Istituto di Ricerche sulla Combustione
Consiglio Nazionale delle Ricerche

Dipartimento
di Ingegneria Chimica,
dei Materiali e della
Produzione Industriale
Università degli Studi
di Napoli Federico II

Production and Stability Assessment of Oxygen Carrier Produced By Sewage Sludge Fluidized Bed Combustion

Antonio Coppola

Università degli Studi di Napoli Federico II, DICMaPI- Napoli (Italy)

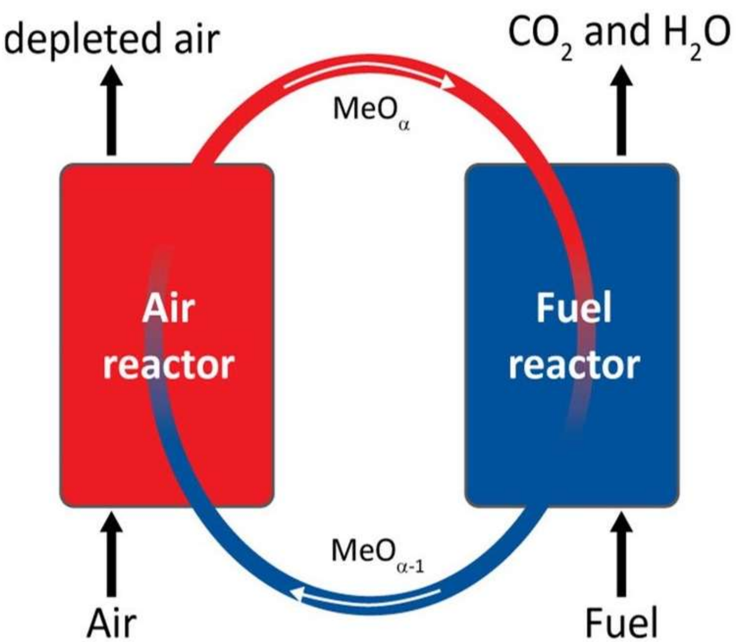
Giovanna Ruoppolo, Massimo Urciuolo, Riccardo Chirone

Consiglio Nazionale delle Ricerche, IRC – Napoli (Italy)

AIChE The Global Home of Chemical Engineers
FLUIDIZATION XVI
May 26 - 31, 2019 | Guilin Shangri-La Hotel | Guilin, China

Introduction: Chemical Looping Combustion

The Chemical Looping Combustion is an innovative technology that allows to burn fuel avoiding the direct contact between it and the oxygen of the air. The process is based on the use of an Oxygen Carrier (OC, typically a metal oxide) to transfer oxygen from the air to the fuel, allowing the formation of burnt gases free of nitrogen and therefore composed mainly of carbon dioxide (concentrated) and water (separable).



Fuel Reactor

$$(2n+m)Me_xO_{y(s)} + C_nH_{2m} \rightarrow (2n+m)Me_xO_{y-1(s)} + mH_2O + nCO_2$$

Air Reactor

$$(2n+m)Me_xO_{y-1(s)} + \left(n+\frac{m}{2}\right)O_2 \rightarrow (2n+m)Me_xO_{y(s)}$$

Properties required of oxygen carriers:

- High reactivity
- High oxygen transport
- Low costs
- Low environmental impact
- High mechanical strength

Introduction: Oxygen Carrier

Typical values of R_O, oxygen ratio (oxygen transport capacity)

- Fe-based OC, R_O=0.045
- Cu-based OC, R_O=0.089
- Ni-based OC, R_O=0.091

$$R_O = \frac{m_o - m_r}{m_o}$$

What are the limits?

- High carrier cost
- Carrier preparation method

Test a low-cost OC by re-using sewage sludge, and evaluate performance in a Chemical Looping Combustion process. The OC was prepared by combustion of sludge in a fluidized bed, and deposition of the ashes on a support of γ-Alumina (Al_2O_3).

OXYGEN CARRIER

CHEMICAL LOOPING COMBUSTION

Aim of the work

- The metals (Fe, Ca, Mn) present in sewage sludge ash have been deposited during sewage sludge fluidized bed combustion on γ-alumina which is characterized by high mechanical resistance and it was used as bed material.

