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Department of Industrial Engineering

ProceedLAB
Processes & Catalysis for Energy & Environment depollution

Microwave susceptible catalytic filters for diesel soot abatement

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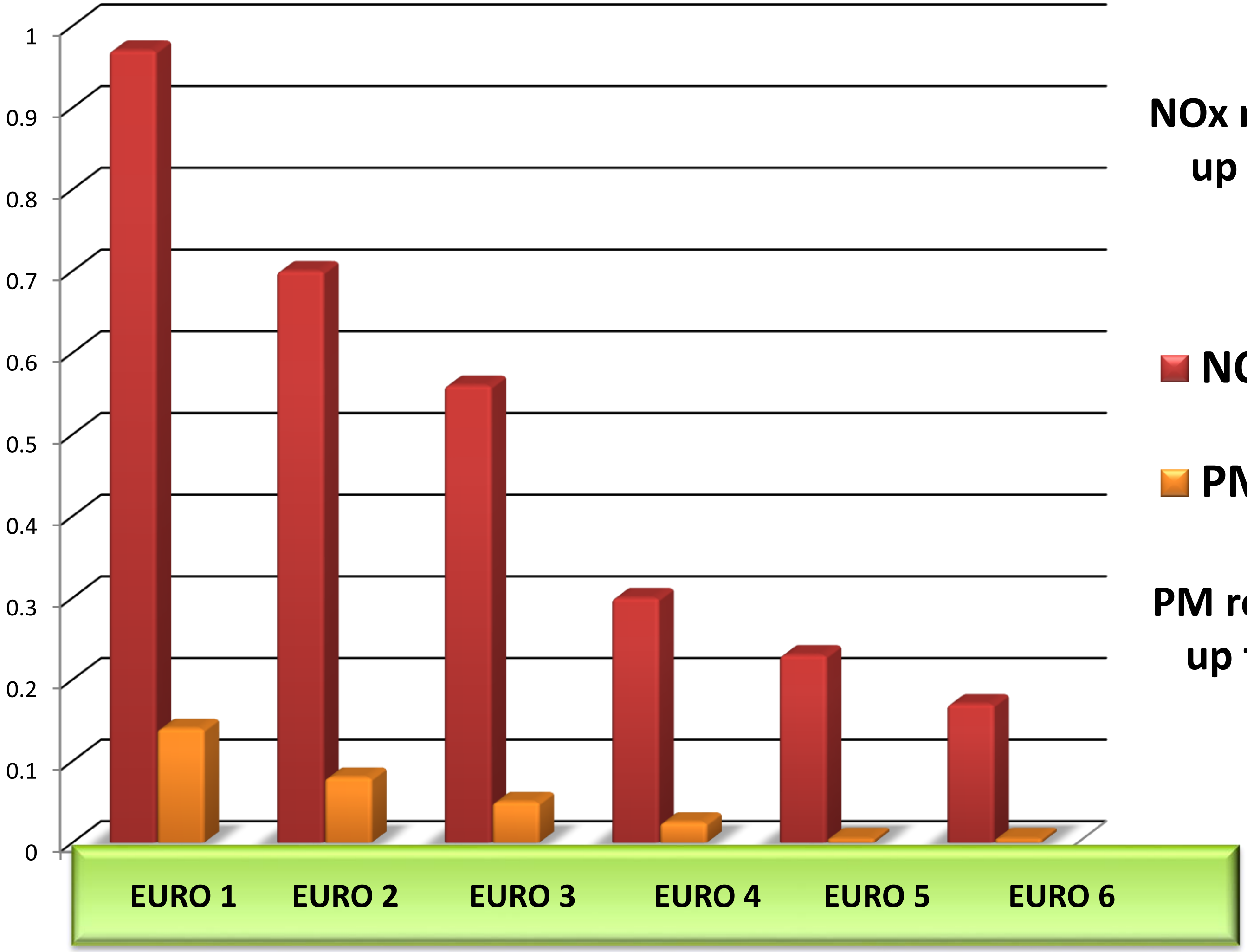
Introduction



1993 **2014**

NOx reduction up to 80%

PM reduction up to 60%

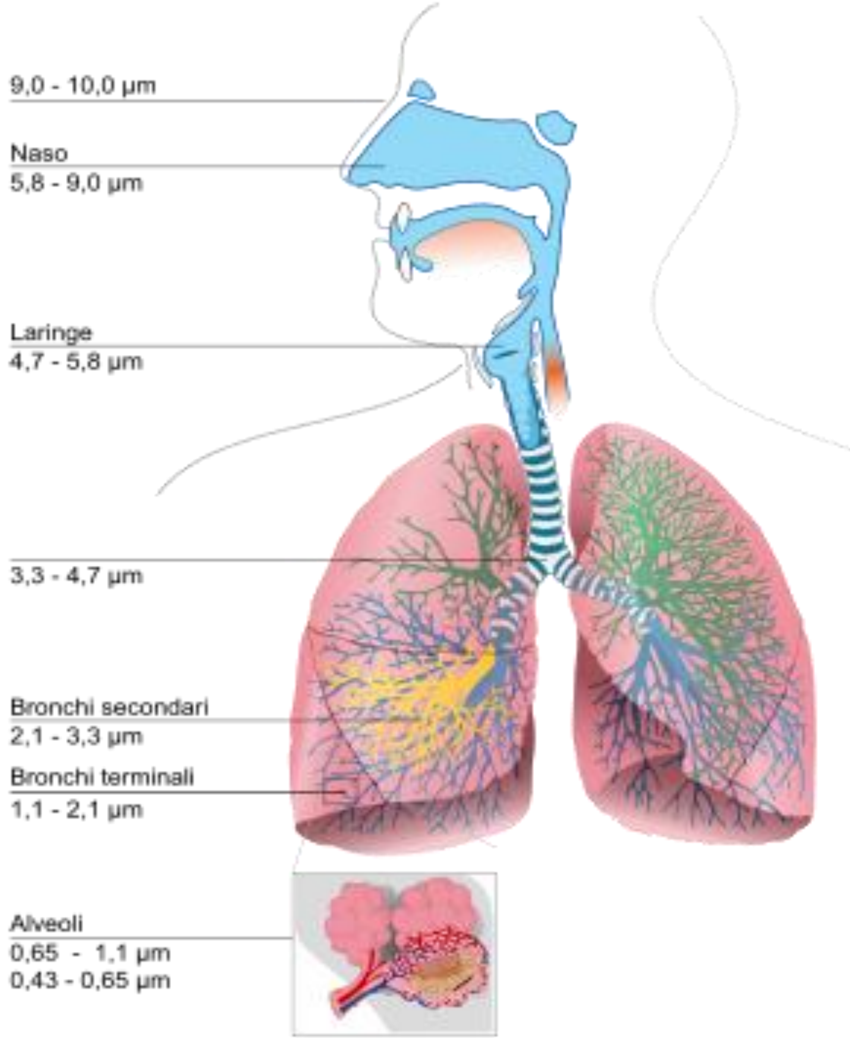
Particulate Matter effects

Effects on human health:

- **diseases of respiratory and cardio-circulatory systems**
- **Increase in cancers**

Effects on environment:

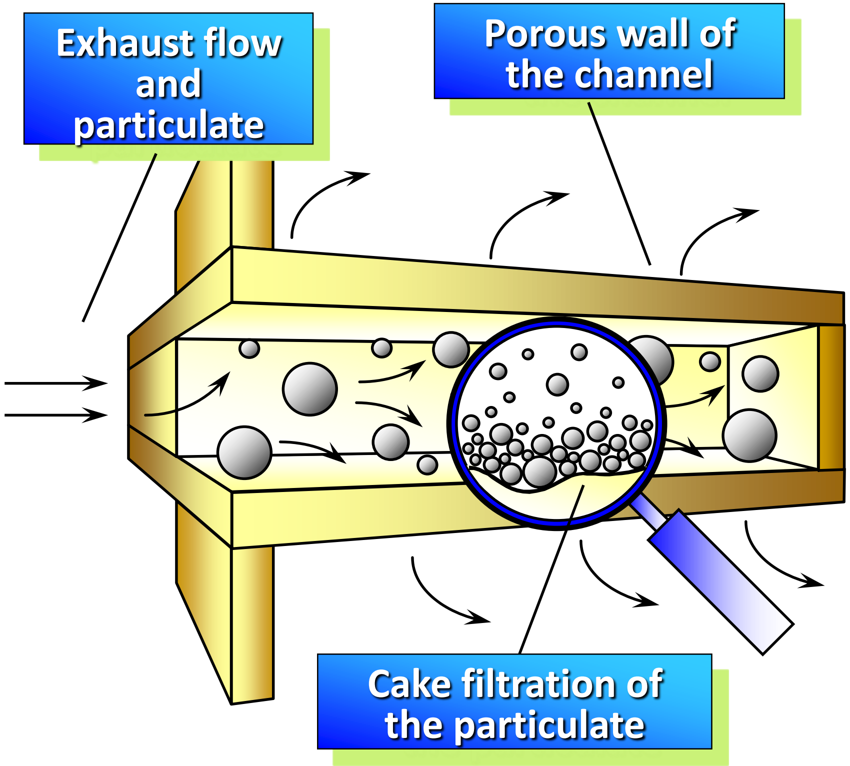
- **disturbances in the propagation and absorption of solar radiation**
- **reduction in atmospheric visibility**



Introduction

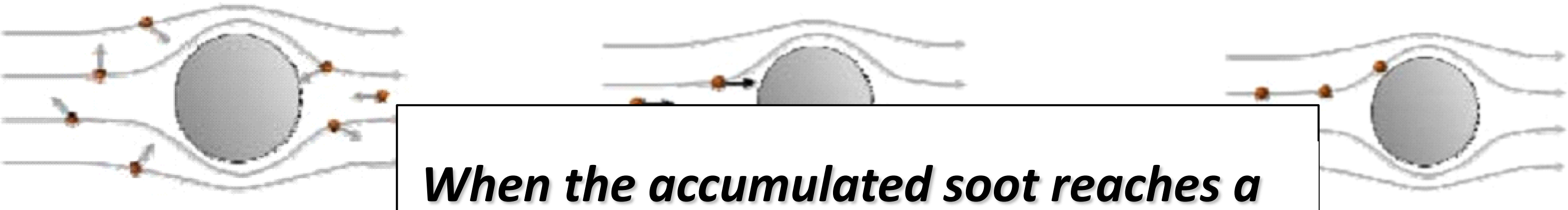
AFTERTREATMENT SYSTEMS FOR DIESEL ENGINES — SAE NAPLES — 27/28 JUNE

The most applied route to reduce particulate emissions under EU standards is the use of the Wall-Flow Diesel Particulate Filters (DPFs).
They consist of ceramic monoliths with alternately plugged channels: so the exhaust gas is forced through the wall and the soot is collected on the surface and inside the porosity of the channels walls.



