Design of a High Porosity SiC Substrate for Future Euro VI Applications

Thomas Wolff[1], Holger Friedrich
AFT Auto Filter Technology GmbH, Bayreuther Str. 9, D-95482 Gefrees, Germany

Shahrokh Hajireza
Thermal & Combustion Technology, Hulda Rasks Vag 11, 237 42 Bjarred, Sweden

Abstract: Due to the increasing demand for space and cost reductions in future Euro VI diesel exhaust systems, there is a need for diesel particle filter (DPF) substrate materials, which are capable of receiving high amounts of wash coat loadings for the additional integration of a DeNOx-functionality. In order to have a base material composition which can easily be modified to meet the special demands in respect to soot mass limit, filtration efficiency, low back pressure and coatability of these future applications, a new SiC substrate was developed. The technology of this new material is based on the reaction forming of SiC by siliconizing carbon. The corresponding, new developed manufacturing process leads to highly porous structures with porosities in the range of 55% - 65% and a unique sponge like morphology of the pore structure, which provides high filtration efficiency even at these high porosities and large pore sizes in the range of 22µm.

The aim of this paper is to give an introduction to this new kind of substrate material. In examples we will show, that it is possible to create materials with membrane like structures to achieve high filtration efficiencies in both the new and a fully regenerated state, as well as to create an open surface structure for applications with focus on low back pressure and high wash coat loadings at high filtration efficiencies. Experimental studies combined with simulation results show the influence of the porosity and the cell design of this material on peak temperature and thermal gradients during severe regeneration modes. Both are important parameters for the DeNOx catalysts which have a restricted temperature stability.

Introduction

In order to be able to cope with future emission legislation and to downsize the whole exhaust system there is the need of further improvement of the DPF substrate materials with respect to reduced back pressure, filtration efficiency, and the capability to receive high wash coat loadings. The best solution for these types of filters would be a material with a high porosity, a high thermal conductivity and a high soot mass limit. A highly porous SiC would be such a material. SiC substrates are available on the basis of recrystallized SiC[2] or in form of silicon bonded SiC[3]. However based on their pore structure a detrimental characteristic of these materials is that they need – at large pore diameters in the range of 25µm and high porosities in the range of 60% - a given loading of soot to achieve a filtration efficiency of more than 90%. An approach to bypass this dilemma is described by Furuta et al[4]. They present a substrate with an additional membrane on the substrate surface to achieve high filtration efficiencies and advanced loading characteristic by pure surface filtration. The disadvantage of this approach is a much higher back pressure level than for the corresponding materials without the inlet membrane, and the cost impact from the additional manufacturing step.

In contrast to that the presented reaction formed XP-SiC substrate material inherently combines the advantages of a highly porous material with large pores and with the filtration and loading characteristic of the solution with the inlet membrane. This can be explained by the special microstructure of this new type of substrate material.

---

[1] To whom correspondence should be addressed

[2] Mey D., Andy P., Tardivat C., Augier C., and Briot A. "Improved DPF Substrate for Washcoat Accomodation", SAE technical paper 2009-01-0288

[3] Ucgikawa A., Uchida Y., Otsuka A., Harada T., Hamanaka T., Nagashima K., and Nagata M. "Material Development of High Porous SiC for Catalyzed Diesel Particulate Filters", SAE technical paper 2003-01-0380

[4] Furuta Y., Mizutani T., Miyairi Y., Yuki K., and Kurachi H., "Study on Next Generation Diesel Particulate Filters", SAE technical paper 2009-01-0292

Reaction forming technology and material characteristics

In contrast to the currently available SiC substrates, which use SiC-particles as raw materials, XP-SiC is made from the precursor materials silicon and carbon. These materials are extruded together with aluminum as an alloy element to silicon together with some additives into a honey comb structure and then they are dried and heat treated to form the reaction formed SiC. This heat treatment is performed under inert atmosphere. A highly porous material with a unique micro pore structure is created which we call XP-SiC. Due to the volume reduction by reaction forming silicon and carbon to silicon carbide and the fact, that the molded structure starts at values of 25% to 30% for the porosity after the pyrolysis process, the porosity of the XP-SiC materials is in the range of 50% to 70%. The pore size distribution of this material has typically a broad feet and a narrow peak. The mean pore diameter can be adjusted by the choice of the mean particle diameter of the starting materials silicon and carbon and the applied heat treatment.

The basic material properties of XP-SiC have been investigated using the standard characterization methods. A summary of measured data can be seen in table 1. The values listed have been determined for a material with a mean pore diameter of 15µm and a porosity of 55%.

Table 1: Material characteristic for a 15µm, 55% porosity material in comparison to a R-SiC with 22µm pore diameter and 48% porosity (Notox MD200HP)

	XP-SiC	R-SiC
Isostatic strength, MPa	5	6
Young modulus, GPa	23	30
Heat capacity (RT), J/gK	0.787	0.750
Heat capacity (400℃), J/gK	1.188	1.250
Thermal Conductivity (RT), W/mK	11	~40
Thermal Conductivity (400℃), W/mK	8	15
Coefficient of thermal expansion (20-1000℃), 10^{-6} 1/K	4,7	4.7
Maximum temperature, ℃	1400	1400

Performance and comparison to a standard SiC

The performance of a XP300 with 60% porosity and 22µm pore diameter with a catalytic coating for passive regeneration called EnviCat2054 was investigated in detail. The coating was applied at an amount of precious metal of 50gPt/cft to the XP-SiC substrate. The size of the filter was 5,66''x7''. The impact of the coating on the back pressure was very low, i.e. less than 3% at a cold flow of 600m³/h. In order to evaluate the substrate material a comparative SiC-filter with the same cell density of 300cpsi, but with a lower cell wall thickness of 12mil and lower values for the porosity and the pore size was used in the same test procedure. The catalytic coating of the standard SiC filter was designed for a LDD application, i.e. for active regeneration. Both filters, had the same size of 5,66''x7''. The tests have been performed at the lab of LAT in Thessaloniki, Greece. The test setup is described in detail in the paper of Hajireza et al[5]. The engine used was a PSA DW12 2.2l EURO 3. Both filters were tested with a Cordierite DOC in front of the DPF. The DOC volume was 0.8 l (diameter: 144mm and length: 51mm) and is normally used together with the comparative standard SiC filter in the LDD application. The filtration efficiency was measured at a low soot emission. To achieve this, the engine was run at a mass flow rate of 150 kg/h and an exhaust temperature of 200℃. At that temperature the catalyst on both filters was not active, i.e. the results were not influenced by any catalytic soot burning. The results of these tests have been verified in a second test at Cambustion, where soot from a diesel burner (DPG) was used.

The striking result is that the filtration behavior is similar to that of the standard SiC, although the standard SiC had a much lower porosity and a lower mean pore diameter. This seemingly contradiction can be explained by the special pore size distribution of the XP-SiC and the geometry of the pores and pore channels in the filter walls.

In addition, loading and incomplete regeneration cycles at Cambustion have shown a much better correlation between soot load and corresponding backpressure. This is an effect of the less pronounced depth filtration of the XP-SiC substrate.

Durability check

In order to check the durability of the XP-SiC a 100-cycle test was performed at the South west ResearchInstitute (SwRI) in San Antonio. A full description of this test can be reviewed in the publication of

---

[5] Hajireza S., Johannesen L.T., Wolff T., Koltsakis G., Samaras Z., Haralampous O., "A Modeling and Experimental Investigation on an Innovative Substrate for DPF Applications", SAE technical paper 2010-01-0891

Zahn et al[6]. The engine used was a 2.2l PSA DW12. In summary 103 regenerations were performed, 80 controlled regenerations at an inlet temperature of 610℃, 8 incomplete regenerations at an inlet temperature of 430℃ and 15 uncontrolled regenerations with an inlet temperature of 610℃ before drop to idle. The filtration efficiency was checked after every 15 cycles using a smoke meter. In addition the integrity was checked using a boroscope. The soot loading for each cycle was 8 ±0.5g/l. The filter tested was again a XP-SiC with 300cpsi, 13mil wall thickness, 22µm of mean pore diameter, 60% porosity and the dimension 5,66''x7'' with the catalytic coating EnviCat2054. The tests were performed with a DOC in front of the filter and supplemental fuel injection in order to get the desired regeneration temperatures. Together with this DOC the filter had a balance point of 300℃.