- Three different combustion tests have been carried out in a 41 mm ID reactor adopting different operative conditions: the fluidization velocity and the particle size, in order to find optimal conditions for the preparation of the OCs.

- The oxygen carriers has been tested in reduction/oxidation tests using methane as fuel.

- The performance of the prepared OCs have been performed using a lab-scale fluidized bed apparatus properly designed for the study of chemical looping processes as close as possible to reality, in terms of cycling of temperatures and of reaction atmospheres.

- The samples have been characterized by TPR analysis, carrying out reduction tests with a mixture of 2% H_2/Ar, and a temperature ramp of 10°C/min up to 850°C.

Materials

Chemical composition

Proximate analysis		Elementar analysis (dry basis)	
Moisture	12,2	Carbon	39,4
Fixed carbon	57,4	Hydrogen	5,6
Volatiles	9,3	Nitrogen	6,7
Ash	21,2	Sulfur	0,8
		Chlorine	0,7
		Oxygen	22,7
		Ash	24,1
Higher heating value, kJ/kg			13484
Lower heating value, kJ/kg			12135

Inorganic elemental analysis of sewage sludge (as received), mg/kg

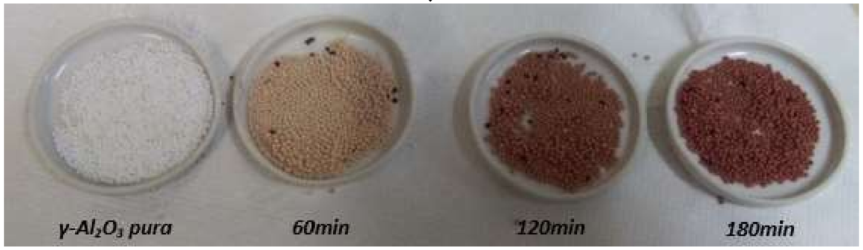
	%		ppm		ppm
AI	0,694	Ba	130	Ni	68
Ca	1,378	B	55	Se	3
Fe	2,671	Cr	81	Sr	70
Mg	0,360	Co	4	Sn	18
P	1,496	Cu	294	Ti	202
K	0,202	Pb	69	Tl	0,03
Si	0,255	Mn	247	V	15
Na	0,043	Hg	3	Zr	3
Zn	0,059	Mo	6		

Experimental Combustion tests

The experiment was carried out in a bubbling fluidised bed reactor in laboratory scale employing air as fluidization gas, using the sludge as fuel and alumina as an inert material bed.

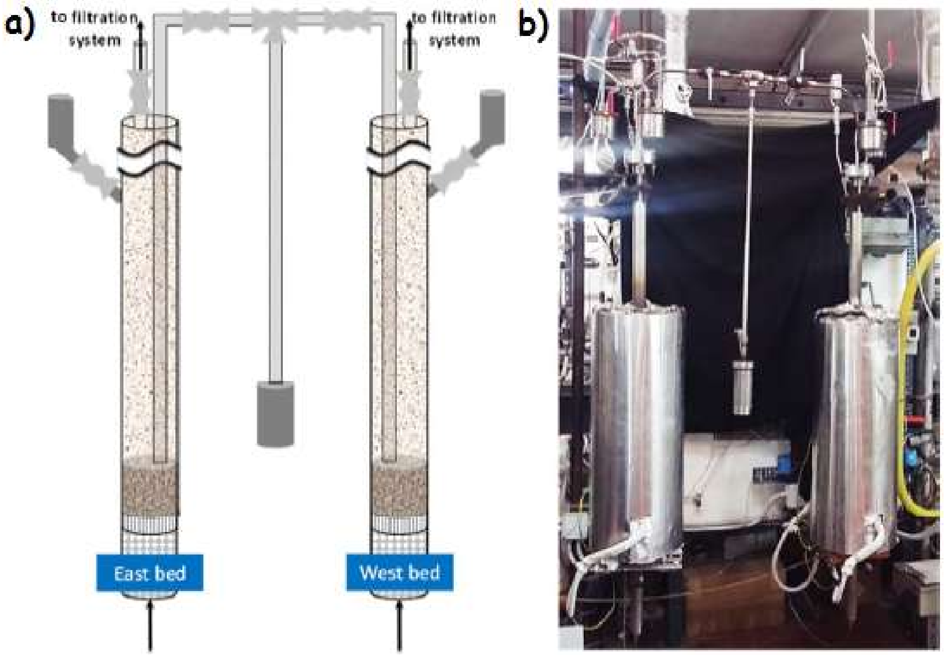
Operative conditions	Test 1	Test 2	Test 3
Temperature [°C]	850	850	850
U_{gas} [m/s]	0.47	0.6	0.6
<*d*> alumina bed [µm]	1000	1000	400–600
Feed [g/h]	100	120	120
Bed weight [g]	180	180	180

