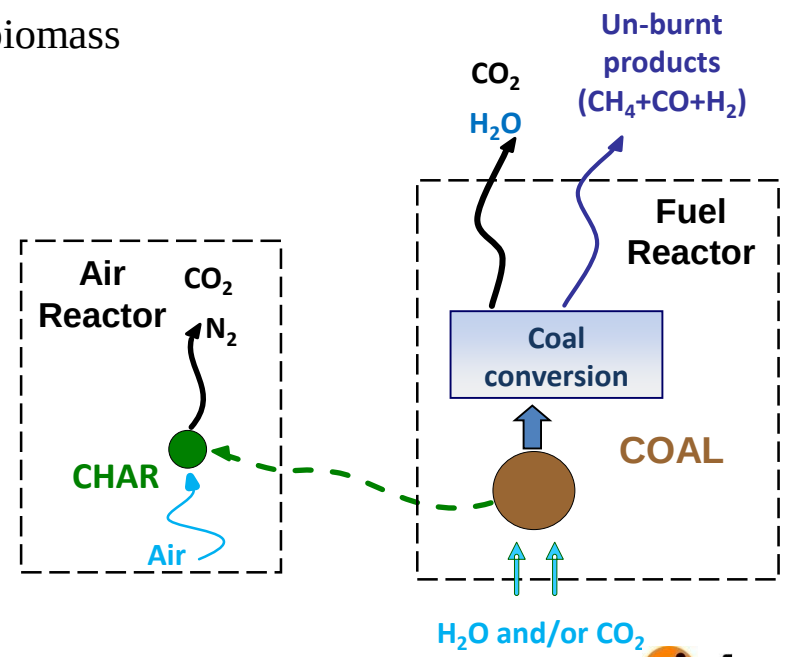

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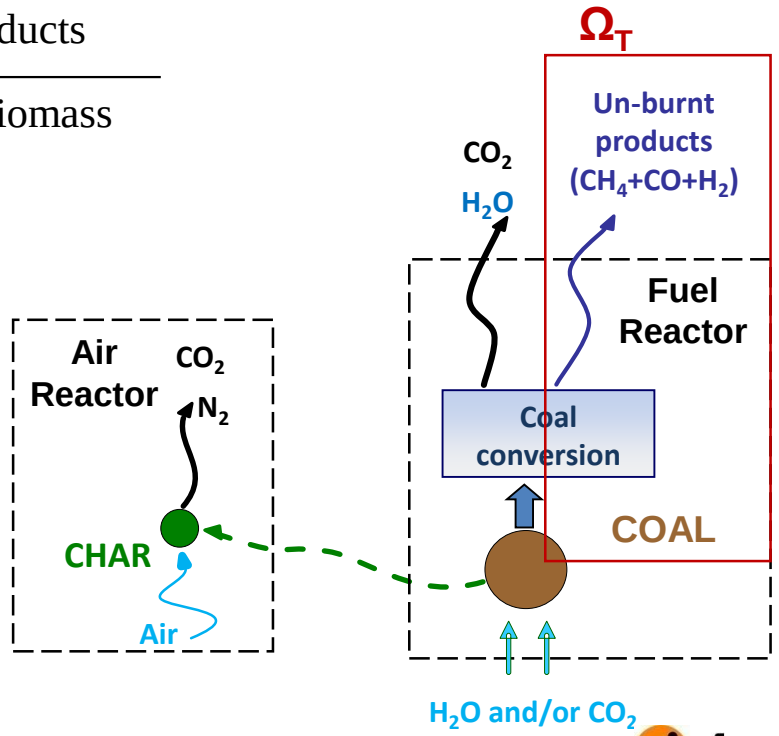

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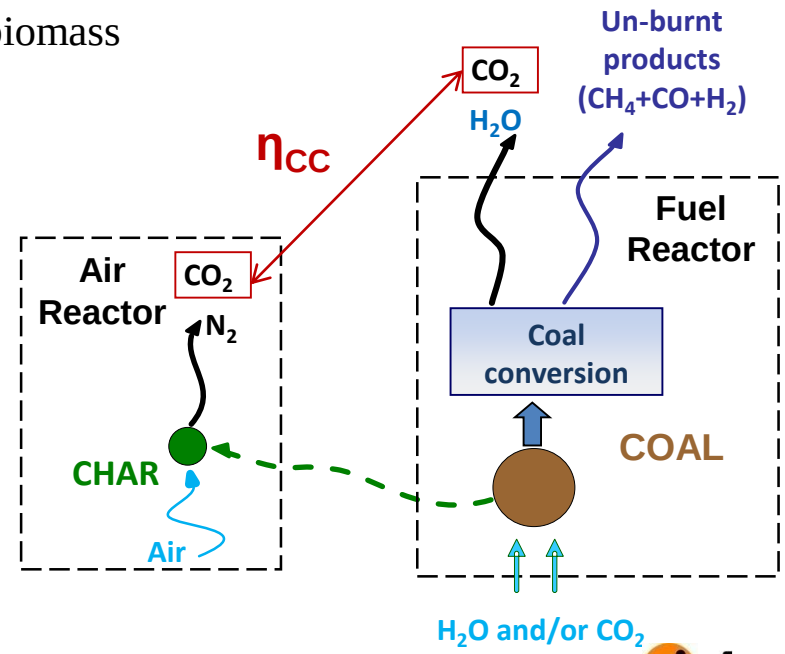

