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UNION POUR LA SCIENCE ET LA TECHNOLOGIE VERRIÈRES

LE VERRE

14 et 15 novembre 2013

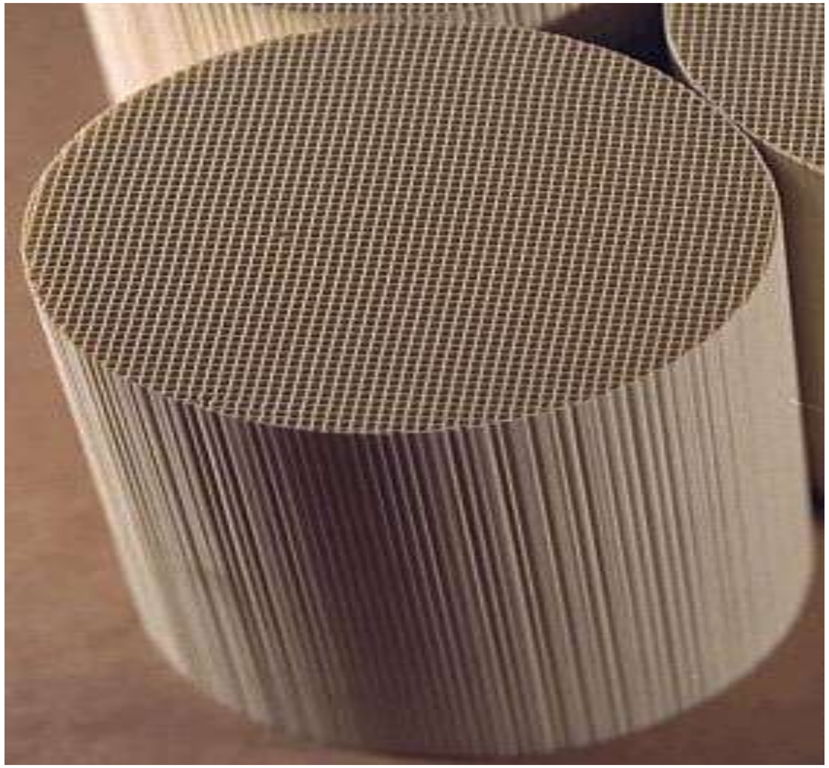
Centre Européen de la Céramique, Limoges

JOURNÉES PLÉNIÈRES USTV - GDR VERRES 3338

Oxide-Based Cellular Ceramics Monolithic Honeycombs Used in Catalysis and Filtration applications

Jean-Jacques Théron
Corning European Technology Center
Avon, France

November 14, 2013



Outline

- Introduction – Corning Overview
- Cordierite monoliths for gasoline engine automotive catalytic converters application
- Oxide-based Diesel Particulate Filters (DPF) applications
- High surface area oxide-based ceramics honeycombs for other applications
- Conclusions

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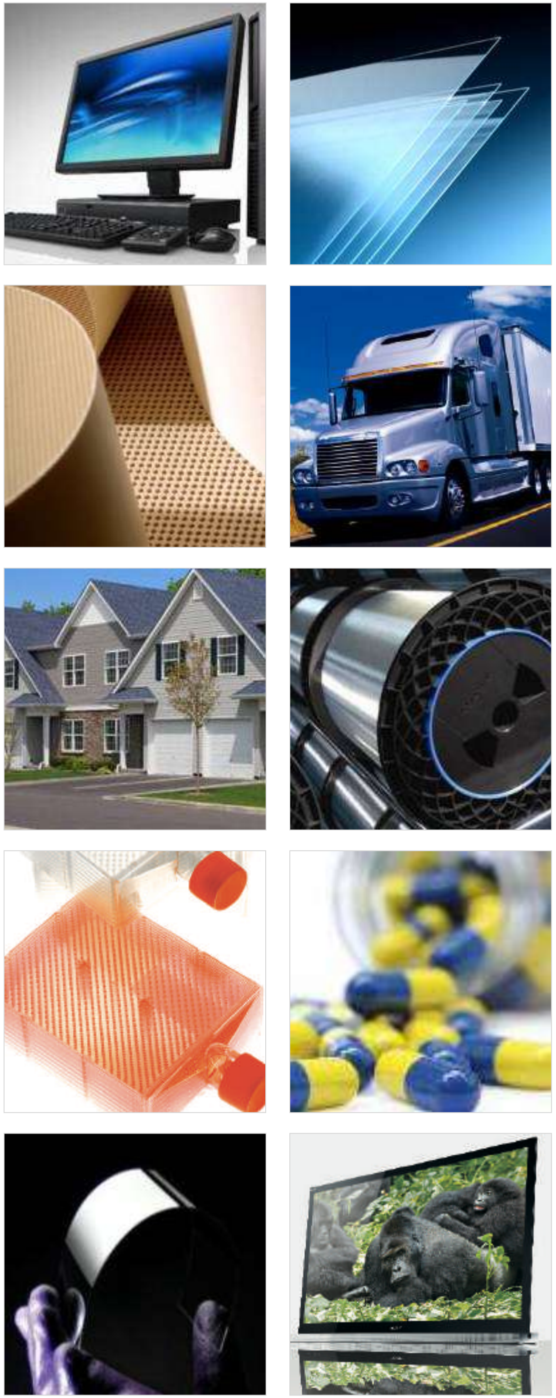
Corning European Technology Center 2013 Overview



Corning Incorporated

Founded:
1851

Headquarters:
Corning, New York

Employees:
~29,000 worldwide

2012 Sales:
$8.0B

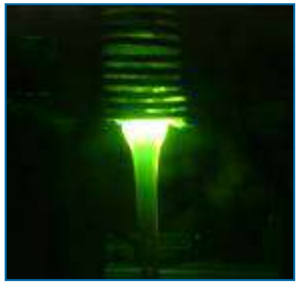
Fortune 500 Rank (2012):
328

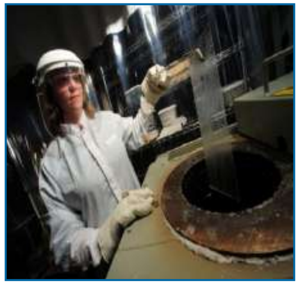
- Corning is the world leader in specialty glass and ceramics.
- We create and make keystone components that enable high-technology systems for consumer electronics, mobile emissions control, telecommunications, and life sciences.
- We succeed through sustained investment in R&D, 160 years of materials science and process engineering knowledge, and a distinctive collaborative culture.

Corning Market Segments and Additional Operations

Display Technology	Telecom	Environmental Technologies	Life Sciences	Specialty Materials	Other Products and Services
• LCD Glass Substrates • Glass Substrates for OLED and high-performance LCD platforms	• Optical Fiber and Cable • Hardware and Equipment – Fiber optic connectivity products	• Emissions Control Products – Light-duty gasoline vehicles – Light-duty and heavy-duty on-road diesel vehicles – Heavy-duty non-road diesel vehicles – Stationary	• Cell Culture and Bioprocess • Assay and High-Throughput Screening • Genomics and Proteomics • General Laboratory Products	• Corning® Gorilla® Glass • Display Optics and Components • Optical Materials – Semiconductor materials – Specialty fiber – Polarcor™ • Optics • Aerospace and Defense • Ophthalmic	• Emerging Display Technology • Drug Discovery Technology • New Business Development • Equity Companies – Cormetech, Inc. – Dow Corning Corp. – Eurokera, S.N.C. – Samsung Corning Precision Materials Co., LTD (SCP)

Centralized R&D Campus: Corning, New York





Designed to integrate our technical capabilities and create keystone components

Sullivan Park Connected Globally in Europe, Asia and the U.S. West Coast

Corning West Technology Center
Silicon Valley, California

Corning European Technology Center
Fontainebleau, France

Corning Advanced Technology Center
Taipei, Taiwan

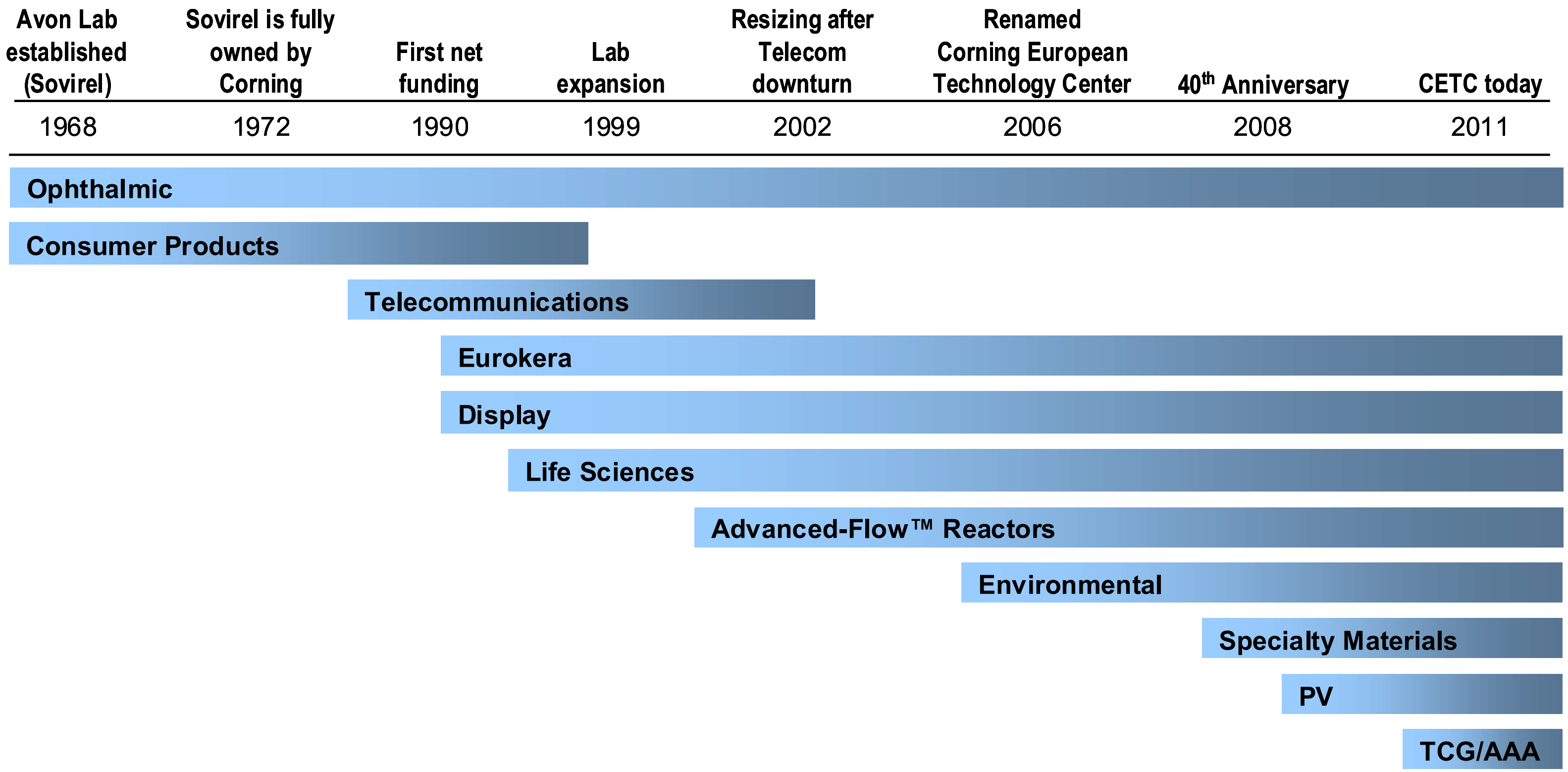
Corning Scientific Center
St. Petersburg, Russia

