# Incorporation of Catalytic Compounds in the Porosity of SiC Wall Flow Filters – 4 Way Catalyst and DeNOx Application examples

## DEER MEETING

**August 15TH-2007 - Detroit (MI)**


| | |
|---|---|
| Jean-Pierre JOULIN | CTI |
| Bruno CARTOIXA | CTI |
| Didier TOURNIGANT | CTI |
| Arnold LAMBERT | IFP |
| Jean-Christophe RUIZ | CEA |
| Anne JULBE | IEM |

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# AGENDA

- **Short CTI presentation**
- **Introduction**
  - Why to concentrate in one or two components all the exhaust gas containing HC, CO, NOx and PM
- **Exploration of 3 different methods of catalyst impregnation inside the pore of a SiC DPF**
  - Supercritical $CO_2$ method
  - Sol Gel impregnation
  - Incorporation of catalyst with the slurry forcing method
- **Zeolith impregnation of SiC DPF for DeNOx function using SCR method**
- **Conclusions**

# SHORT CTI PRESENTATION

CTI is specialized in perfecting the design of a wide range of technical ceramics often porous, whose applications are mainly in environment, filtration, catalysis fields and SOFC.

These include :

- ***Liquids filtration*** : membranes supports in ultra and micro filtration.
- ***Gas and particles filtration*** : tubular, flat, honeycomb, foam filtration carriers, **diesel particulate filter**.
- ***Catalysts supports*** : pellets with high specific area, honeycombs, smooth and grooved porous rings.
- ***Liquid metals filtration*** : honeycombs and foams refractories.
- ***Special refractories*** : withstanding temperatures higher than 1 600°C.
- ***Special ceramic washcoast for COx, DeNOx, VOC treatment and SOFC applications.***

***Factory area*** **: 6 000 m²**

***Laboratory and pilot area*** **: 1 000 m²**

- Scientific manager : JP. JOULIN
- Adm. & Financial Manager : N. DELBIANCO
- Dr in Catalysis & membranes : E. LOURADOUR
  D. TOURNIGANT
- 4 Ceramic engineers : L. ESPIN
  B. CARTOIXA
  F. PEY
  G. GAUDRY
- Quality insurance : S. ENJOLRAS
- 10 Technicians & laboratory people

**Created** : 8th of march 1990

**Independent SME . French Institute Of Petrol as Share holder**
**Capital** : 220 000 €

**Numbers of employees**: 75

***Industrial and laboratory equipment*** **:**

**mixers (1 to 1200Kg), extrusion press (1 to 400L), high frequency and microwave dryers, gas and electric kilns (0.4 to 10m³ until 1700°C), laboratory equipment, ...**

# Membrane materials and design for High temperature applications ( > 500°C)

**Inert porous supports (mainly for filtration):**

$Al_2O_3$, $SiO_2$, $TiO_2$, SiC, $ZrO_2$, $Y_2O_3$….

**Geometry design**

Honeycomb, flat, tubular,

granules, foams, tablets,
washcoat, membrane

**Active materials (for catalysis)**

$CeO_2/ZrO_2$

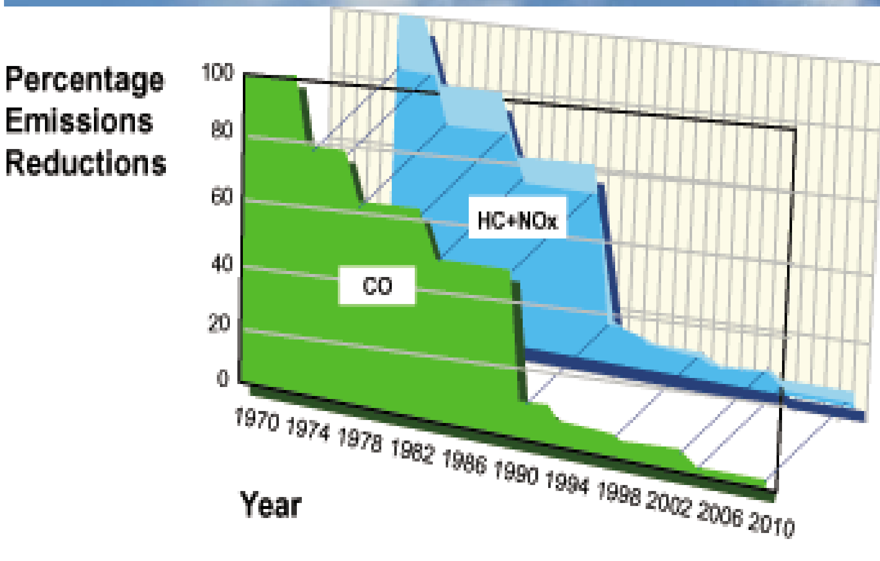
CeO2/$Al_2O_3$/Pt, $CeO_2$/Gd zeolithes,

ZnO, $V_2O_5$

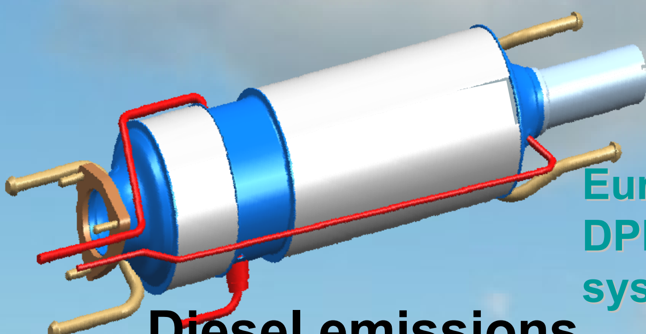
Perovskites (LSM), …..

# INTRODUCTION

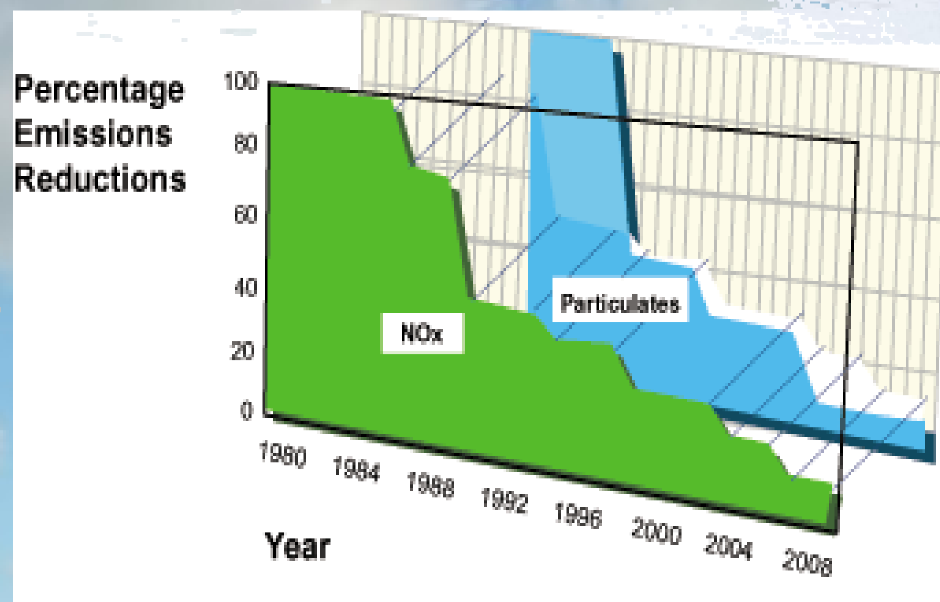
# Vehicle's environmental progress







Euro4 UF DPF system

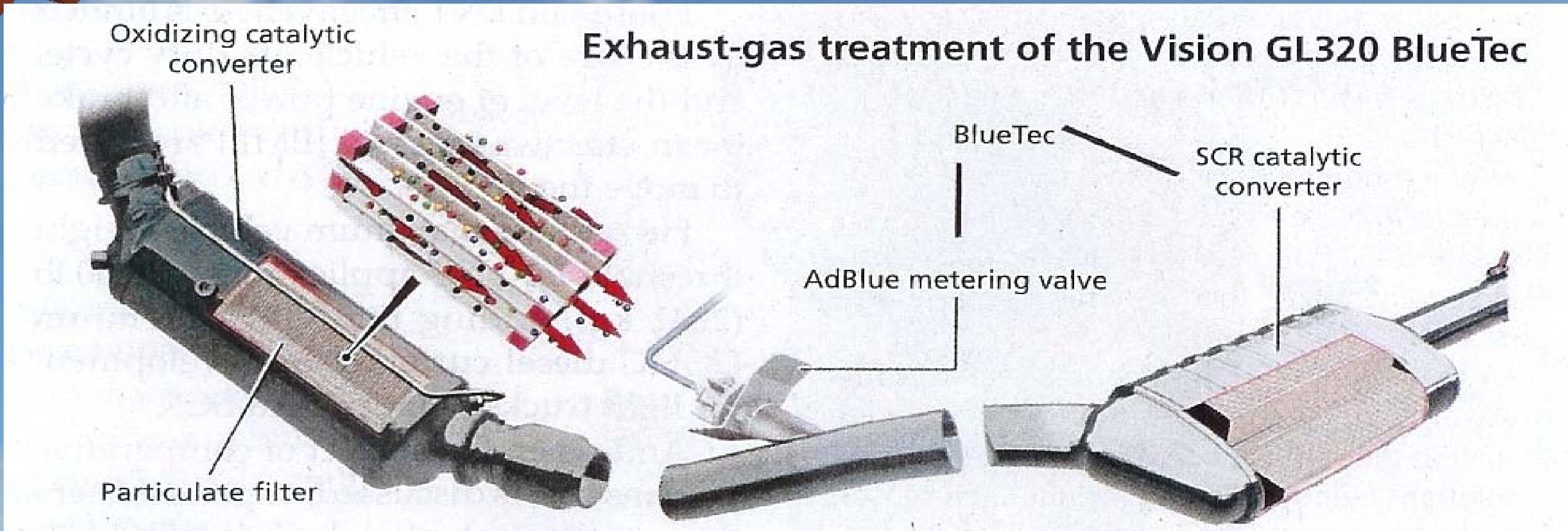


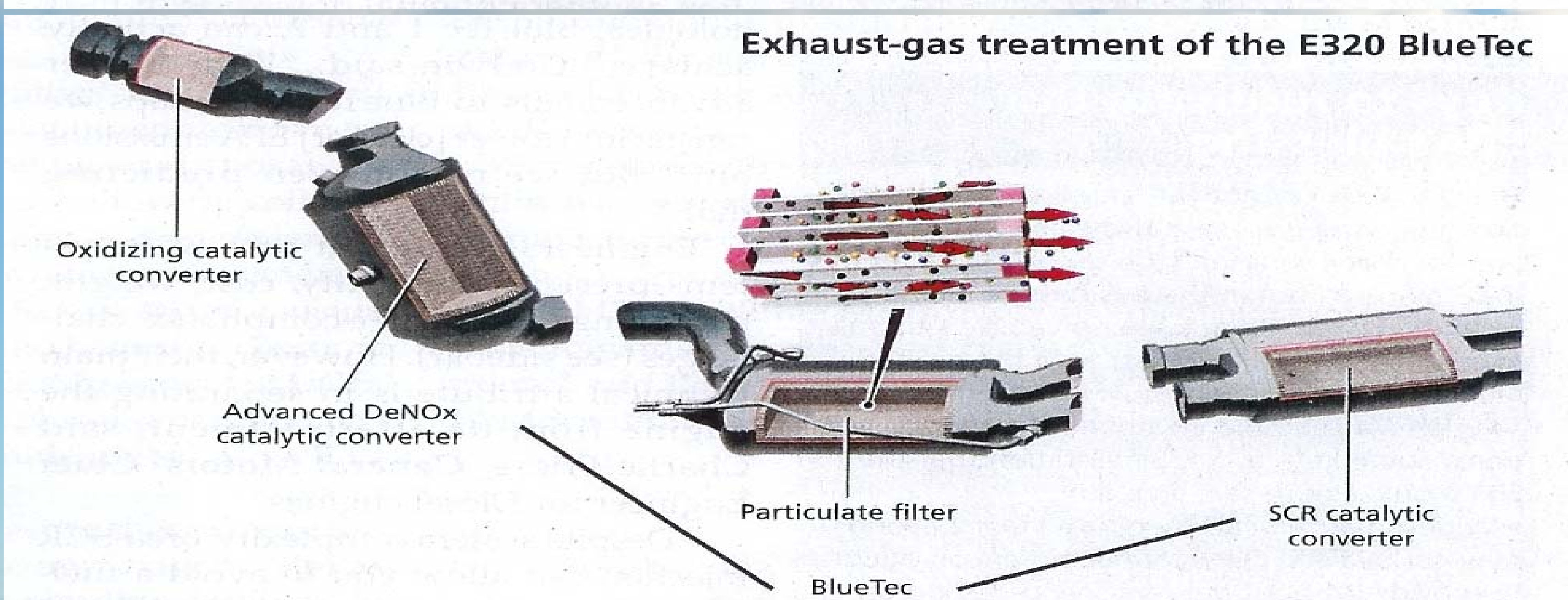

**Diesel emissions reduction legislation trends in Europe**



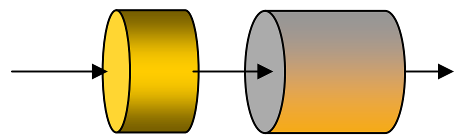
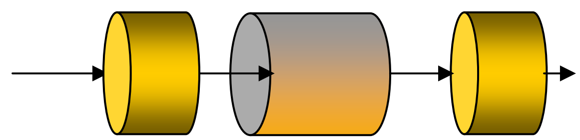
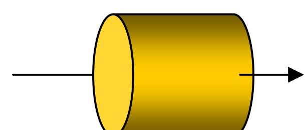
Fiat courtesy

