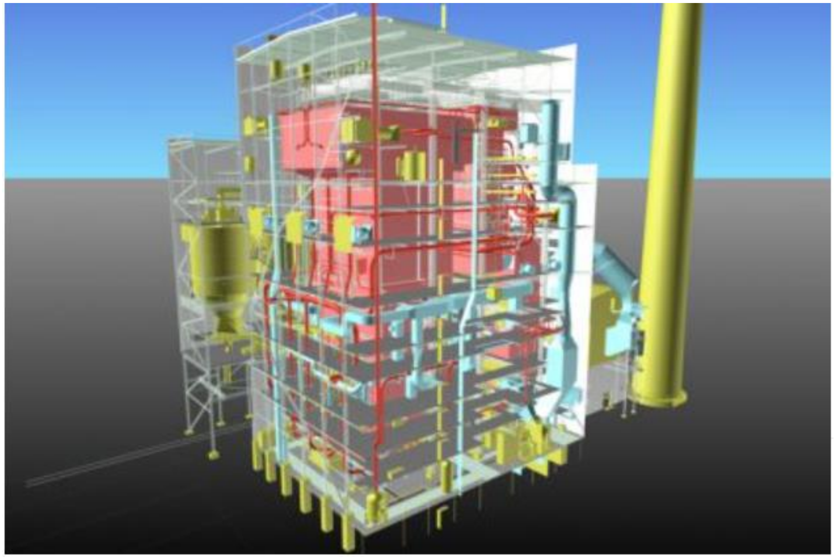
FLEX FLORES:
Innovative Refractories for use in combustion plants operating under flexible conditions

FLEX FLORES

Why?

To move towards a more eco-friendly approach in power generation

Development of innovative concepts to improve the flexibility of Circulating Fluidized Beds technology



- **Retrofitting of existing plants**
- **Design of new plants**

Flexibility → Fuels, Operations → Materials

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Why?

Refractories resistant to flexible fuels in terms of cofiring

- Ability to operate with low rank fuels in combustion and co-combustion conditions

> Lignite

> Biomass (straw pellets)

Why?

Flexibility implies severe conditions for the materials used in CFB, namely refractories for inner lining (lateral wall, roof of boiler, Intrex, separator)

Refractory criticalities → Increased thermal stresses
Increased chemical degradation

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How?

- Testing the current commercial materials (i.e., static/dynamic)
- Identify the most performant solutions
- Identify an industrial by product suitable for reusing
- Manufacturing Compositionally Graded Refractories
- Validation of CGRs during a field campaign
- Additive manufacturing of CGRs

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identification of commercial refractories

Adequate Refractories for lining the inner of boilers for flexible plant operations

- ✓ Able to withstand aggressive action of low rank fuels and biomass

Refractory samples before and after test with fuel ashes

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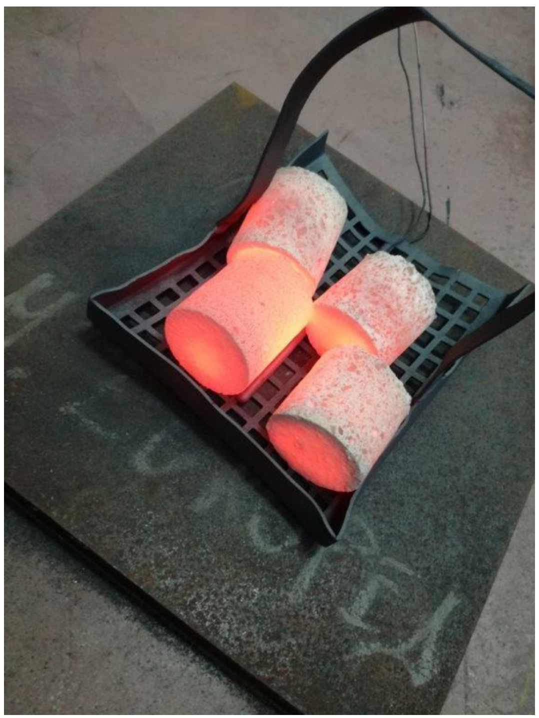
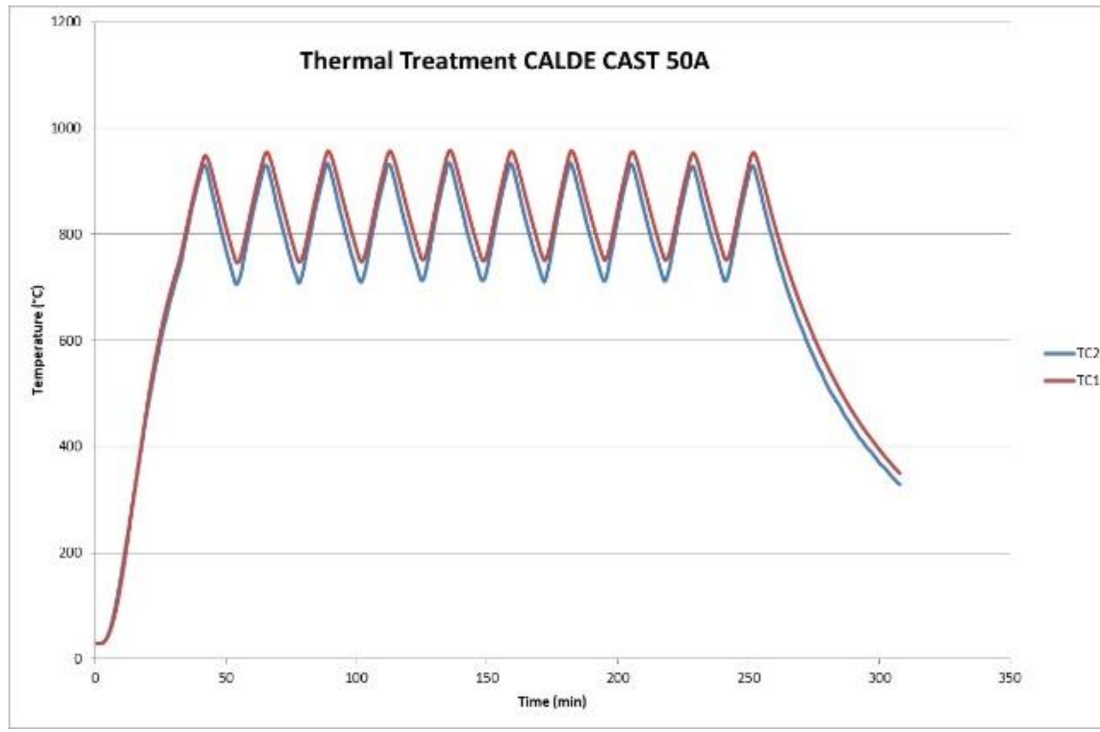
identification of commercial refractories