Fontainebleau-Avon, France

Corning European Technology Center – Founded in 1968

- 185,000 sq. ft.
- Materials & process focus
- Most core technologies
- Pilot plant
- ≈100 permanent employees

CETC business collaborations



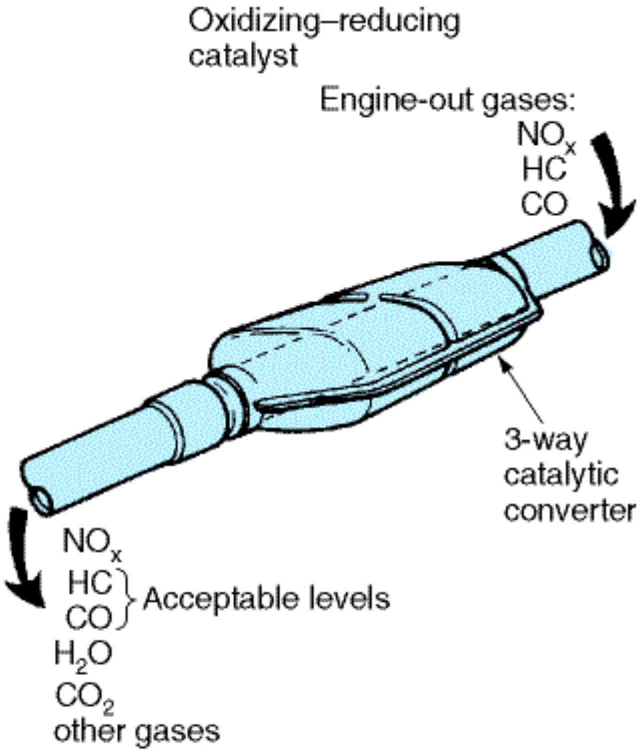
Most of Corning's businesses are present at CETC today

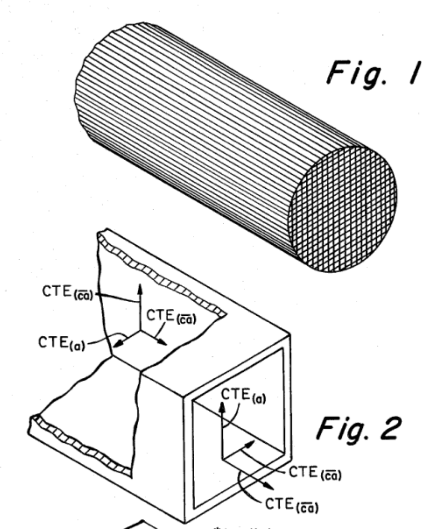
Cellular ceramics honeycombs

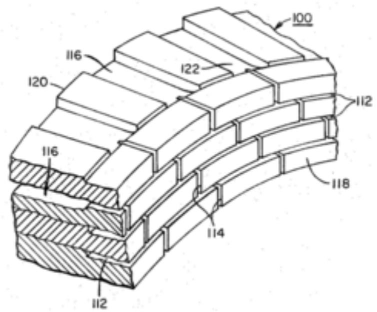
- Catalyst support for air-pollution control
  - Mobile emissions
    - Automotive catalytic converter & Diesel Particulate Filters
  - Stationary emissions
    - Reduction of NOx emission from power plants

Cordierite ceramic honeycomb based catalytic converters

- Flow through chemical reactor integrated in the exhaust pipe
  - Convert CO, HC and NOx into N_2, H_2O and CO_2
- Technology and process invented in the mid 1970's







R.D. Bagley, Method of Forming an Extrusion Die - US Patent 3803951A,1974

I.M. Lachman and R.M. Lewis, Anisotropic Cordierite Monolith - US Patent 3,885,977a, 1975.

National Medal of Technology

Corning Incorporated

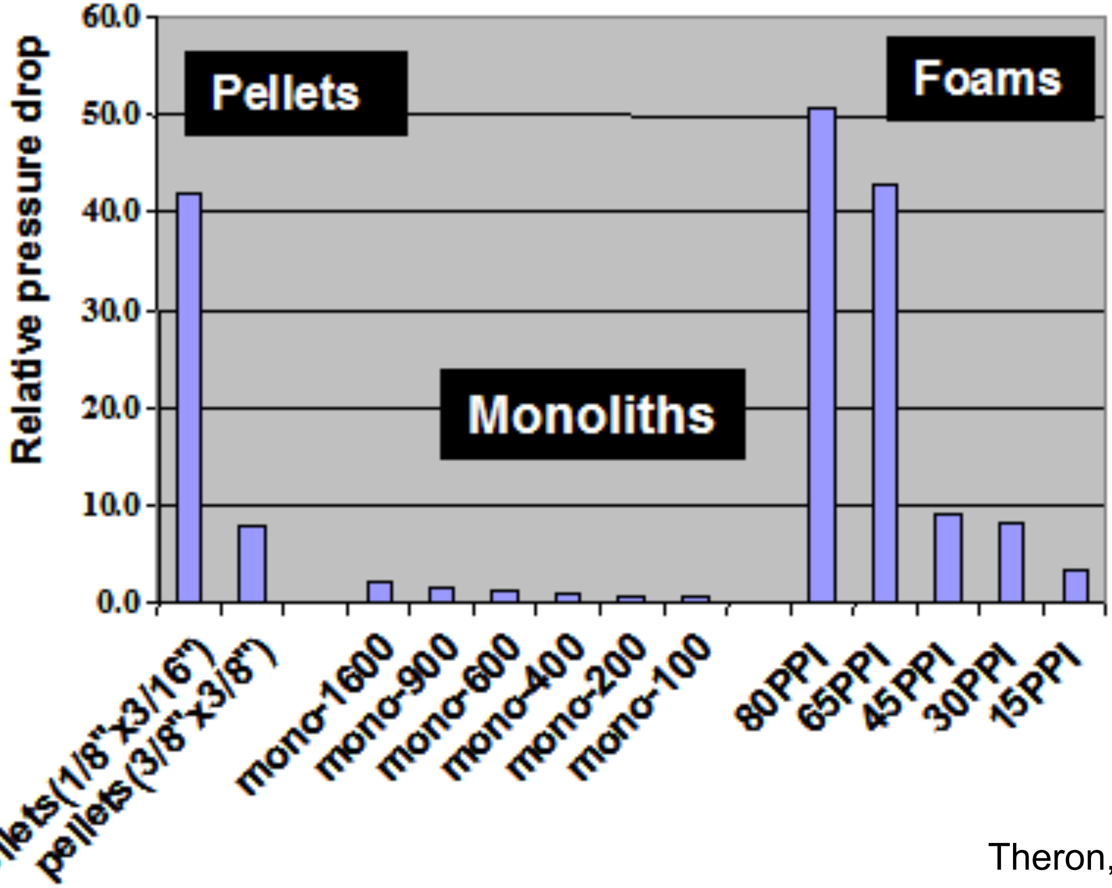
Environmental Technologies

2003

R.D. Bagley
I.M. Lachman
R.M Lewis

Monolithic porous ceramics as catalyst substrates for air pollution control

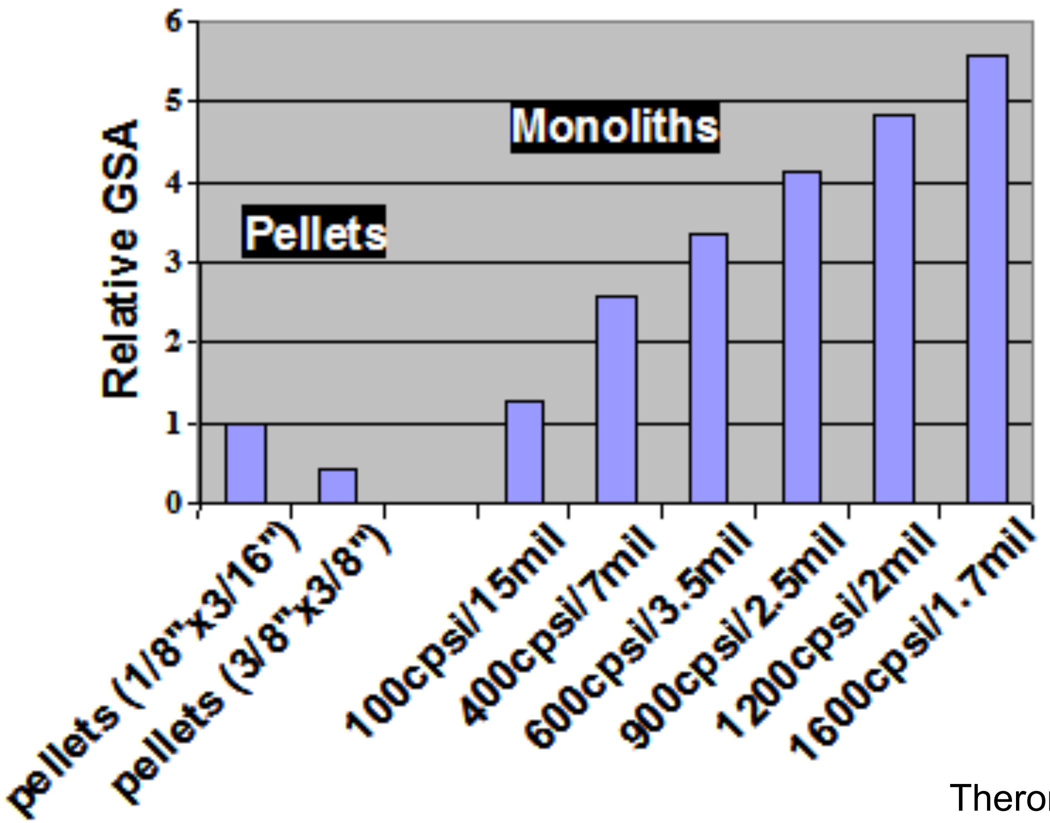
- Monolithic or honeycombs materials have a pressure drop advantage over conventional pellet-shaped catalysts