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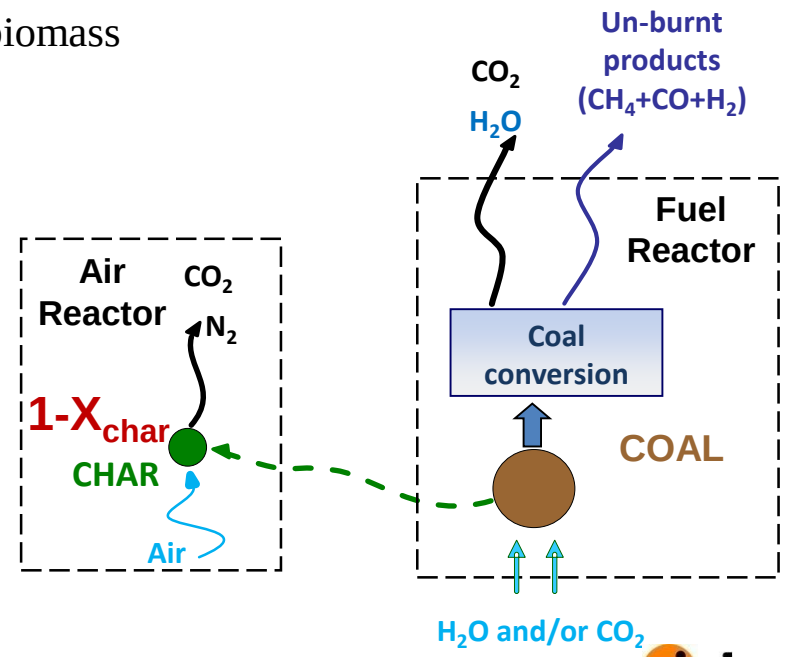

Coals used

	ANT	BIT-MV	BIT-HV	BIT-HV-pre	SUB	LIG
Proximate analysis (wt.% raw matter)						
Moisture	1.0	3.5	7.5	2.3	14.8	12.5
Volatile matter	7.6	25.5	34.0	33.0	33.1	28.7
Fixed carbon	59.9	55.3	49.9	55.9	36.1	33.6
Ash	31.5	15.7	8.6	8.8	16.0	25.2
Ultimate analysis (wt.% raw matter)						
C	60.7	66.3	70.8	65.8	51.5	45.4
H	2.1	3.6	3.9	3.3	3.4	2.5
N	0.9	1.8	1.7	1.6	0.7	0.6
S	1.3	0.5	0.5	0.6	0.3	5.2
$O^{(a)}$	2.5	8.6	7.0	17.6	13.3	8.6
LHV (kJ/kg)	21880	24930	25880	21900	18680	16250
Ω_{coal} (kg O/kg coal)	1.8	2.0	2.2	1.9	1.5	1.4