Previous status

Adequate Refractories for lining the inner of boilers for flexible plant operations

✓ Resist under steady and cycling operations,





Innovative, environmental friendly, and cost effective refractory solutions

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Adequate refractories for flexible plant operations

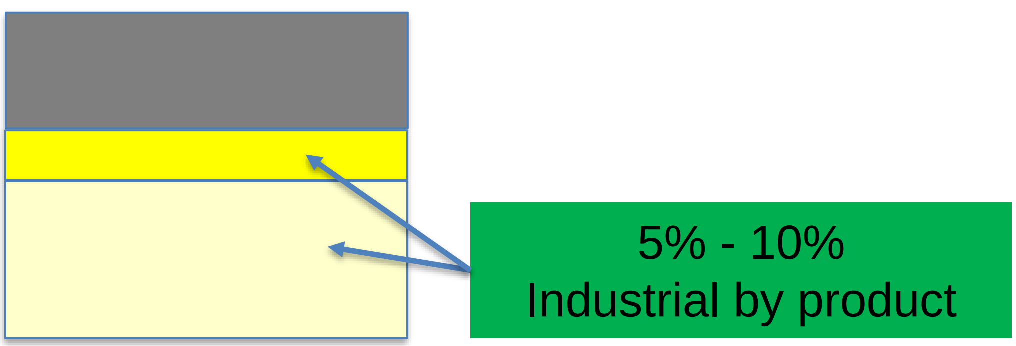
- Compositionally Graded new Refractory solutions for lining CFB plant

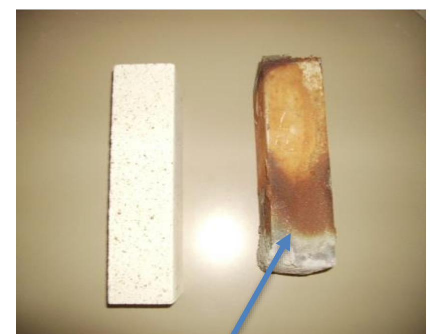
New refractories have been conceived in order to guarantee an optimal performance in terms of **resistance to chemical** and **mechanical aggression** when in service allowing at the same time a **cost reduction** and giving the possibility of **reuse of industrial by- products.** Different industrial by-products have been tested before identify the best one

CGR

Fire side

Back side





By-product (spent refractory)
Up to 5÷10% in new CGR layers

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CGRs tested at pilot scale plant

Useful results after field campaign at 1MWth pilot plant by co-firing lignite with straw pellets

- Innovative refractory materials: no cracks, no corrosion phenomena are visible on the refractory samples after field campaign: there is only a thin brown deposit on the exposed surface of all samples

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CGRs tested at pilot scale plant