Theron, 106th ACerS Meeting, 2004

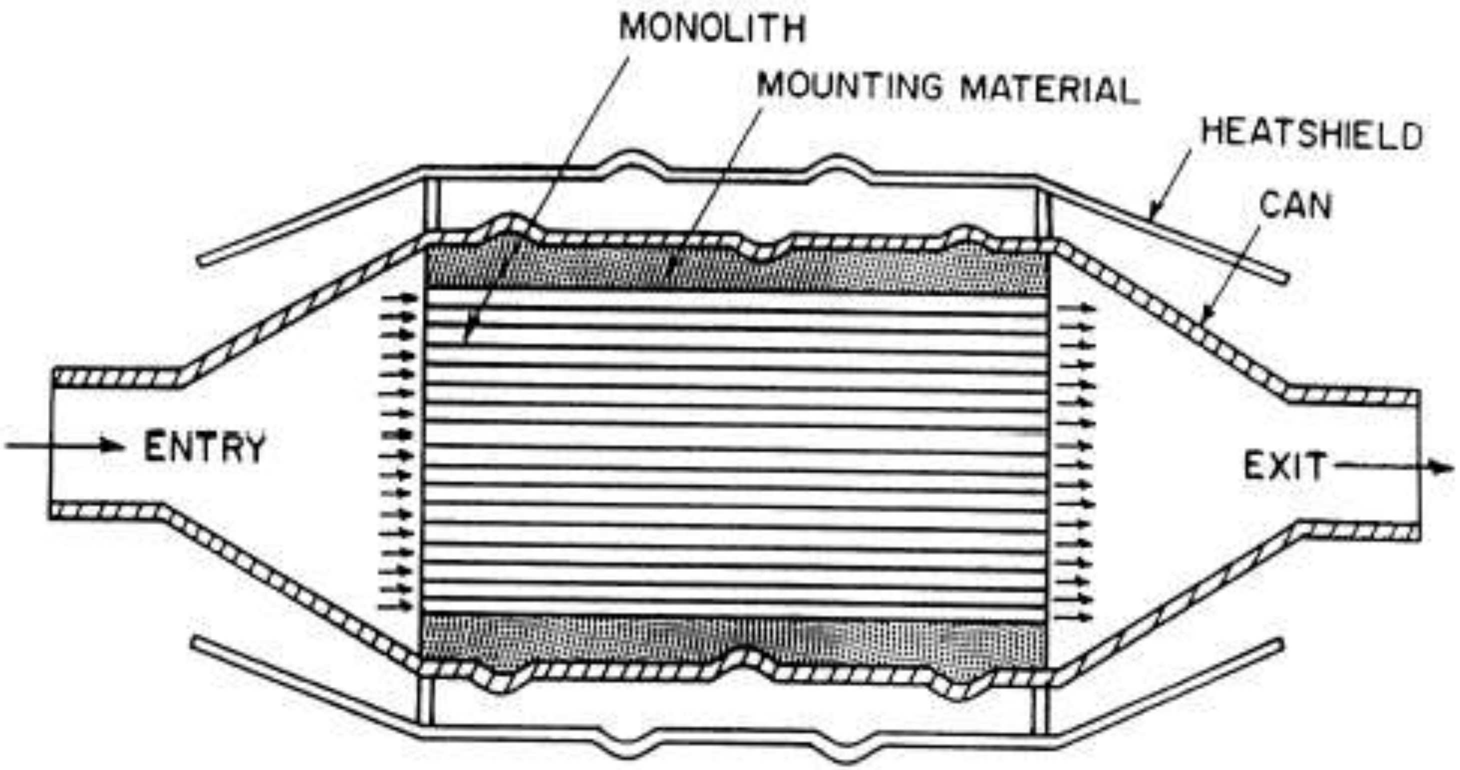
Monolithic porous ceramics as catalyst substrates for air pollution control

- Monolithic or honeycombs materials offers a higher relative geometric surface area than conventional pellet-shaped catalysts



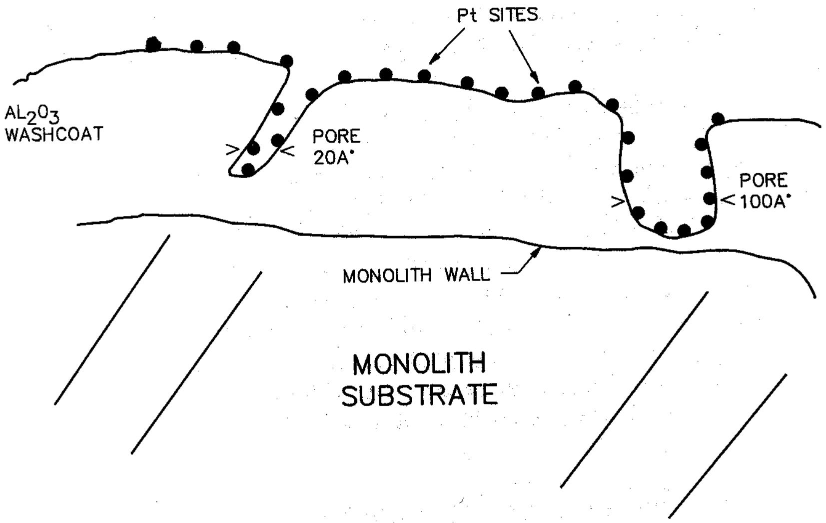
Theron, 106th ACerS Meeting, 2004

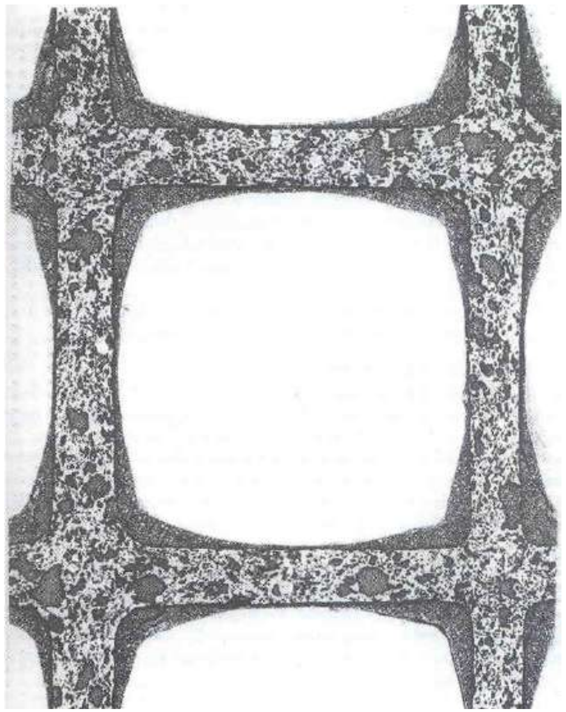
Monolithic Converter System



Monolithic porous ceramics as catalyst substrates for air pollution control

- Ceramic monoliths have well designed pore structure (3-4 µm pores) which allow chemical and mechanical bonding to the washcoat:
  - High surface area carrier such as Al_2O_3
  - Further impregnated with a catalytic component such as Pt





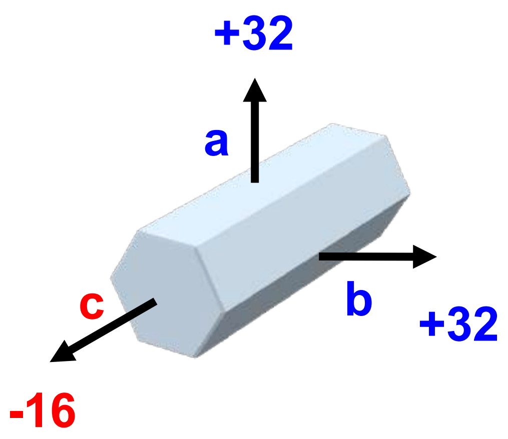
Farrauto et al., Catalysis Today, 51,351-360,1999

Cordierite as a macro-cellular body for exhaust catalyst support : Celcor®

- Extruded synthetic Cordierite $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$
  - Thermal shock resistance
    - Can be made with very low CTE < $10.10^{-7}/^{o}C$
    - Proper crystal orientation and micro-cracks development
  - Mechanical strength
    - Typical monolith axial strength > 3000 psi
  - High Melting point: >$1300^{o}C$
  - Catalyst compatibility as a catalyst support
    - Pore structure to allow chemical and mechanical bonding to the washcoat
    - No migration of chemical component in the ceramic into the catalyzed washcoat
  - High volume throughput via low cost extrusion