d_p: 0,2-0,3 mm

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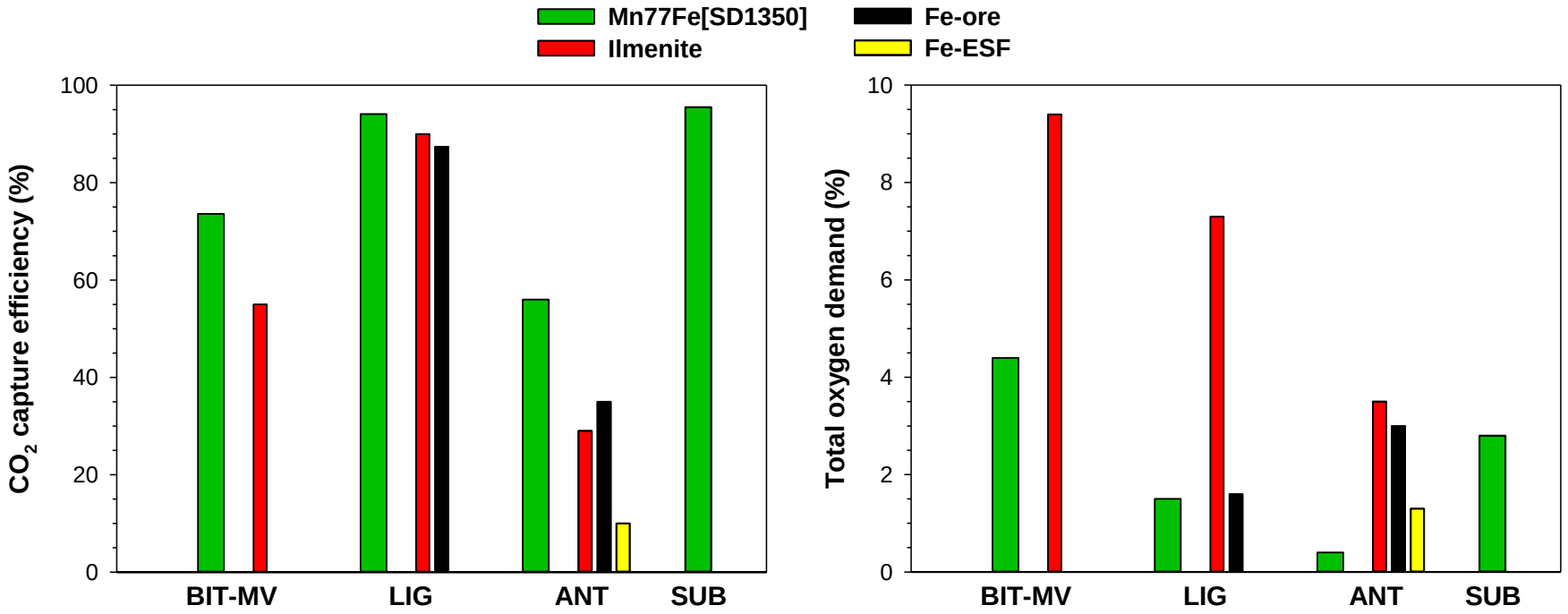
Results

Carbón		BIT-MV	LIG	ANT		SUB
Test		1	2	3	4	5
η_{CC}	%	73,6	94,1	56,0	62,6	95,5
X_C	%	68,3	91,9	55,4	62,1	93,5
Ω_T	%	4,4	1,5	0,4	0,3	2,8
$\eta_{comb.,\ RR}$	%	94,2	98,4	99,2	99,5	97,1
$\eta_{carbón}$	%	99,2	98,3	93,4	97,1	98,0
$\xi_{C,\ fijo}$	%	1,0	2,3	6,7	2,9	2,8

Fuel reactor – 900 ºC
Air reactor - 950 ºC
Φ - 1.0
No carbon stripper

- CO_2 capture efficiencies depended on coal rank. It were high for high reactivity coals as lignite.
- Oxygen demands Ω_T lower than 4.5 %

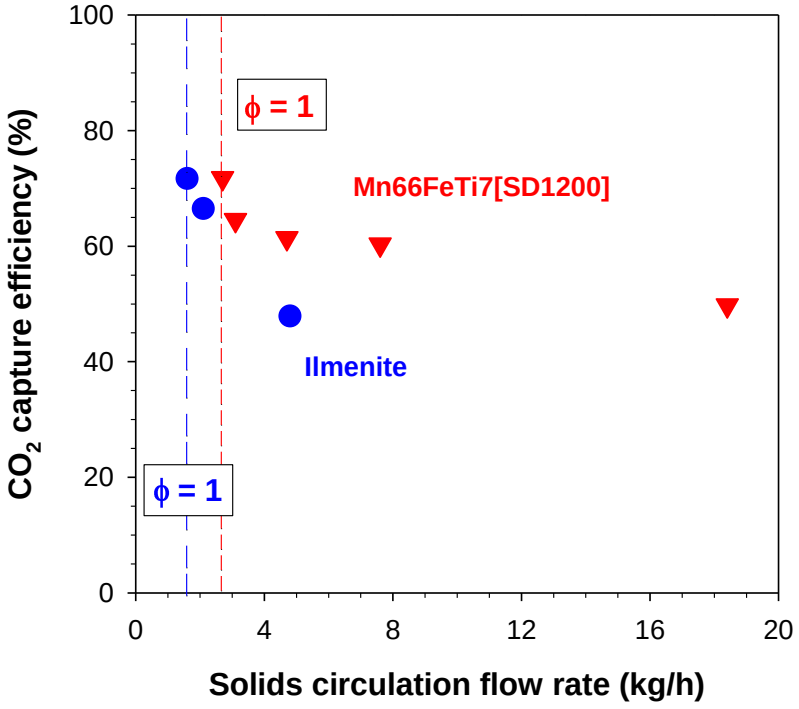
Comparison of performance with low cost oxygen carriers