Each test was approximately carried out for 3 hours. Three samples were taken, in order to evaluate the effect of time on the degree of covering sludge / alumina ashes



Experimental :CLC tests

TWIN BEDS Apparatus



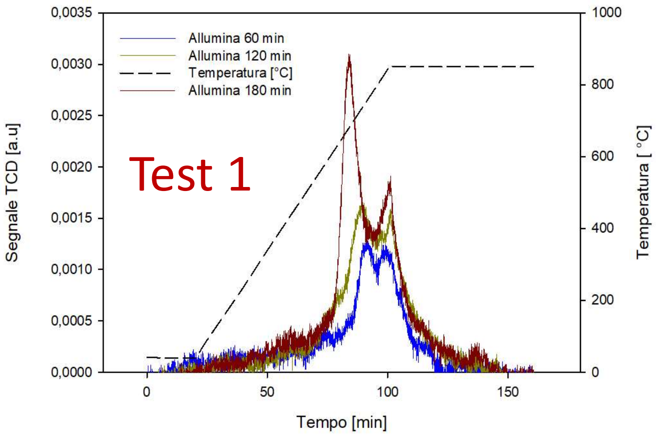
	Air Reactor	Fuel Reactor
***T*, °C**	850	750/800/850
***Q*, NL/h**	617	677/646/617
***U*, m/s**	0.5	
Fluidization Gas	Air	2%vol CH_4/N_2
Reduction/Oxdidation cycles	5	
Time, min	10	25

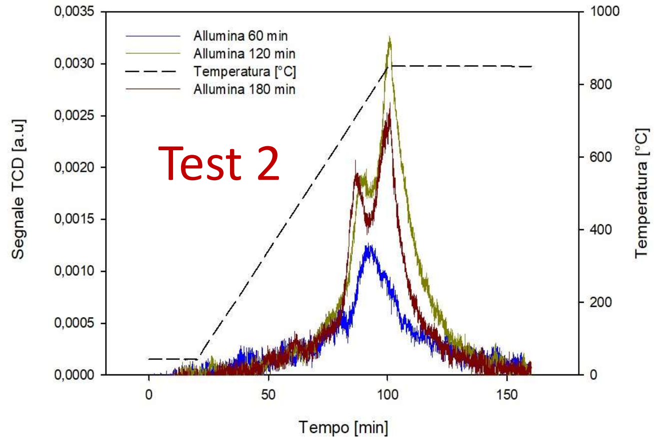
Experimental: TPR analysis and reduction/oxidation cycles

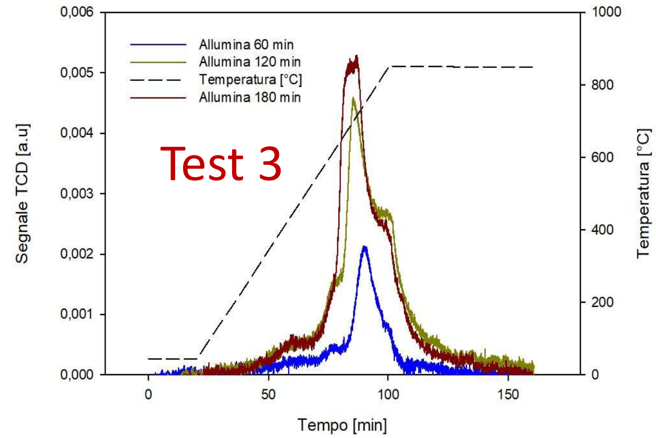
Micromeritics Autochem II TPD/TPR analyzer
110 mg OC
2% H_2/Ar mixture (50 $Ncm^3\ min^{-1}$)
10 °C min^{-1} up to **850 °C**.
1 h in air (50 $Ncm^3\ min^{-1}$) at 850 °C before the experiment.