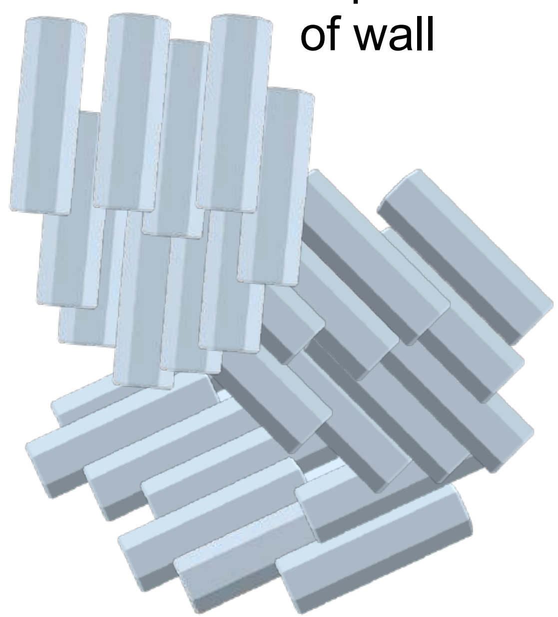
Cordierite Thermal Expansion

Crystal Lattice CTE



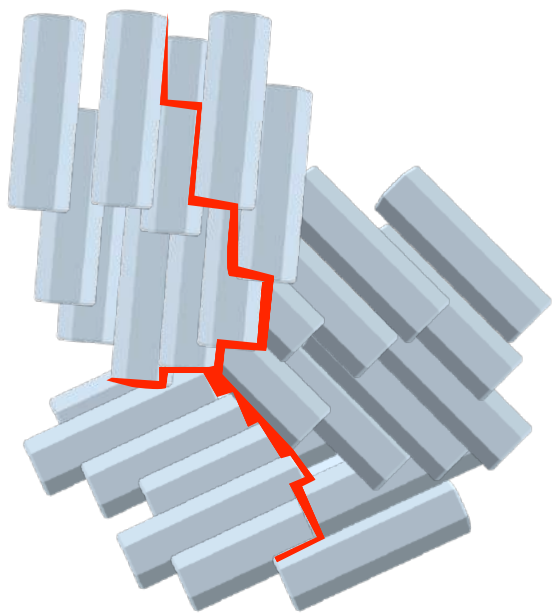
Average = $16 \times 10^{-7}/^{o}C$
Anisotropic

Oriented Domains



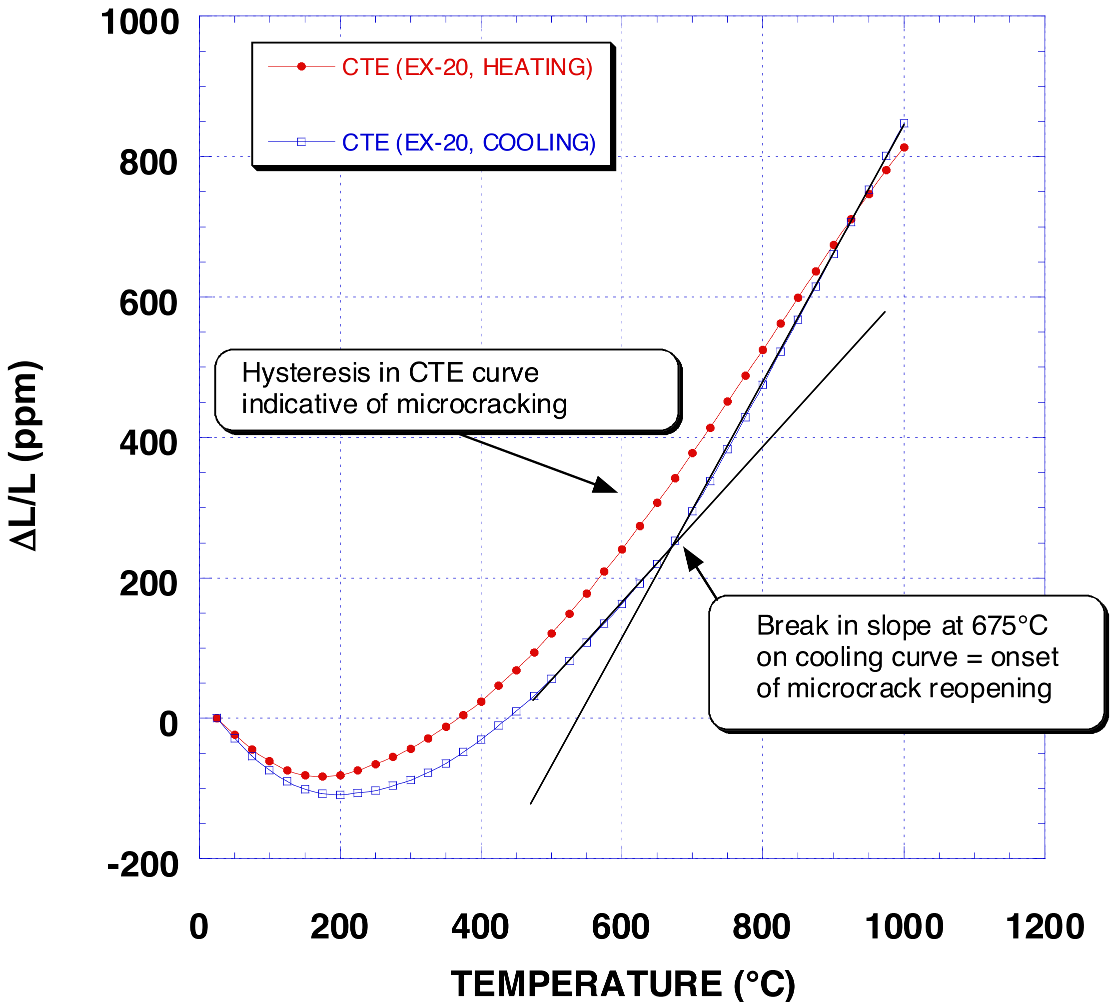
Average within plane
= 8 to $12 \times 10^{-7}/^{o}C$

Microcracking



Average within plane
= 2 to $7 \times 10^{-7}/^{o}C$

Influence of Crystal Orientation & Micro-cracks
Engineering Strain as a Function of Temperature



High volume extrusion process

Mixing
Blending of raw materials with binders and other additives

↓

Plasticizing
Water or other solvents

↓

Pre-Extrusion
Extrude rods for more uniform mixing

↓

Extrusion
Extrude through monolith die

↓

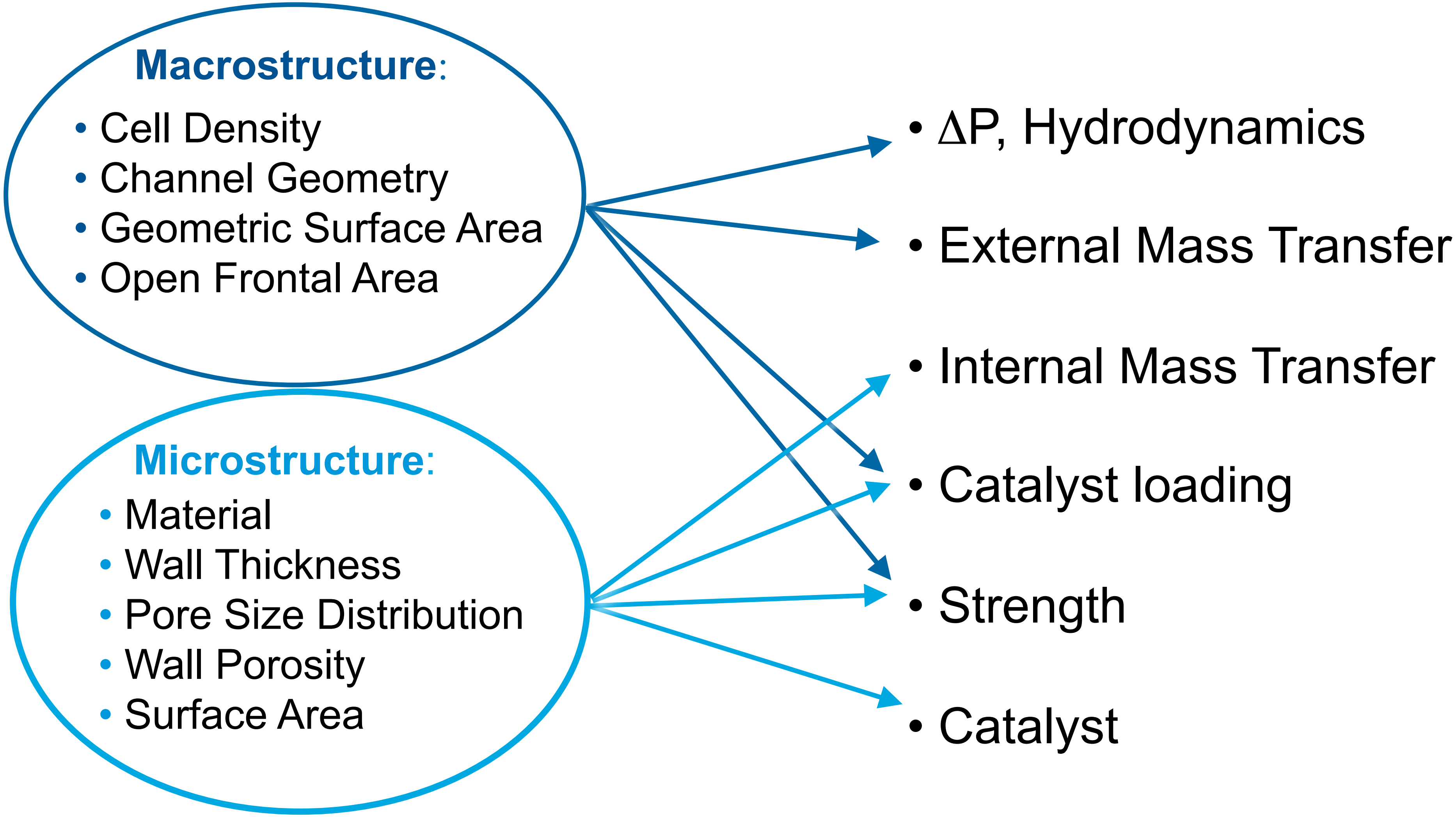
Drying
Uniform drying for green strength and to prevent cracking

↓

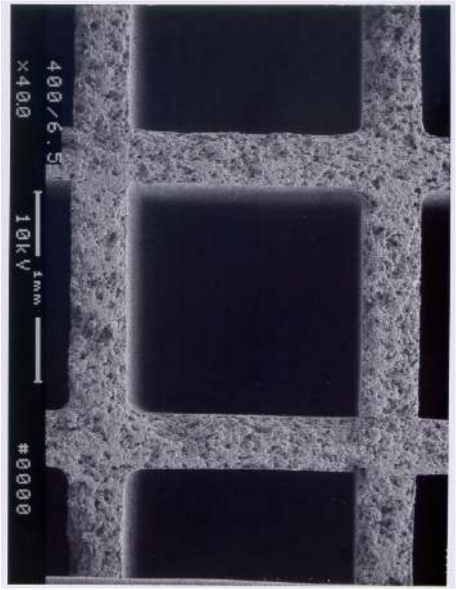
Firing
Set temperature and heating rate for desirable crystalline phase and physical properties