Wall Flow Filtration Mechanism

Depth filtration

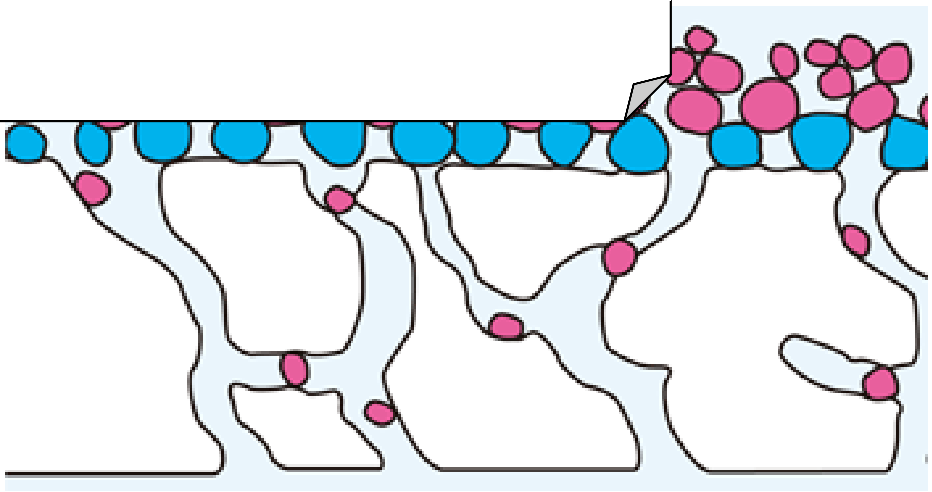


Diffusional deposition

e interception

When the accumulated soot reaches a critical level, DPF must be regenerated to maintain efficient engine operation

Cake filtration



DPF Regeneration… Drawbacks

- High temperatures (> 600°C) are required for filter regeneration
- The combustion often generates moving high temperature waves, the temperature of which may exceed in some cases the melting temperature of the filter
- Also for a catalyzed DPF the temperature necessary for soot removal is higher than the average exhaust gas temperature

It must be added energy!!

Currently the regeneration process is performed by post-injection and "fuel-born" catalysts resulting in ….

- ***complex engine management cycle***
- ***higher fuel penalty***

Hence, in addition to the post-injection further active method of regeneration are under investigation.

Innovative catalytic DPF regeneration technology

- **Catalyst: $CuFe_2O_4$**

- **Microwave assisted regeneration: selective and instantaneous heating, function only of the dielectric properties of the materials.**

Material	Dielectric constant ε’	Dielectric loss factor ε’’
Diesel soot	10.700	3.600
Quarzo	3.800	0.001
Cordierite	2.900	0.140
Alumina ceramic Al_2O_3	8.900	0.009
SiC	30.000	11.000

Objectives

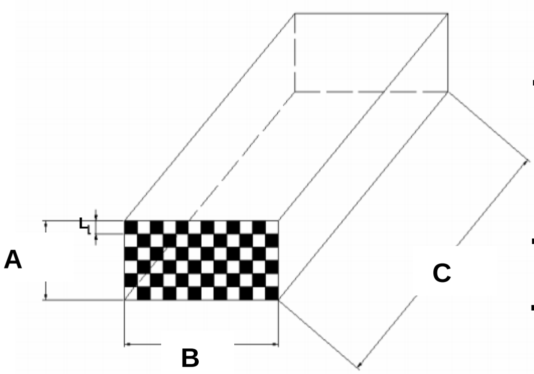
To Prepare and characterize a specifically MW sensible catalytic SiC-WFF, loaded with Copper-Ferrite

To perform On-line soot deposition and regeneration tests to demonstrate the use of microwave heating for DPF regeneration

To Compare the energy required for the regeneration of the catalytic filters

Materials

Commercial SiC Wall Flow Filters with 150 cpsi by Pirelli EcoTechnology



Total channels	Open channels	Channel lenght (L) [mm]	Filter wall thickness [mm]	a [mm]	b [mm]	c [mm]
585	277	1.5	0.6	36	80	124

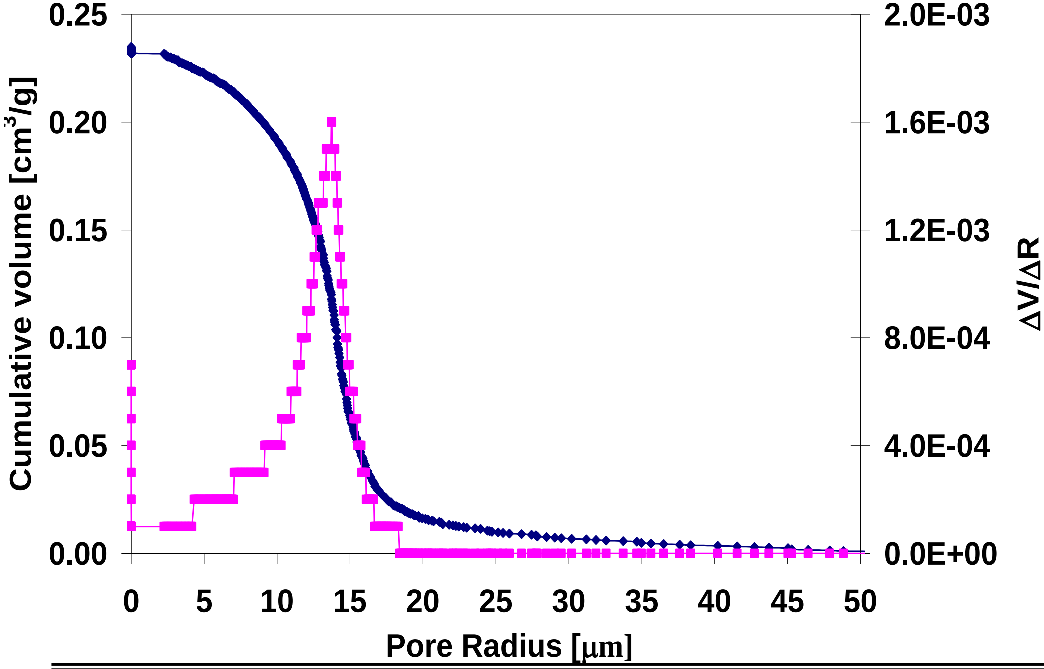
Engine

(Lombardini LDW 502)

The engine used is a 505 cm^3 bi-cilindrical city car water cooled diesel engine with 7kW@3600 r.p.m.

Materials and Engine Characterization

by Hg porosimetry test on WFF…



	Total porosity [%]	Average pore radius [Å]	Weight density [g/cm³]	Apparent density [g/cm³]
Untreated filter	37	$1.44*10^5$	1.59	2.55
Heat-treated filter	41	$1.7*10^5$	1.52	2.61

Opacity, soot concentration and filtration efficiency at various operating conditions, for two different engine load

Low load

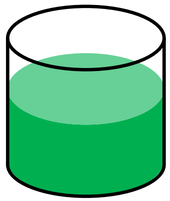
rpm	$Opacity_{in}$ [%]	C soot [mg/m³]
600	15.1	34.3
1100	13.2	29.8
1500	10.7	23.9
1900	7.1	15.5

High load

rpm	$Opacity_{in}$ [%]	C_{in} [mg/m³]	$Opacity_{out}$ [%]	C_{after} [mg/m³]	Eff [%]
600	58.9	143.1	0.3	0.5	**99.7**
1100	24.9	58.2	0.2	0.4	**99.4**
1500	29.5	69.3	0.1	0.1	**99.8**
1900	13.8	31.2	0.1	0.2	**99.7**

Catalyst preparation: wet impregnation

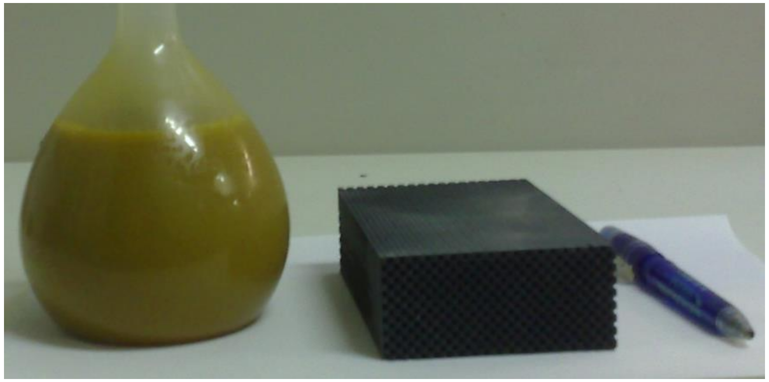
Sic filters were catalysed by:



Impregnation
60°C - 30 min

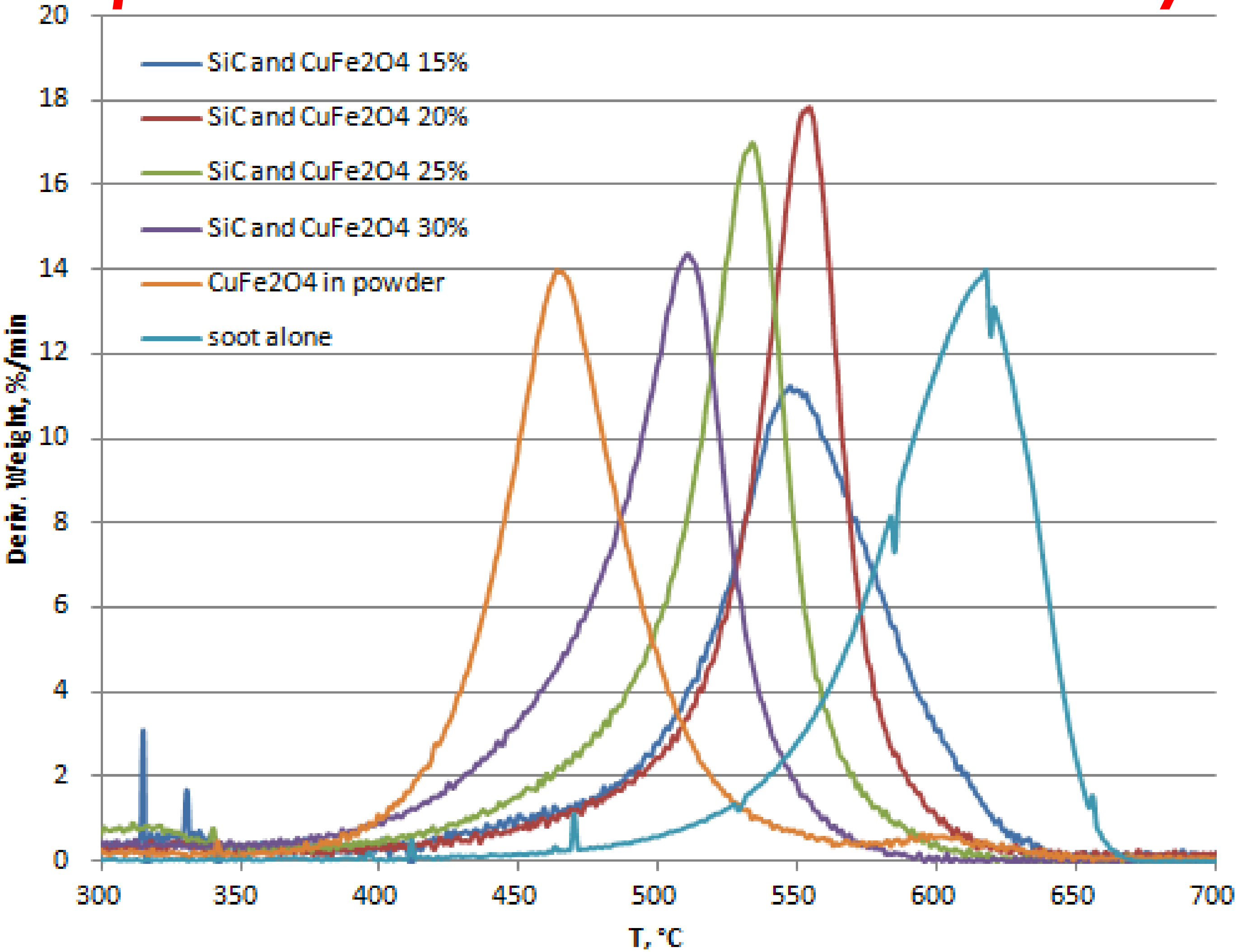
Drying
60°C - 9 h

Calcination
1000°C - 30 min



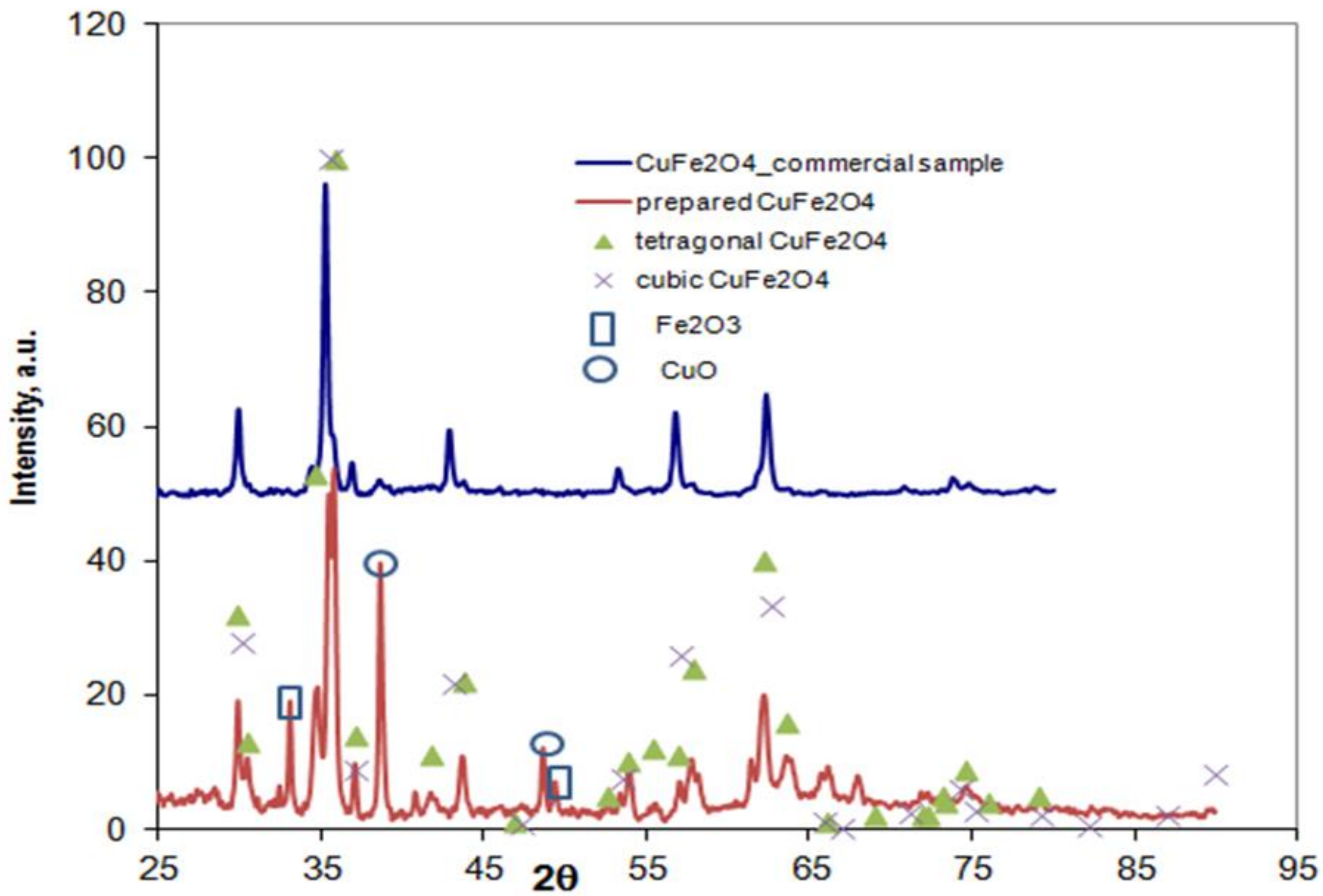
The final value of the active species on the WFF is up to 30%wt.

Samples Characterization: TG-DTA Analysis



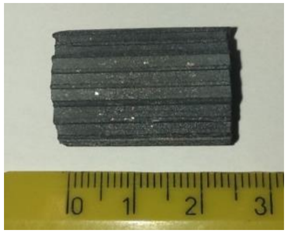
The TG curve of soot alone shows very low reactivity, with the ignition temperatures of about 550°C and the maximum of reaction rate at about 620°C. The TG curves of soot and SiC-$CuFe_2O_4$ mix show that, by increasing the load of active species, the ignition temperature and the temperature of maximum combustion rate (T_m) are lowered, as well as the combustion reaction rate is increased.

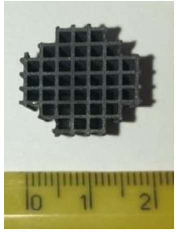
XRD analysis



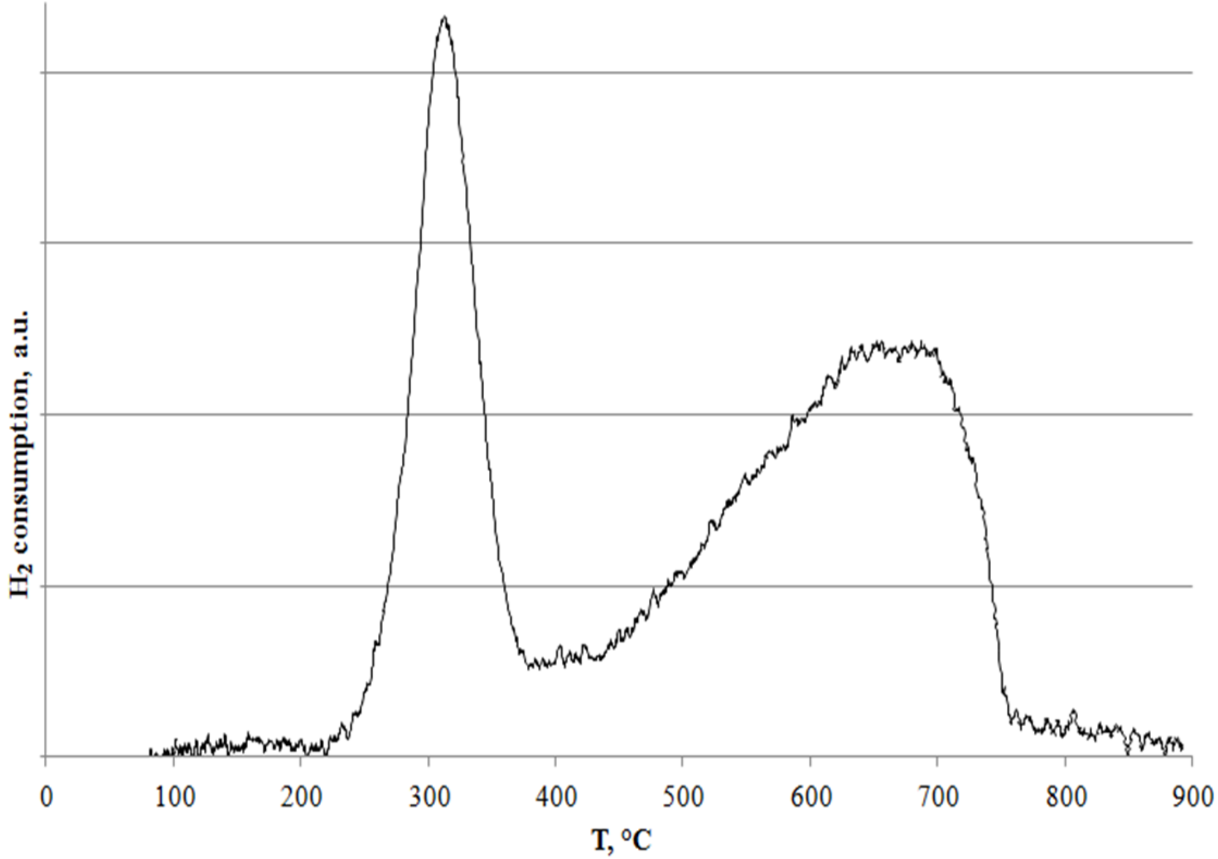
XRD analysis shows the typical peaks of $CuFe_2O_4$ in the tetragonal and cubic form, and the presence of two other peaks, corresponding to CuO and Fe_2O_3.

TPR analysis





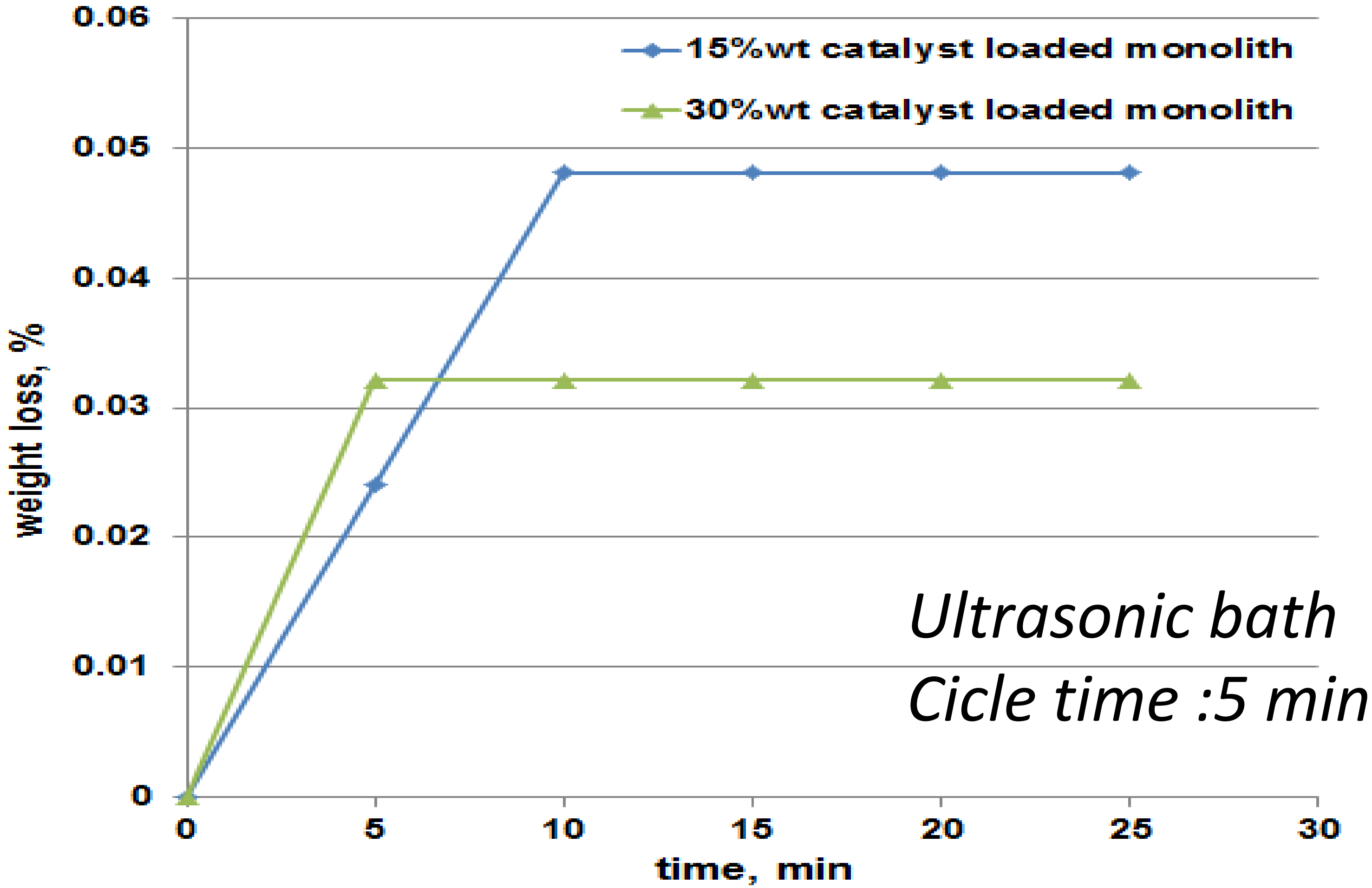
Heating: 5°C/min
Tamb →900°C
Gas: 5%H_2
95%He