FlexFlores

Useful results after field campaign at 1MWth pilot plant

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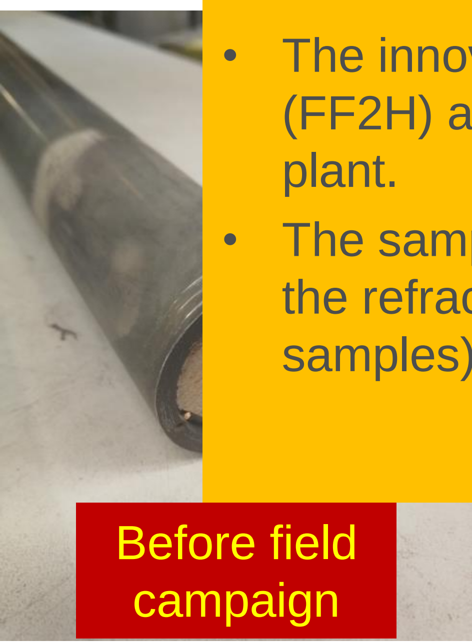
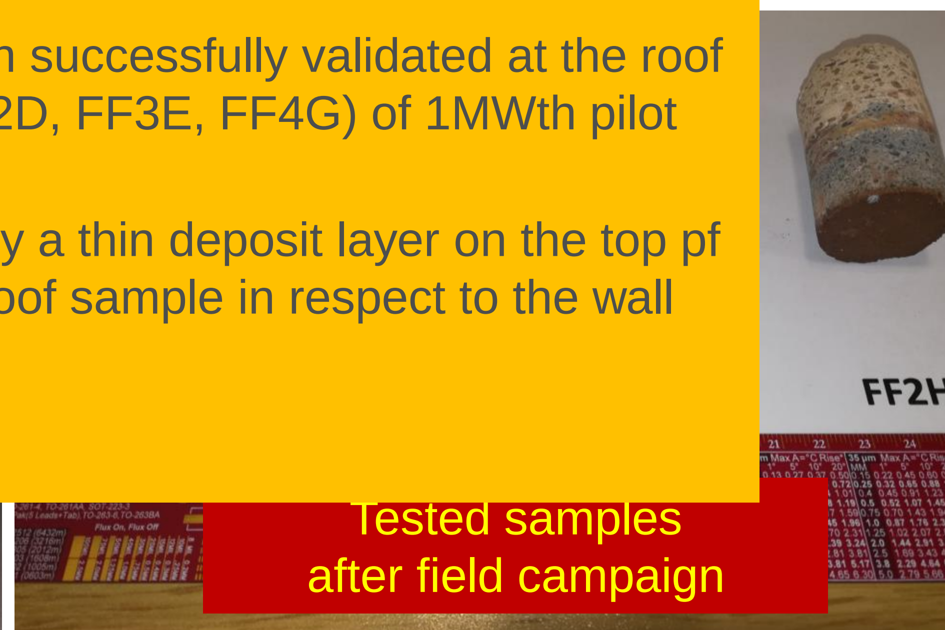
Validation of CGR materials

- The innovative CGRs have been successfully validated at the roof (FF2H) and lateral wall (i.e., FF2D, FF3E, FF4G) of 1MWth pilot plant.
- The samples after test show only a thin deposit layer on the top pf the refractories (thicker on the roof sample in respect to the wall samples)



Before field campaign

After field campaign



Tested samples after field campaign

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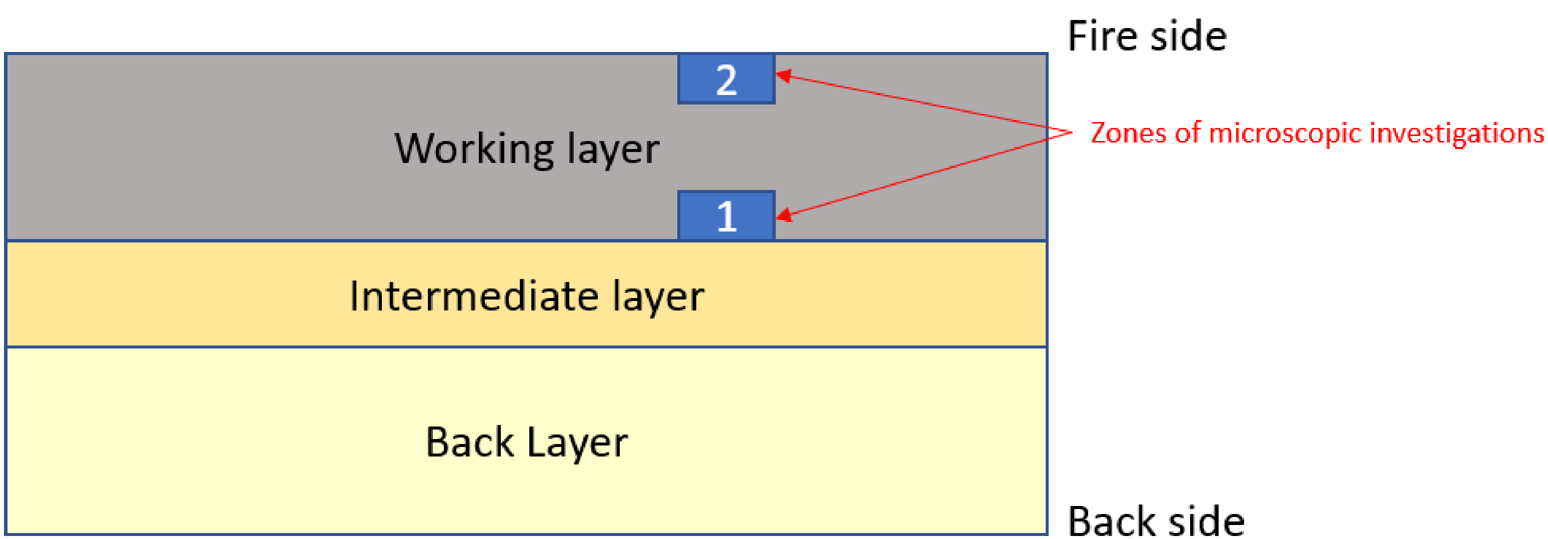
CGRs tested at 1MWth pilot plant during a field campaign