Williams et al., 17th Nat. Symposium on catalysis , Bhanagar, 2005

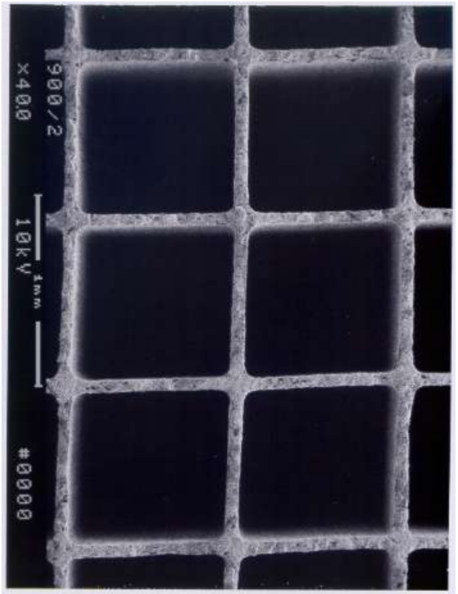
Monolith Properties can be Tailored for Optimum Catalyst and Reactor Performance



Reduction of the Wall Thickness

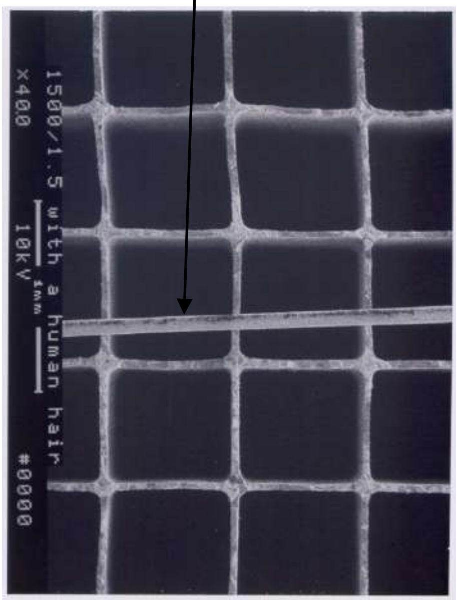


400cpsi/165µm



900cpsi / 50µm

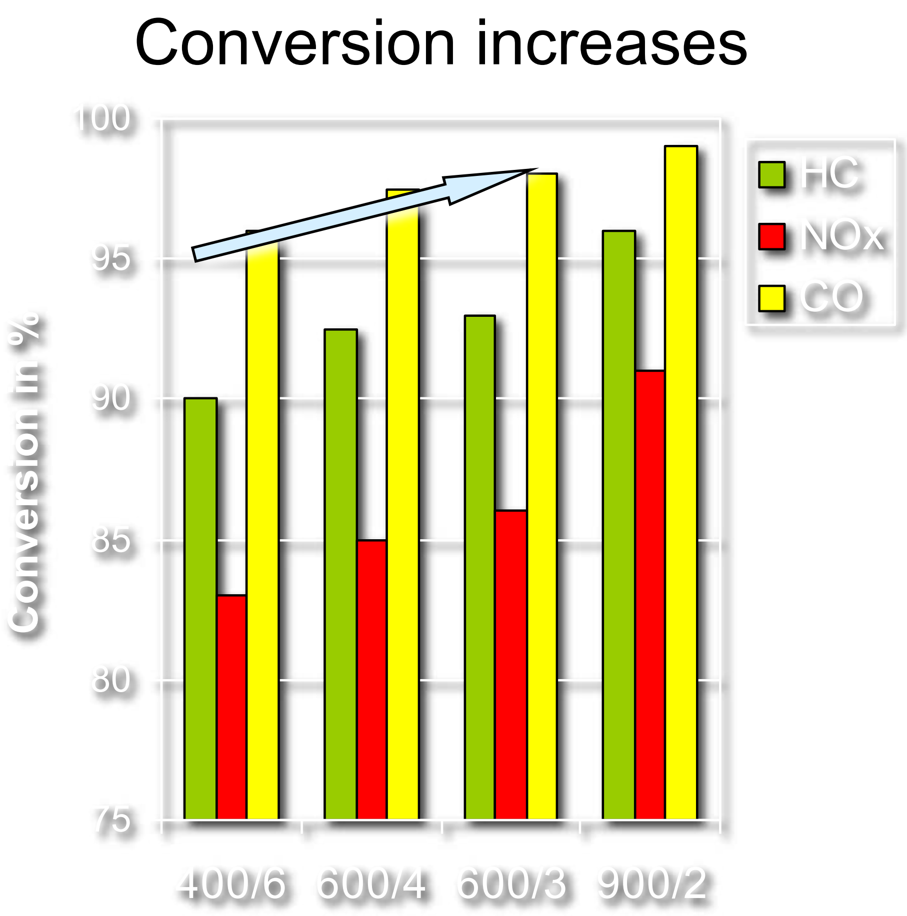
Human Hair

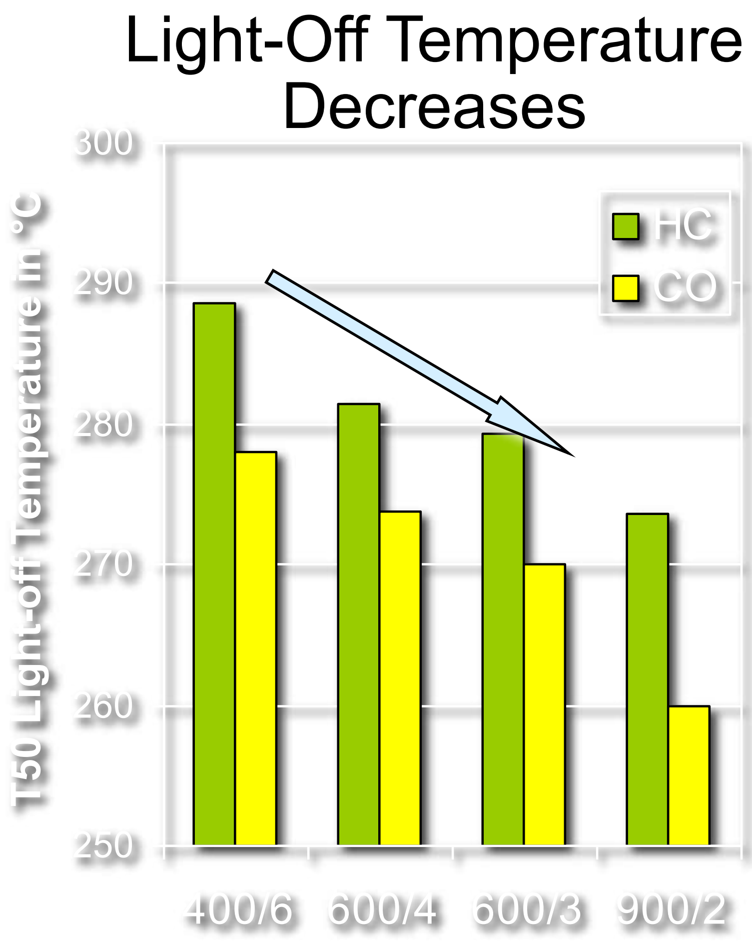


1500cpsi / 38µm
with human hair

Gulati, SAE comm. 99001, SAIT Puna, 1999

Advanced substrates reduce emissions





Will et al., SAE 2000-01-0502

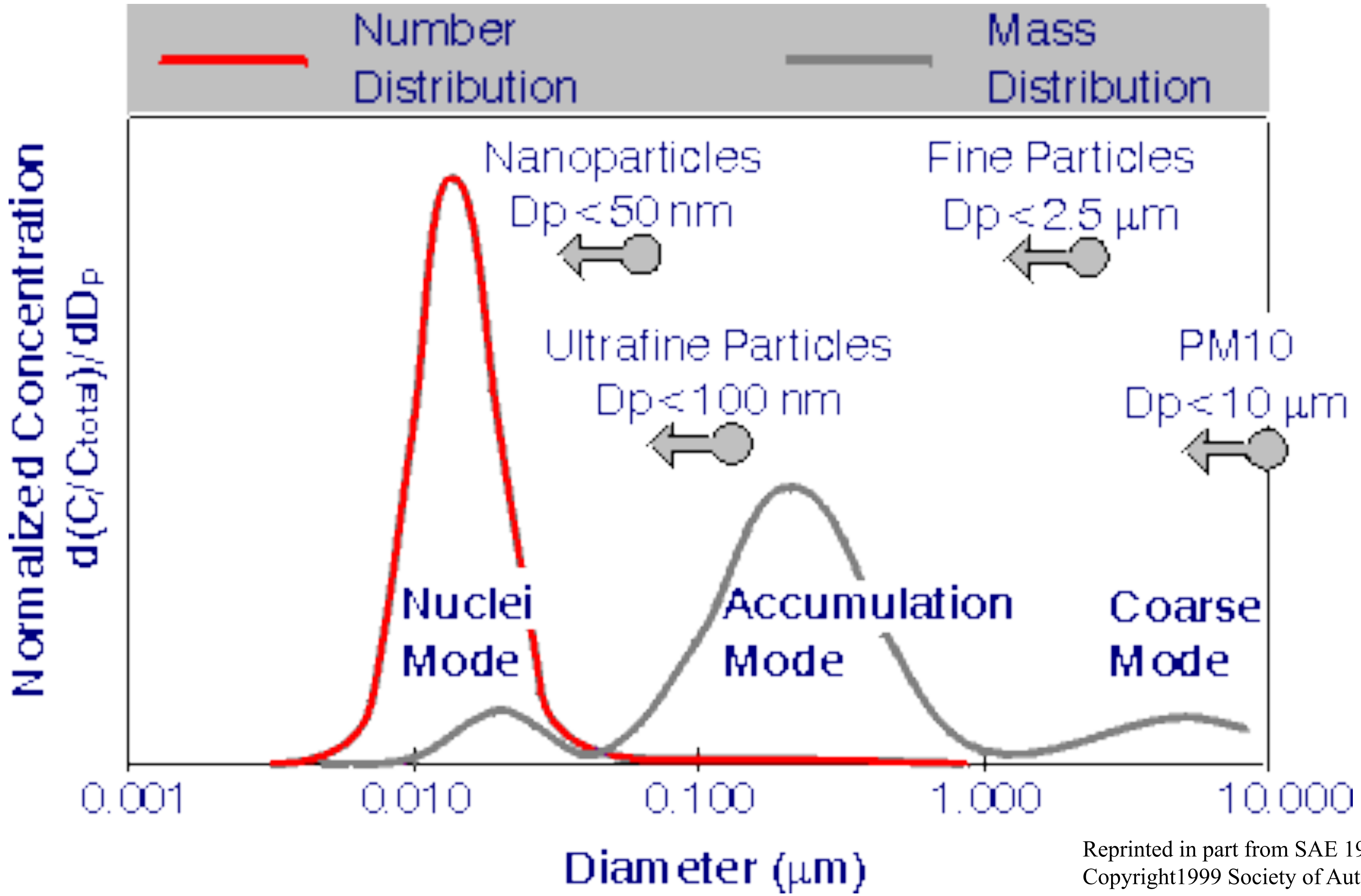
Health Risks of Diesel Particulate Matter