The samples have been characterized by TPR (temperature programmed reduction) analysis, to study the reactivity of the carriers and to evaluate the amount of reducible material deposited on the support.

Results Combustion tests



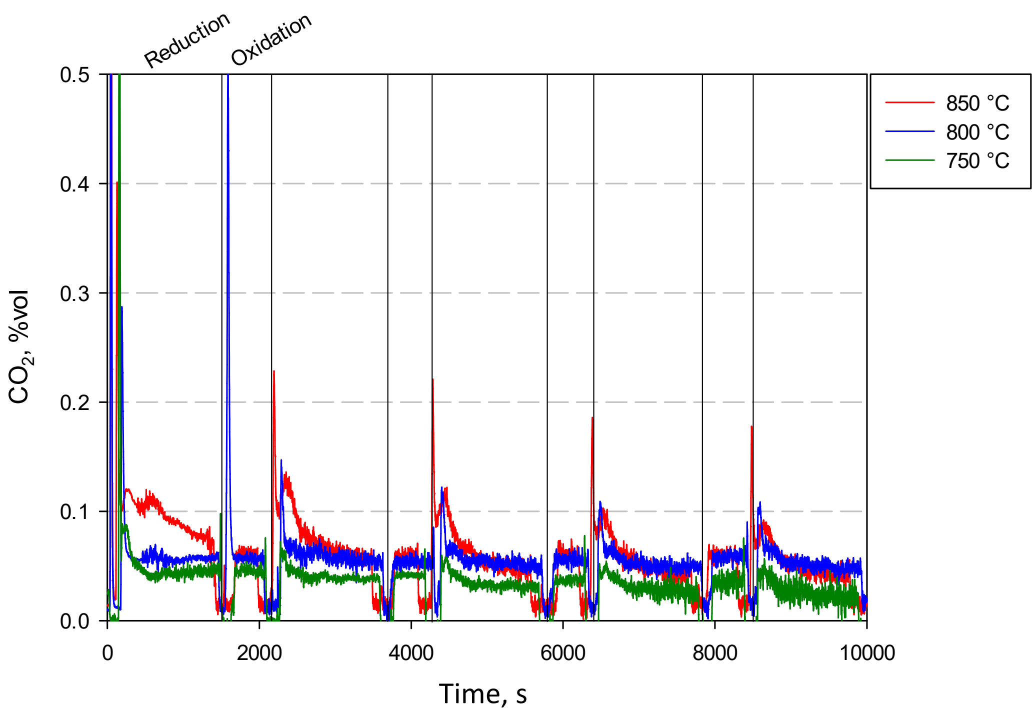


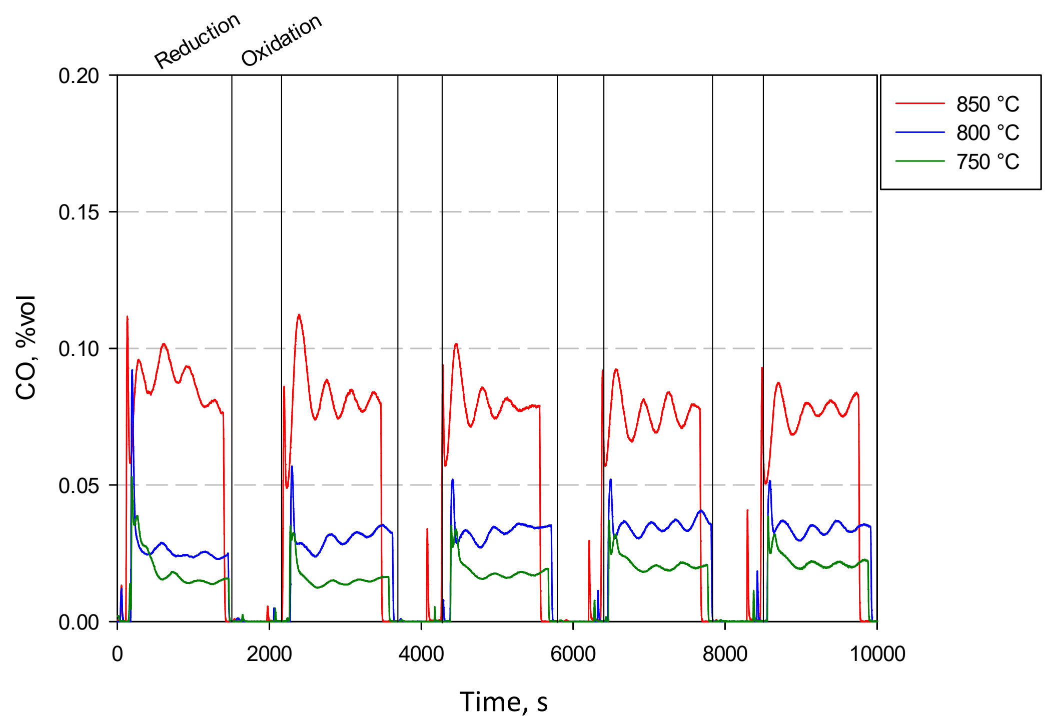


	60 min		120 min		180 min	
	µmol H_2	mg H_2/g_c	µmol H_2	mg H_2/g_c	µmol H_2	mg H_2/g_c
Test 1	7.26	**0.13**	10.17	**0.19**	13.46	**0.26**
Test 2	8.67	**0.16**	16.41	**0.30**	12.88	**0.24**
Test 3	7.47	**0.13**	23.61	**0.38**	24.11	**0.43**

$$R_O=3.4\times10^{-3}$$

Results CLC tests