General approach leading the microscopic investigation in cross section

- Identification of possible phases due to the chemical interaction of the fire side layer components with products and/or reactants due to the operating environment
- Investigation of possible undesired effects within the material itself. In particular, the use of part of industrial by-product in the inner layers of CGR could be cause of contamination due to the diffusion of species towards the fire side layer. In this case, the formation of cracks caused by local inhomogeneities could be the worst case.

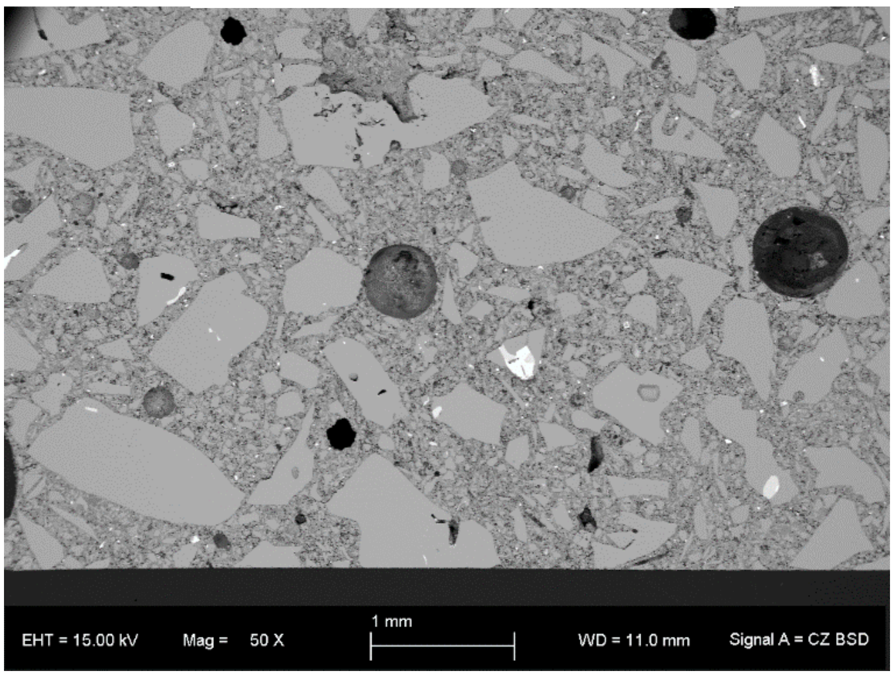


CGRs tested at 1MWth pilot plant during a field campaign

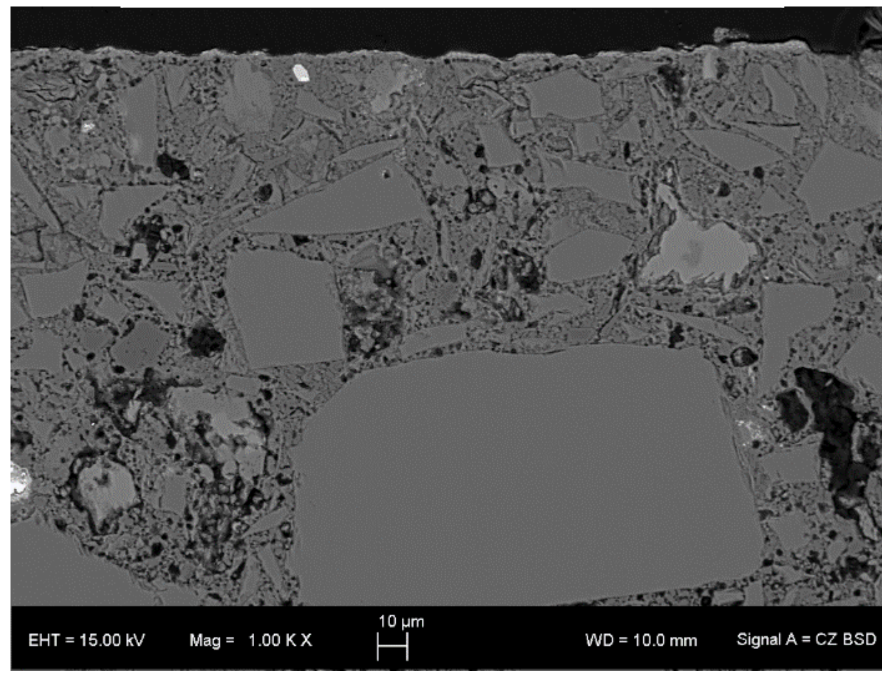
Typical appearance of the working layer in the CGR post mortem