Two pronounced reduction peaks at about 300°C and 610°C, due to the reduction of $CuFe_2O_4$ to Cu and Fe_3O_4, and, subsequently, the reduction of Fe_3O_4 to Fe

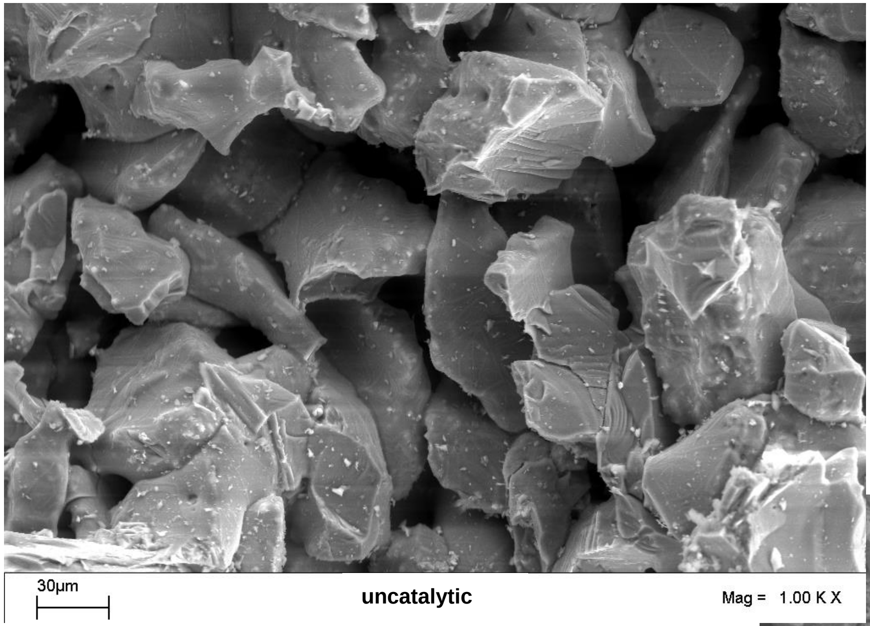
The consumed H_2 corresponds to about 17%wt of $CuFe_2O_4$, which is in a quite good agreement with the estimated 15%wt of $CuFe_2O_4$ on the monolith

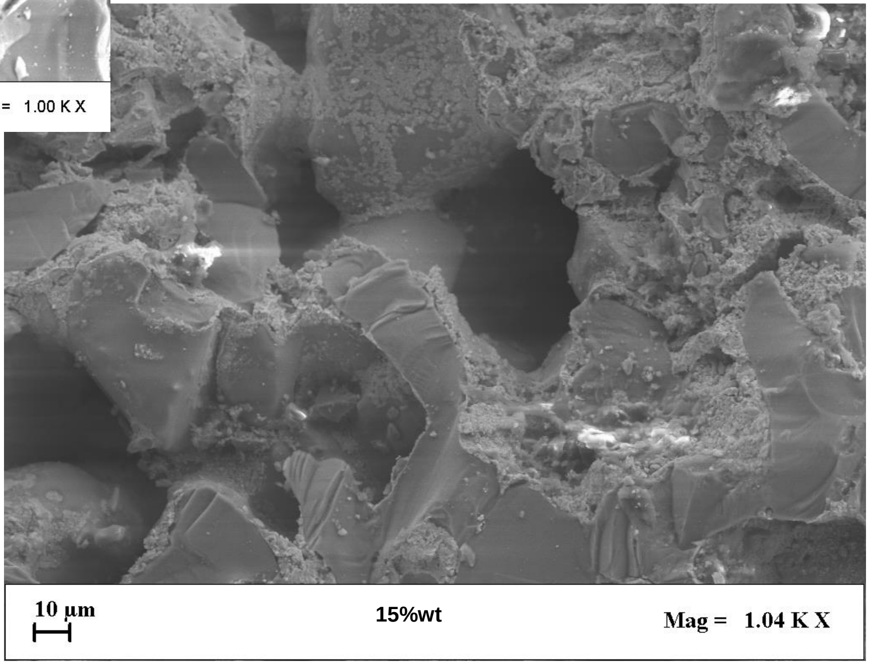
Active species adhesion test



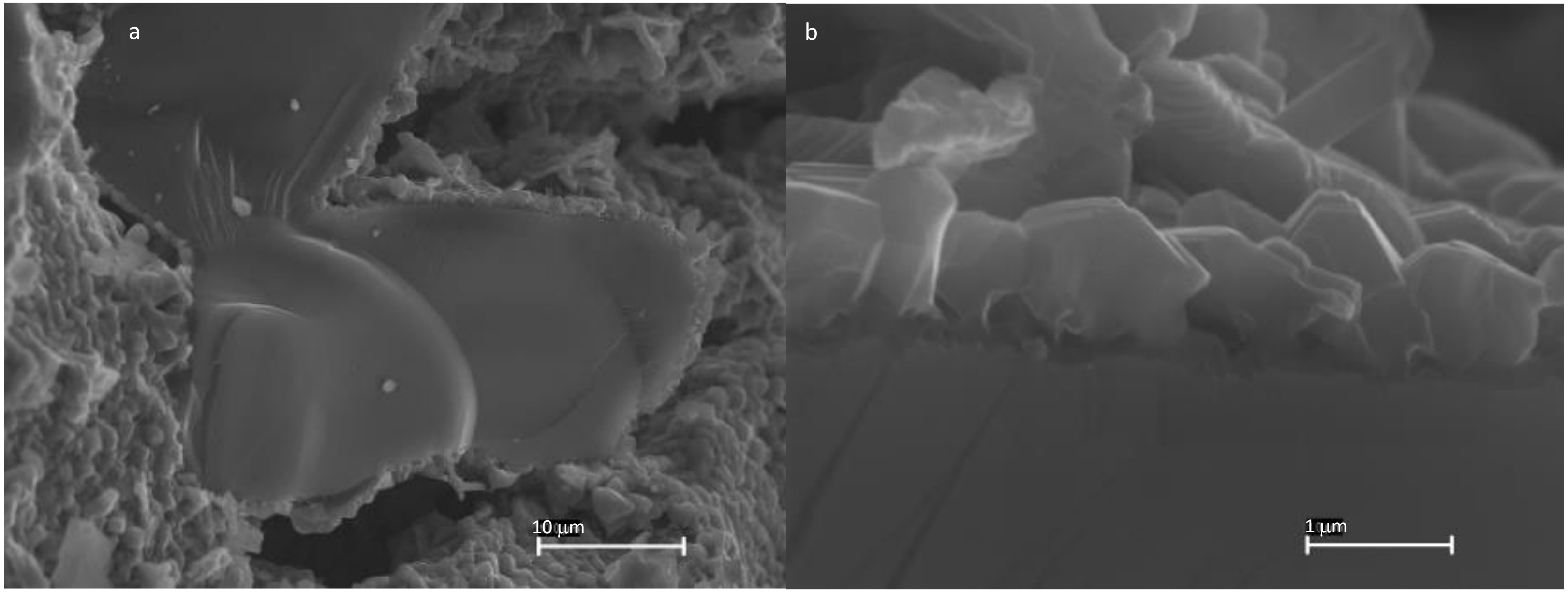
- Very low weigt losses
- The active species were deposited on the monolith **without any washcoat**