# CURRENTLY DPF SYSTEM + DeNOx TRAP



# CURRENTLY DPF SYSTEM + DeNOx TRAP

| SYSTEMS | | PROCESS |
|---|---|---|
| **Catalysed DPF** | Cordierite Catox + SiC DPF  | - Soot Oxydations with $NO_2$ with or without catalysis |
| **SCRT System (JM)** | Cordierite Catox + SiC/cordierite DPF+SCR-$NO_x$  | -Soot Oxydations with $NO_2$<br>$NO_2$+PM $\rightarrow$ $CO_2$+$N_2$<br>-Catalytic reduction of $NO_X$ |
| **DPNR System (Toyota)** | Cordierite Catox + DPF+$N0_x$ trap  | **4 WAY CATALYSIS** |

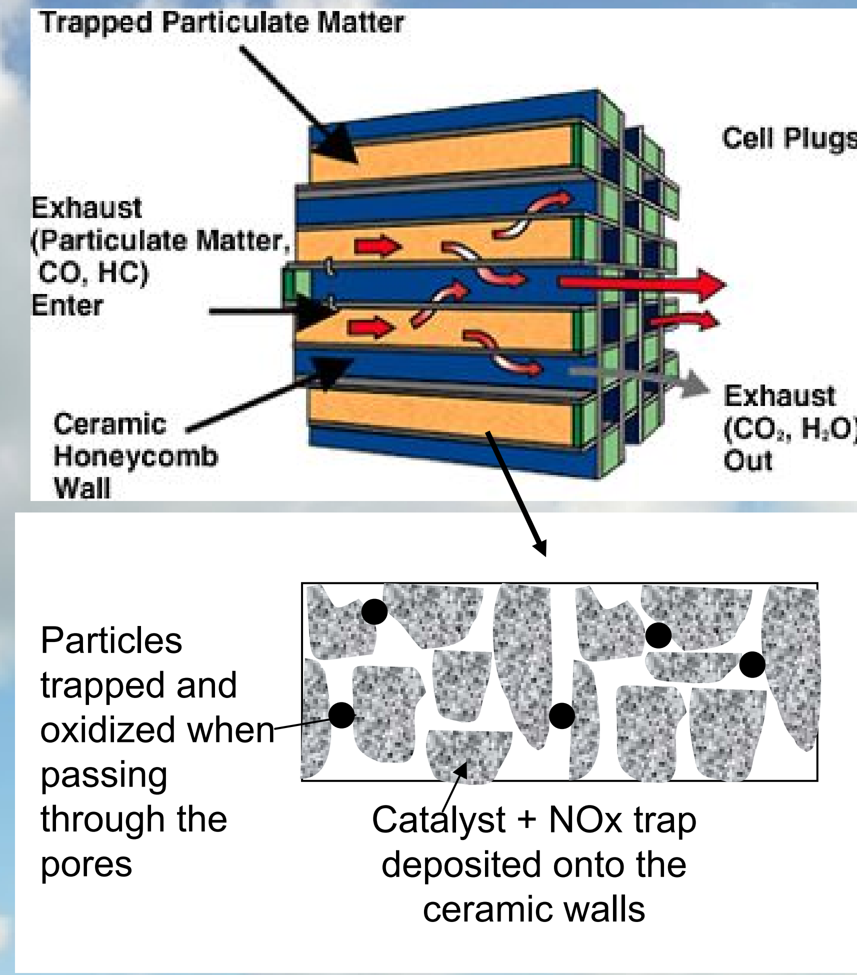
# 4-WAY CATALYSIS : eliminate HC, CO, NOx and PM with a single treatment device

**Catalytic phase impregnation + $NO_X$ deep trapping within the pores of the filtering support**

- Favor the NOx trapping and the oxidative catalysis in terms of volume (high $S_{BET}$) together with the important function of absolute particles filtering (no thick covering of the surface that would desactivate the catalyst and blocks the NOx trapping).
- Favor the synergy effect between $NO_X$ trapping and particles oxidation

**Interest of nanophased materials :**

- **Homogeneous materials, finely divised with high $S_{BET}$**
- **specific properties (surface activity highly increased)**



CTI has developed a new composite SiC DPF able to be easily catalysed. The catalyst is impregnated inside the porosity of wall flow :

- Porosity of the CTI SiC DPF is around 46% and pore size around 17/19 µ.

- The great advantage of CTI'SiC composite product is to be already treated against all the oxidation attacks and so to preserve the catalyst performance during ageing.

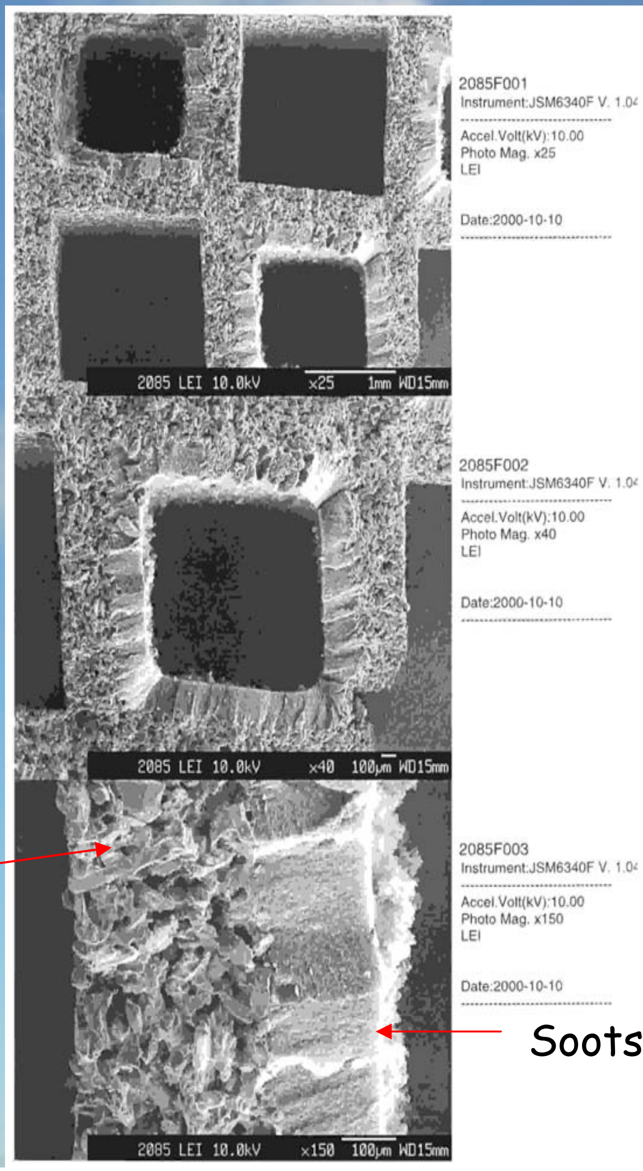
# EXPLORATION OF 3 DIFFERENT METHODS OF CATALYST IMPREGNATION INSIDE THE PORE OF A SiC DPF

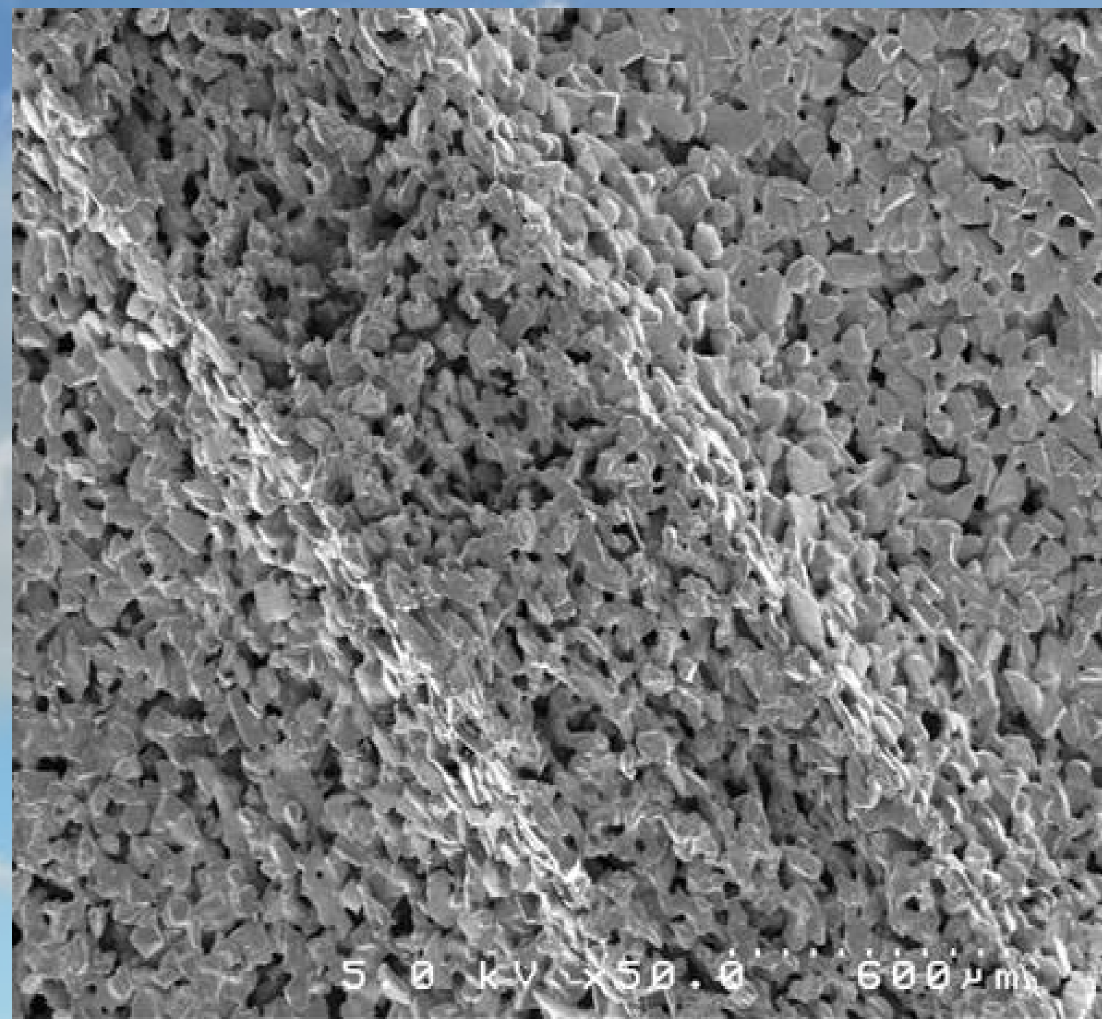
Since 2003 CTI has explored 3 different ways of catalysis impregnation :

- $CO_2$ supercritical impregnation with CEA (Pierrelatte, Atomic Energy Center)
- Sol gel impregnation with IEM Montpellier (European Institute of membrane)
- Forced slurry method with IFP (French Petroleum Institute) (patented)

# SEM PHOTO OF A CTI'S DIESEL PARTICULATE FILTER (DPF)

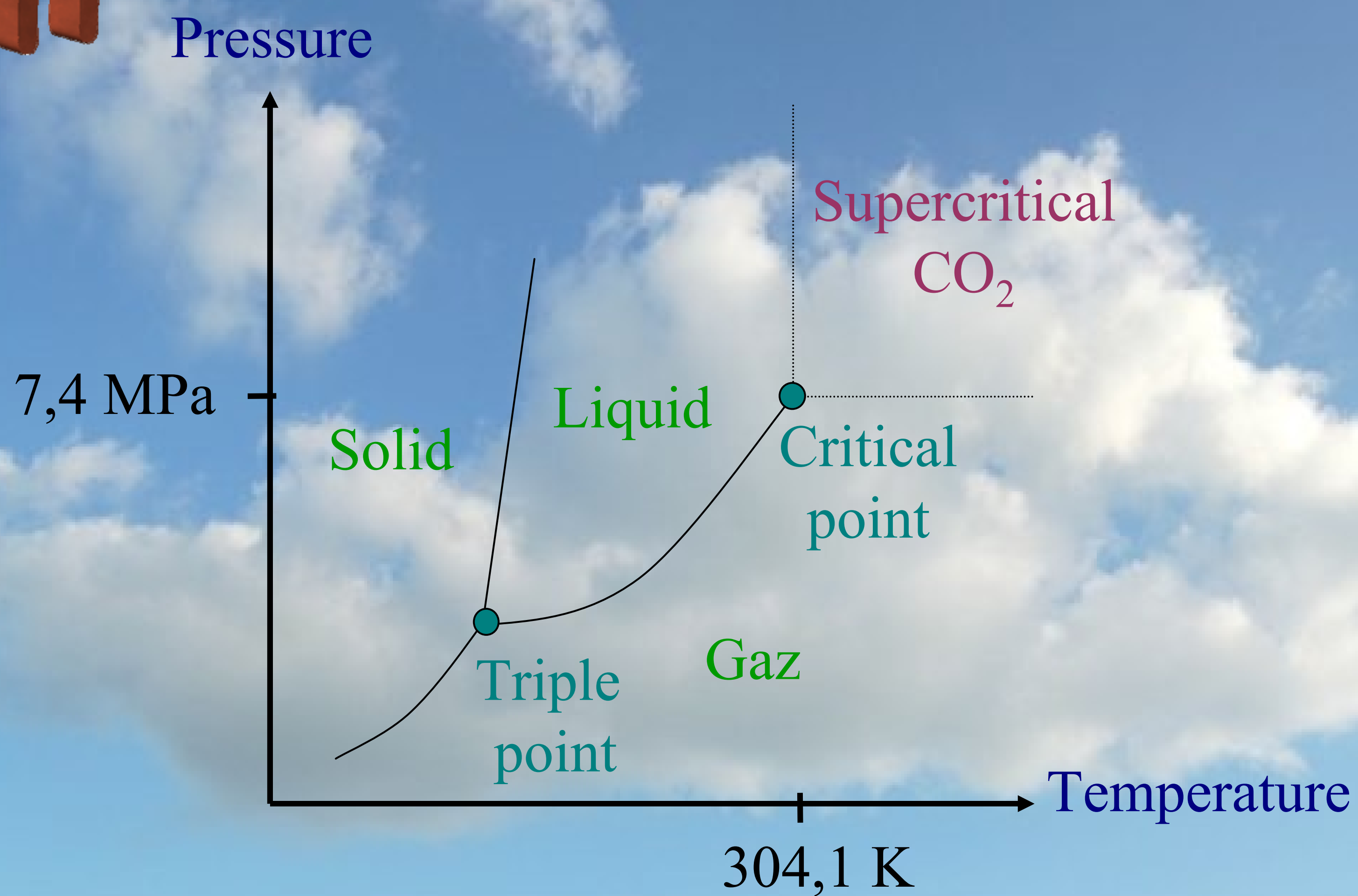
## Soot Deposit configuration before regeneration