Sample	Mutagenicity	DNA Damage	Chromosomal Damage
Diesel PM	+	(+) toxic	-
Gasoline PM	+	+	+
Diesel SVOC	weak	-	-
Gasoline SVOC	weak	(+) toxic	+

SVOC: semi-volatile organic compound

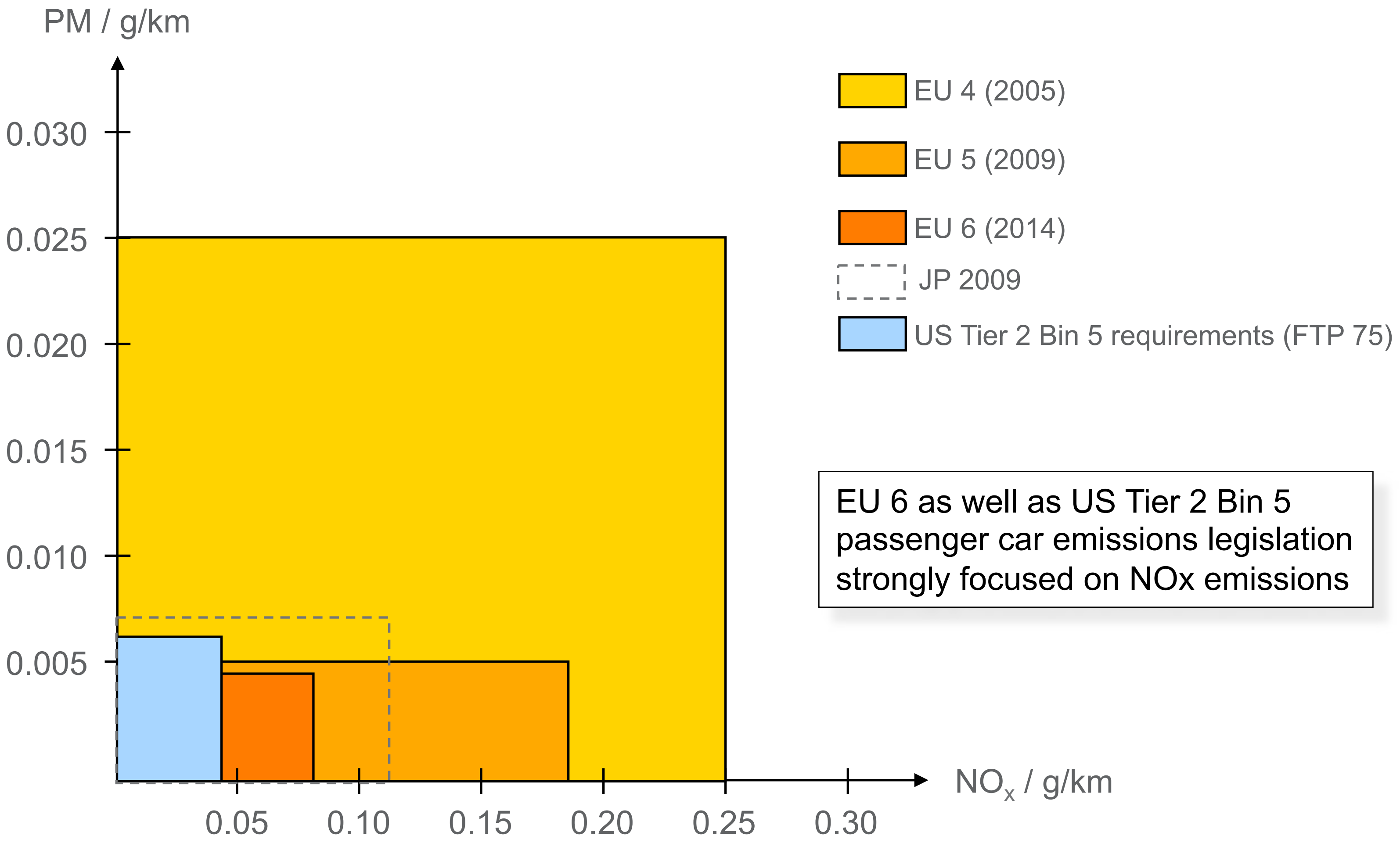
W. Wallace, US Department of Energy Diesel Engine Emission Reduction Conference, San Diego, August 2002.

Typical Diesel Particle Size Distribution



Reprinted in part from SAE 1999-01-1142, Copyright1999 Society of Automotive Engineers

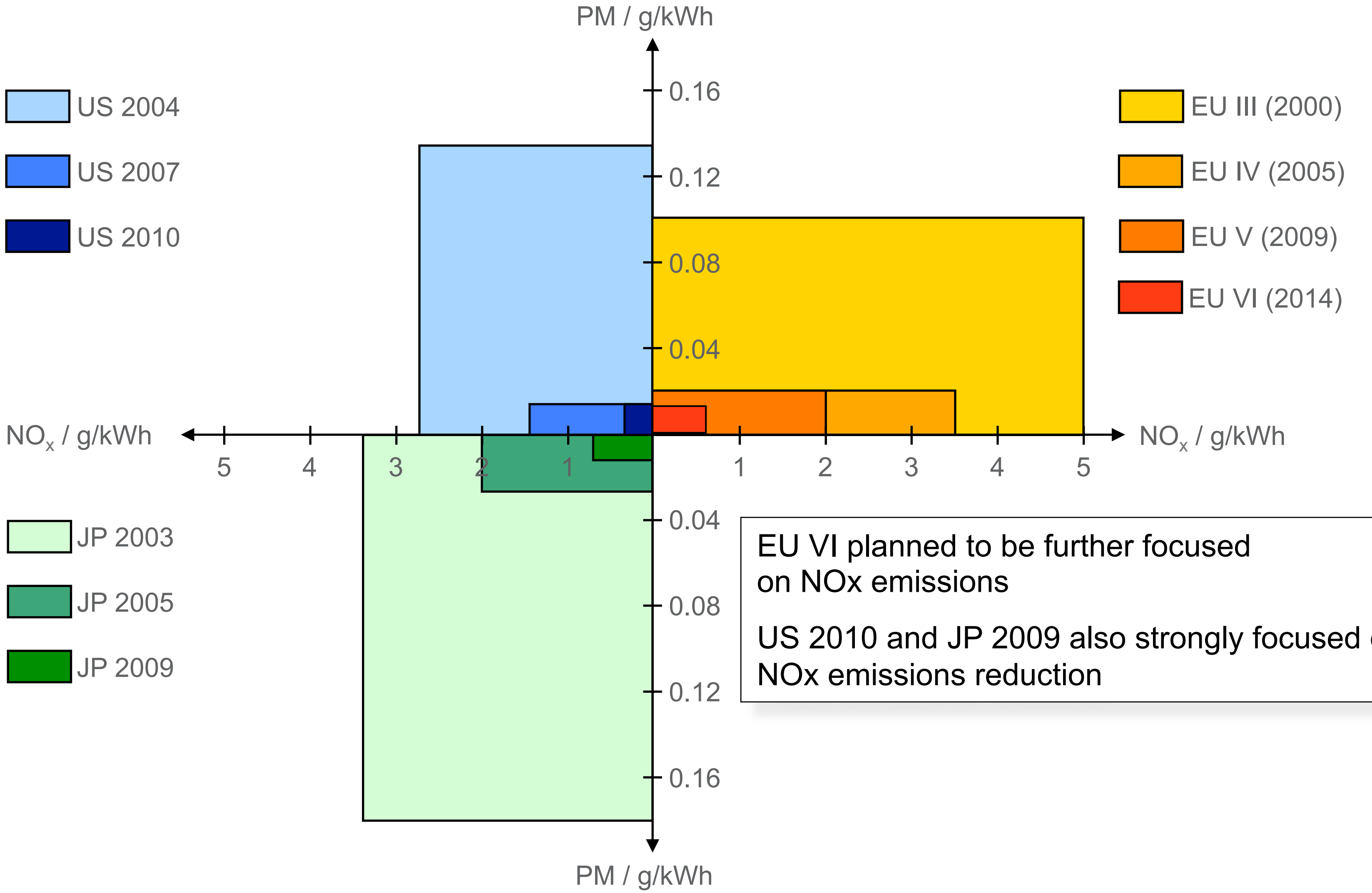
PM & NOx Emissions Legislation for Passenger Cars



EU 6 as well as US Tier 2 Bin 5 passenger car emissions legislation strongly focused on NOx emissions