SEM images



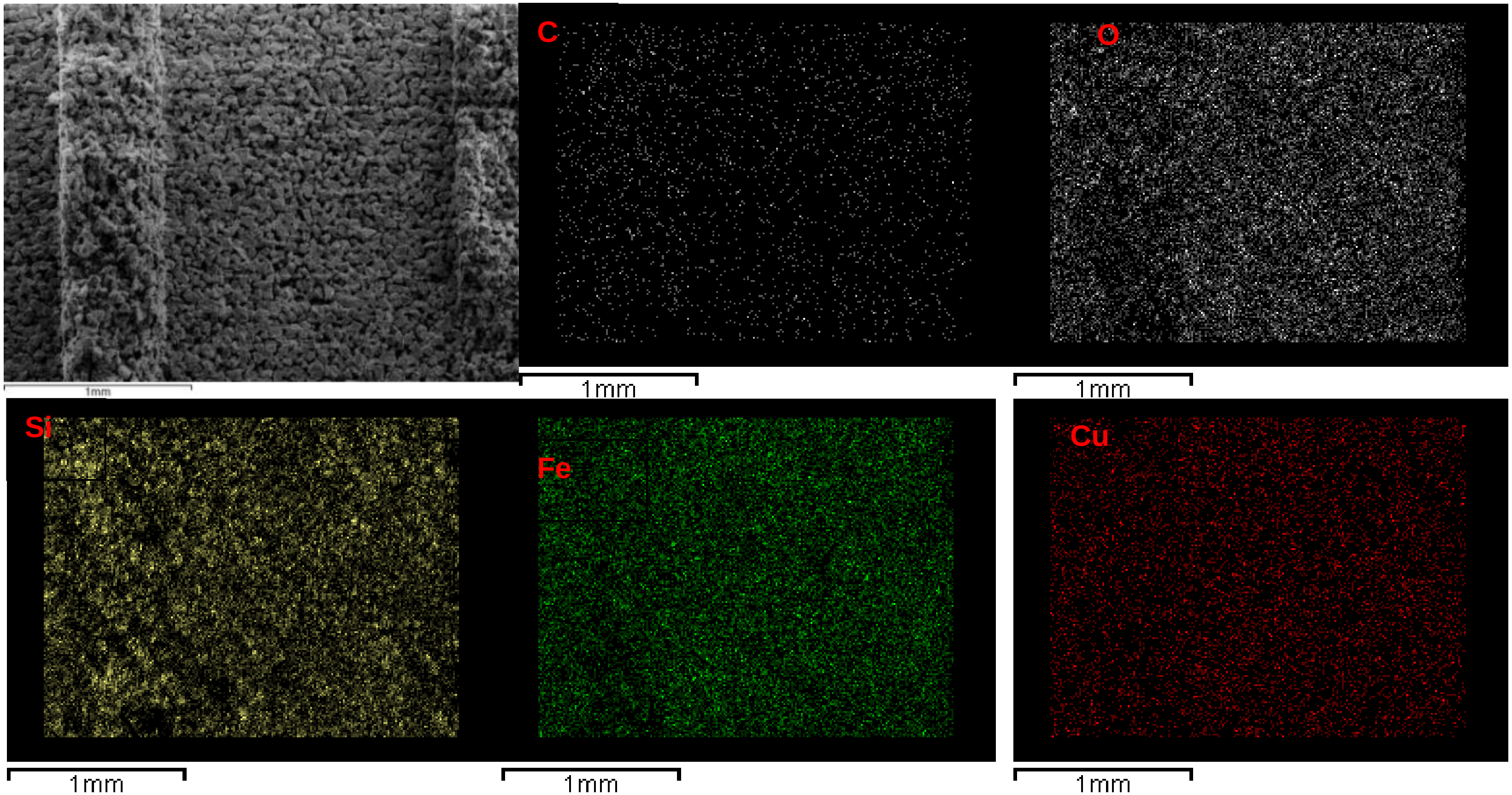


SEM images



- Homogenous distribution and good adhesion of the active species on the SiC granules
- Tight contact between the active species and the SiC granules
- Average thickness of the catalyst layer is of about 3 micrometers

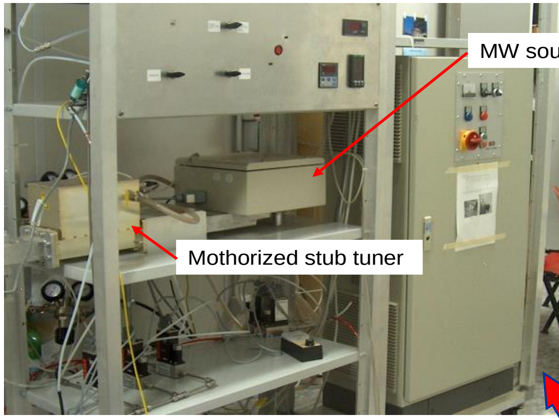
SEM-EDAX analysis

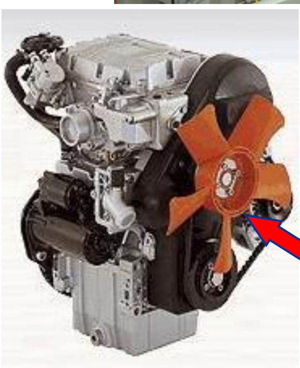


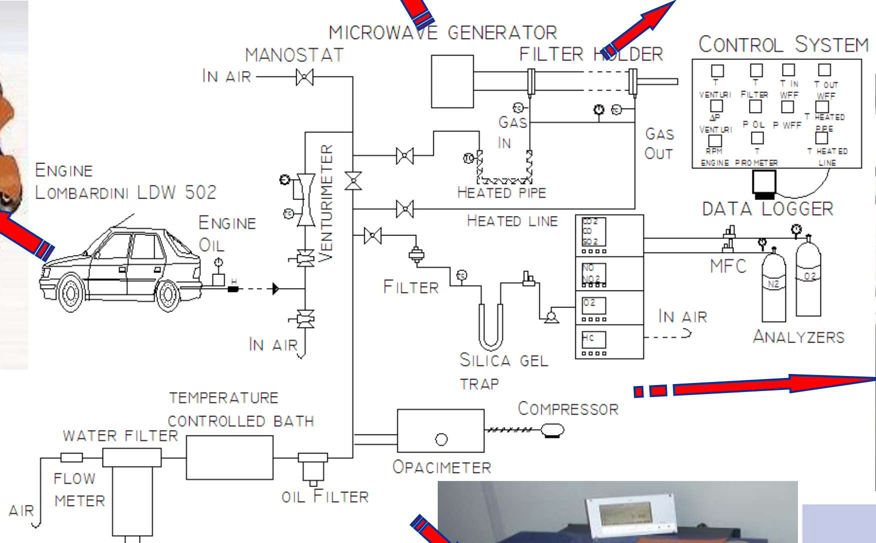
The elements which are evidenced by EDX are the ones of the structural material of the filters (C, and Si), as well as the ones of the catalytic active species (Cu and Fe)

Experimental Plant

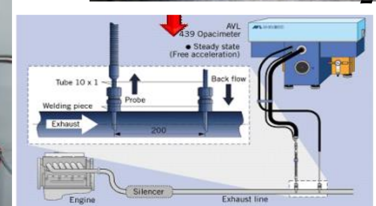
On-line SOOT deposition and DPF regeneration test







AVL 439



Regeneration step in two different ways:

- *by pre-heating the diesel exhaust stream with the electrical resistances*

by heating the WFF only with the microwave generator (2kW max)

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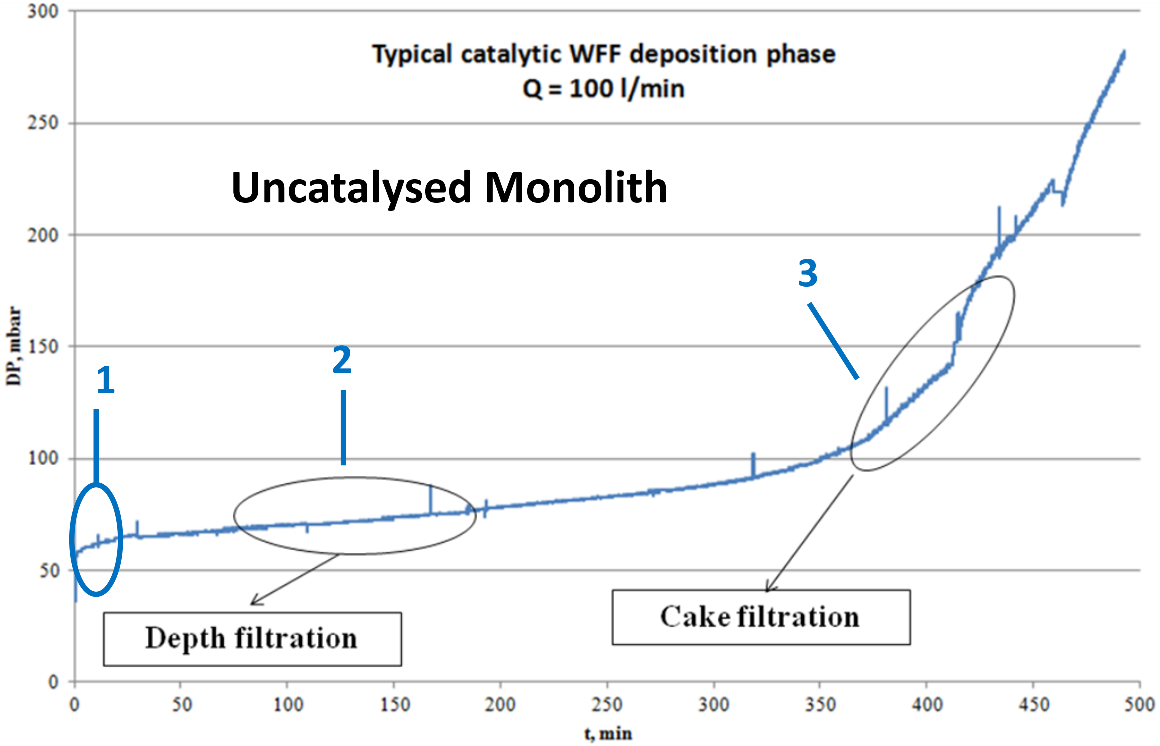
Typical soot loading on a SiC WFF



The average opacity at the DPF inlet: 22% (Csoot : 45 mg/m^3)

The average opacity at the DPF outlet: 0.02% (Csoot : 0.04 mg /m^3)

Average filtration efficiency higher than 99%

Transient time is lower than 3 min.

Three different stages of soot loading in the DPF:

1. the soot starts to fill the pores in the WFF

2. the soot layer is forming on the surfaces of the WFF

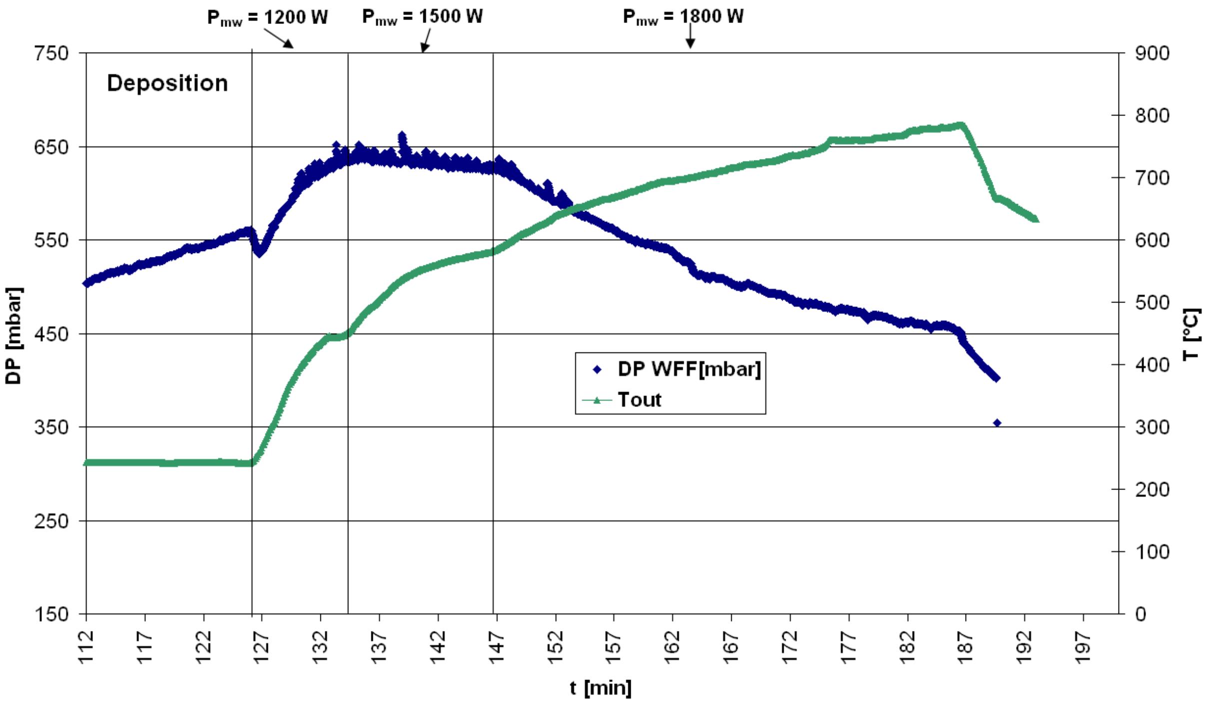
3. the soot layer reaches an appreciable thickness, and starts to act itself as a filter