# SUPERCRITICAL $CO_2$ METHOD

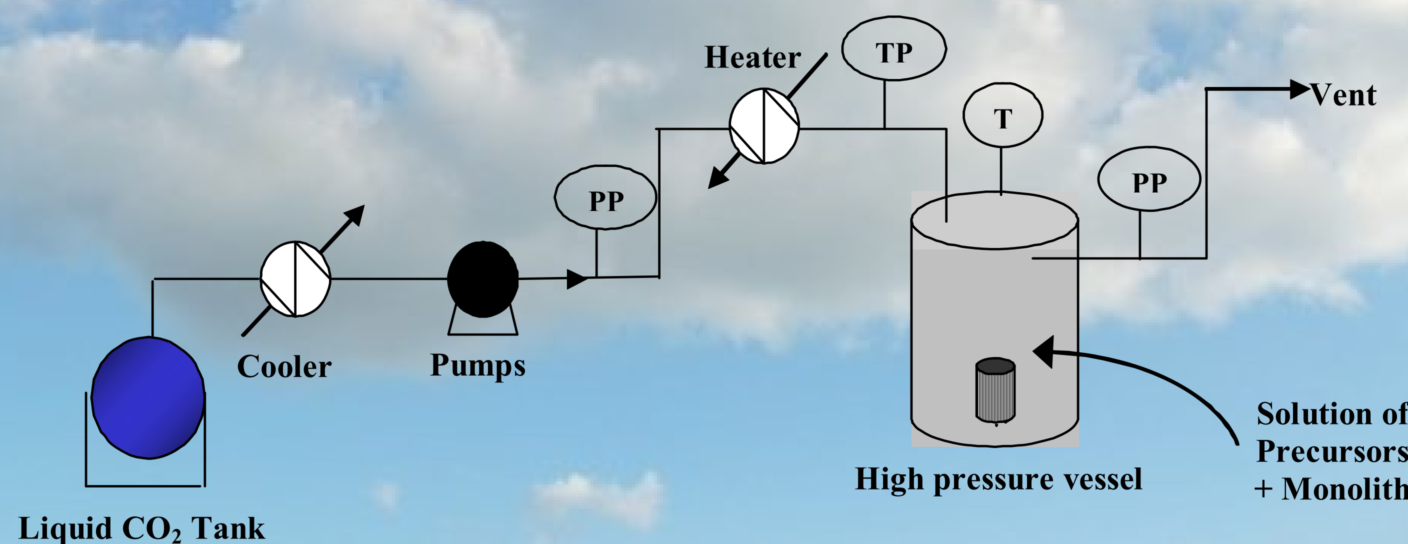
with collaboration of CEA Pierrelatte - 2004



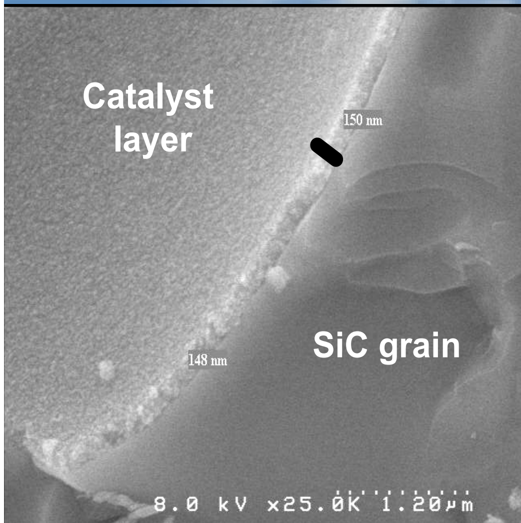

Phase diagram of supercritical $CO_2$

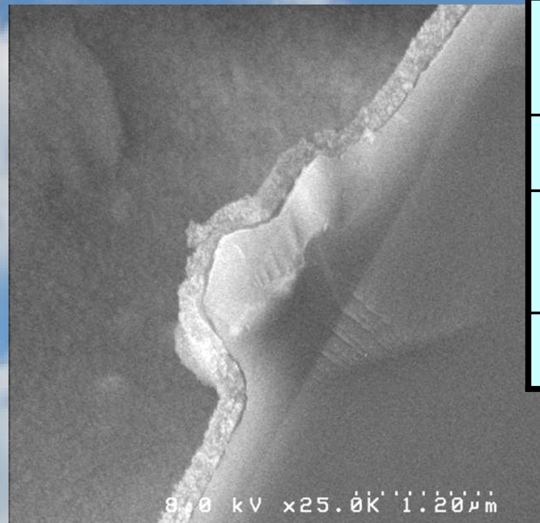
# MATERIALS

Particularity : The synthesis and macroporous support impregnation was carried out in a single step, in a 1 litre high-pressure vessel. After introducing a specific amount of selected catalyst formulation in the autoclave containing the monolith, the liquid $CO_2$ was pumped into the vessel up to the operating pressure of 30 MPa. The reaction temperature was regulated at 573 K using an external electric heater. The contact time of the reactants in SC $CO_2$ was 1 hour



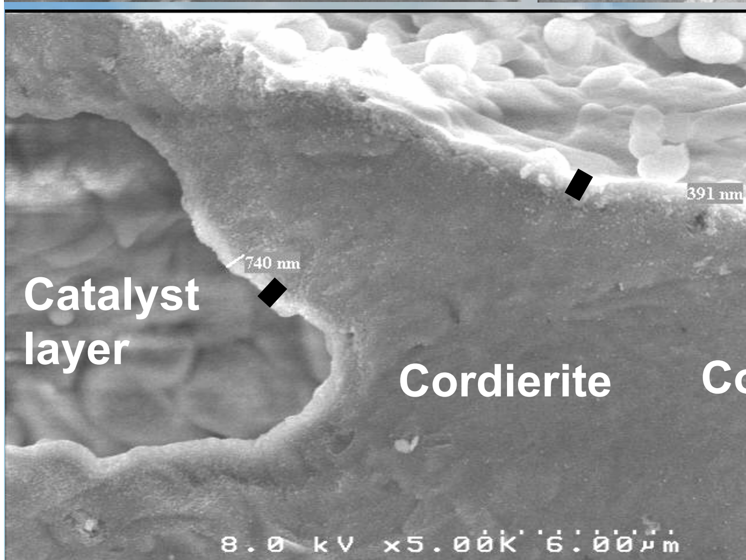
# RESULTS – SEM –
# SiC and Cordierite analysis