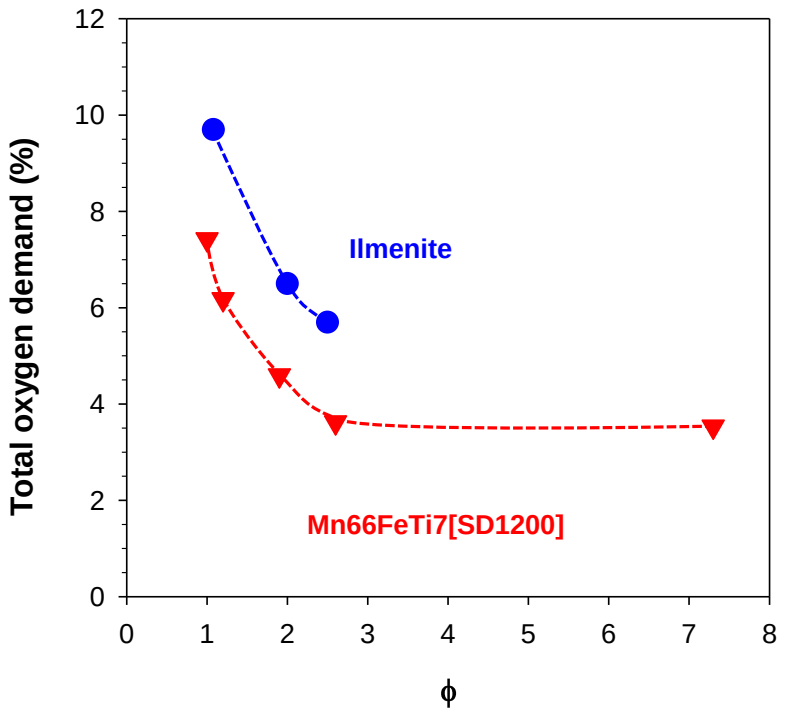


- CO_2 capture efficiencies were higher than those found with other low cost oxygen carriers
- Oxygen demand was lower than those found with low cost oxygen carriers

CLaOU con Mn66FeTi7[SD1200]

Effect of solid circulation flowrate





- CO_2 capture efficiency decreased when solid circulation increased .
- CO_2 capture efficiencies higher than those found with ilmenite

- Total oxygen demand decreased when ϕ increased because more oxygen was available
- Significant improvement with respect to ilmenite.

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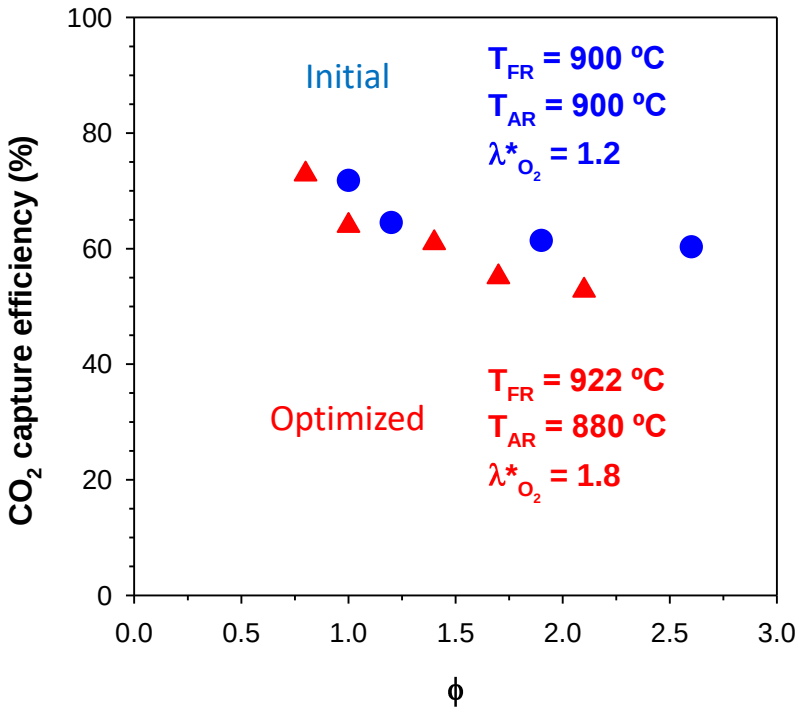
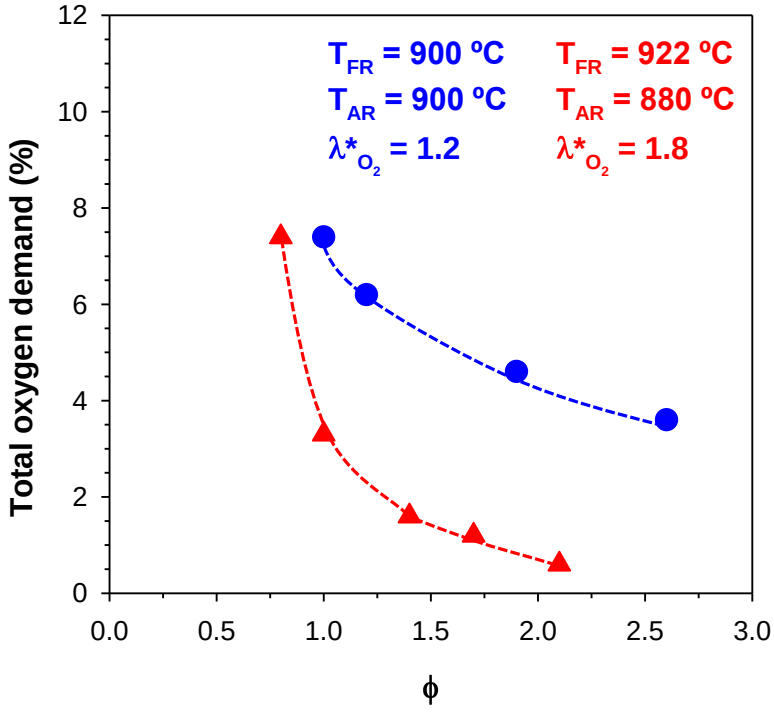
Optimization of the operating conditions