From this point, an additional increase in the pressure drop curve slope is observed

MW assisted regeneration tests for uncatalytic filters

operating engine conditions:

- *deposition: 600 rpm, High load, flow rate 100 l/min*
- *regeneration: 600 rpm, Low load, flow rate 100 l/min*
- *Starting Soot load : 5g/l*



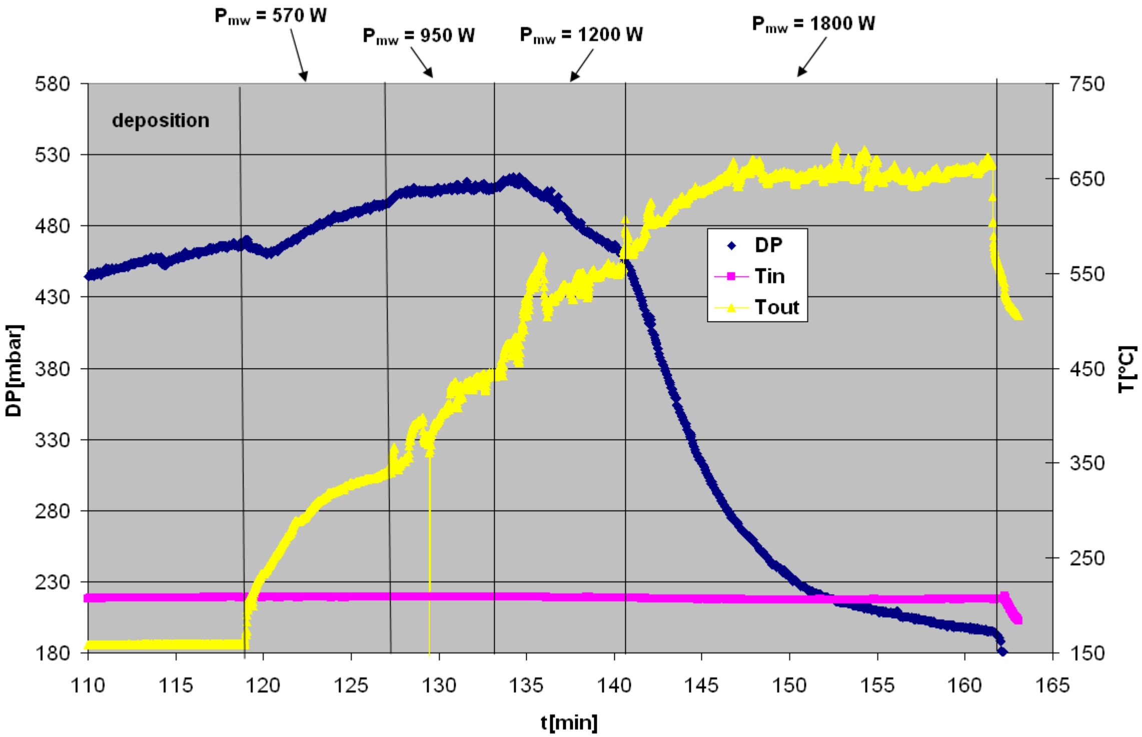
In the range of 200-450°C the temperature increase results in a further pressure drop increase.
A sensible decrease in the pressure drop is only observed at outlet temperature higher than 550°C, corresponding MW power higher than 1500W.

The MW power was raised from 1200 W to 1800 W to obtain the filter regeneration

After about 70 minutes the regeneration phase is not yet completed.

MW assisted regeneration tests for 15%wt catalytic filter

operating engine conditions:
- *deposition: 600 rpm, High load, flow rate 100 l/min*
- *regeneration: 600 rpm, Low load, flow rate 100 l/min*
- *Starting Soot load : 5g/l*



The complete filter regeneration is obtained in about 30 min.

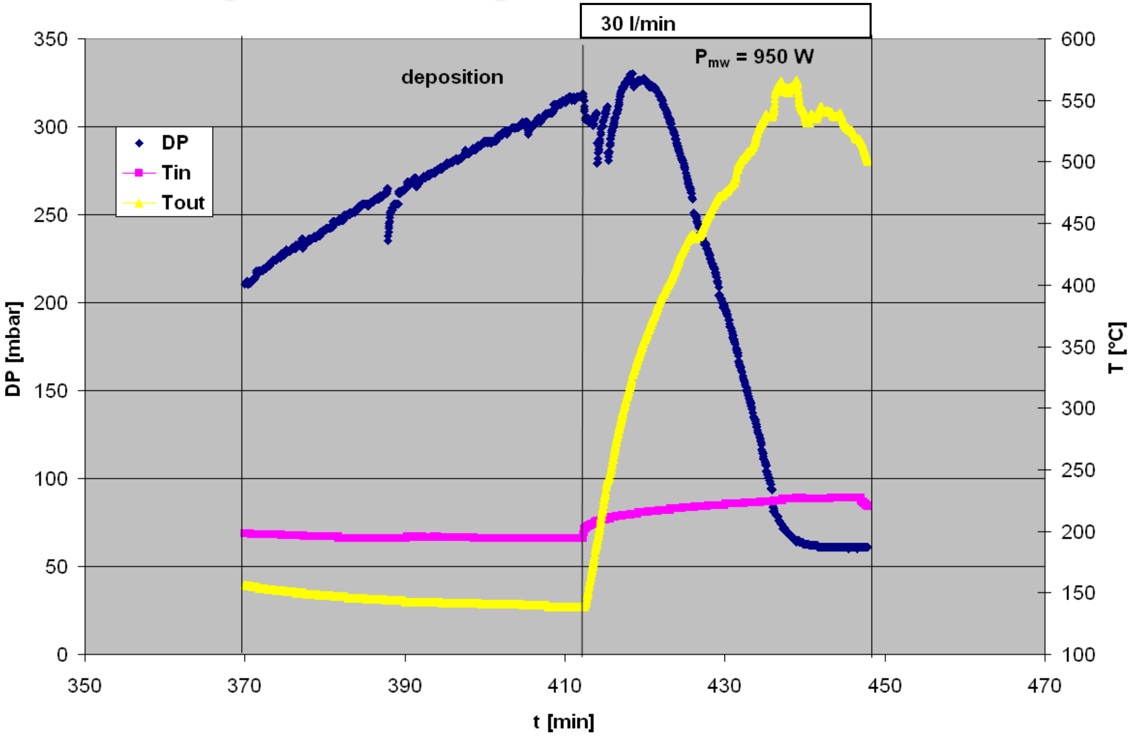
A similar pressure drop behaviour as function of time is obtained for the catalytic filter but..

1. *the regeneration starts at lower temperatures*
2. *the MW power required to ignite the system is lowered*
3. *at the same MW power value the regeneration rate is very higher*

The influence of the gas flow rate on the MW assisted regeneration tests for catalytic WFF:

operating engine conditions:

- *deposition: 600 rpm, High load, flow rate 100 l/min*
- *regeneration: 600 rpm, Low load, flow rate 30 l/min*
- *Starting Soot load : 5g/l*



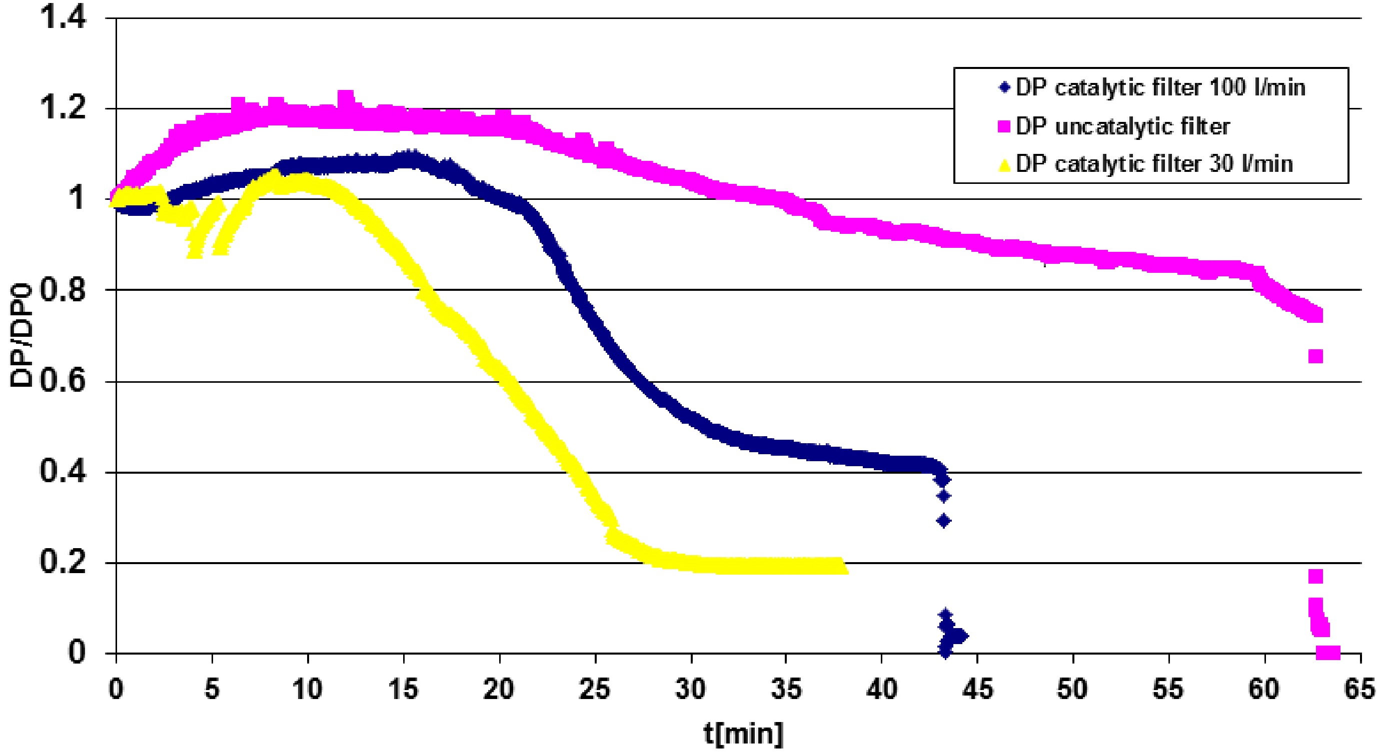
very fast regeneration: all the regeneration phase lasts about 20 minutes

Reducing the gas flow rate from 100 to 30 l/min..