Depending on the effective soot load the peak temperatures inside the filter during the uncontrolled regenerations have been in between 800℃ and 1070℃ . The maximum thermal gradient which could be observed was at 100℃/cm in radial direction at the filter outlet. As the final result no decrease in filtration efficiency and no appearance of any cracks could be observed.

Simulation

The high porosity of this material can be used for high wash coat loadings, especially for the integration of DeNOx functionality in form of SCR catalysts or a NOx storage catalyst. These type of catalysts are known to be sensitive against high temperatures. The results for the uncontrolled regenerations at SwRI have shown, that a material with 60% porosity even at a large cell wall thickness of 13mil shows already at 8g/l a peak temperature of more than 1000℃. We therefore investigated the peak temperature at different high porosity levels and cell wall thicknesses by simulation work. We used the commercial code Axitrap for detailed simulation of severe regeneration. The effect of the catalytic coating on the thermal behaviour of the filter was taken into account and for the calibration of the chemical parameters, we used the engine test bench data from SwRI, where the internal temperature in the filter was measured by thermocouples on different locations. The porosity varied from 58% up to 65% and the cell wall thickness from 11.5mil up to 13mil. As one result the peak temperatures for all cases were higher than 1000℃ and for the substrate with the lowest thermal weight it was close to 1250℃. In addition the influence of the heat up ramp before drop to idle on maximum wall temperature and thermal radial gradient was investigated.

As an additional case a XP300 with 60% porosity and a SCR washcoat was investigated. In the simulation code, we replaced the precious metal coating by a Fe-zeolite SCR coating with an amount of 100g/l. Calibrated Fe-zeolite SCR reaction mechanism according to Koltsakis et. al.[7] were used. Three reactions for standard, fast and slow SCR as well ammonia oxidation was implemented in the model. The thermal field inside the filter was predicted in the same way as for the previous cases. As the result we saw a slight change in the maximum wall temperature and a strong decrease in the maximum radial thermal gradient.

Conclusions

A new type of SiC substrate has been developed which can cope with current and future emission legislation. Its key characteristics are its high filtration efficiency at low back pressure levels together with a low back pressure increase under loading (negligible wall filling) combined with a high porosity and a reduced thermal weight which enables easy light off at acceptable soot mass limits. The unique microstructure of this material, which is based on its special processing technology, is the basis for its filtration performance and the new combination of filter key properties.

One advantage of this new material is the usage of the high porosity for the integration of additional wash coat with DeNOx functionality. Simulation work based on the results at SwRI predicts high peak temperatures up to 1250℃ for high porosity levels in combination with precious metal catalysts. The results for a model of a XP-SiC substrate with 60% porosity and a SCR catalyst coating of 100g/l indicate that the substrate itself survive severe regenerations at a soot load level of 8g/l but that the catalyst will be probably damaged by peak temperatures, which are still above 1000℃.

Contact:

AFT Auto Filter Technology GmbH, T. Wolff, e-mail: two@notox.com, phone: +49 9254 275 99 11
Thermal & Combustion Technology, S. Hajireza, e-mail: dr_hajireza@hotmail.com, phone: +46 707 551 164

---

[6] Zahn R., Eakle S., Spree K., Li C., and Mao F., “Validation Method for Diesel Particulate Filter Durability”, SAE technical paper 2007-01-4086

[7] Koltsakis, Koutoufaris, and Haralampous, “Evaluation of multi-functional deNOx systems using advanced simulation tools”, MinNOx conference 2010

AUTO FILTER TECHNOLOGY

Design of a High Porosity SiC Substrate for Future Euro VI Applications

Thomas Wolff, Holger Friedrich
Shahrokh Hajireza

14th ETH-Conference on Combustion Generated Nanoparticles
August 1st – 4th 2010

Motivation for a new SiC type

Requests for future applications (Euro 6)

- High wash coat levels for integration of additional functions
- High filtration efficiency with max 6 × 10^{11} km^{-1} (PMP method, NEDC test)
- Applications with high SML ~8g/l

Drawbacks of "current" solutions

- High filtration efficiency only by small pores or additional filtration layers (membrane filters)
- Low soot mass limit for most high porosity materials
- Deficient correlation: porosity (pore size) ↔ filtration efficieny

→New type of SiC with unique microstructure

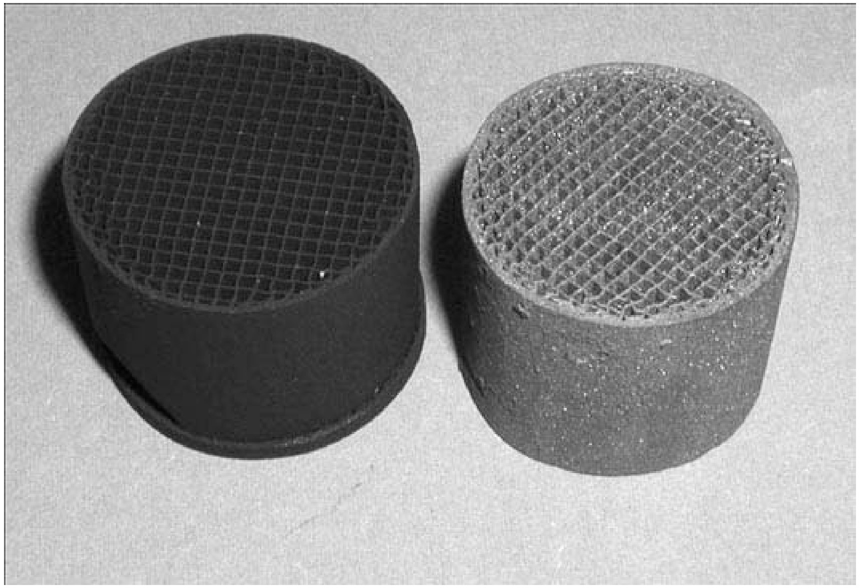
Outline

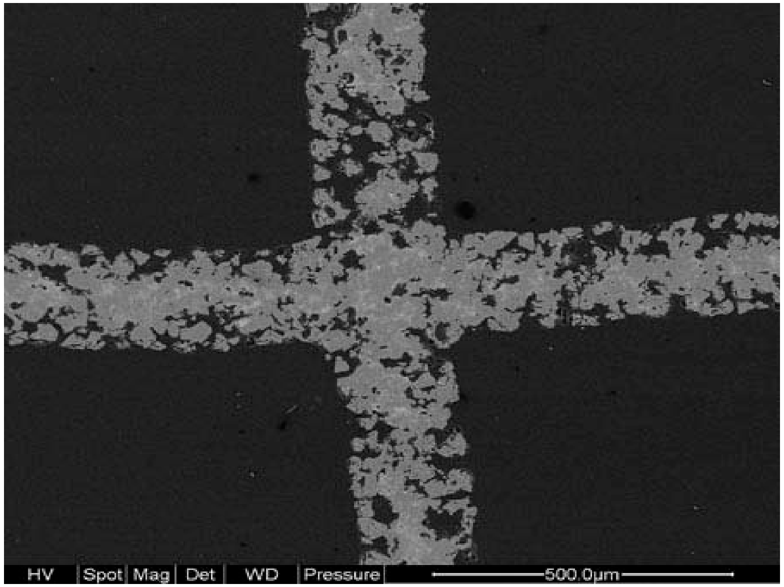
- Process and material / substrate characteristics
- Performance in comparison to a standard SiC
- Durability check
- Simulation:
    - Impact of high porosity on thermal behaviour
    - Model for a SCR coated XP300 with 60%

Classic reaction forming process

$$\mathbf{Si}_{\text{infiltrated}} + \mathbf{C}_{\text{resin}} \rightarrow \mathbf{SiC}$$