The reactivity of the OC increases with temperature and decreases as the number of cycles growths.

Results CLC tests

T Fuel Reactor	Cycle	CH_4 conversion degree, %	mmol O/ g OC	mmol CO/ g OC	mmol CO_2/ g OC
850°C	1	10.0	1.582	0.237	0.218
	2	8.3	1.282	0.226	0.151
	3	8.3	1.163	0.217	0.128
	4	8.8	1.040	0.202	0.109
	5	10.1	1.107	0.198	0.128
800°C	1	10.4	0.713	0.071	0.125
	2	5.9	0.596	0.085	0.085
	3	8.6	0.753	0.090	0.121
	4	7.4	0.746	0.095	0.115
	5	8.7	0.785	0.092	0.127
750°C	1	3.8	0.285	0.045	0.037
	2	4.1	0.654	0.048	0.127
	3	4.0	0.603	0.057	0.108
	4	3.9	0.581	0.065	0.096
	5	5.0	0.531	0.067	0.083

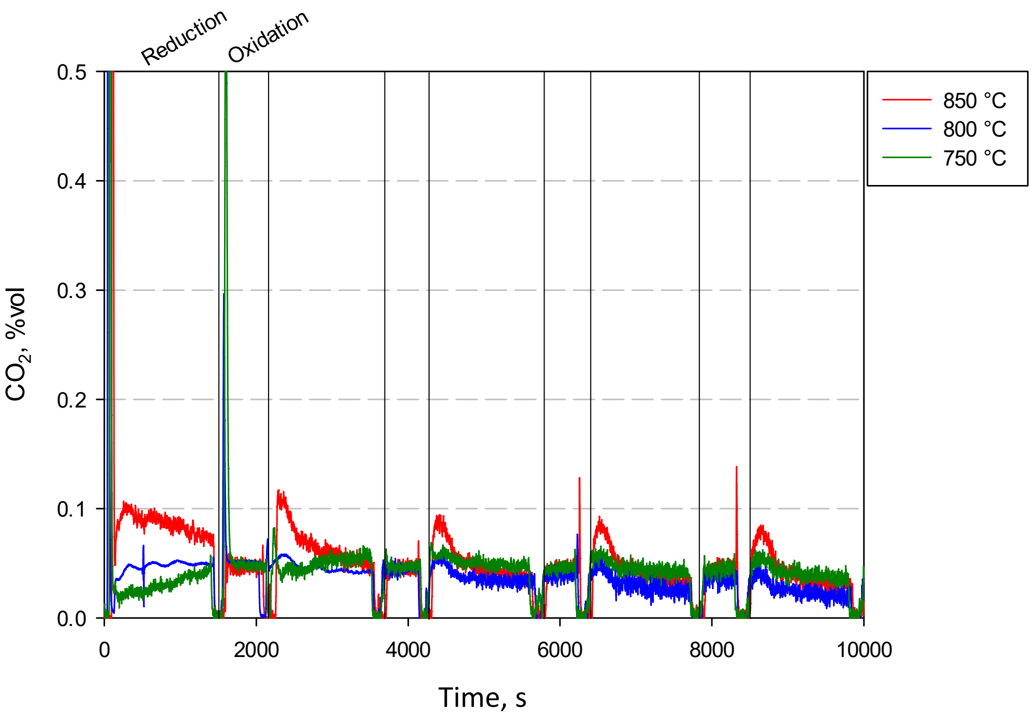
- $R_{O,max}=25.3\times10^{-3}$
- Fresh material: 4.5×10^{-3}