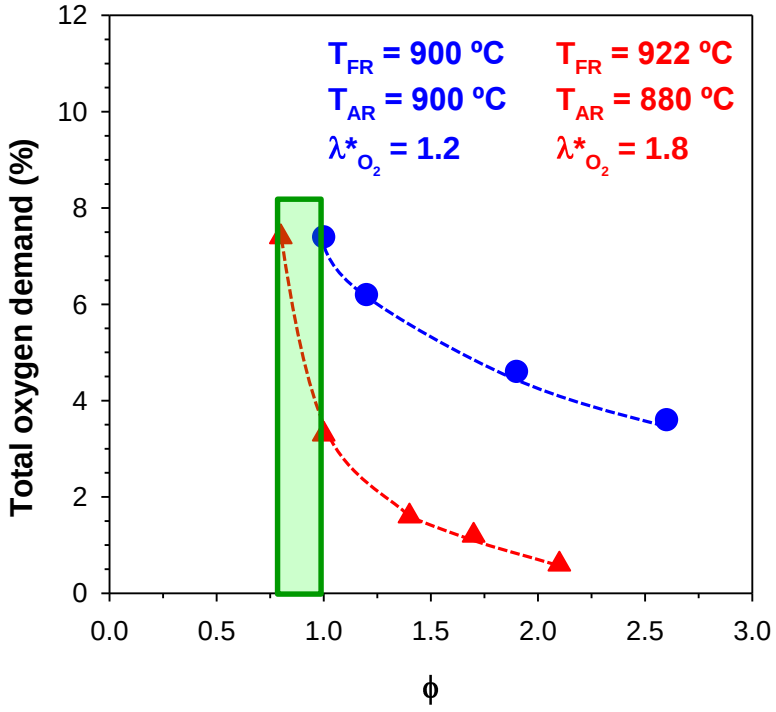
- Reducing temperature in the air reactor
- Increasing oxygen concentration in the air reactor λ^*_{O2}
- Increasing Φ
- Small effect on the CO_2 capture
- Carbon stripper continues being necessary

Optimization of the operating conditions



- Significant effect on the oxygen demand due to higher oxidation conversion in the air reactor that increases O_2 generation.
- Ω_t =0.5 % with Mn66FeTi7.
- Lowest oxygen demand obtained with low cost oxygen carriers.

Optimization of the operating conditions



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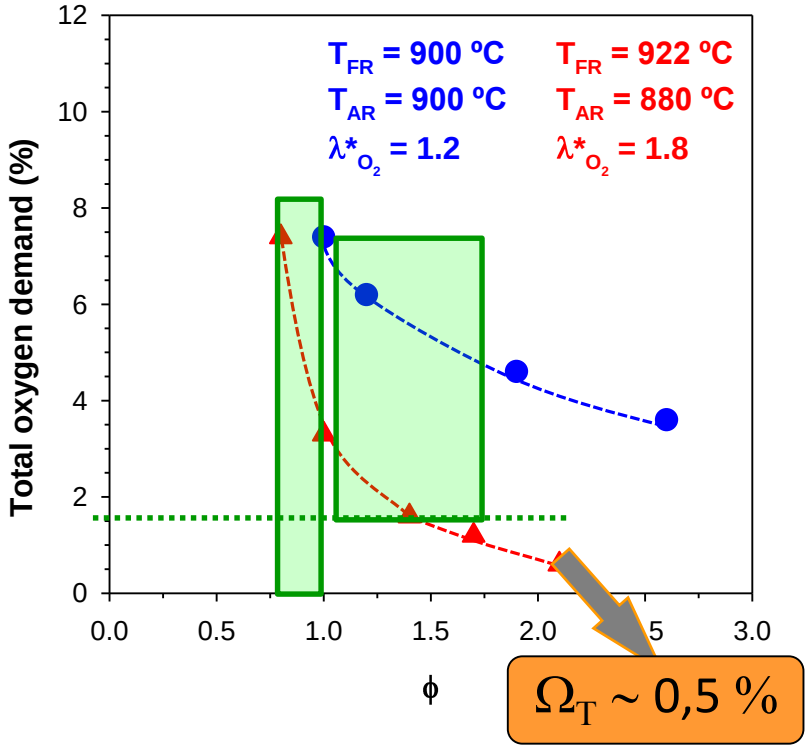