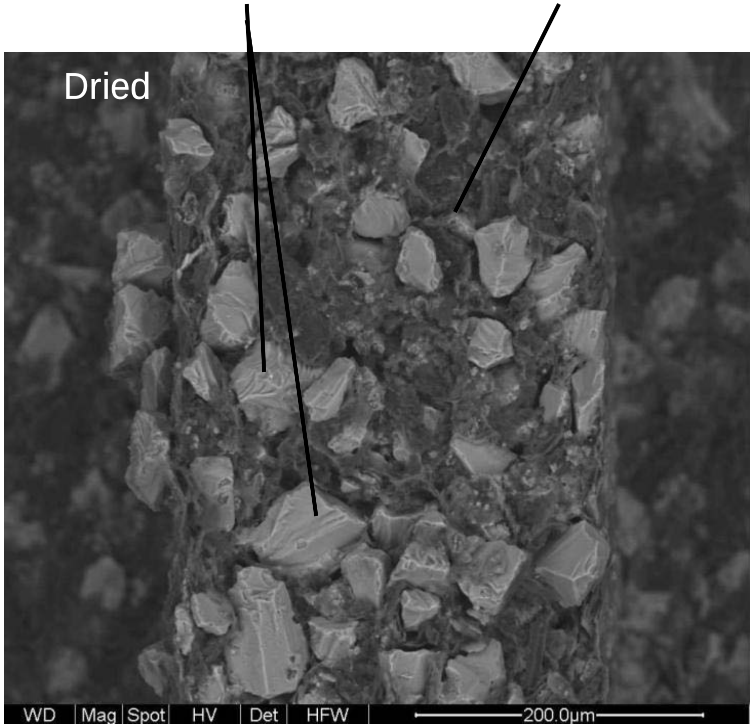
Known technology:
Infiltration of a porous carbon structure by Si in vacuum
→ ceramic brake discs for passenger cars
→ space mirror technology

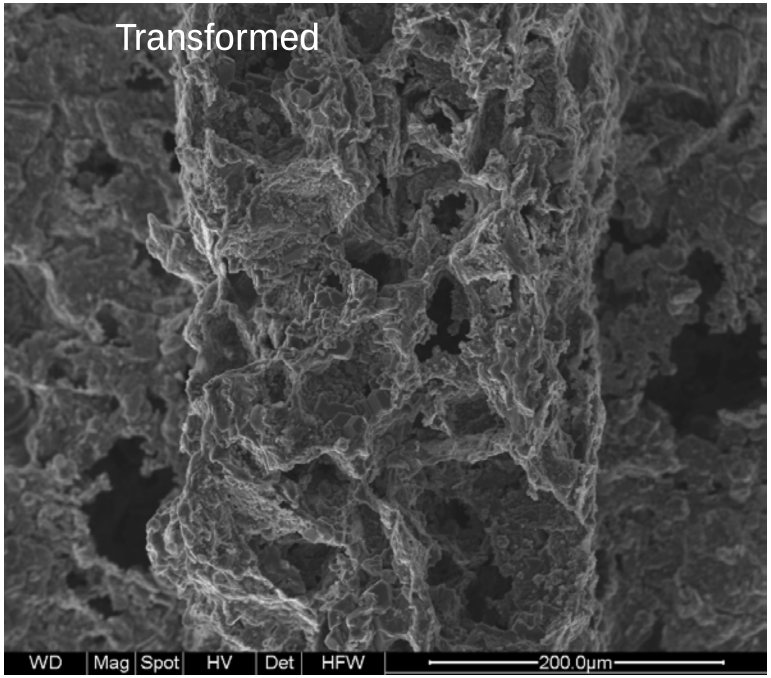




Modified reaction forming process

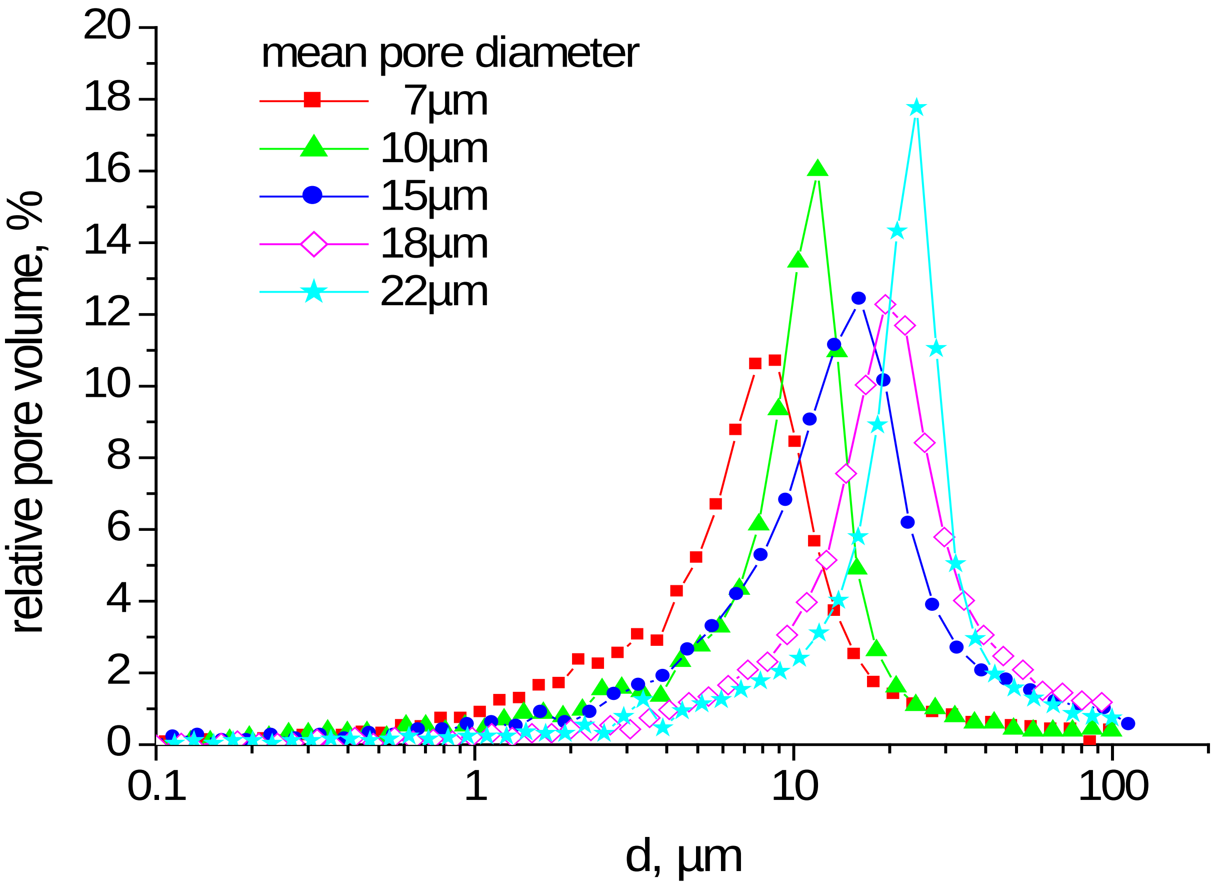
$$\mathrm{Si} + \mathrm{C} \xrightarrow{+\,\mathrm{Al}} \mathrm{SiC}$$ **=XP-SiC**

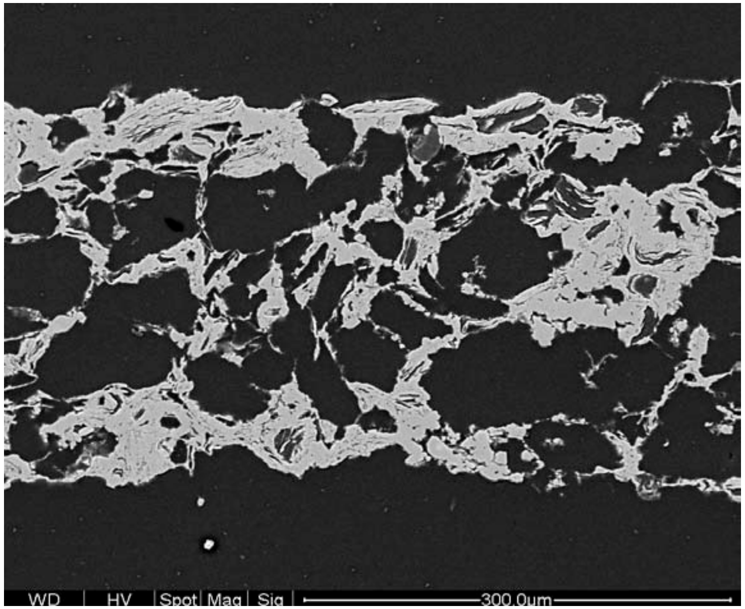




Components are co-extruded
Al improves wetting and reduces reaction temperature

Characteristic pore size distributions





Pore size distribution can be engineered by:
raw materials and processing conditions