FF3E

Zone 1



Zone 2



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CGRs tested at 1MWth pilot plant during a field campaign

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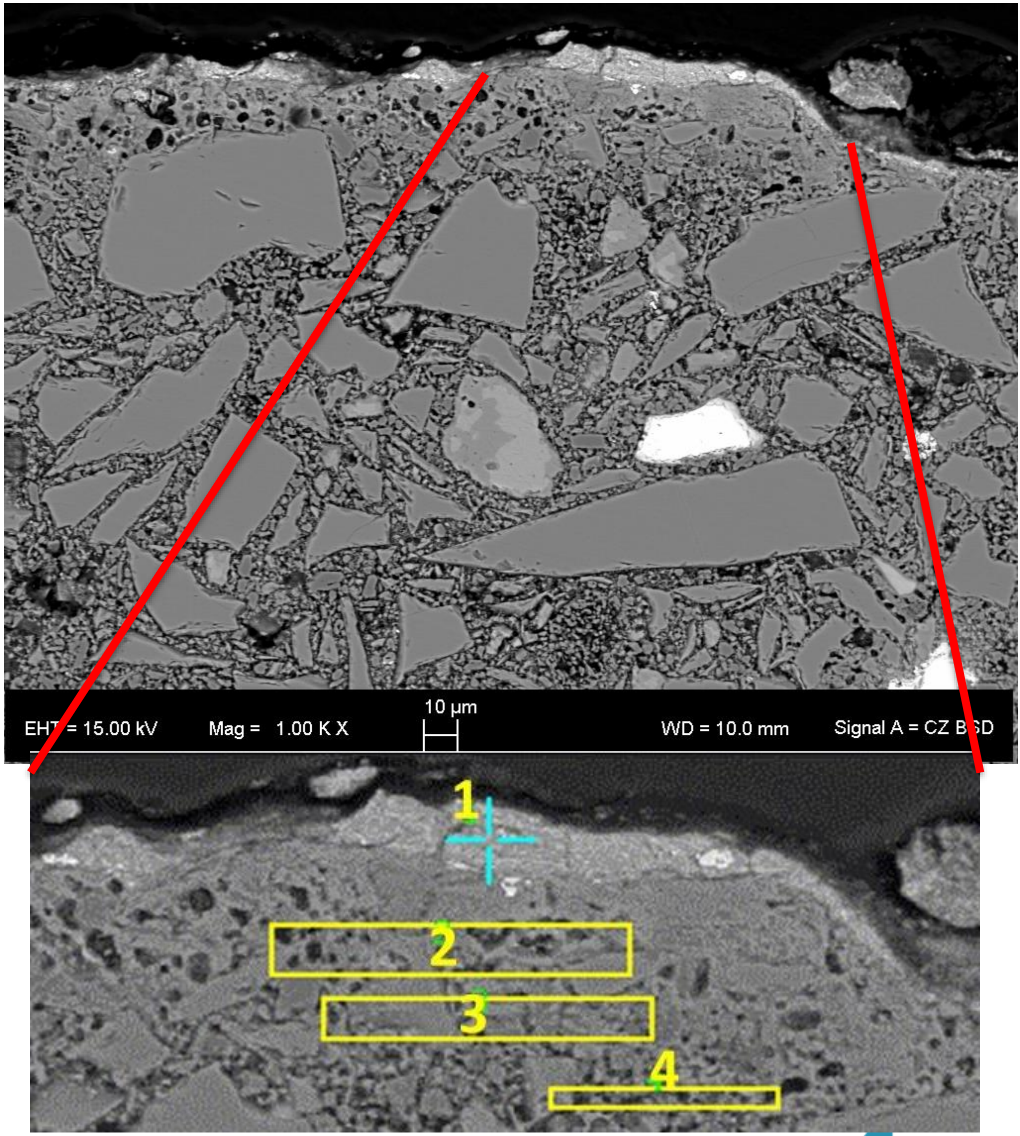
FF2H

Typical chemical composition of the deposit and first layer of refractory (cross section of exposed surface)

	1	2	3	4
	Wt%	Wt%	Wt%	Wt%
CK	18.38	13.67	13.30	22.73
OK	28.20	31.91	34.45	24.47
MgK	01.13	01.40	01.62	
AlK	02.15	02.23	02.30	09.38
SiK	01.41	01.30	01.18	39.05
PK				00.53
SK	18.30	18.00	16.99	01.20
CaK	21.56	22.44	20.79	02.64
FeK	08.88	09.03	09.38	