EU 6: 6x10^{11}#/km PM and 4.5 mg/km

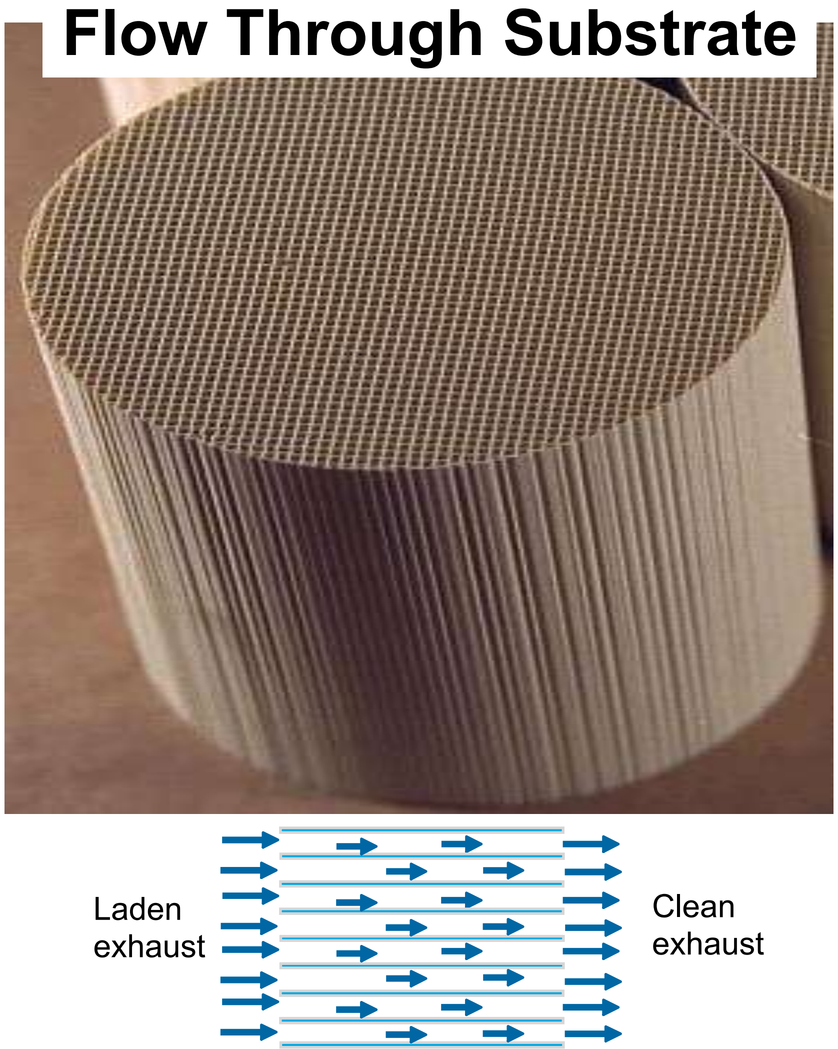
Current and Future HDD Emissions Legislation

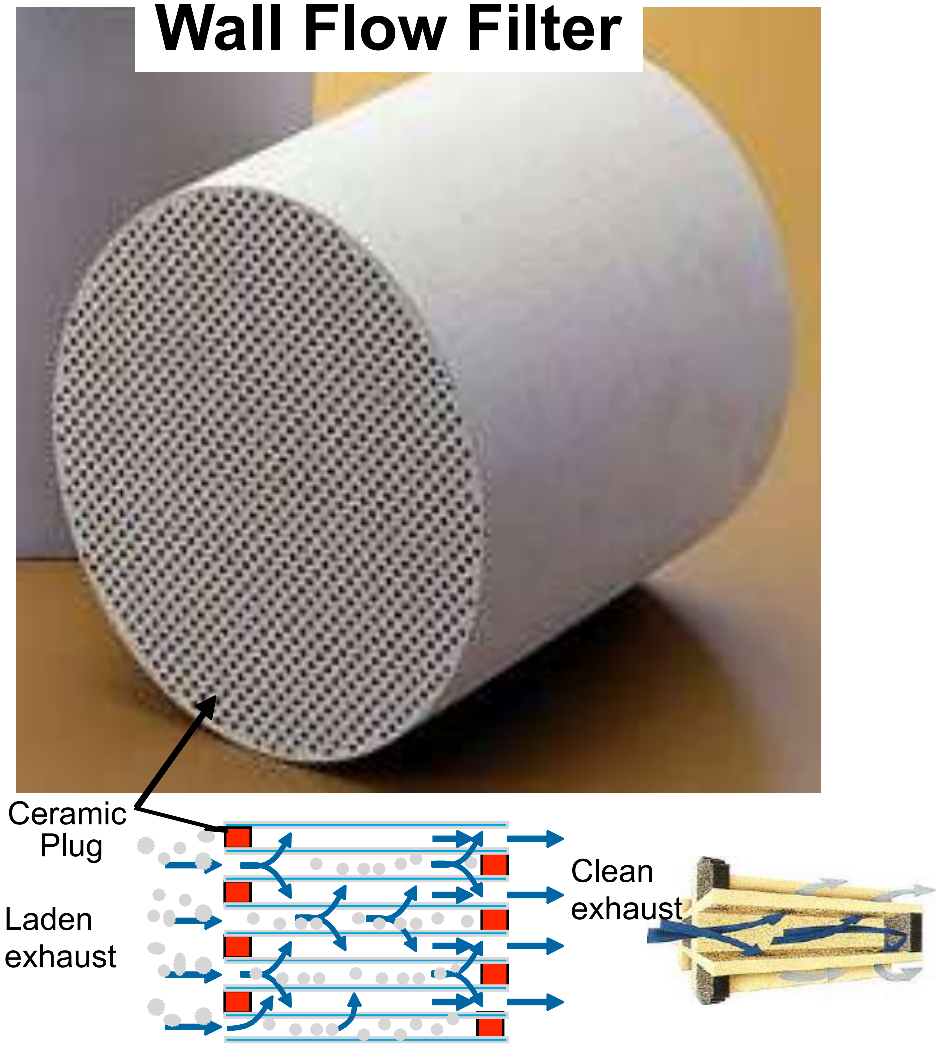


EU VI planned to be further focused on NOx emissions

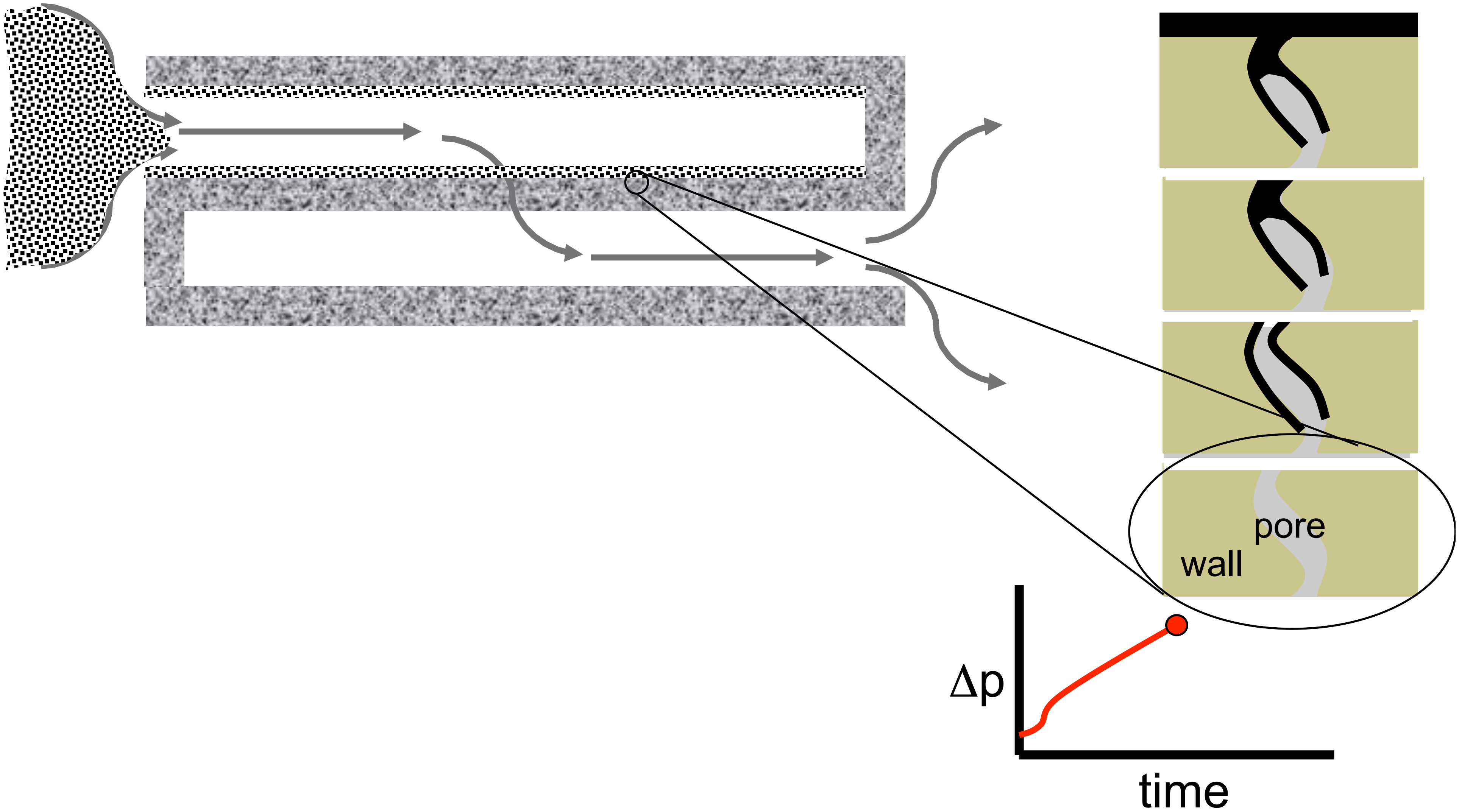
US 2010 and JP 2009 also strongly focused on NOx emissions reduction