Product specification

	XP materials			
Porosity	58%	57%	60%	65%
Pore diameter	12µm	20µm	22µm	22µm

CPSI / mil	200 /16	560g/l	610g/l	550g/l	510g/l
	300 / 13	530g/l	560g/l	510g/l	460g/l
	300 / 11.5	480g/l	510g/l	460g/l	415g/l
		specific weigh			

Comparison of efficiency and loading characteristics

to a standard Silicon Carbide

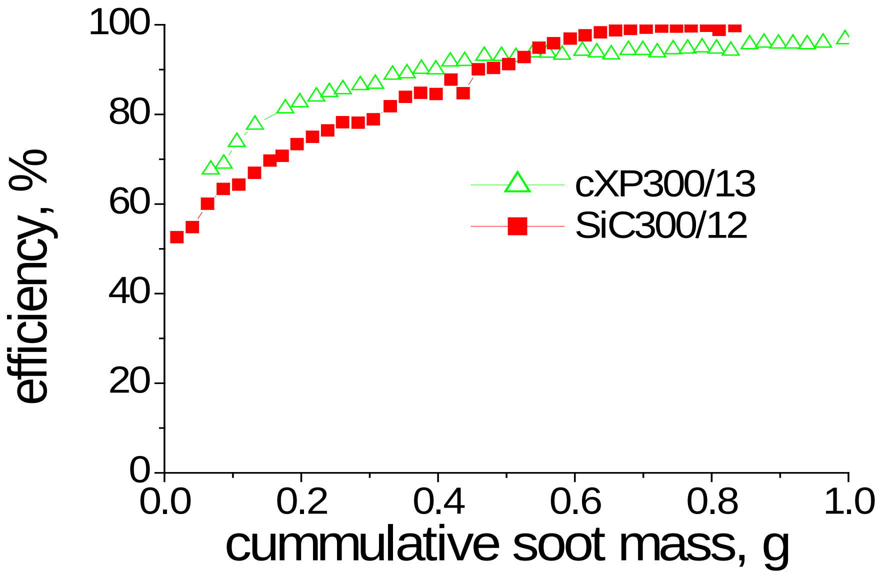
	Cell density / wall thickness	Mean pore diameter	Porosity	catalytic coating
SiC300/12	300cpsi/12 mil	15µm	50%	for active reg.
XP300/13	300cpsi/13 mil	22µm	60%	Envicat2054
	300cpsi/12mil	22µm	60%	uncoated

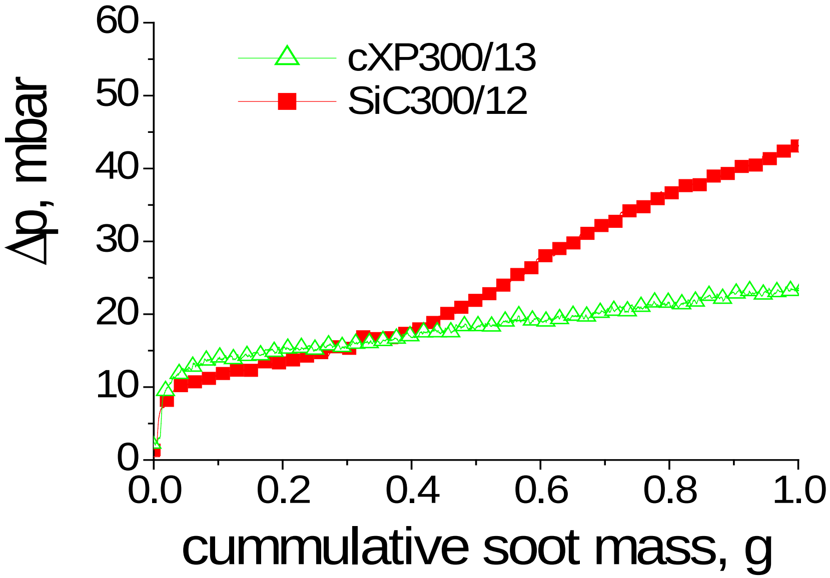
Performance of XP-SiC in comparison to std. SiC

AUTO FILTER TECHNOLOGY

tests at LAT, engine: PSA DW12 2.2l
150kg/h, DPF inlet temp. 200°C

Filter size: 5,66''x7''

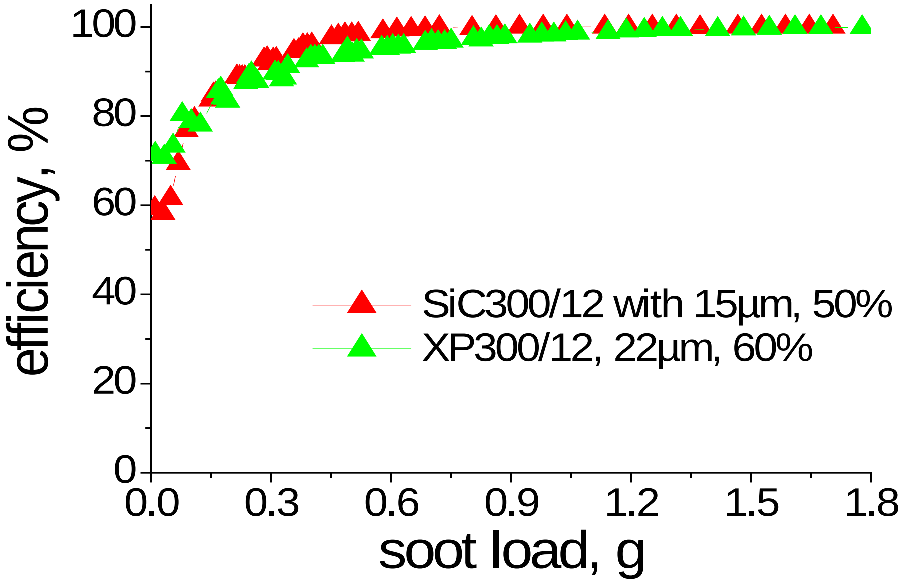




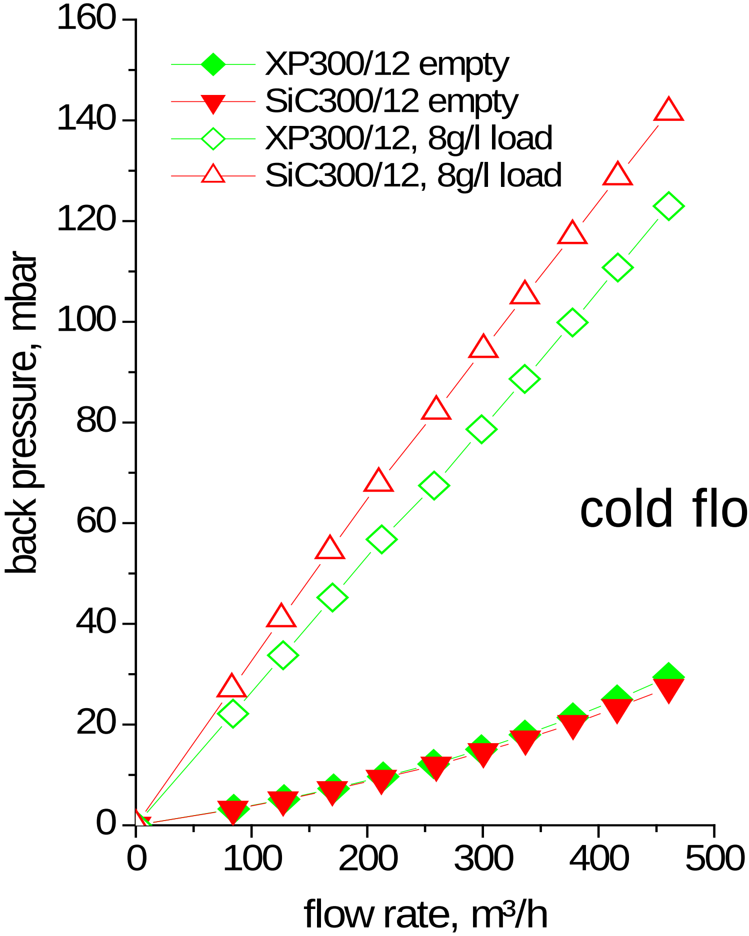
Significantly improved loading behavior (lower increase of pressure drop) at similar high filtration efficiency.