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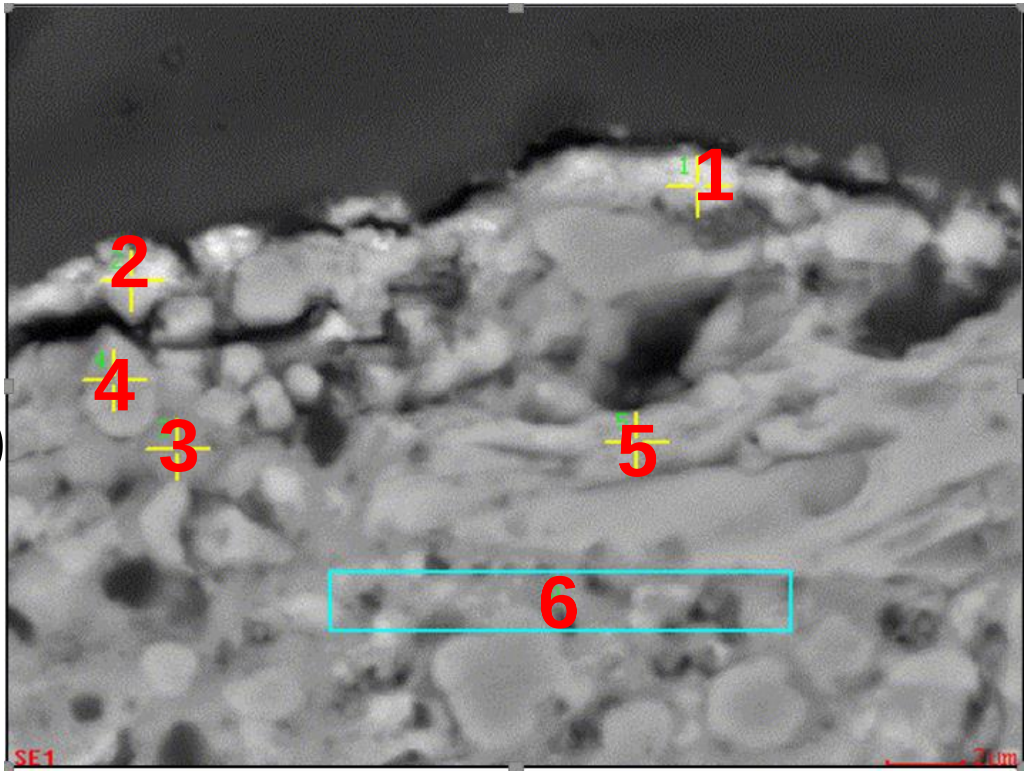
CGRs tested at 1MWth pilot plant during a field campaign

FF2D

Typical chemical composition of the deposit (cross section of exposed surface)

	1	2	3	4	5	6
Element	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%
CK	23.65	28.28	13.44	13.05	39.60	17.39
OK	35.21	34.81	37.19	42.25	03.74	26.49
NaK	00.41	01.05	04.03	00.62		02.54
MgK	01.14	00.60	00.36			00.35
AlK	06.29	06.64	20.14	41.47	01.05	13.51
SiK	04.09	09.06	17.14	01.82	55.61	32.03
PK	00.56	03.08	05.48	00.78		03.40
SK	09.85	03.95				
KK						01.30
CaK	15.13	11.10	02.22			03.00
FeK	03.67	01.42				

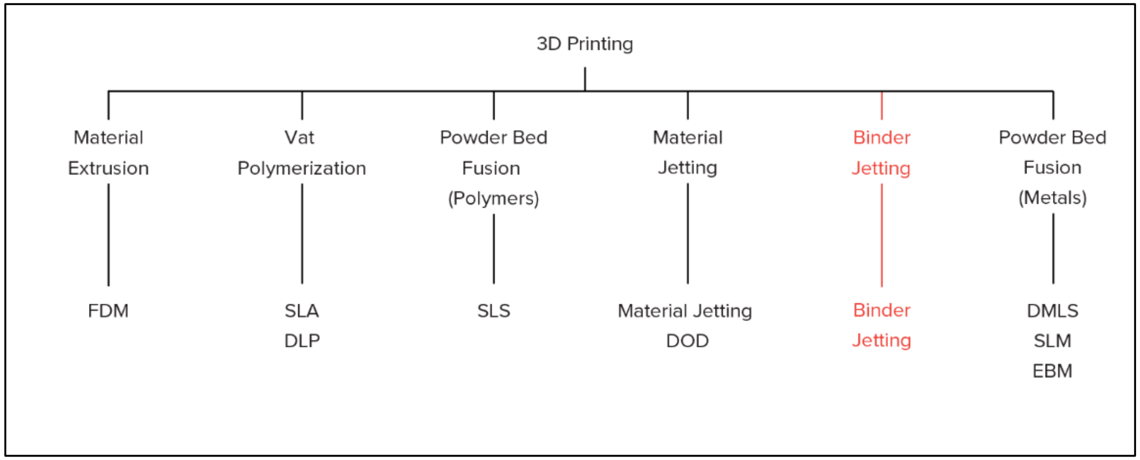


Intro:
Additive Manufacturing

Exploring a new way to produce CGR materials:

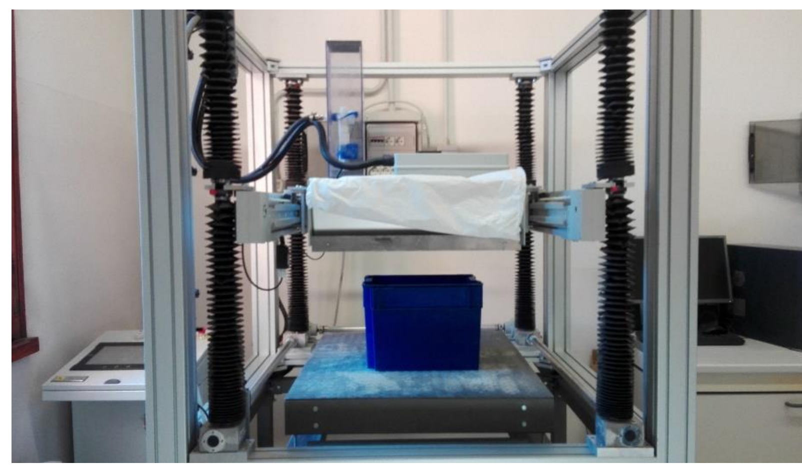
Additive Manufacturing

Innovative solutions:
Refractories Production by Additive Manufacturing



Binder jetting methodology to produce CGRs from raw materials

Thanks to collaboration with
Prof. Paolo Colombo
University of Padua



Innovative solutions:
Refractories Production by Additive Manufacturing

Lateral resolution: 3 mm

Slice thickness: 1-20 mm

Printing envelope:

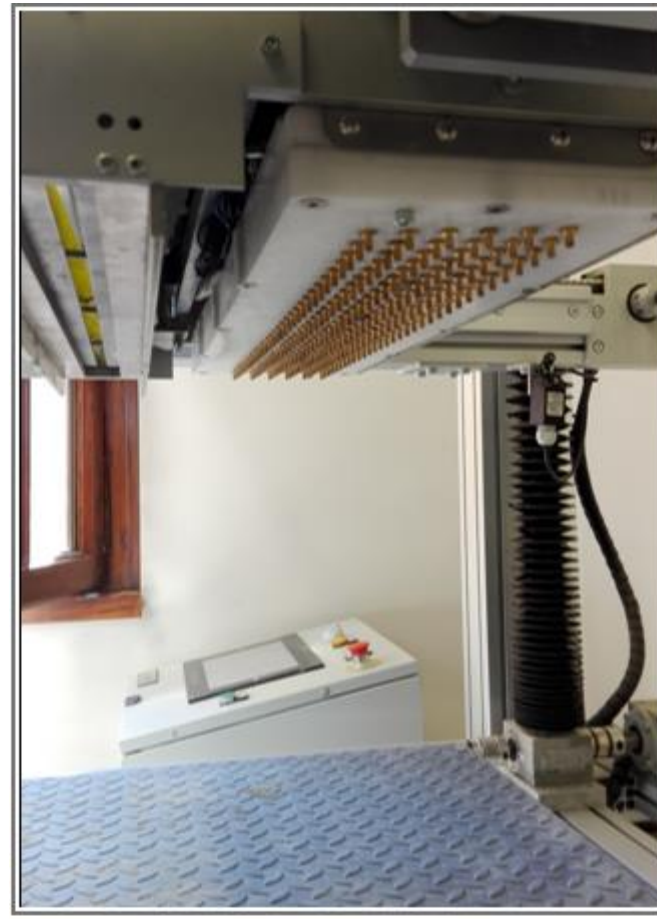
- 80 cm (height);
- 60x60 cm (plane)
- 192 nozzles

Printing medium:

- water

Additive Manufacturing technology:

- Binder Jetting



Innovative solutions:
Refractories Production by Additive Manufacturing

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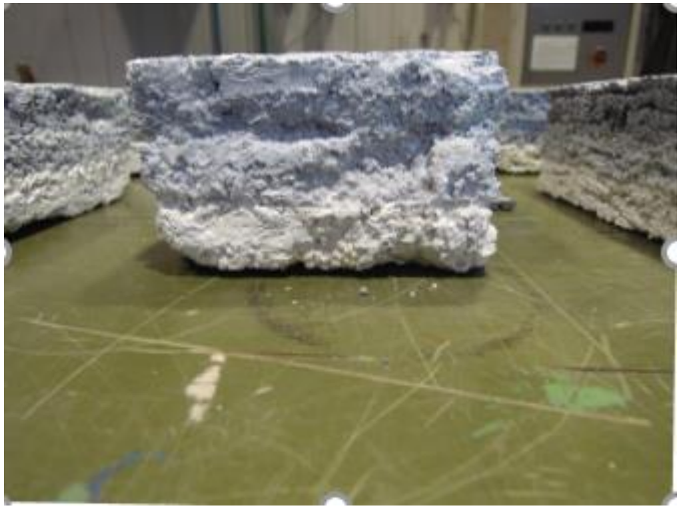
- The produced CGRs have been thermal treated at 1200ºC, the samples have been cut in halves to produce other four samples.
- These samples have been infiltrated with colloidal alumina in order to reduce porosity thanks to a further heat treatment at 1200ºC.