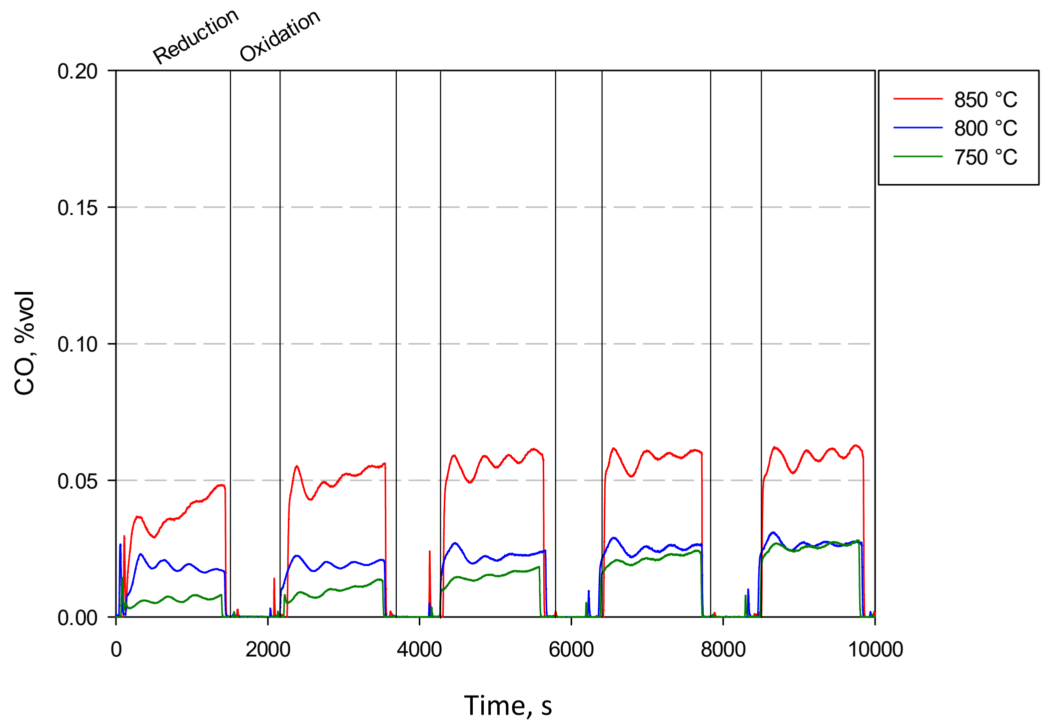
⇩

Support reactivity?

Results CLC tests

Results (using the support only)