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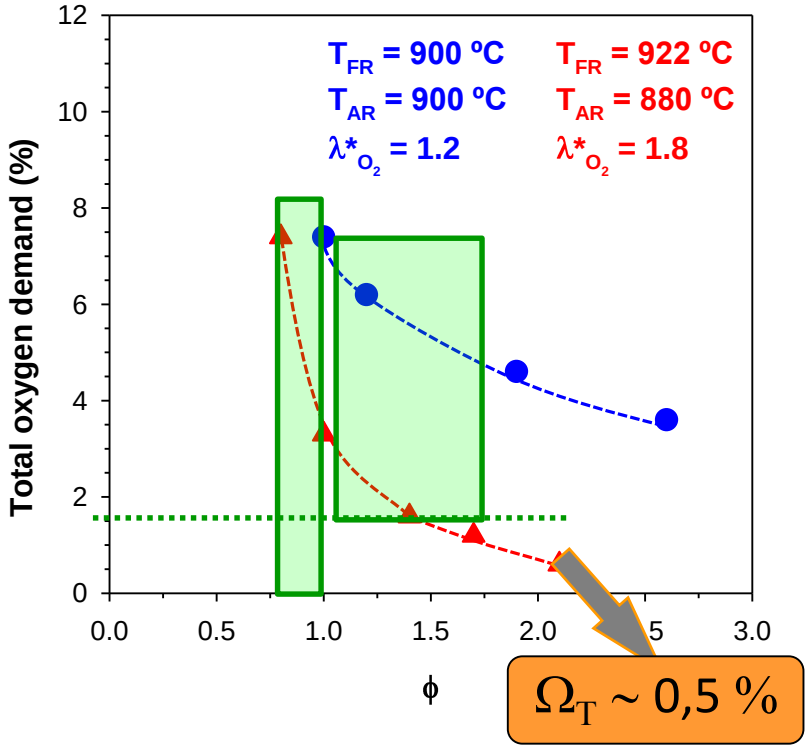
CL*a*OU con Mn66FeTi7[SD1200]

Optimization of the operating conditions



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- Lowest oxygen demand obtained with low cost oxygen carriers.

CLaOU- Chemical looping Combustion assisted by Oxygen Uncoupling Combustion

coal *i*G-CLC + one small CLOU contribution that allows to reduce unburnt gases.

Total oxygen demand Ω_t

*i*G-CLC > CLaOU > CLOU

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Conclusions

- Two Fe-Mn mixed oxygen carriers with magnetic behavior have been developed and tested in a continuous unit burning coals of different rank
- Mn77Fe (SD1350) was suitable for *i*G-CLC and showed better performance than low cost Fe based oxygen carriers
- Mn66FeTi7(SD1200) has some CLOU behavior and was suitable for CLaOU process
- With this material very low total oxygen demand (Wt=0.5 %) was obtained

Thanks For Your Attention

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Solid fuel CLC

Combustion of solid fuels using Chemical Looping Technology has experienced one important development in the last decade.

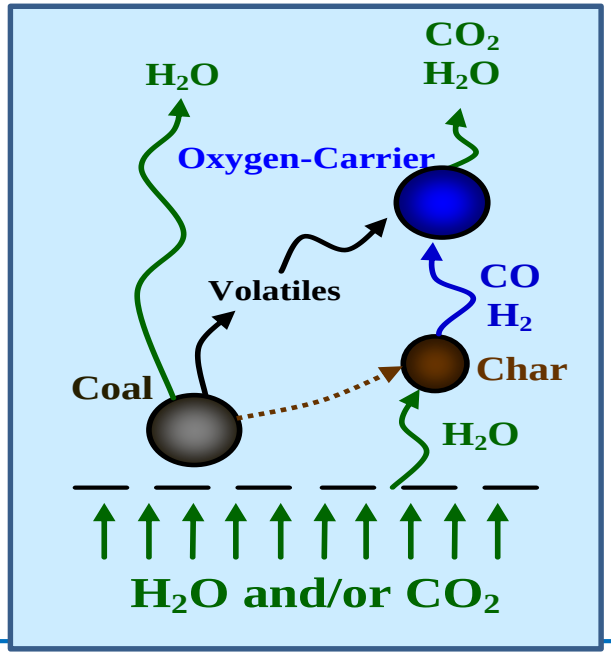
Two options depending on the mechanism on the mechanism of solid conversion