Verification with soot from a DPG (diesel burner)

tests at Cambustion
with soot from a diesel
burner (DPG)
@ 2g/h, 250kg/h,
DPF inlet temp. 240°C

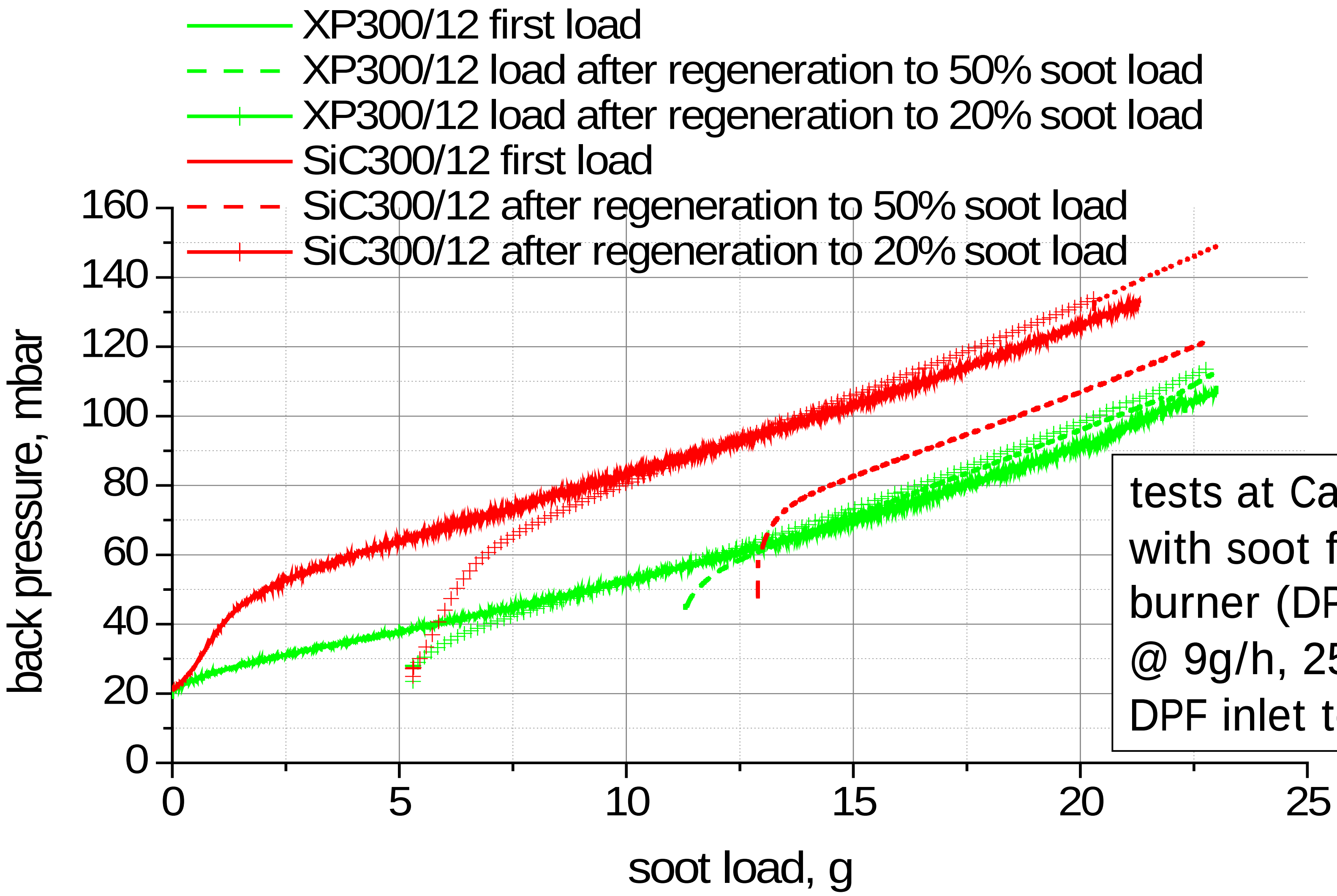


Filter size: 5,66''x7''



cold flow test

Loading after active regeneration

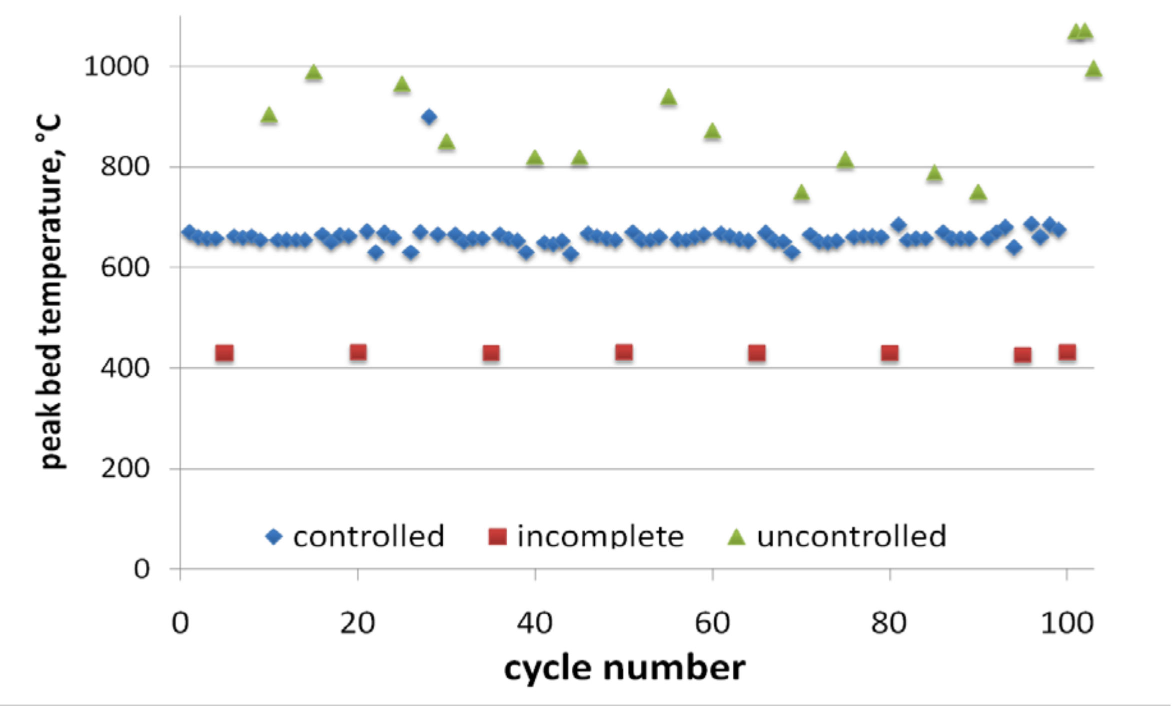


tests at Cambustion
with soot from a diesel
burner (DPG)
@ 9g/h, 250kg/h,
DPF inlet temp. 240°C

Durability check at SwRI

Durability test according to
SAE-paper 2007-01-4086
„Validation Method for Diesel
Particulate Filter Durability“

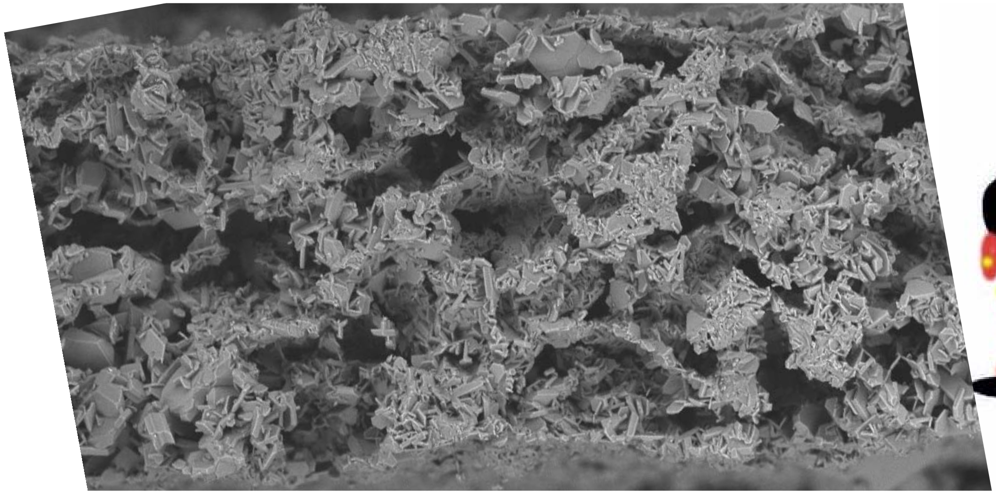
Tested filter:
XP300/13, 22µm, 60%
Coated with EnviCat2054