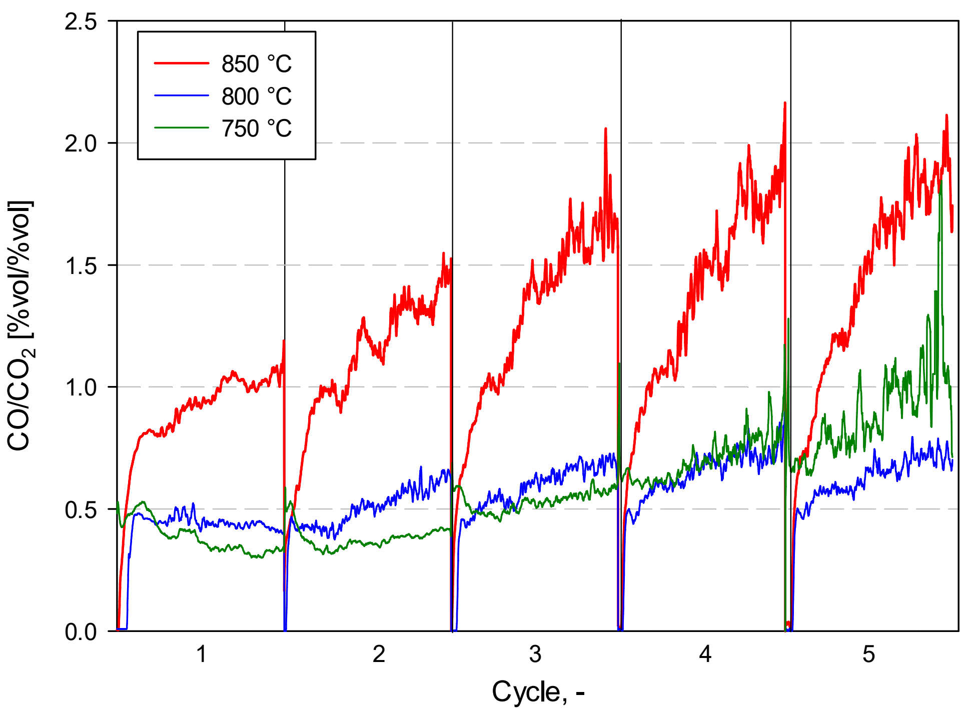




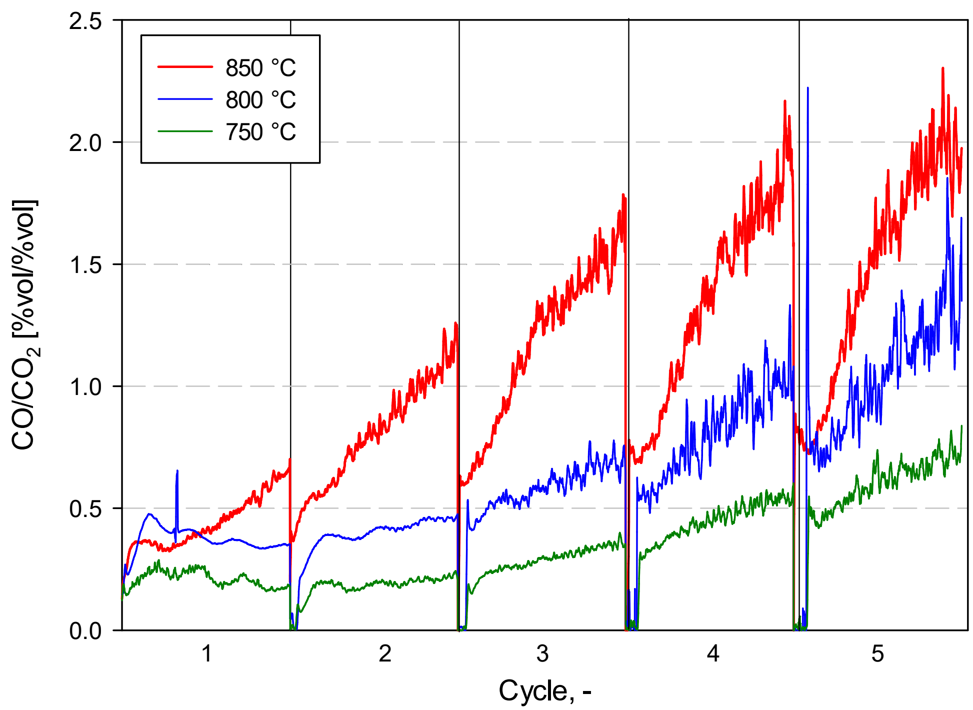
Alumina reactivity increases with the temperature increase and with increasing the number of cycles.