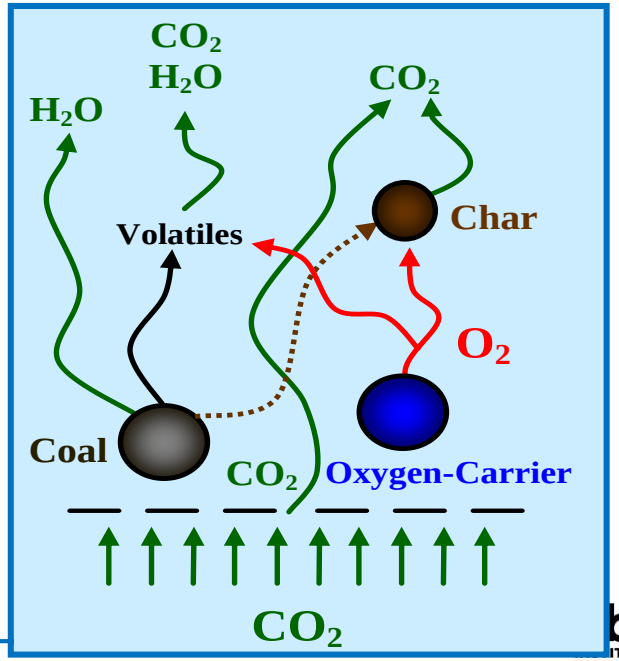
iG-CLC - in-situ Gasification Chemical Looping Combustion

Solid fuel is gasified inside the fuel reactor by H_2O and/or CO_2 and the oxygen carrier oxidizes gasification products (CO, H_2, CH_4, volatiles) to CO_2 and H_2O

CLOU - Chemical Looping with Oxygen Uncoupling

Solid fuel is burned with gaseous oxygen released by the oxygen carrier



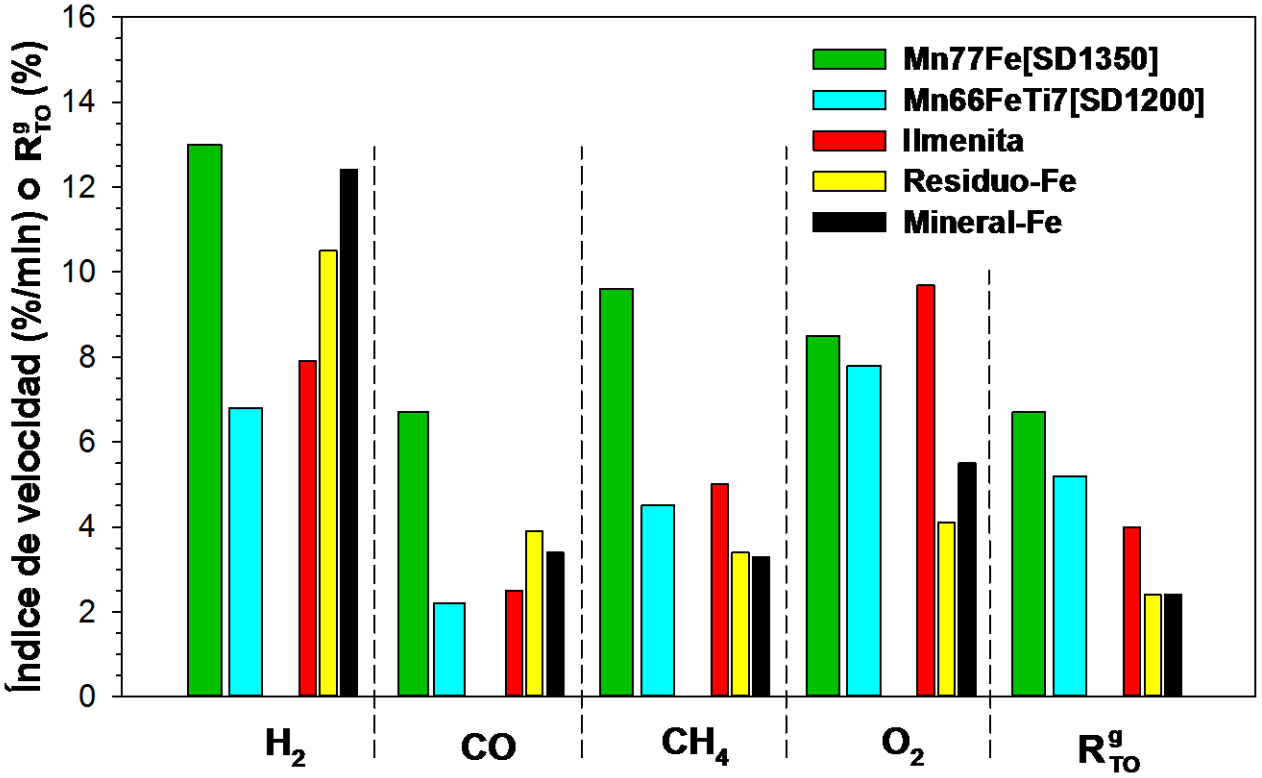


Performance of solid fuel CLC

- Results obtained in pilot units show that iG-CLC and CLOU processes can be carried out with coals of different rank from lignite to anthracite and also with biomass using ores and synthetic oxygen carriers.
- ***Incomplete CO_2 capture*** both in iG-CLC and CLOU. Part of unconverted char in FR is transfered to the AR, in which is converted to CO_2 emitted to atmosphere.
- ***Incomplete combustion of gases coming from FR***, that force the use of one oxygen polishing step to finish the combustion to CO_2 and H_2O. The need of oxygen has one significant energy penalty.
- Presence of ***ashes in coal significantly reduces the effective lifetime*** of the oxygen carriers