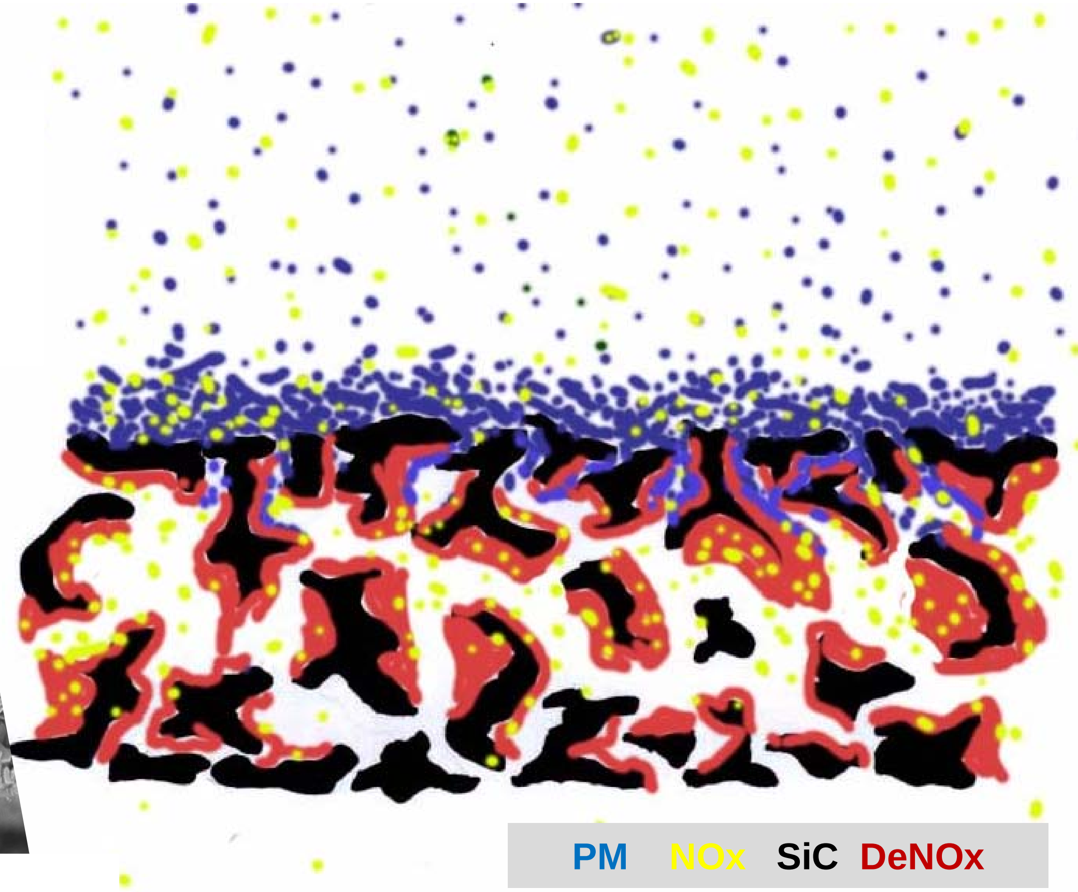


- ☐ maximum peak bed temperature: 1070°C
- ☐ integrity check with boroscope and smokemeter every 15 cycles
- ☐ check of PN efficiency after the last test cycles
  - → no cracks observed, no decrease of PN efficiency
  - → indication for soot mass limit in the range of 8g/l

Usage for high wash coat loadings

Bone like structure with large pores inside and smaller surface- and transition pores