1. *MW power required to ignite the system is further lowered*
2. *similar regeneration behavior obtained with only about 900W instead of 1800.*

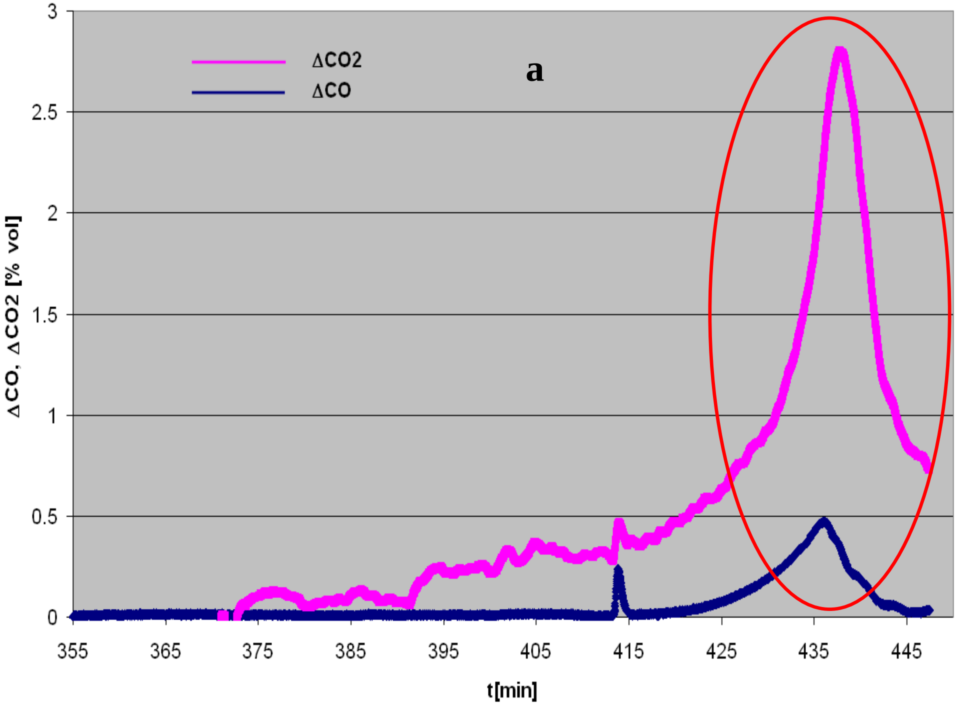
reduced quenching effect of the cold gas flow through the filter

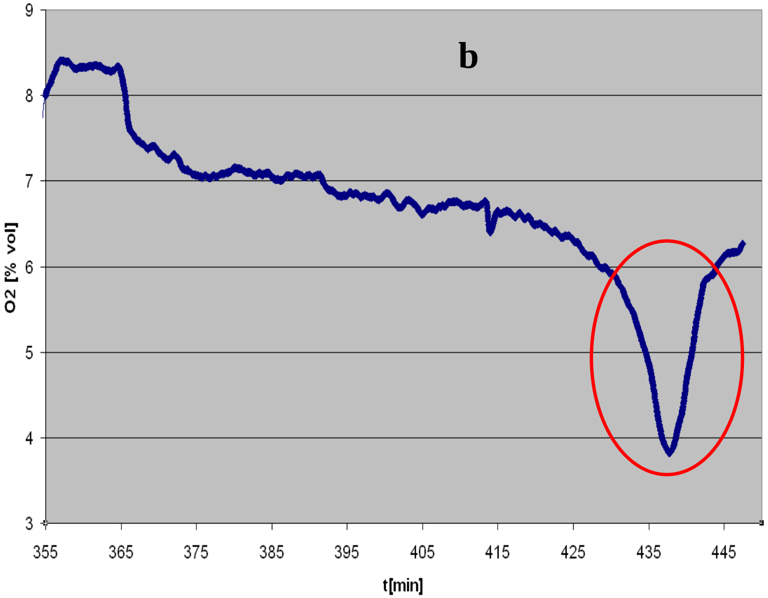
MW assisted regeneration phase



- For the uncatalysed case the regeneration starts for MW power higher than 1500 W After about 1h the regeneration is not yet completed
- The 15%wt catalyst load allows simultaneously to regenerate at lowered MW power and higher reaction rate giving the complete soot removal in about half time
- At lower gas flow rate the MW energy is used mainly for the soot combustion allowing an higher energy saving and a regeneration time further reduced

Regeneration phase: exhaust gas analysis

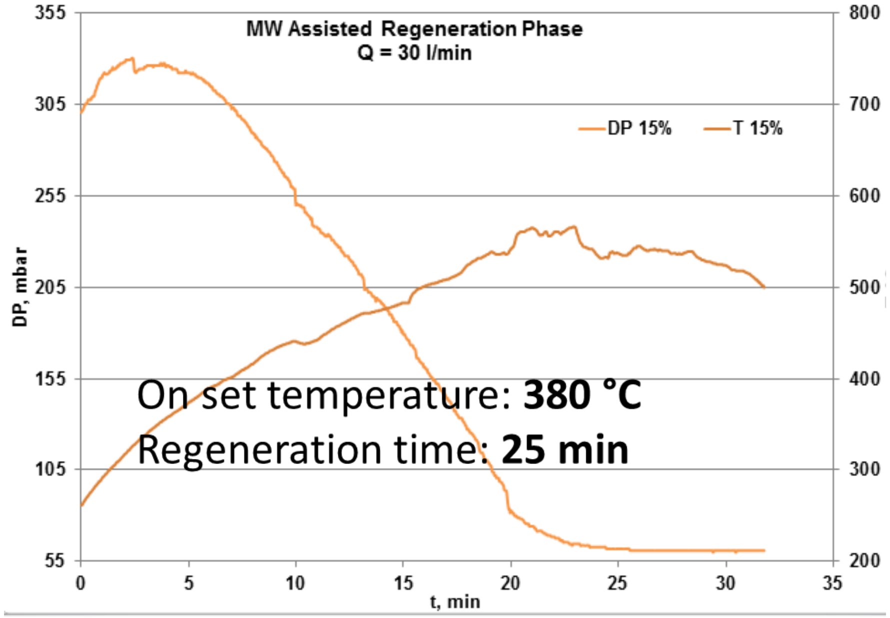


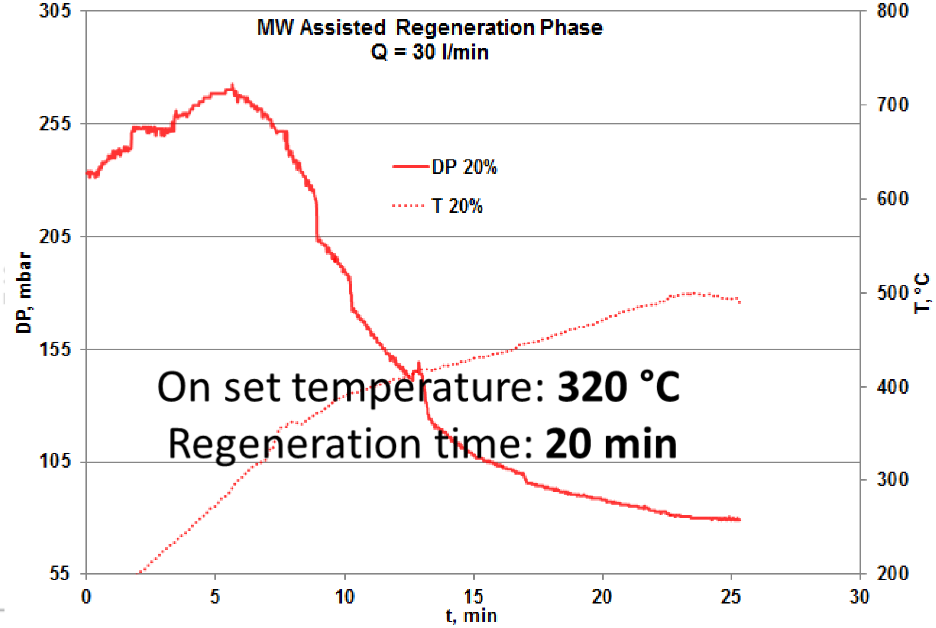


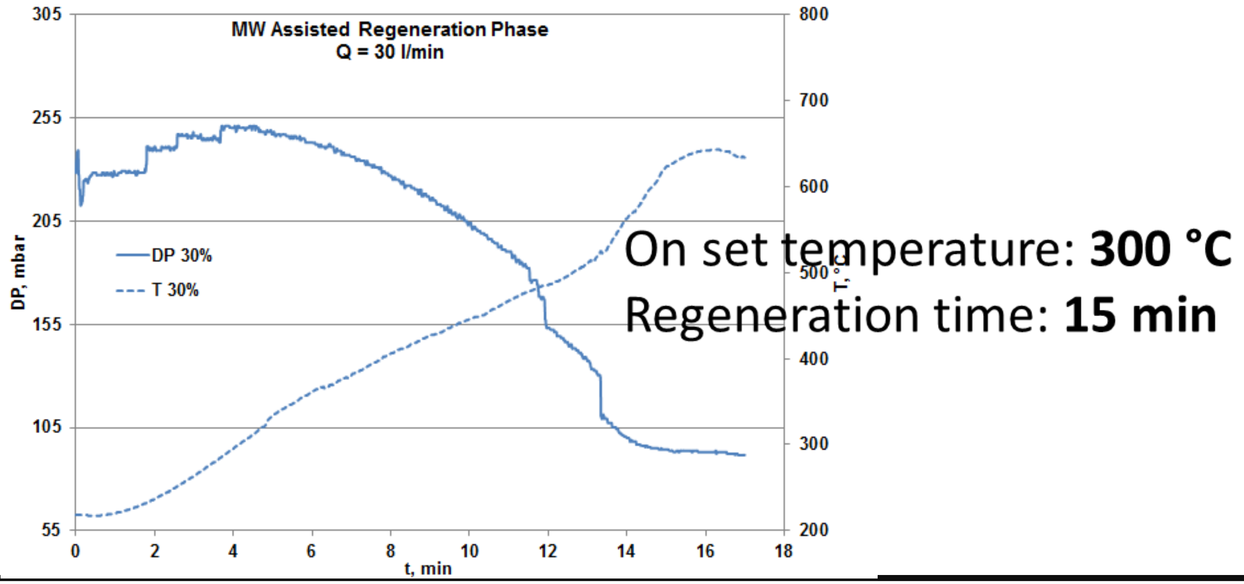
Very good oxygen balances verified

Very high selectivity to CO_2 likely due to the lowered temperature and to the catalyst presence.