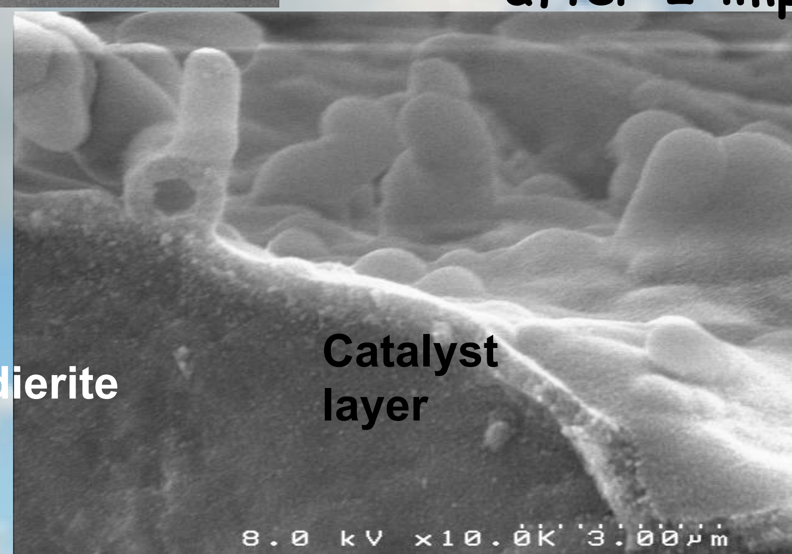



| | | |
|---|---|---|
| | | |
| | | |
| | 400 - 700 | |
| | 550 | |

**thickness of the active layer
after 2 impregnations



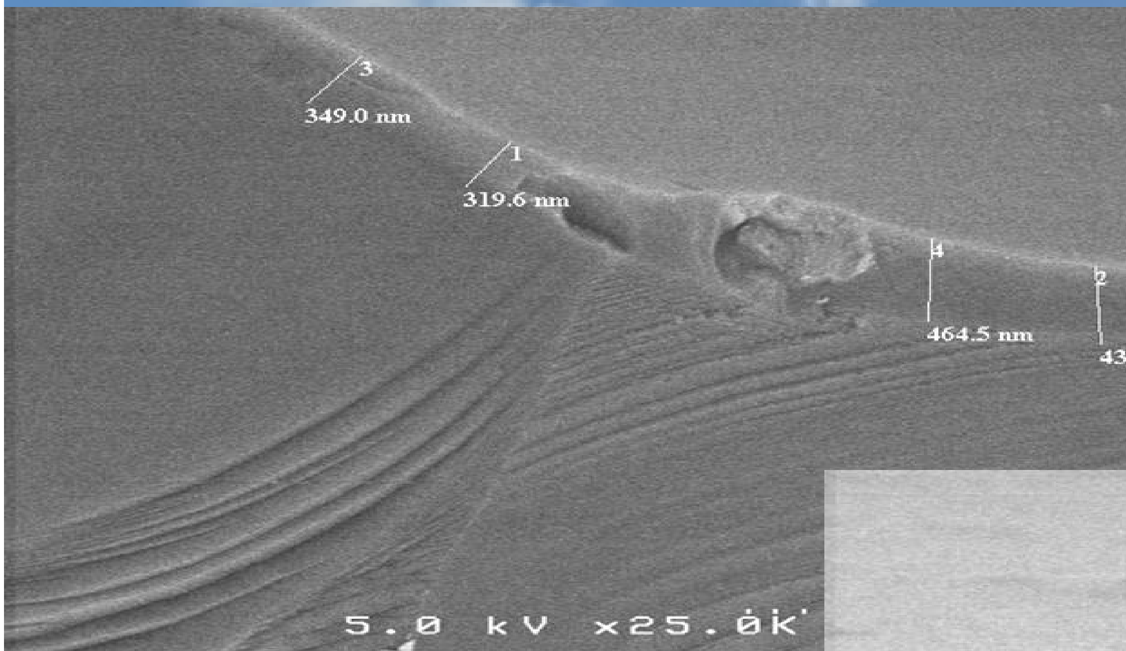



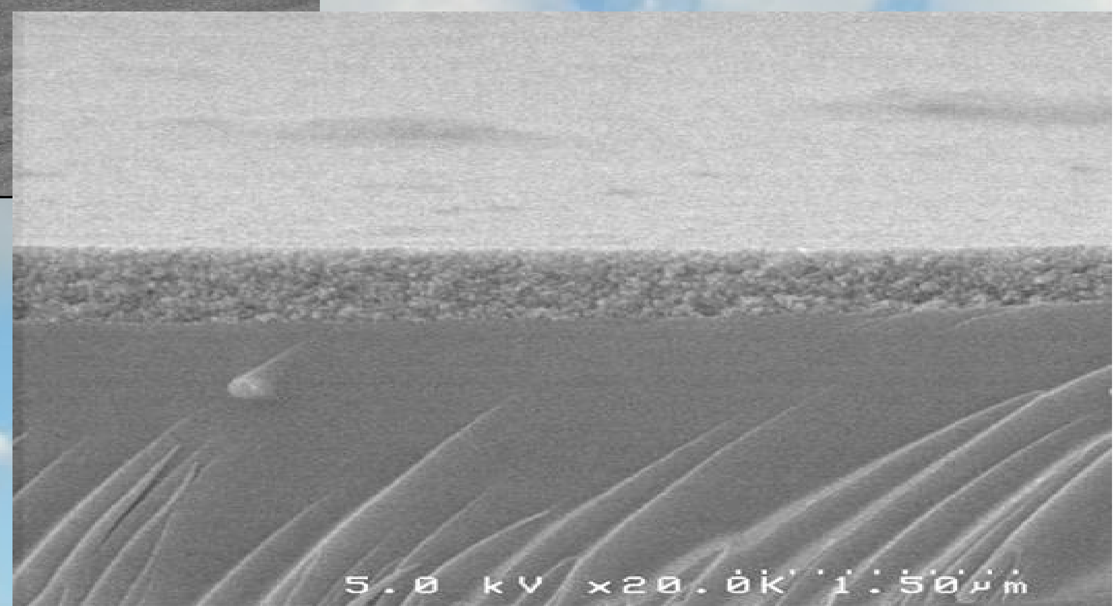

Sol composition : Alumina – Zirconia – Ceria – Baryum oxyde

# SOL GEL IMPREGNATION

with collaboration of IEM Montpellier

# CERAMICS GRIT IMPREGNATED WITH NANOPHASE CATALYST (350 nm layer) ON HONEYCOMB FILTER 1/2

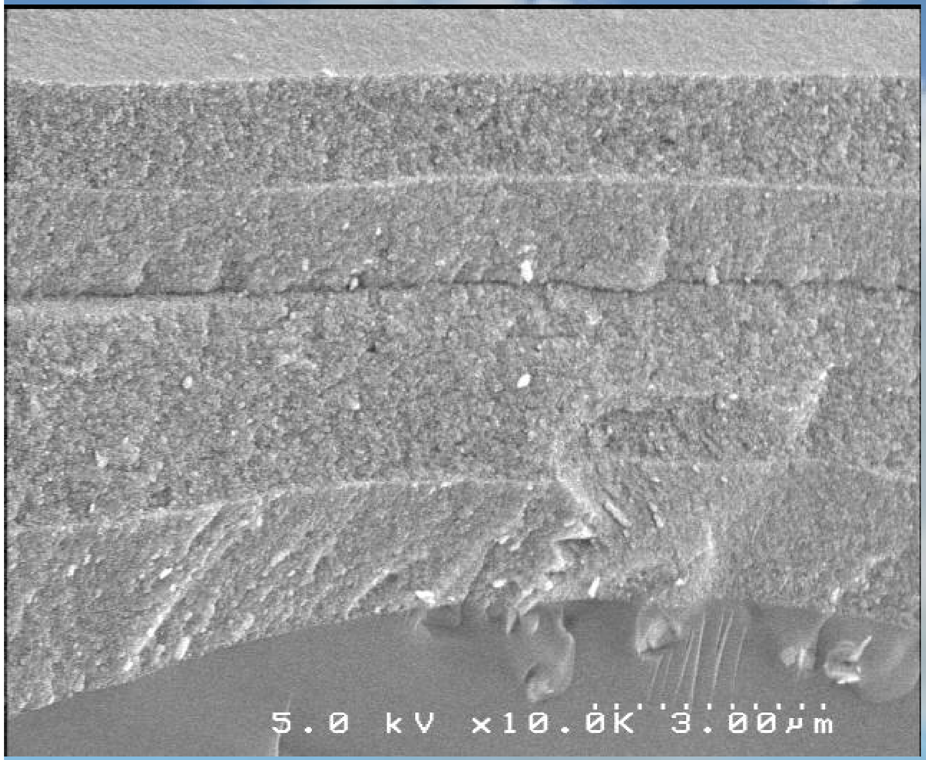


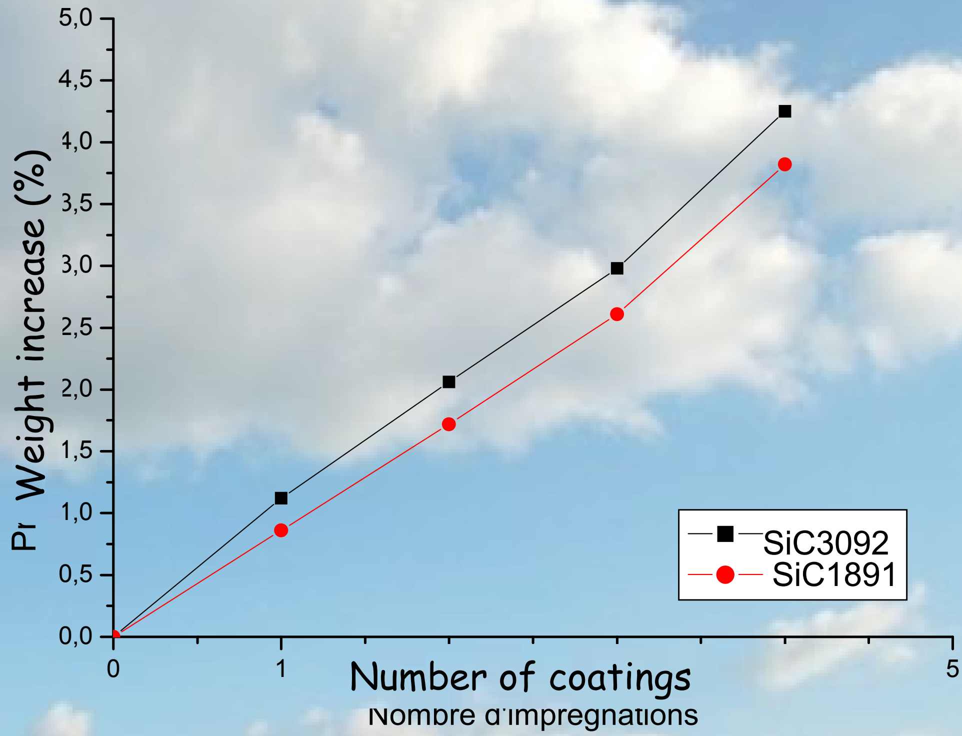




**Sol gel composition Alumina, Ceria, Zirconia, Baryum oxide**

# CERAMICS GRIT IMPREGNATED WITH NANOPHASE

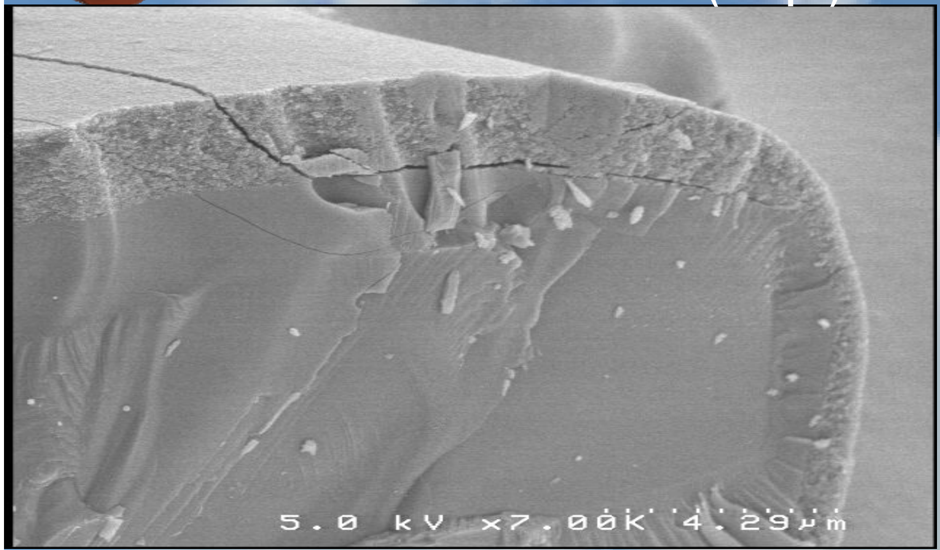
## CATALYST (350 nm layer) ON HONEYCOMB FILTER 2/2



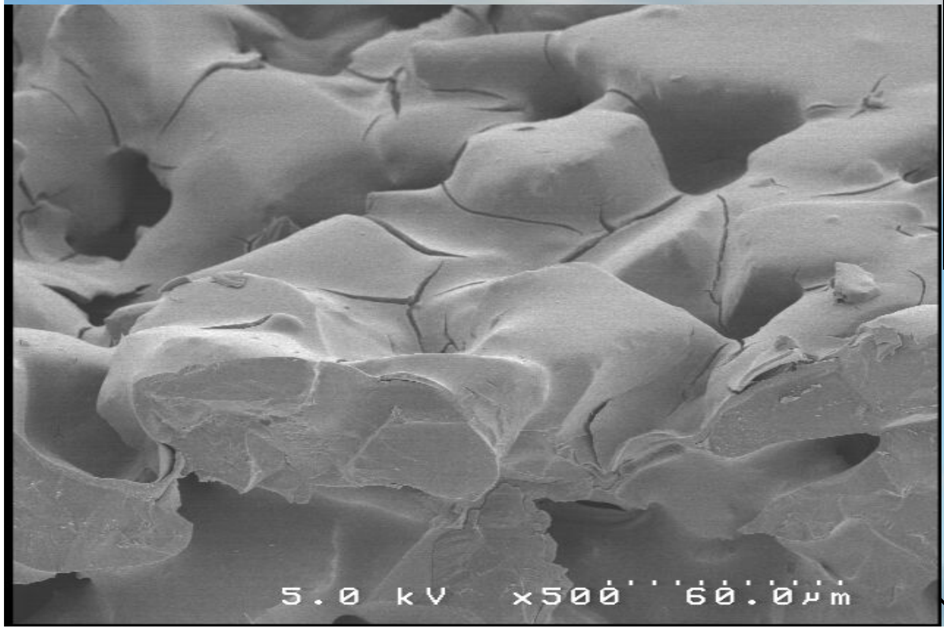



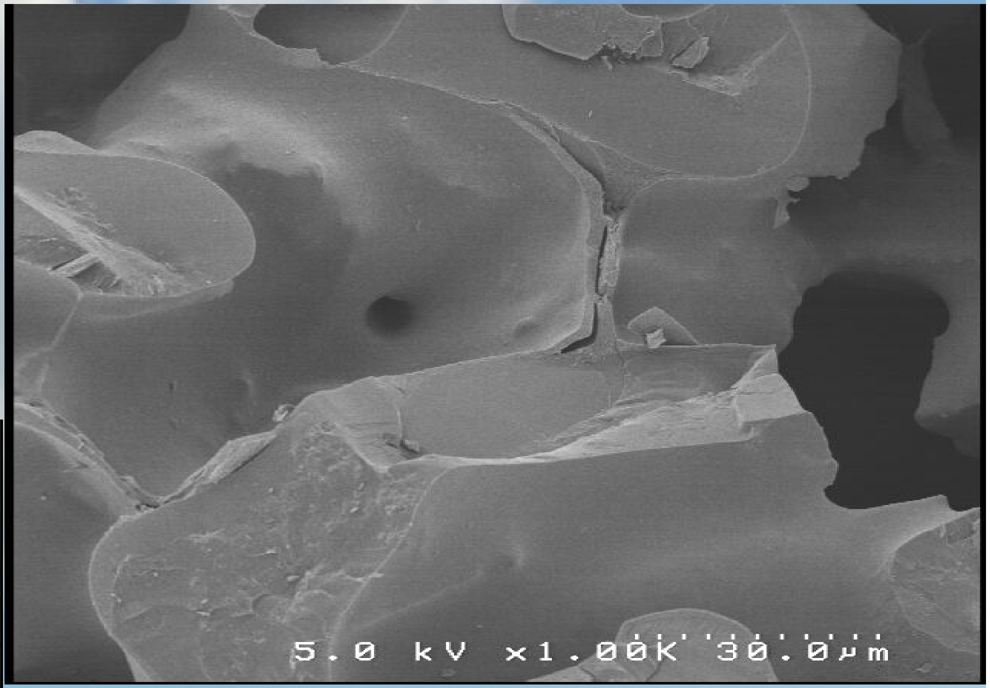
# MULTI IMPREGNATION RESULTS

4M18SiC3092-3 (coupe)




4M18SiC3092-2 (coupe-surface)




4M18SiC3092-9 (cloison)

* Layer thickness is around 2µ after depositio

*** Cracks can appear up to 4 layers**

INCORPORATION OF CATALYST

WITH THE SLURRY FORCING METHOD

with collaboration of IFP (French Petroleum Institute)

Incorporation of a NOx-trap type catalytic formulation inside the porosity of a SiC wall flow filter (WFF) has been performed, forcing a slurry of the catalyst through the substrate.

# SLURRY PREPARATION

NOx trap formulation :

Precious metal Pt, Pd, Rh

Catalyst oxide :BaO - $CeO_2$ - $ZrO_2$ - $Al_2O_3$

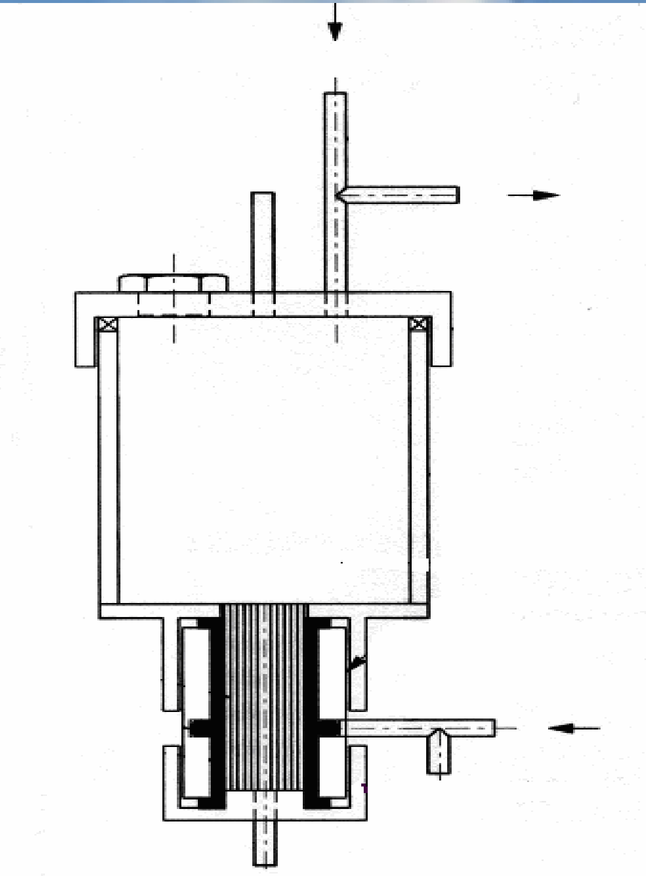
Adjust the viscosity and particle size distribution

- fluid enough
- $Dv_{90}$/Dpores < 0.25

$Dv_{90}$ : measured by laser diffraction

Dpores : mean pore size of the WFF, measured by Hg porosimetry

# IMPREGNATION



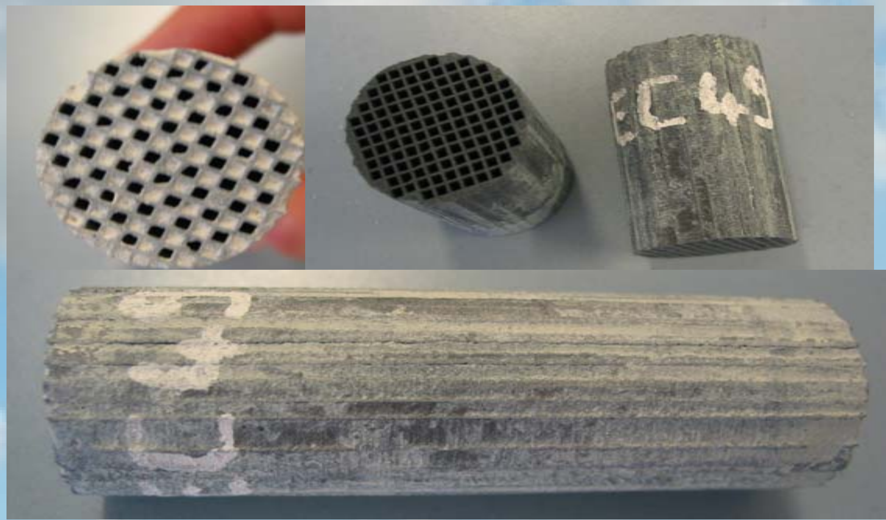
impregnation unit

SiC cores characteristics:

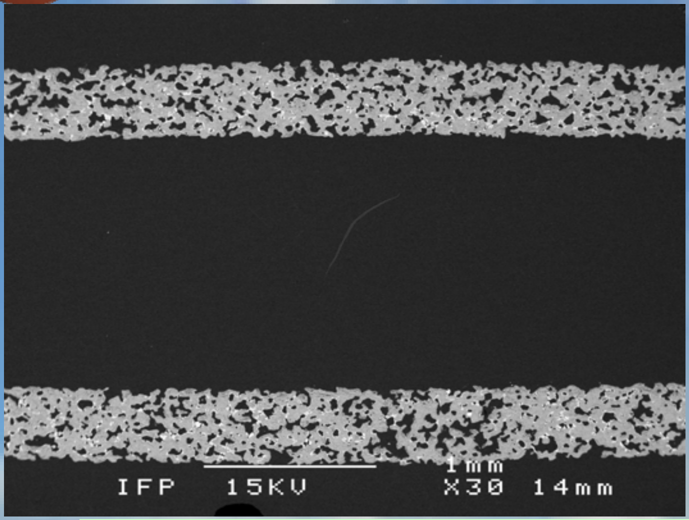
1" diameter, 3" length, 180 cpsi,

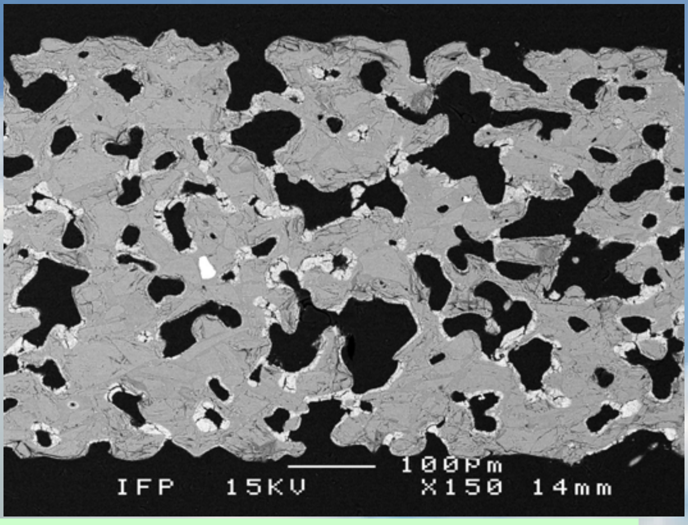
20 µm mean pore diameter,

55% porosity



# CHARACTERISATION / TESTING

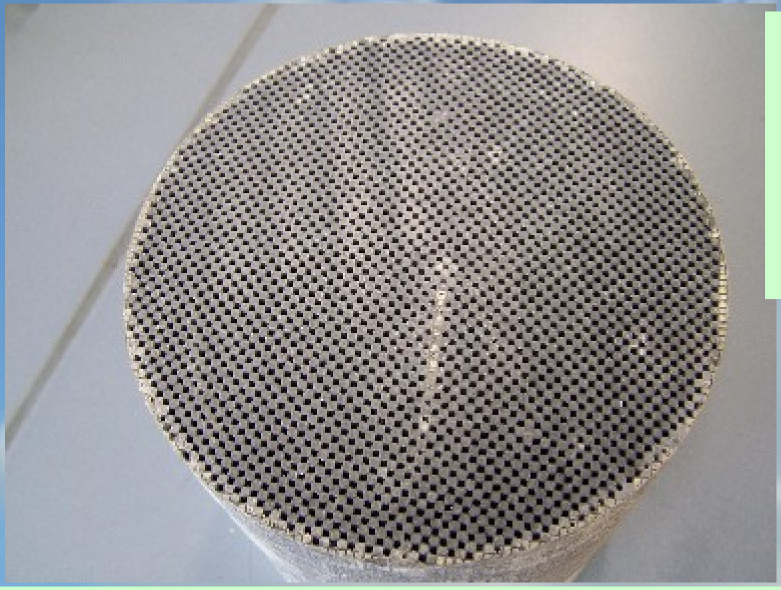



SEM pictures of a core loaded with 159 g/l catalyst

- Washcoat inside the porosity
- Whole SiC surface coated
- Thickness 1 to 8 µm

# SCALE UP



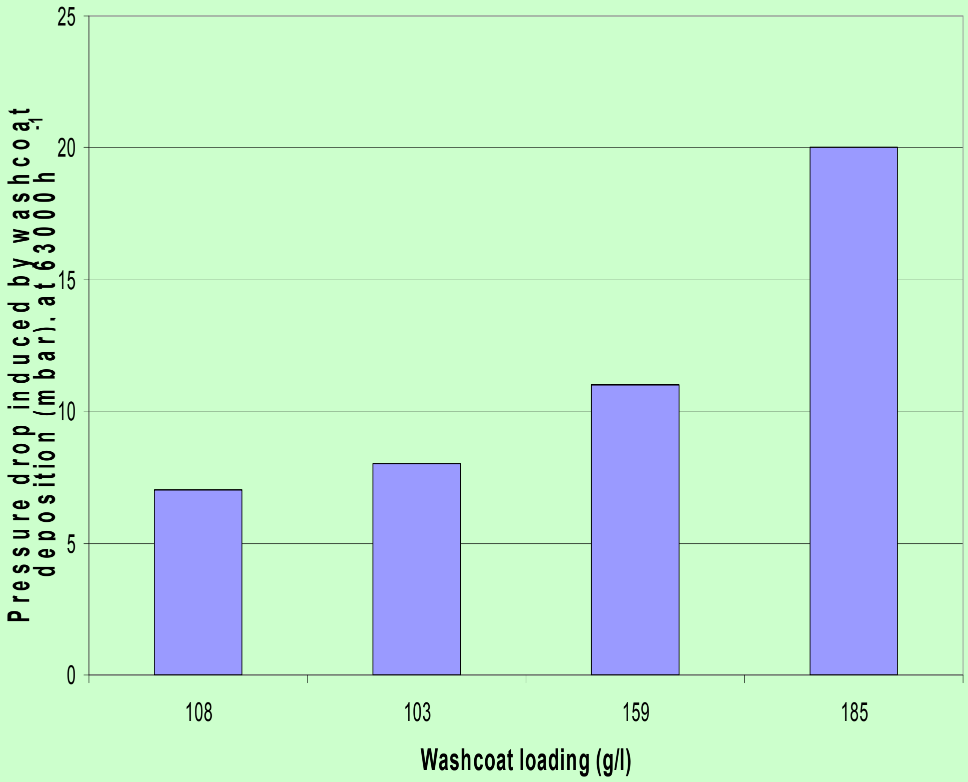
5"66 diameter, 6" length, 180cpsi, 19 µm mean pore diameter, 50% porosity

washcoat loading : 190 g/l

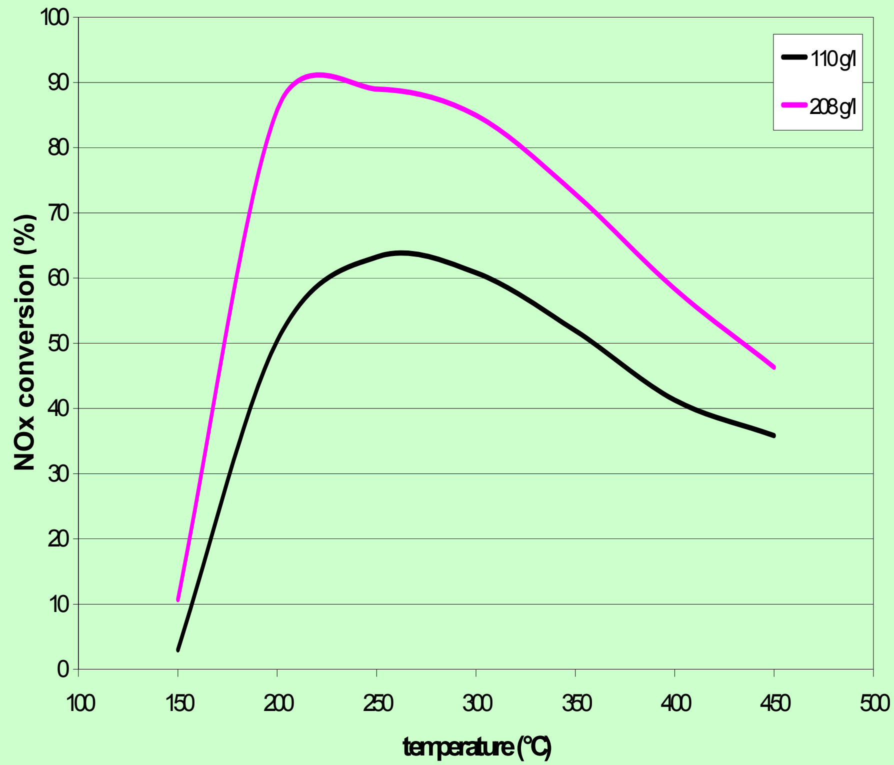
washcoat-induced pressure drop : 15 mbar (50000 $h^{-1}$)

Scale up succeeded

- high loading
- low pressure drop




Pressure drop as a function of washcoat loading




Synthetic gas bench testing of deNOx activity

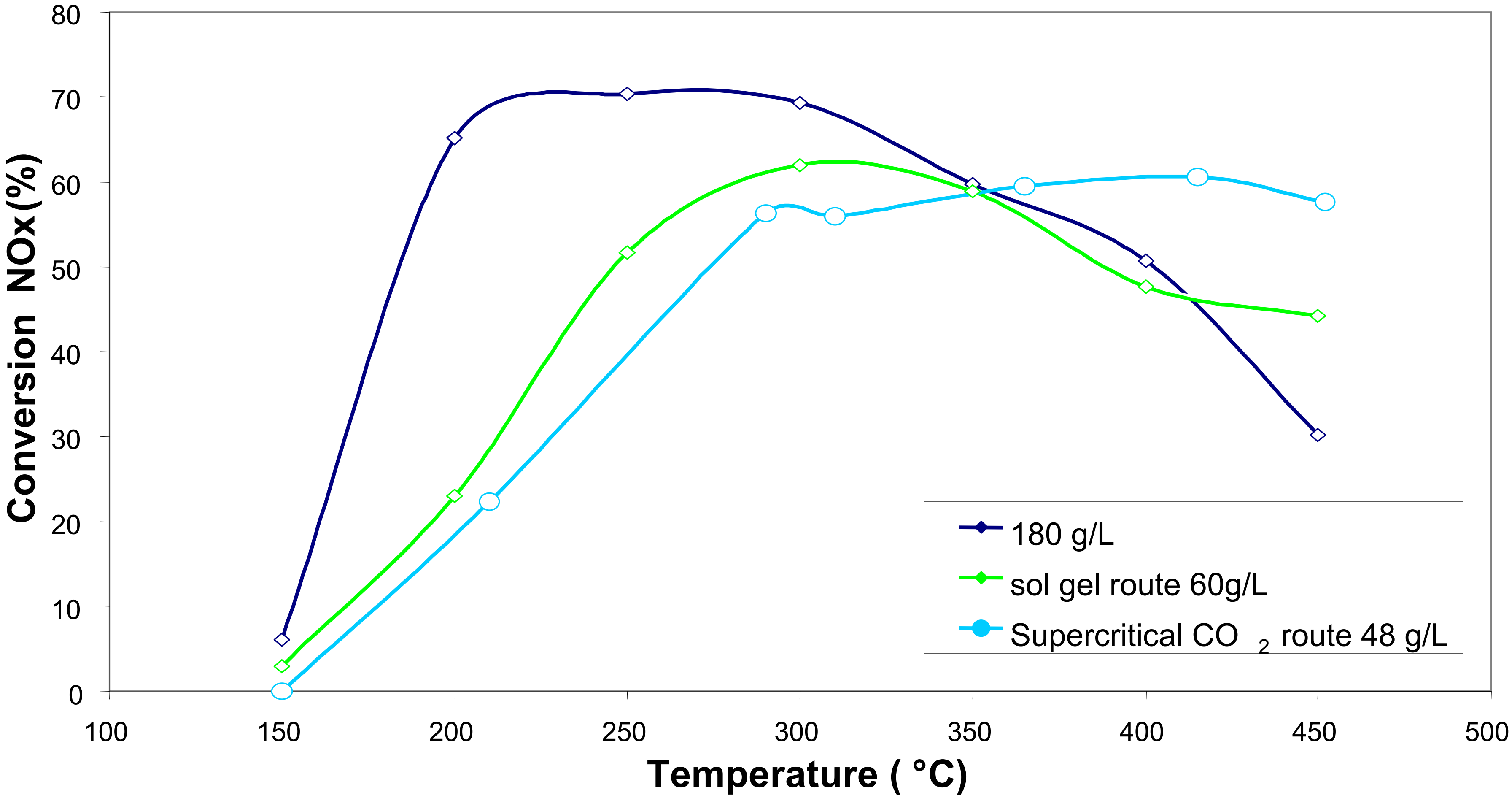
- Low pressure drop at high loading
- DeNOx activity comparable to that of flow through monoliths

# CONCLUSIONS OF IFP/CTI METHOD

- Versatile method to deposit any type of catalytic formulation inside the porosity of wall flow filters
- Method has been scaled up to real size filter
- Key point resides in adapting the slurry's particle size distribution to the mean pore size of the substrate.