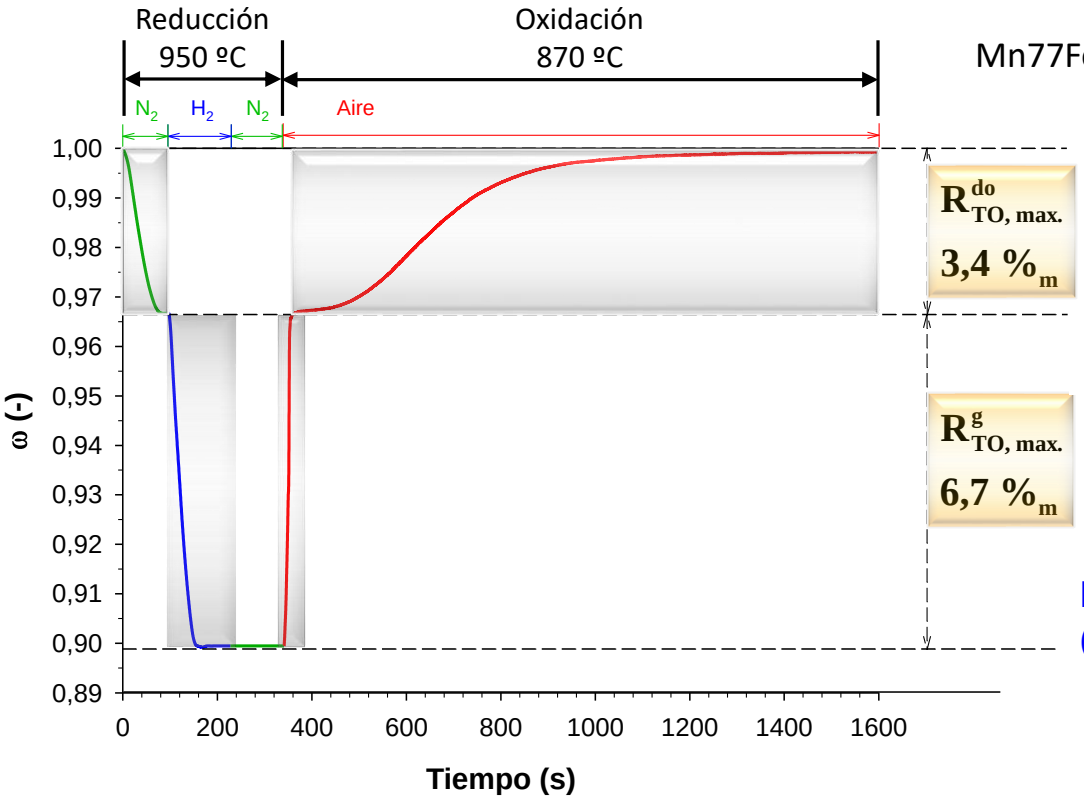
TGA reactivity

Reactivity of low cost oxygen carriers



- Mn77Fe[SD1350] is more reactive than Fe-based oxygen carriers.

Reactivity by TGA



Bixbyíta
$(Mn_{0,77}Fe_{0,23})_2O_3$

$R^{do}_{TO,\,max.}$ 3,4 $\%_m$

Espinela
$(Mn_{0,77}Fe_{0,23})_3O_4$

$R^{g}_{TO,\,max.}$ 6,7 $\%_m$

Mangano-Wustita
$(Mn_{0,77}Fe_{0,23})O$

$$R^{t}_{TO} = R^{g}_{TO} + R^{do}_{TO}$$

$6\,(Mn_xFe_{1-x})_2O_3 \rightarrow 4\,(Mn_xFe_{1-x})_3O_4 + O_2$ → **Capacidad de transporte de oxígeno desacoplado:** R^{do}_{TO}

$(Mn_xFe_{1-x})_3O_4 + H_2 \rightarrow 3\,(Mn_xFe_{1-x})O + H_2O$ → **Capacidad de transporte de oxígeno con gases:** R^{g}_{TO}

$6\,(Mn_xFe_{1-x})O + O_2 \rightarrow 2\,(Mn_xFe_{1-x})_3O_4$ → vía CLC

$4\,(Mn_xFe_{1-x})_3O_4 + O_2 \rightarrow 6\,(Mn_xFe_{1-x})_2O_3$ → vía CLOU