Typical properties of the colloidal alumina: commercially available product

TYPICAL PROPERTIES	AL20
(AlO(OH)), wt%	23.5
Aluminum content expressed as Al_2O_3, wt%	20
Particle Size, Z-Average, nm	60 – 90
Particle Charge	+
pH	4.0
Specific Gravity	1.19
Viscosity, cP	4 – 11

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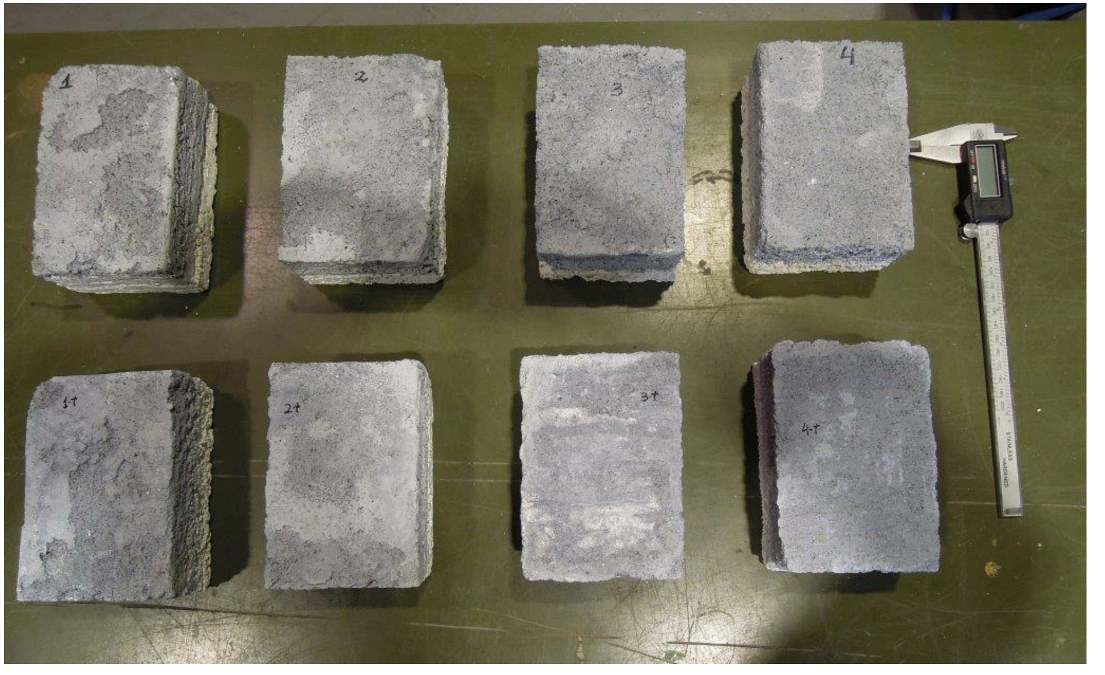
Innovative solutions: Prototypes by Additive Manufacturing

- 8 CGR prototypes have been produced by AM.
- 4 of these 8 have been infiltrated by colloidal alumina in order to reduce porosity.



Density and porosity:
Production by Additive Manufacturing

- The density is ranging
  - 1.57 ÷ 2.16 g/cm^3
- The porosity is up to 40 %.

The infiltrated samples (T samples) seem to be less porous than untreated samples

sample	density	theoretical density	relative density	porosity
	[g/cm^3]	[g/cm^3]	%	%
1	1,57	2,575	61,1	38,9
2	1,92	2,575	74,5	25,5
3	1,60	2,612	61,4	38,6
4	1,57	2,612	60,0	40,0
1 T	1,97	2,575	76,6	23,4
2 T	1,77	2,575	68,6	31,4
3 T	1,77	2,612	67,8	32,2
4 T	2,16	2,612	82,8	17,2

This procedure helps in increase density of the Additive Manufactured materials

Conclusions

1. **Refractories** for boiler have been successfully tested at pilot scale plant. **CGRs** withstand well the aggressive flexible operating conditions tested at 1MWth pilot plant (co-combustion of straw pellets with lignite).

2. **Additive Manufacturing** has been used for the production of CGR prototypes. Despite the results achieved are encouraging, further improvements are required before applying these prototypes in the industrial combustion plants since the current produced prototypes are too much porous.

Thank you very much for your kind attention

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Research Fund for Coal & Steel