Regeneration phase: effect of catalyst load





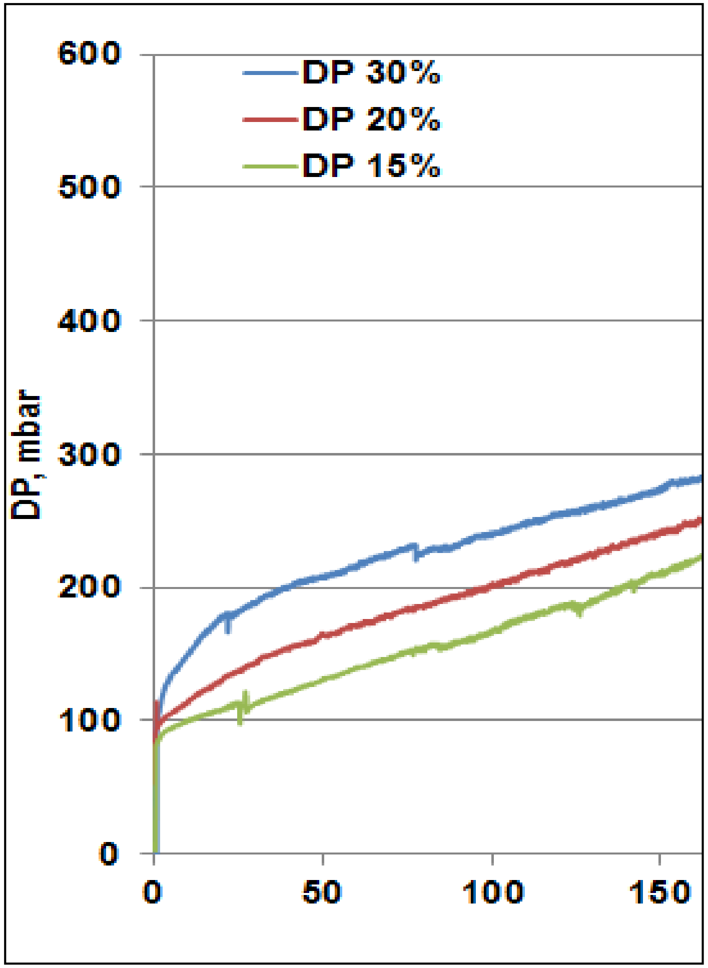


Energy comparison

By integrating the instantaneous MW power as function of time one can obtain the overall energy applied for the regeneration phase.

Fuel post-injection	• 7400 kJ/DPF liters
15%wt loaded DPF	• 5700 kJ/DPF liters
20%wt loaded DPF	• 3300 kJ/DPF liters
30%wt loaded DPF	• 2300 kJ/DPF liters

Deposition phase: effect of catalyst load



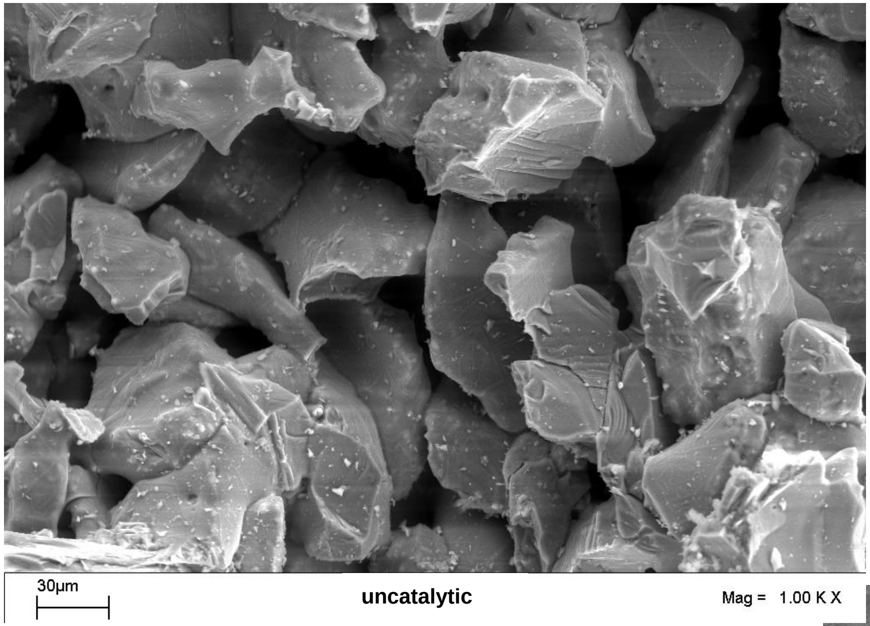
- Higher initial pressure drop at the increase of the catalyst load
- Same trend during the deposition phase

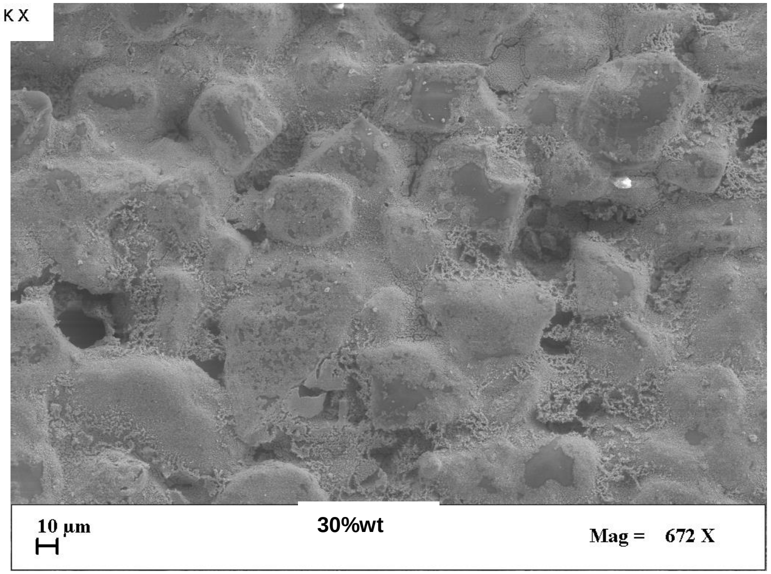
Textural properties

Sample	*BET Surface Area (m^2/gr)*	*Average pore diameter (μm)*
Powder of $CuFe_2O_4$	*1.3*	
Bare SiC monolith	*0.3*	*17*
Catalytic DPF with 15%wt of $CuFe_2O_4$	*0.5*	*15*
Catalytic DPF with 20%wt of $CuFe_2O_4$	*0.9*	*13*
Catalytic DPF with 30%wt of $CuFe_2O_4$	*0.9*	*12*

- The increase in the catalyst load results in the increase of the specific surface area and in the decrease of the average pore diameter

SEM images





Porosimetric tests

Uncatalytic monolith Duration of acid treatment [min]	Pores average diameter [µm]
0	17.0
2	18.0
4	19.0
6	20.0
8	21.0
10	22.0
20	23.0
30	24.0
35	24.5

WE DEVELOPED A DEDICATED CHEMICAL TREATEMENT TO REALIZE THE ACIDIC CARRIER LEACHING AND OBTAIN A CONTROLLED EROSION TO MODIFY THE INITIAL AVERAGE PORES DIAMETER

20% wt $CuFe_2O_4$ loaded SiC monolith	Pores average diameter [µm]
No acid treatment	13
After 30 min of acid treatment	17

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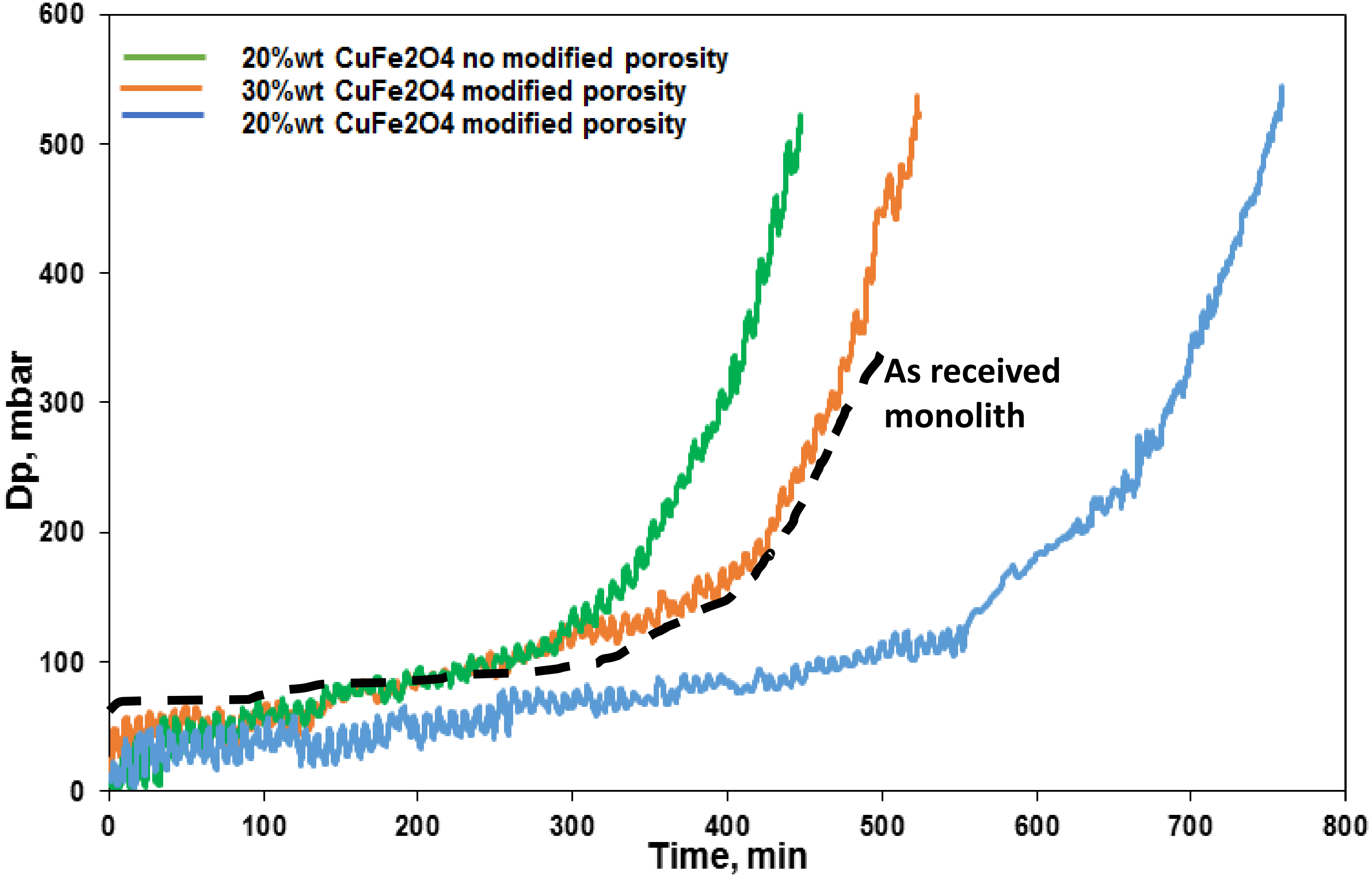
Catalytic Filters with modified porosity



- *Increased duration of the deposition phase*
- *Decrease of the frequency of DPF regeneration phases*

Conclusions

- *MW sensible catalytic Wall Flow Filters were prepared by depositing Copper Ferrite on commercial SiC monoliths (Pirelli Ecotechnology)*
- *The catalyst allowed to decrease the soot ignition temperature up to about 300 °C.*
- *Very high filtration efficiency as in the case of the original monolith,*
- *The designed experimental apparatus allowed us to verify that is possible to achieve the complete filter regeneration employing only microwaves*
- *The higher catalyst load allowed to decrease the time required for the MW regeneration stage (from 40 min up to 20 min) and lowered the energy needed to regenerate the filter, also with respect to fuel post-injection*
- *A dedicated chemical treatement to realize the acidic carrier leaching and obtain a controlled erosion to modify the initial average pores diameter Was developed*

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THANKS FOR YOUR ATTENTION

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