# FIRST QUALITATIVE CATALYSIS RESULT FOR NOx CONVERSION

## COMPARISON OF THE DIFFERENT METHODS



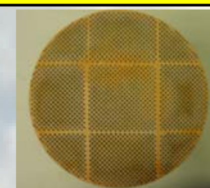
# OTHERS ' IMPREGNATION TRIALS WITH THE SAME TECHNOLOGY

**Zeolith impregnation of CTI SiC DPF for DeNOx function using SCR method.**

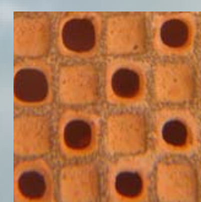
# IMPREGNATION

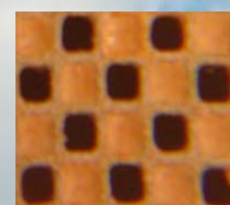
| N° Filter CTI | CTI 039/06 | CTI 031/06 | CTI 033/06 |
|---|---|---|---|
| N° Filter IFP | **EC89** | **EC90** | |
| Mass before impregnation (g) | 1817 | 1877 | 1811 |
| Mass after impre + Calcination IFP (g) | 2156,4 | 2059,5 **non calcined** | **Non** |
| Mass after impre + Calcination CTI 500°C/2h00 (g) | | 2048,2 | |
| Masse addes cata in g | 339,4 | 171,2 | **Impregnated** |
| Volume of the filter in liter | 2,47 | 2,50 | 2,47 |
| **Content cata in g/liter** | 137,41 | 68,48 | 0 |

Sight face



Sight cells

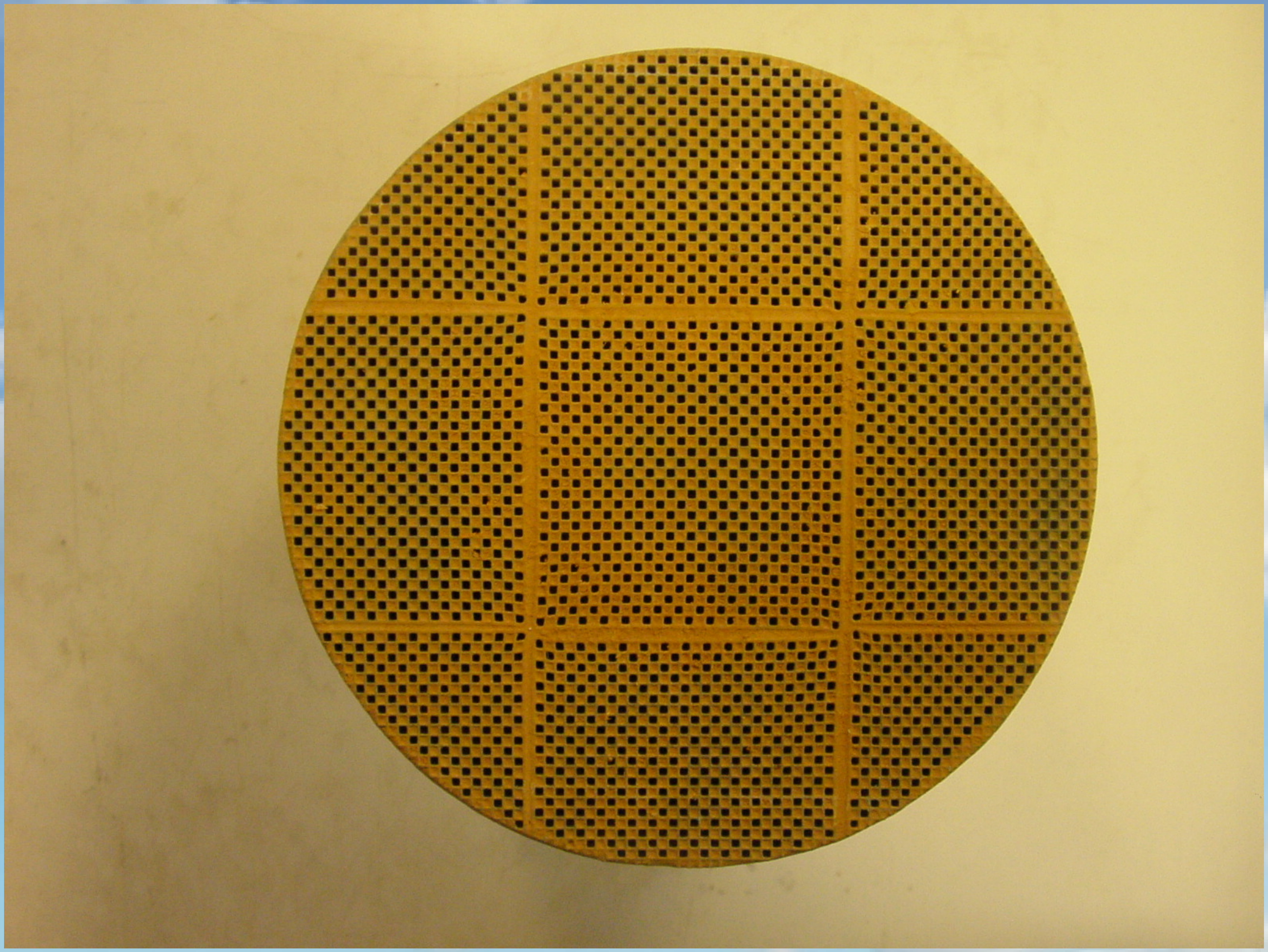




ΔP - mb

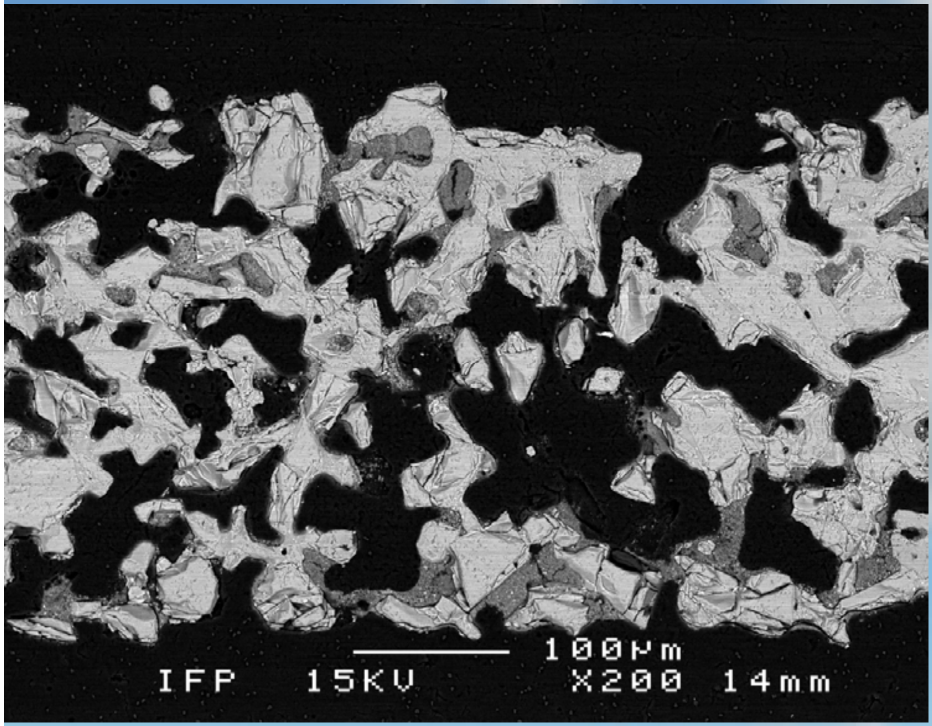
| | | | | |
|---|---|---|---|---|
| Stream of air co-current to the direction of impregnation | Flow 100 $m^3/h$ | 7 | 5 | 3 |
| | Flow 200 $m^3/h$ | 16 | 12 | 9 |
| | Flow 300 $m^3/h$ | 27 | 21 | 16 |
| Stream of air against the current of the direction of impregnation | Flow 100 $m^3/h$ | 6 | 5 | 3 |
| | Flow 200 $m^3/h$ | 15 | 13 | 9 |
| | Flow 300 $m^3/h$ | 26 | 22 | 16 |

# PHOTO OF THE CTI'S DPF AFTER IMPREGNATION

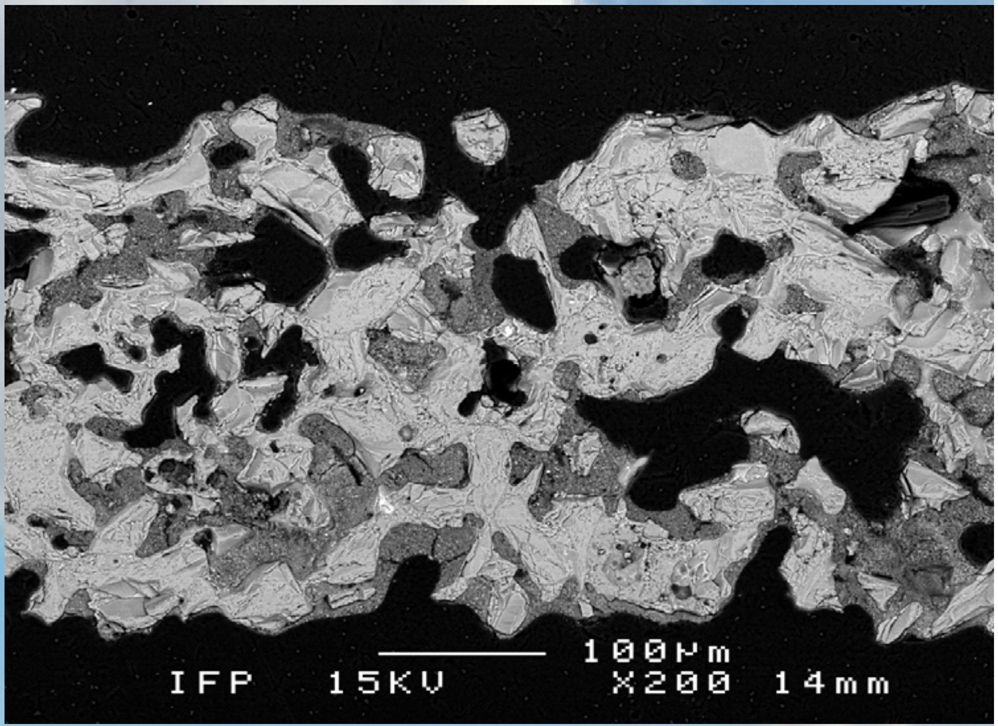


# IMPREGNATION
# MEB PHOTO

**Total zeolith deposition is inside the pore. There is no layer at the surface. Porous cavity of the support are sometimes plugged by the zeolith depending on the concentration.**