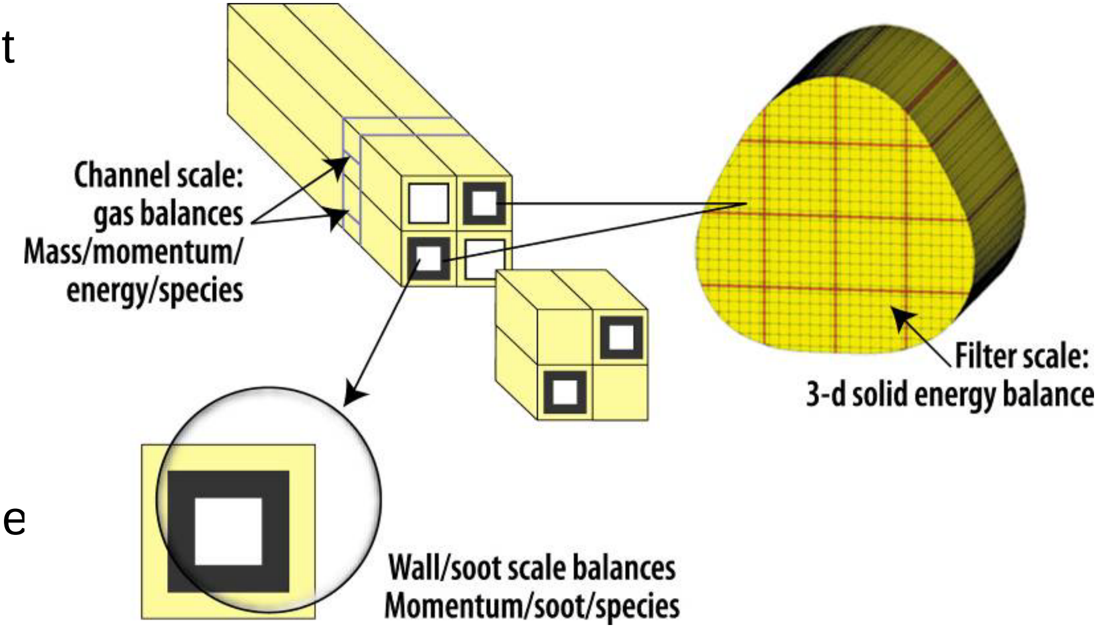




Important for Catalyst: temperature during regeneration

Calculations for investigation of peak temperature

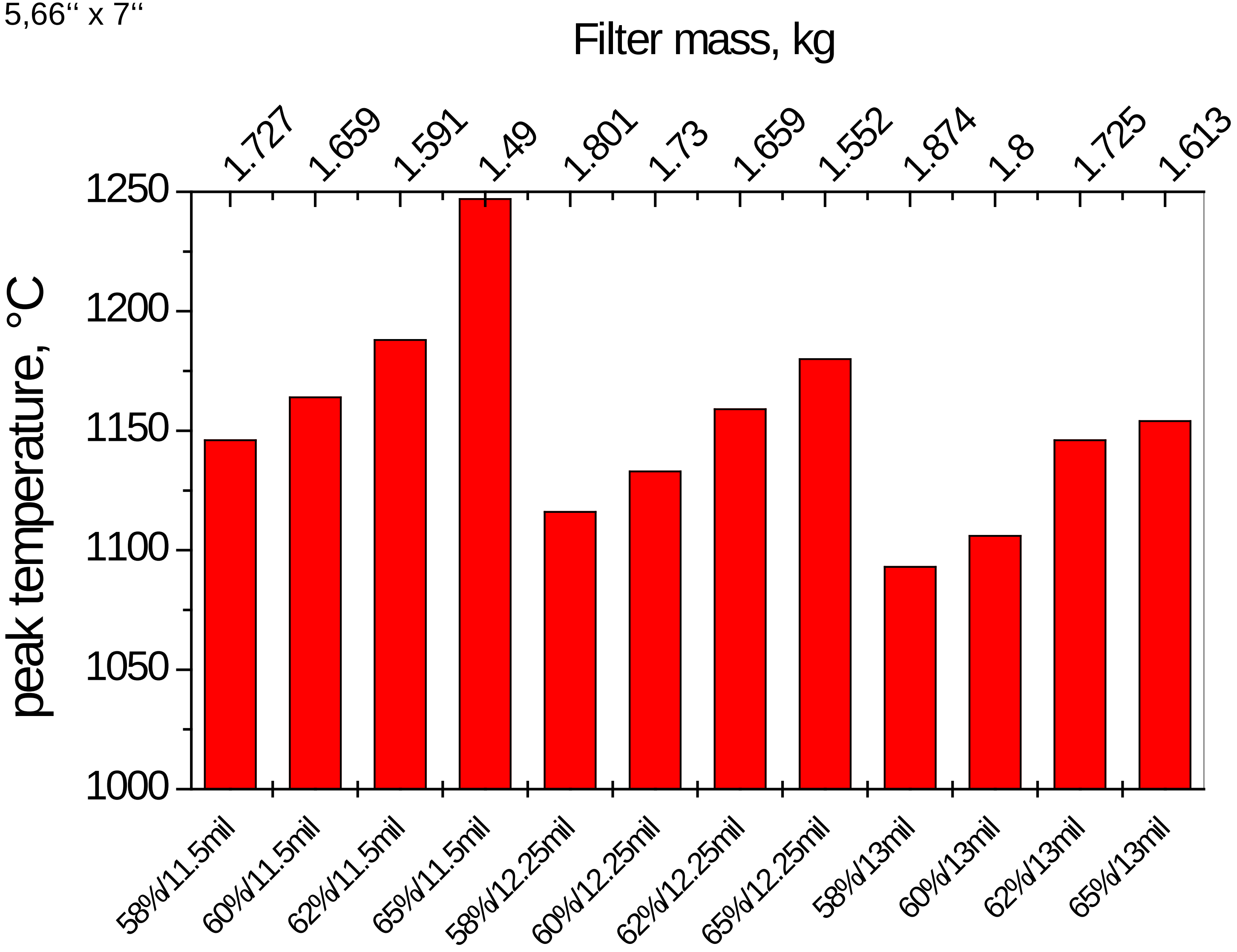
- Commercial code axitrap was employed
- Soot oxidation chemistry parameters were calibrated by means of engine test bench data of SwRI
- The governing equations of mass, momentum, energy and species were considered in three scales:
  filter – channel – wall
- An intra-layer model was adapted for the effect of diffusion and reactions in the soot layer and catalytic wash-coat



Hajireza et al, SAE technical paper 2010-01-0891

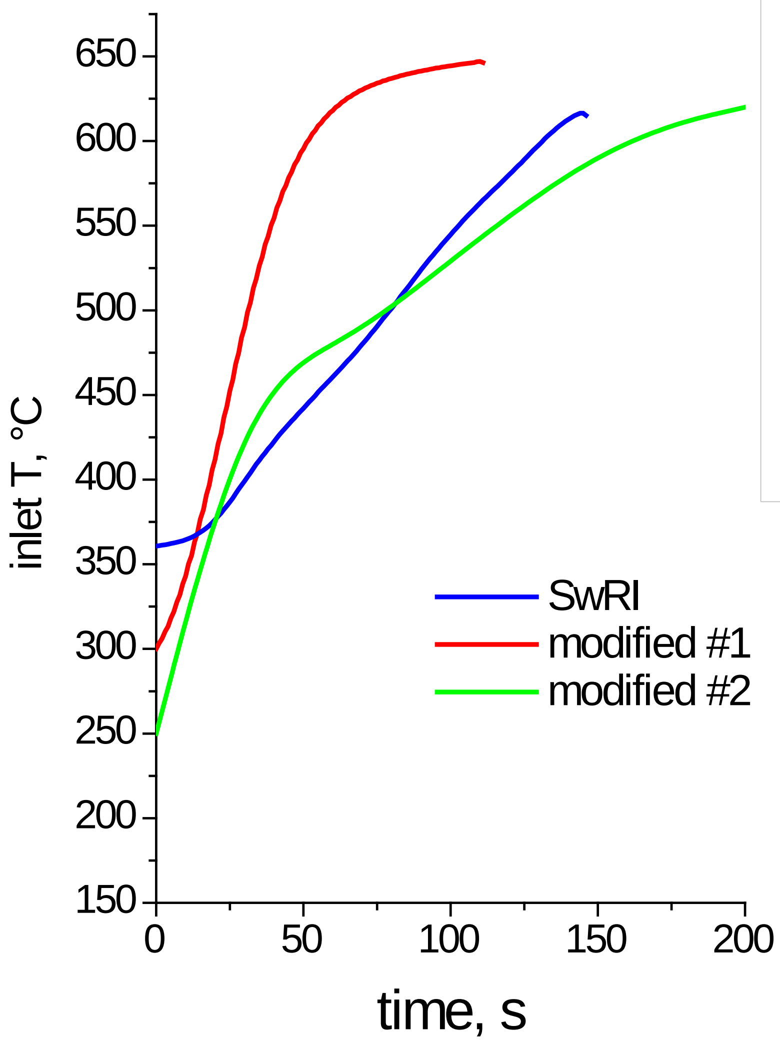
Peak temperature in dependance of thermal mass