Results :CLC tests

Oxygen Carrier

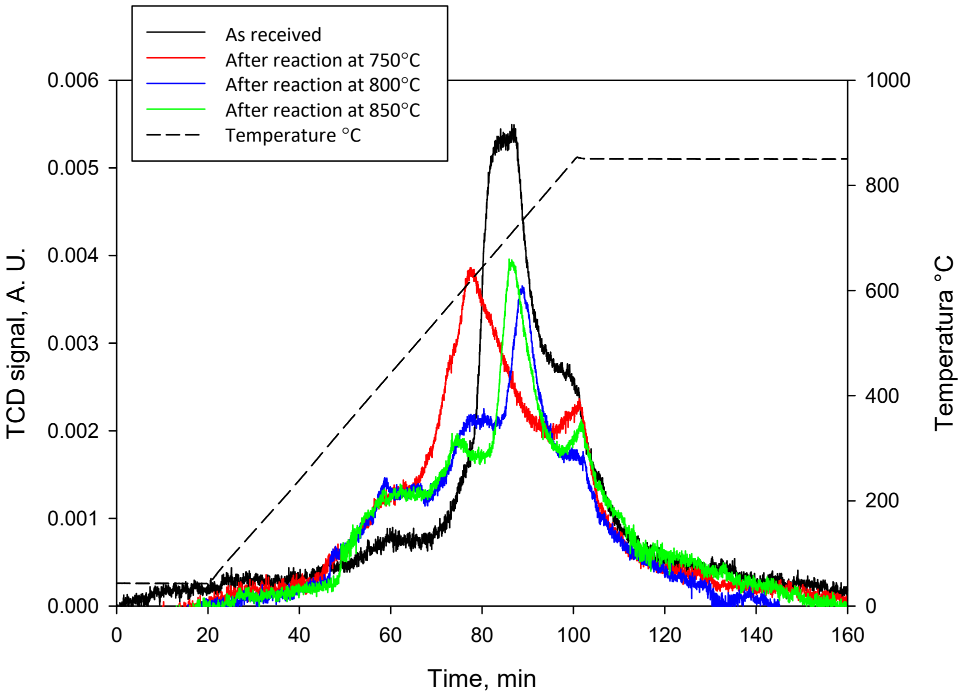


Allumina



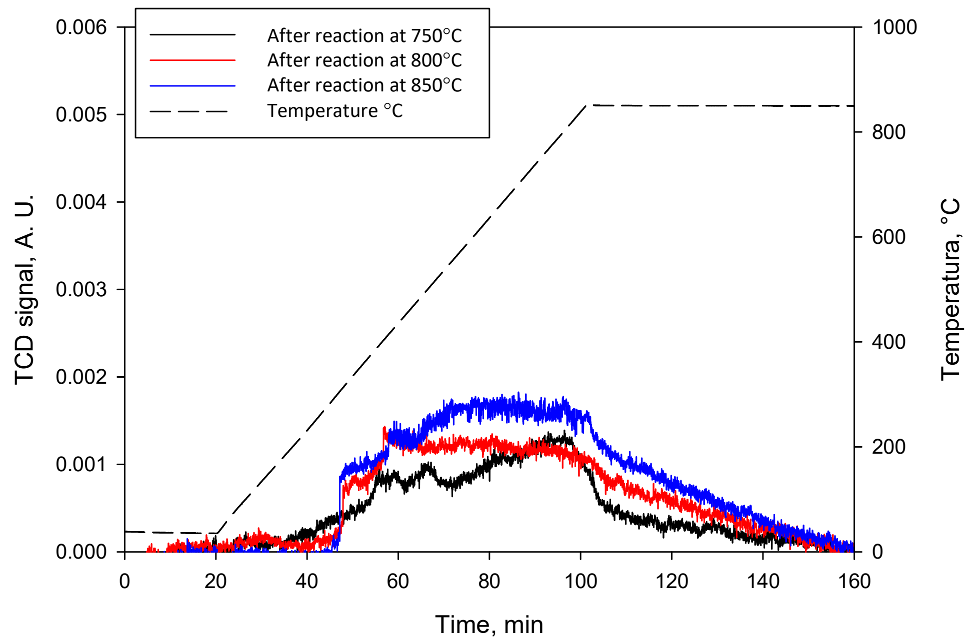
Results :CLC tests

Oxygen Carrier



The material undergoes structural changes

Alumina



Unchanged profile

Conclusions

- Sewage sludge fluidized bed combustion can be considered a feasible and reliable strategy for the preparation of low-cost CLC oxygen carriers.
- The reactivity of the OC increases with temperature increase and decreases with the number of cycles
- R_O,max=25.4×10^{-3}, lower than the values reported in the literature → it is necessary to improve the deposition process.
- From the TPR analysis we note that the material undergoes structural changes following the looping process.

Istituto di Ricerche sulla Combustione
Consiglio Nazionale delle Ricerche

DICMaPI
Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale
Università degli Studi di Napoli Federico II

Thank you for your kind attention