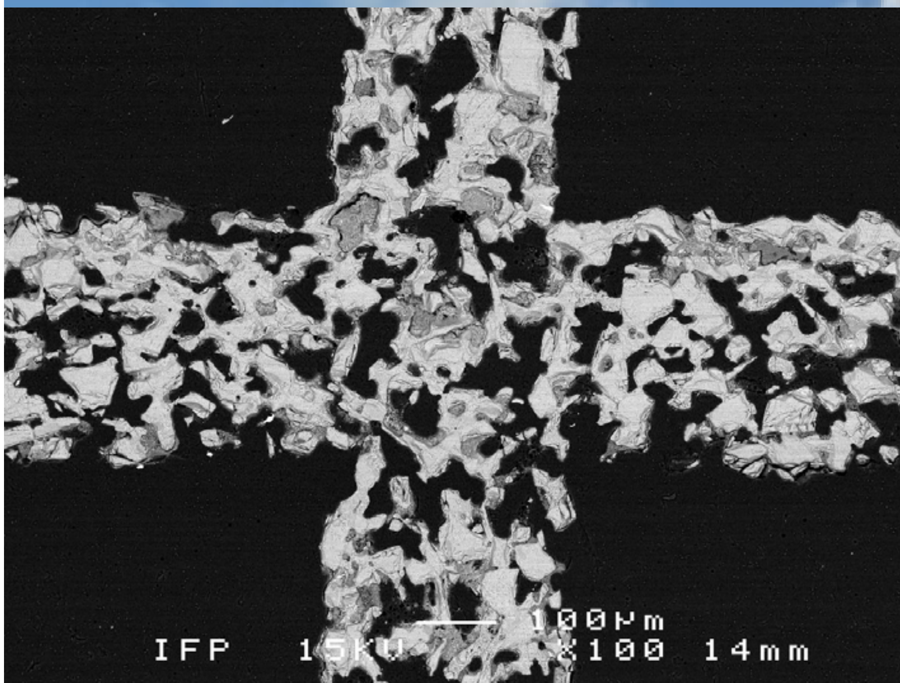



68g/l

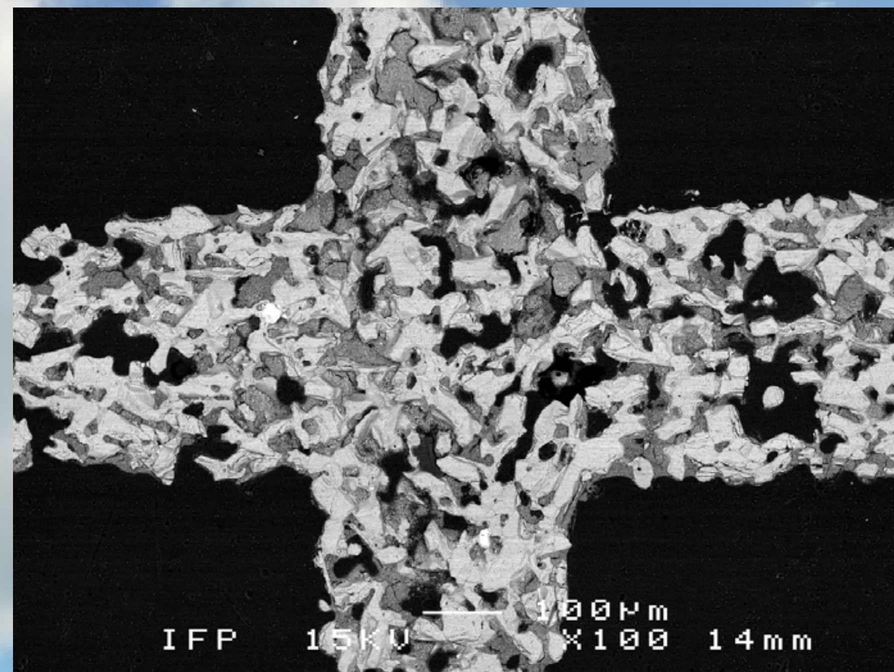



279g/l

# IMPREGNATION
# MEB PHOTO



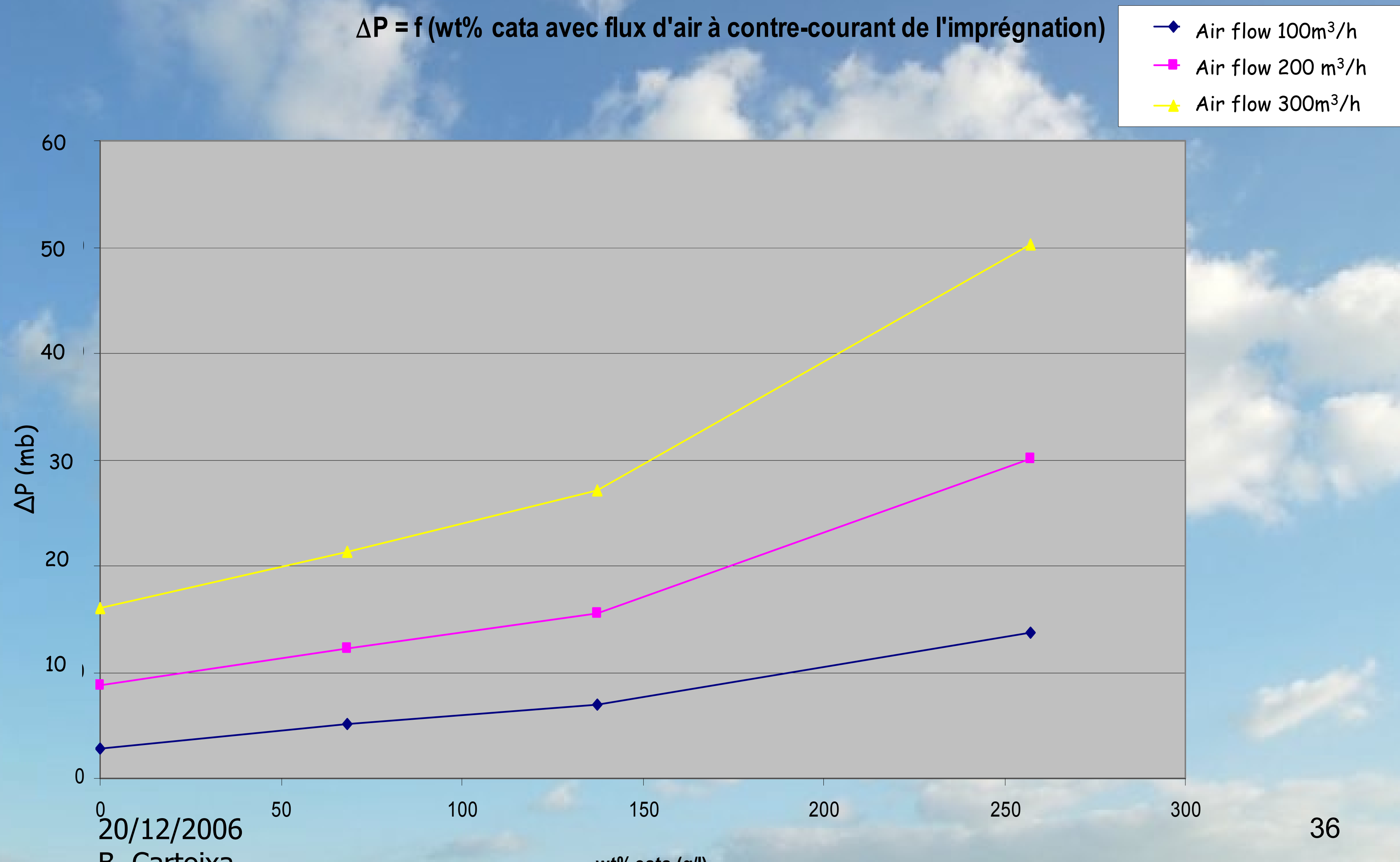

68g/l



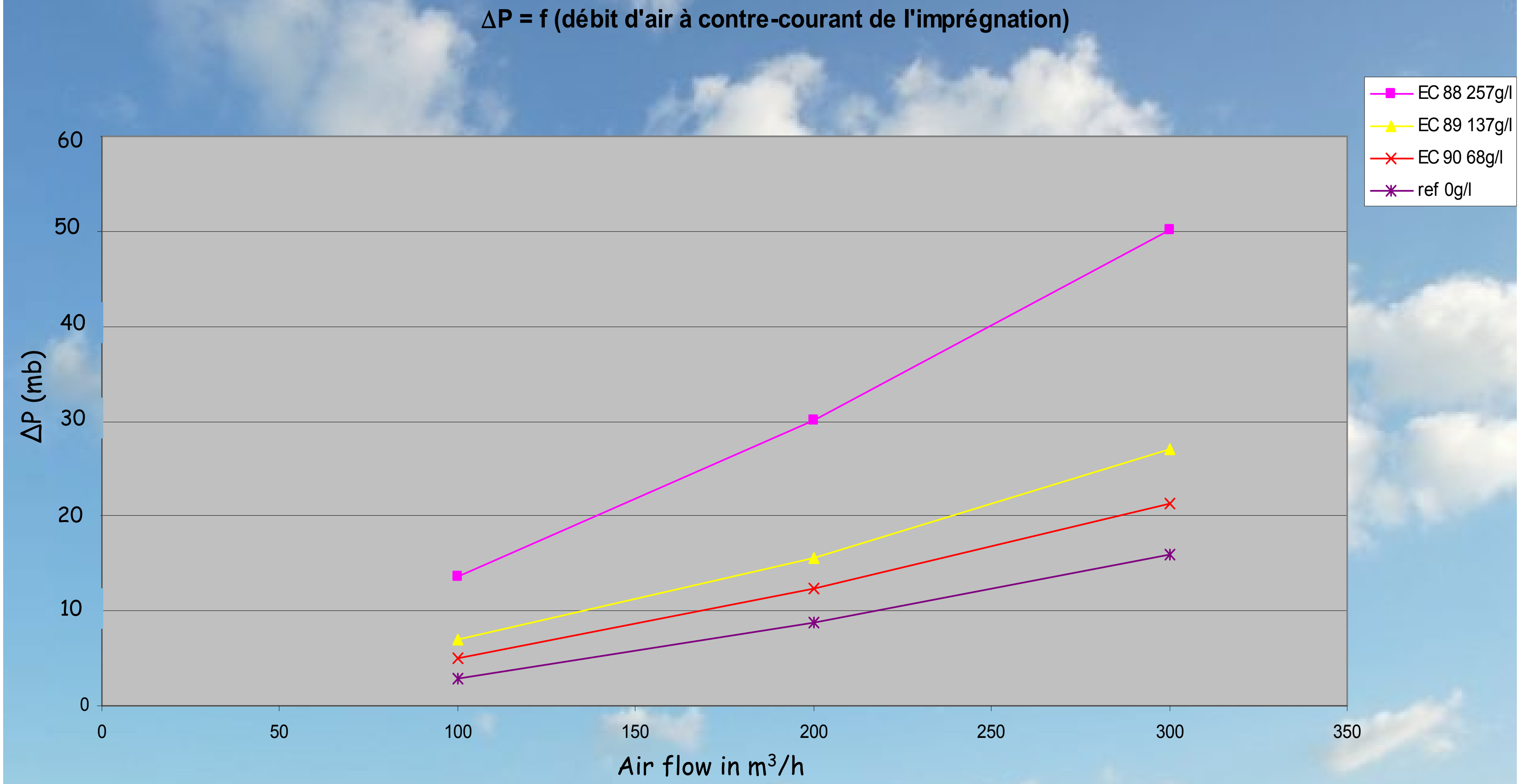

279g/l

Excellent catalyst penetration with partial plugging of some pores, depending of the slurry concentration

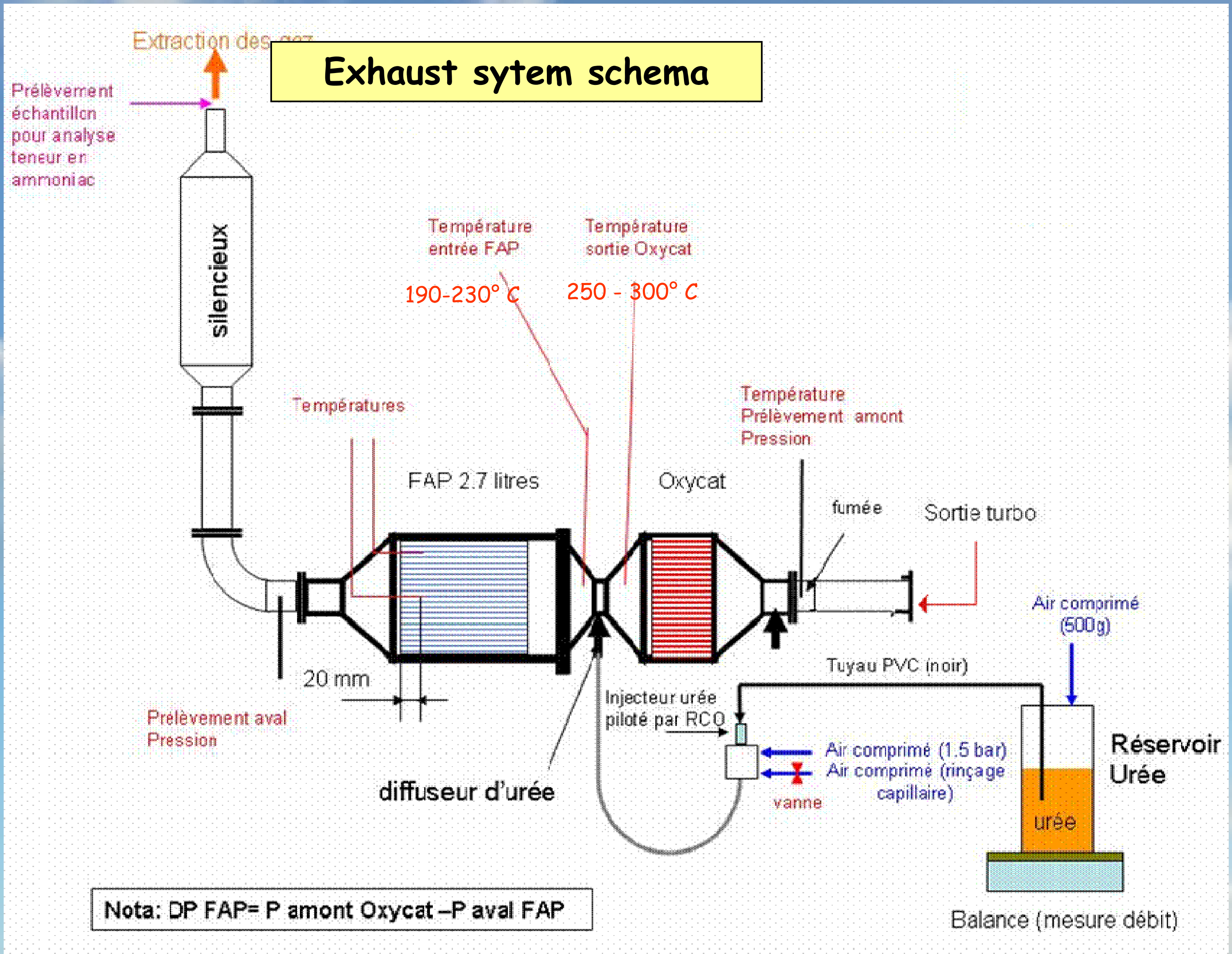
# IMPREGNATION
# BACK PRESSURE MEASUREMENT