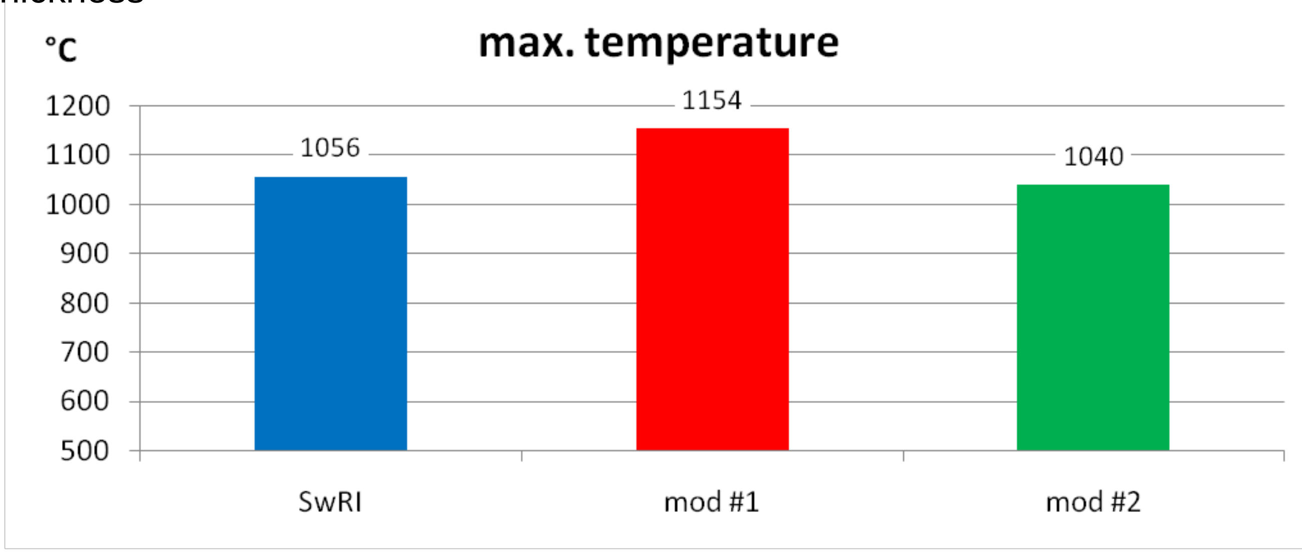
Filter design: 5,66‘‘ x 7‘‘

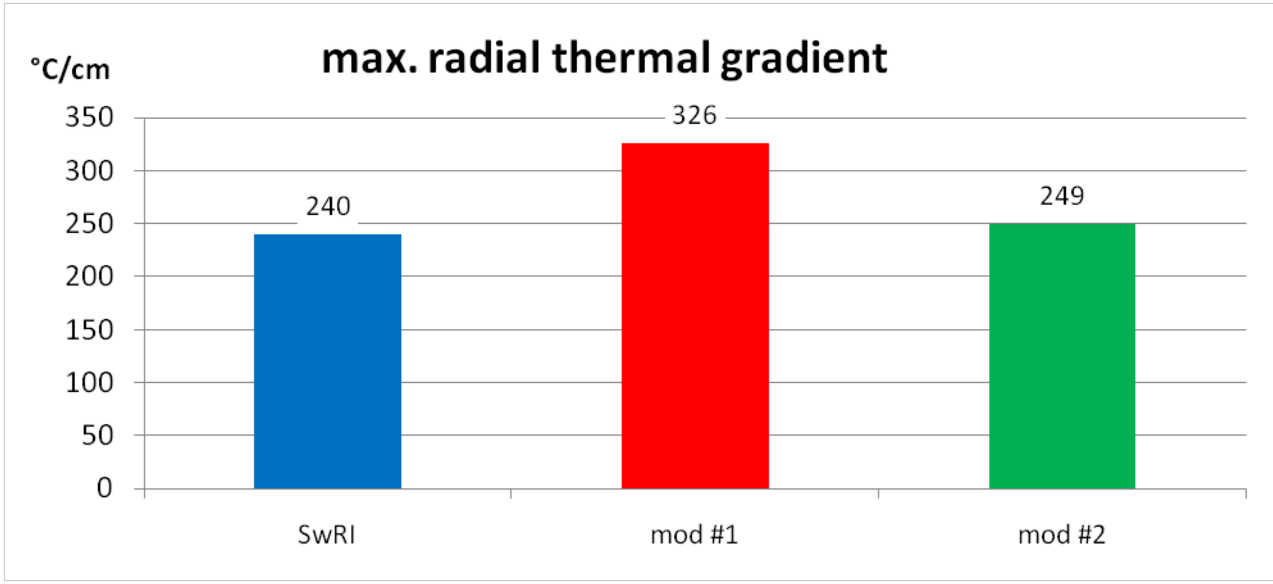


Influence of heat-up ramp

Substrate type: 60% porosity, 11.5 mil wall thickness



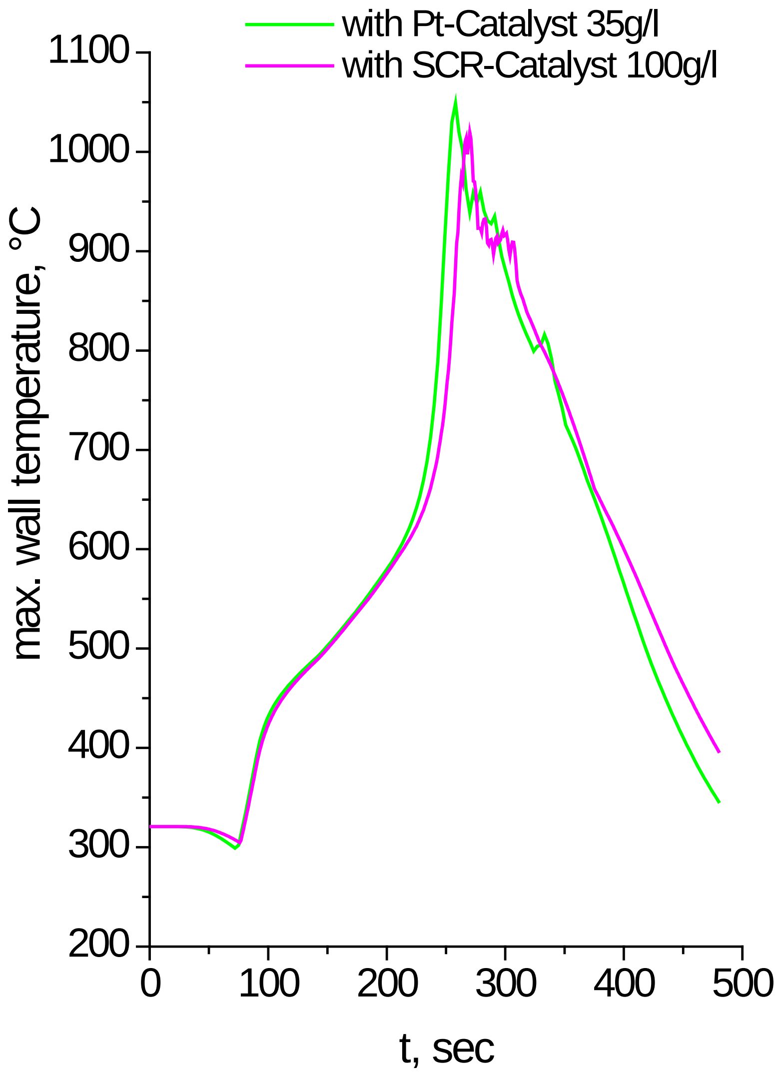


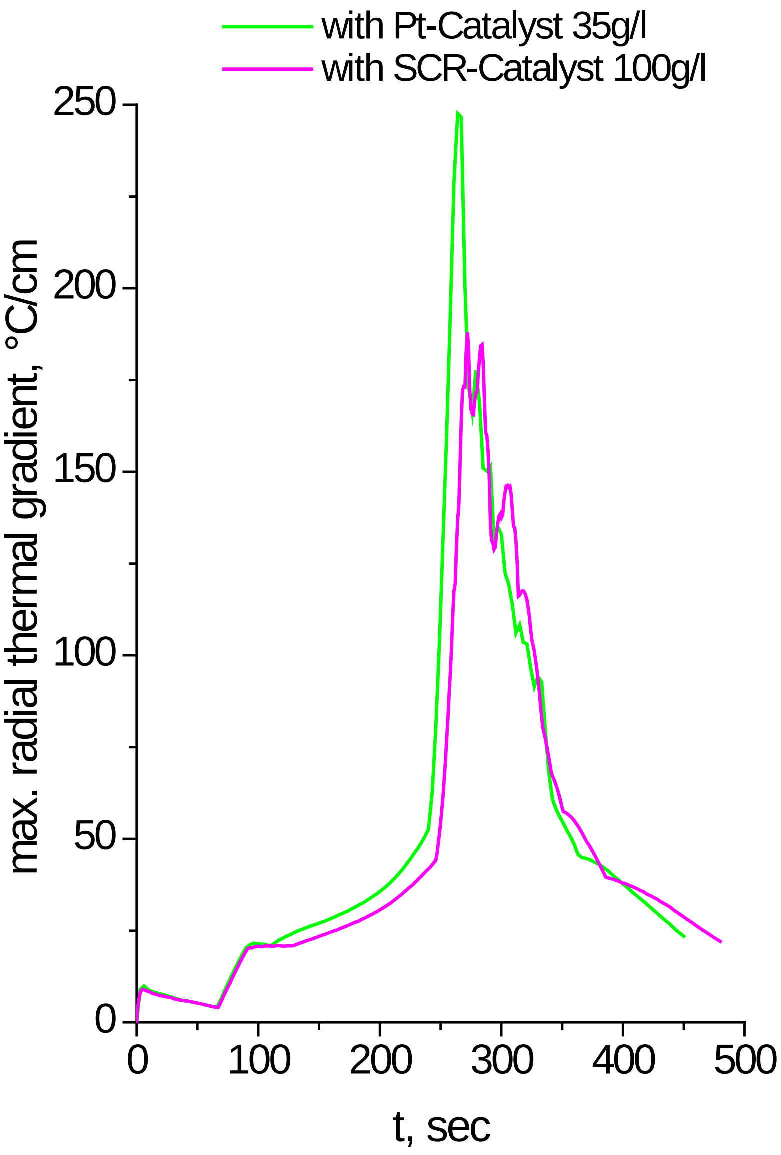


Calculation of a XP300 - 60%-11.5mil with SCR coating

- Substrate density was adjusted for the amount of wash-coat loading
  The assumed wash coat level was 100 g/l
- Fe-Zeolite SCR kinetics was adapted according to
  "Koltsakis, Koutoufaris and Haralampous, MinNox Conference 2010"
- Standard, fast and slow SCR reactions as well as NH_3 slip reactions were implemented
- heat-up ramp mod. #2 was taken

Comparison Oxicat – to SCR coated XP300-60%-11.5mil





Summary

- **A new type of SiC** was presented
  - Modified reaction forming process leads to high porosity levels and a unique pore structure.

- **Unique pore structure** leads to characteristic features
  - Reduced depth filtration, improved correlation Δp to soot load
  - High filtration efficiency at high porosity and large pore sizes.
  - Usage of high porosity for high wahcoat loadings for DeNOx

- A durability check of a XP-SiC with 60% porosity indicates a **soot load limit of 8g/l**.

- Simulations have been performed to investigate the impact on the catalyst.
  - High wash coat levels reduce thermal gradients and peak temperatures during severe regeneration.