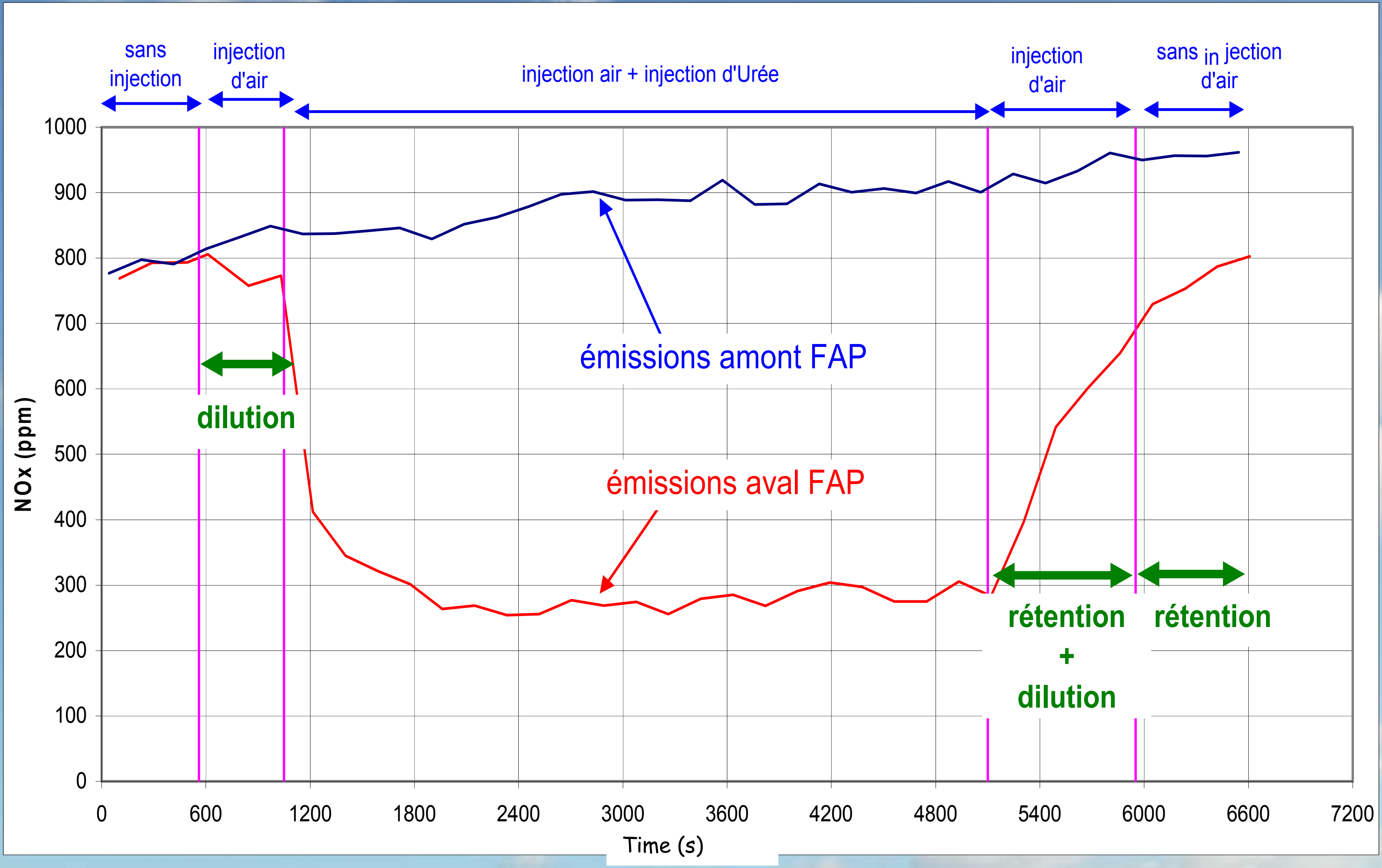
# IMPREGNATION CHARACTERISATION DP



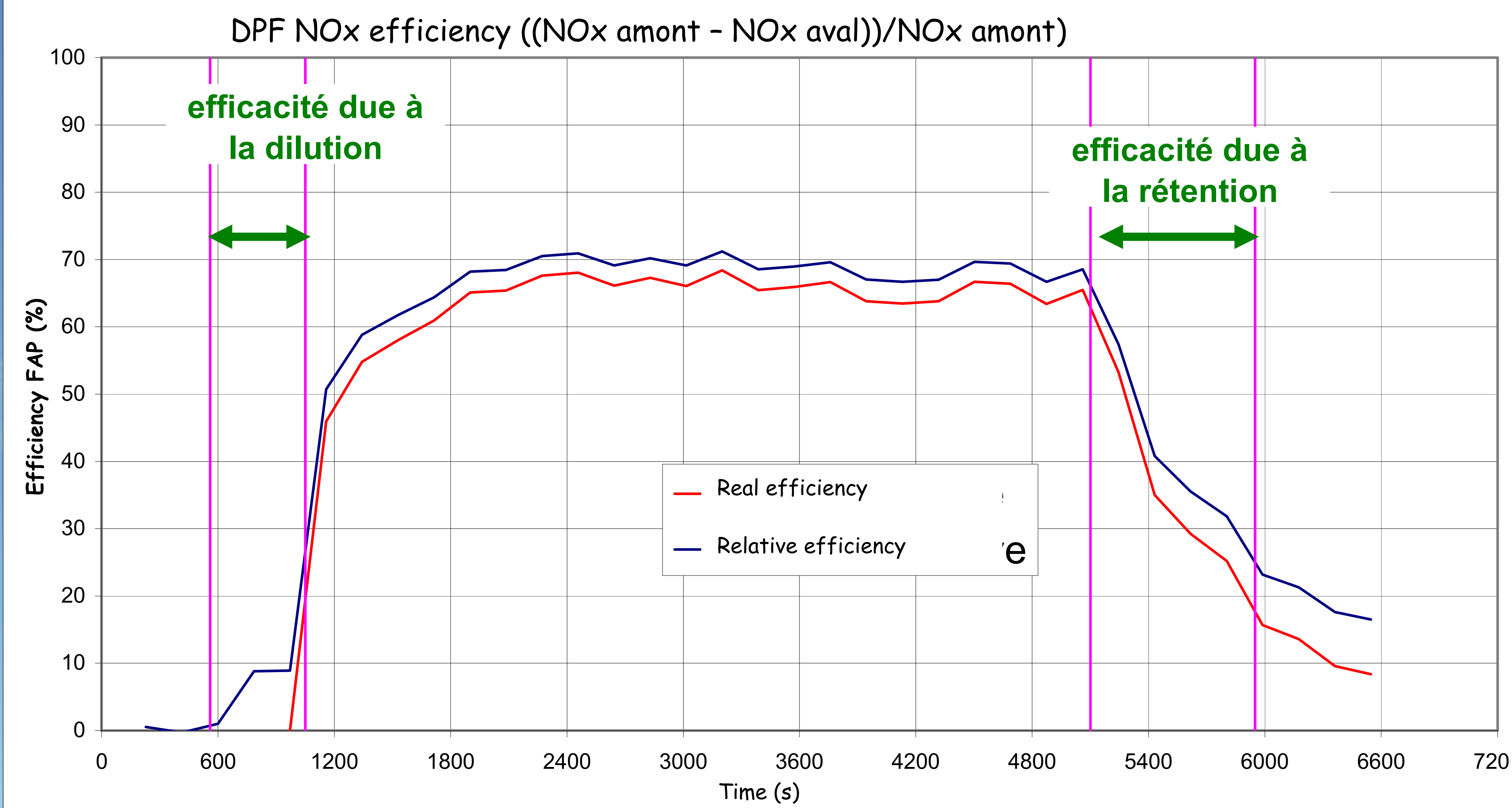
# • MOTOR BENCH TEST FOR ZEOLITH DeNOx DPF Content 137 g/l



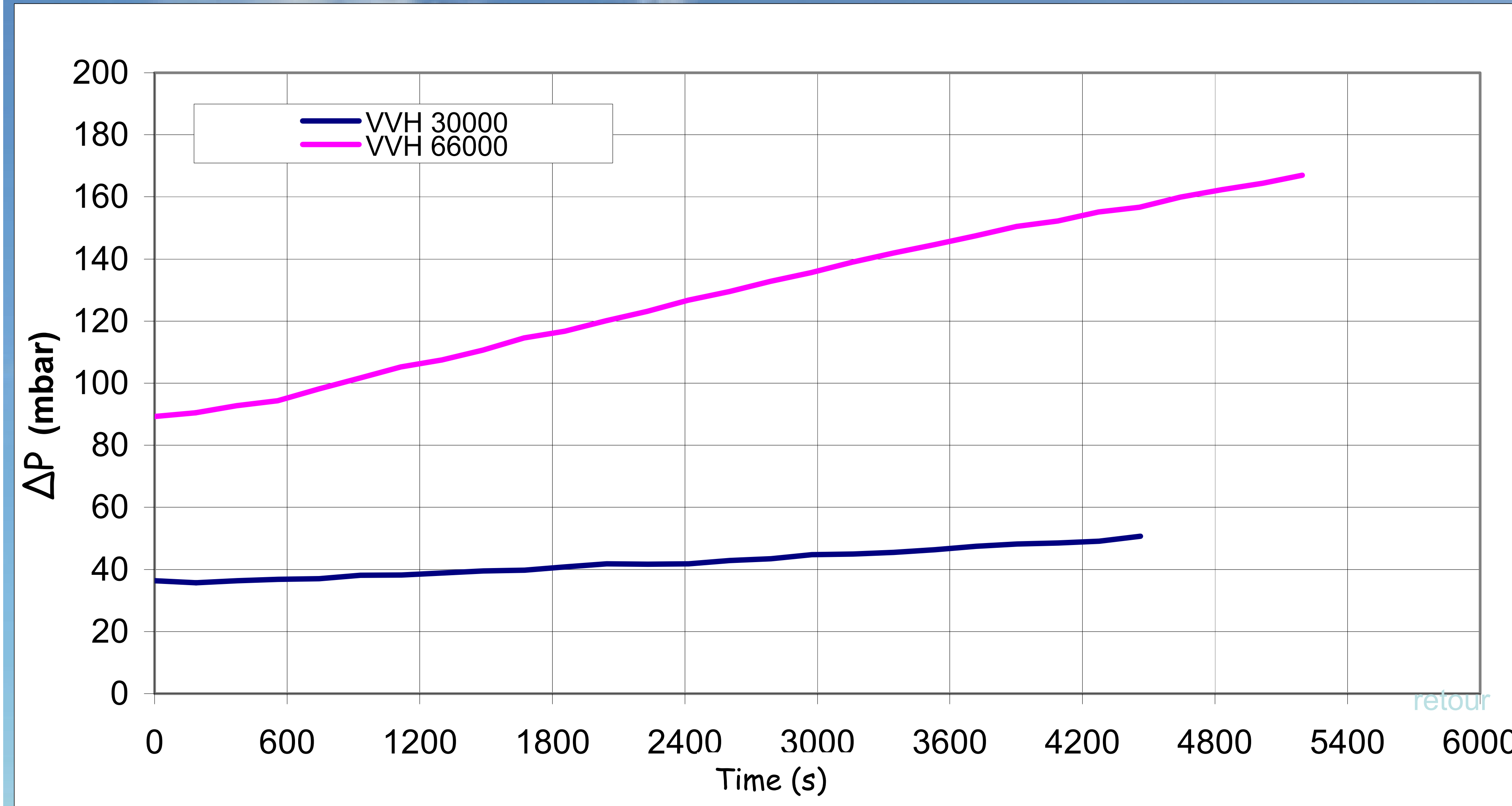
# NOx EMISSION
# BEFORE AND AFTER DPF



# REAL AND RELATIVE EFFICIENCY



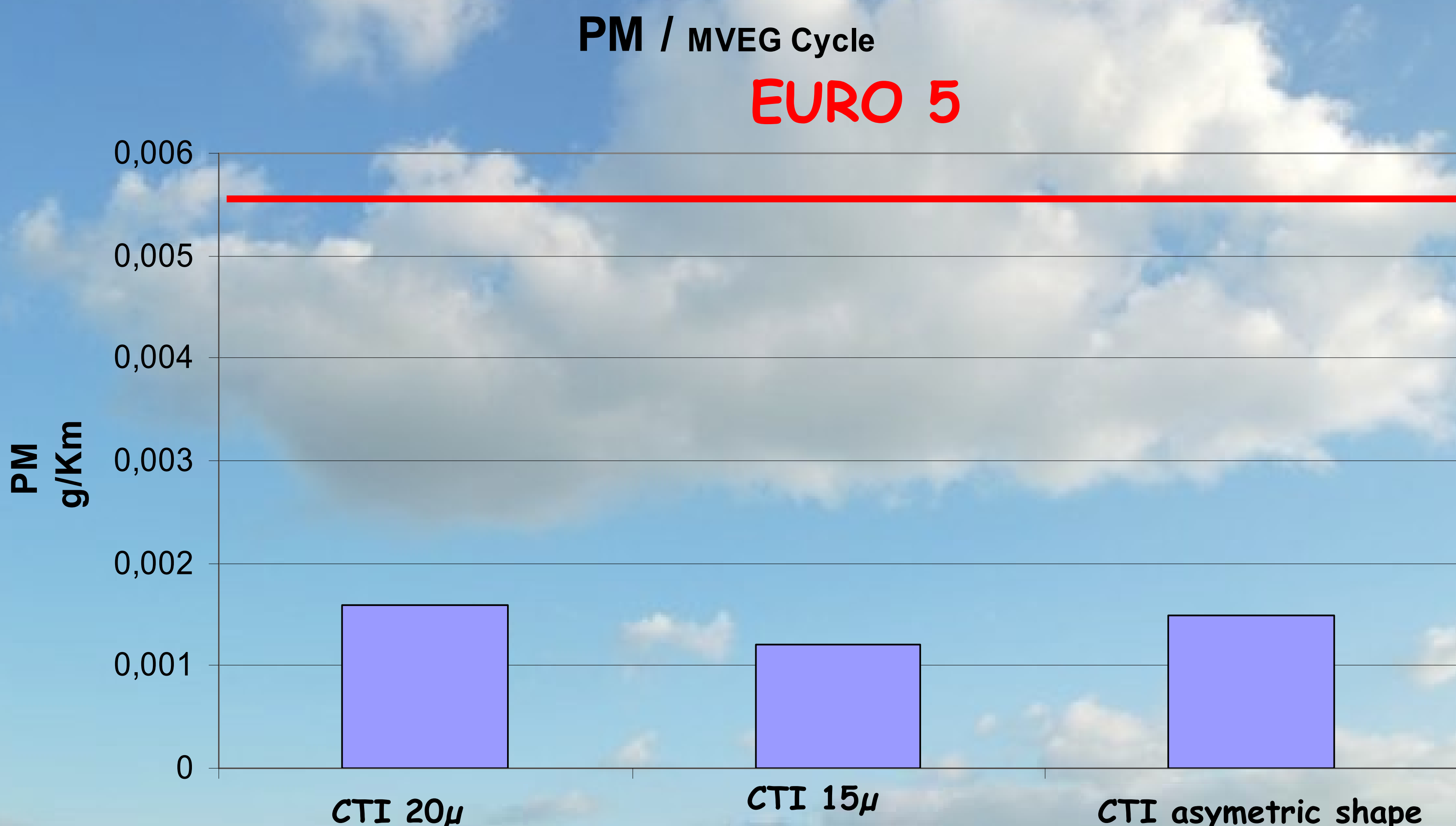
# DELTA P EVOLUTION OF THE DPF



# PM EFFICIENCY OF THE PARTICULATE FILTER

**(test made by IFP)**

**The CTI product when it is virgin (worst condition) is 3 to 4 time below the upper limit requested for Euro V in 2009 (SMPS test done by IFP).**



# CONCLUSIONS

- The 3 different impregnation methods shows a real industrial potential for 4 way catalysis technology or separatively CatOx + DPF DeNOx function.

- Today the most easy and cheapest method seems to be the slurry forcing technology (Patent IFP – CTI)

- CTI's composite SiC product could be easily impregnated with catalyst with very low increase of back pressure.

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# CERAMIQUES TECHNIQUES ET INDUSTRIELLES S.A.

THANK YOU FOR YOUR ATTENTION

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