New challenges are being posed by Diesel Particulate Filters

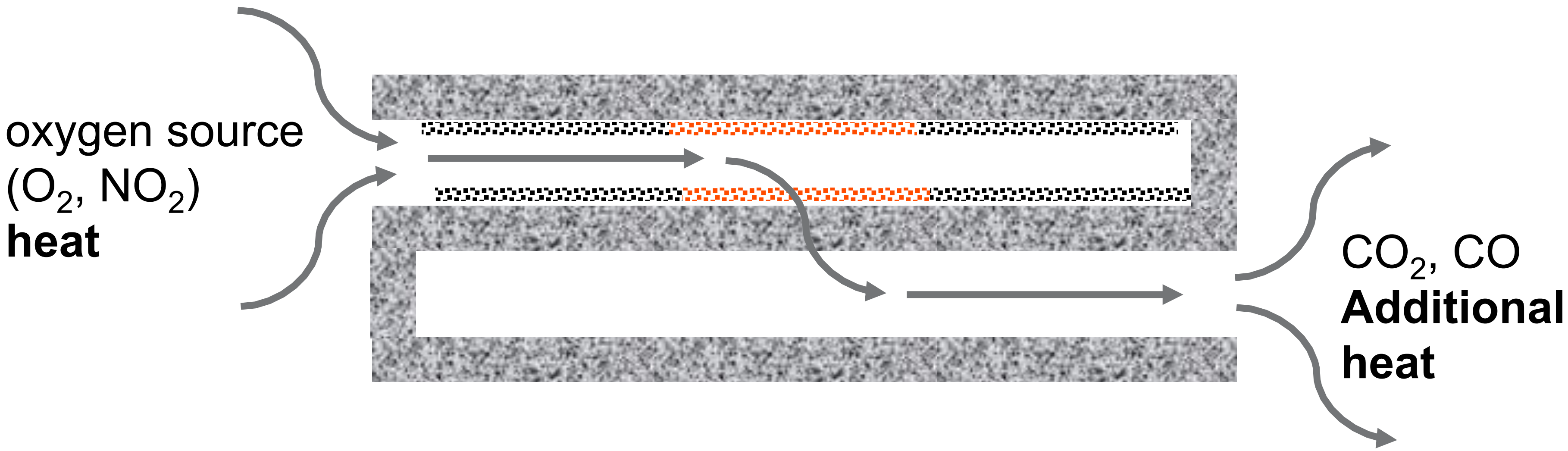


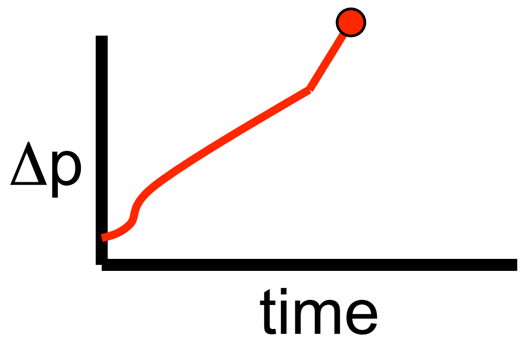


Filtration and Soot Loading

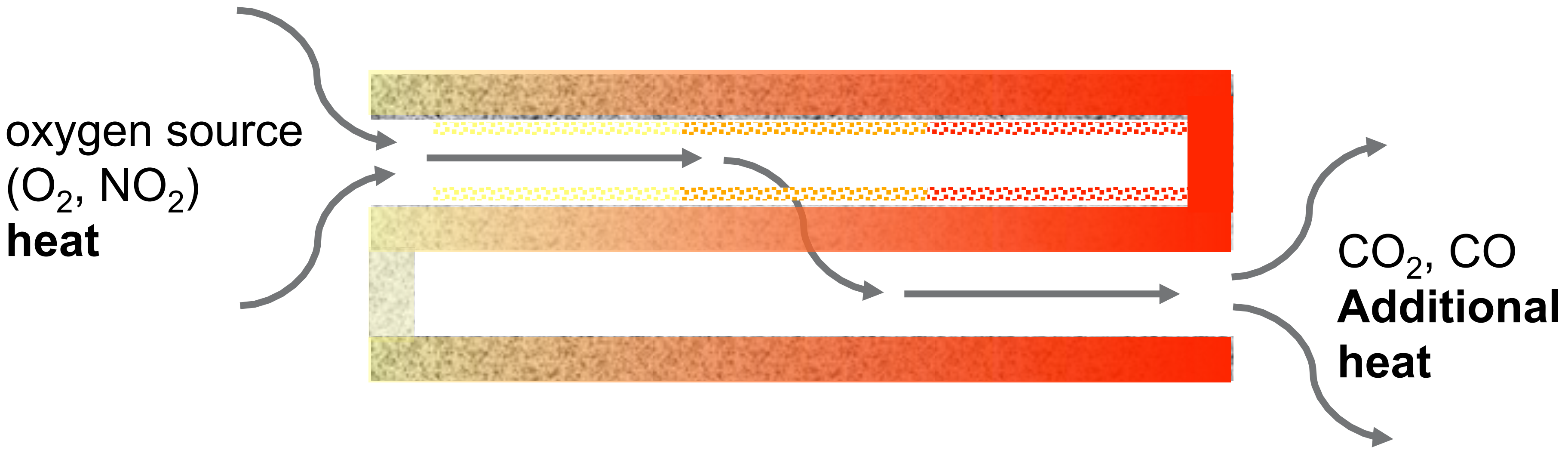


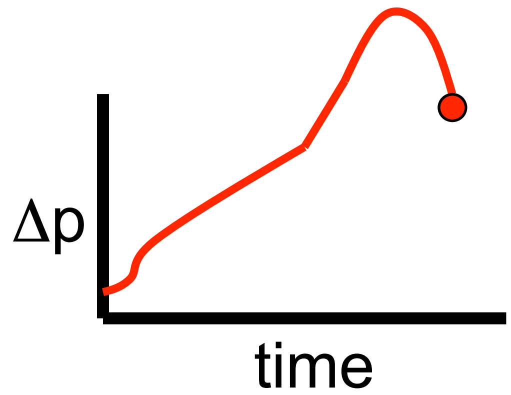
Regeneration



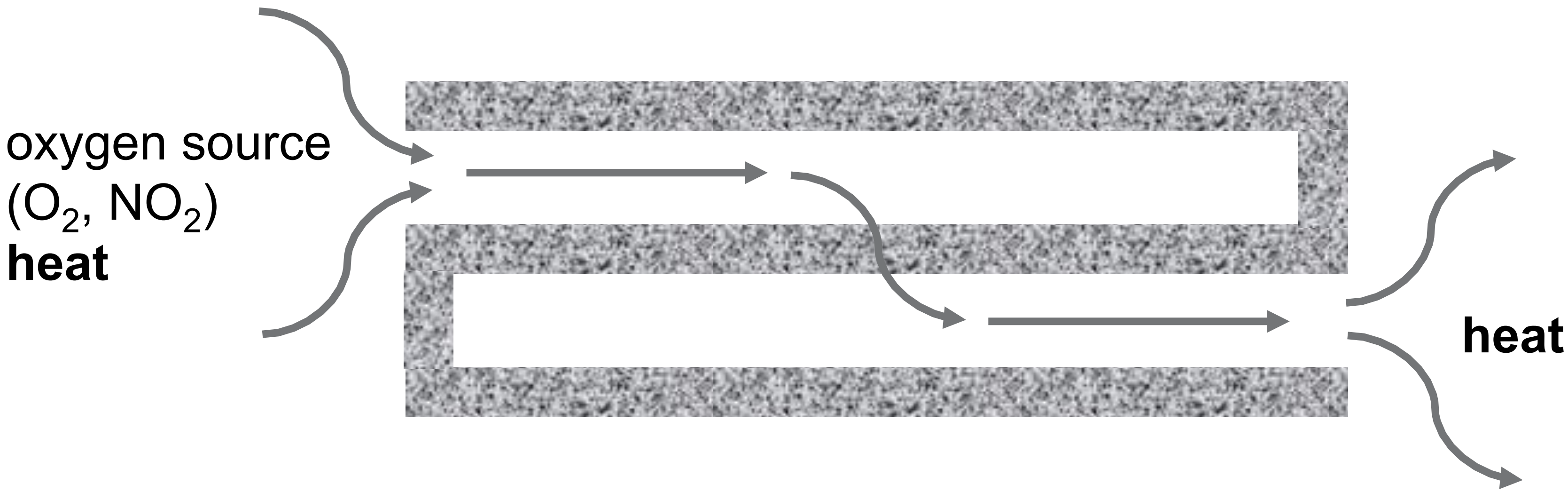


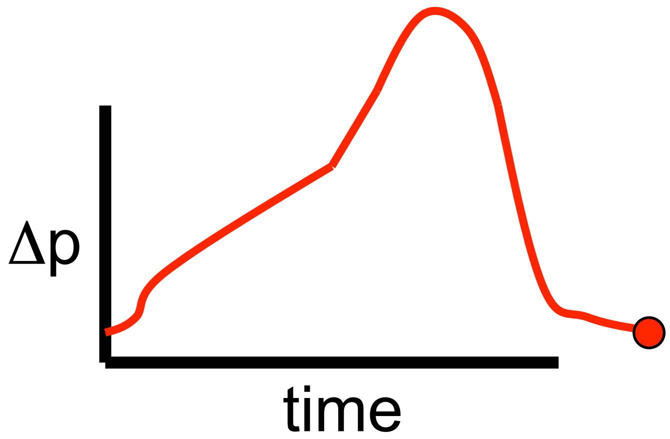
Regeneration





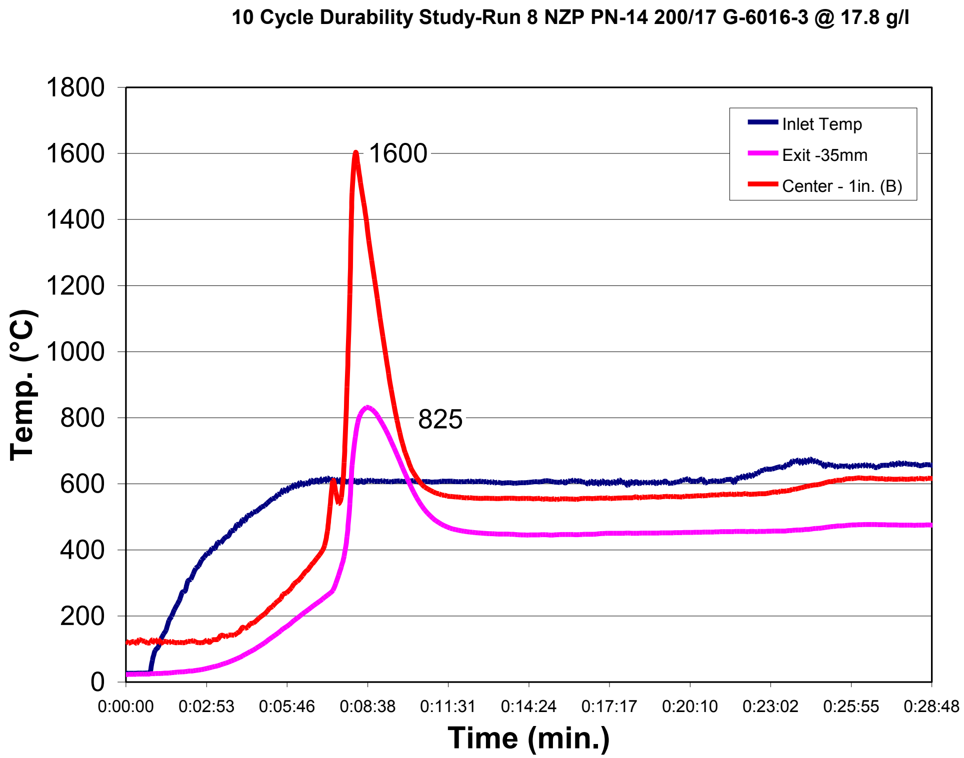
Regeneration





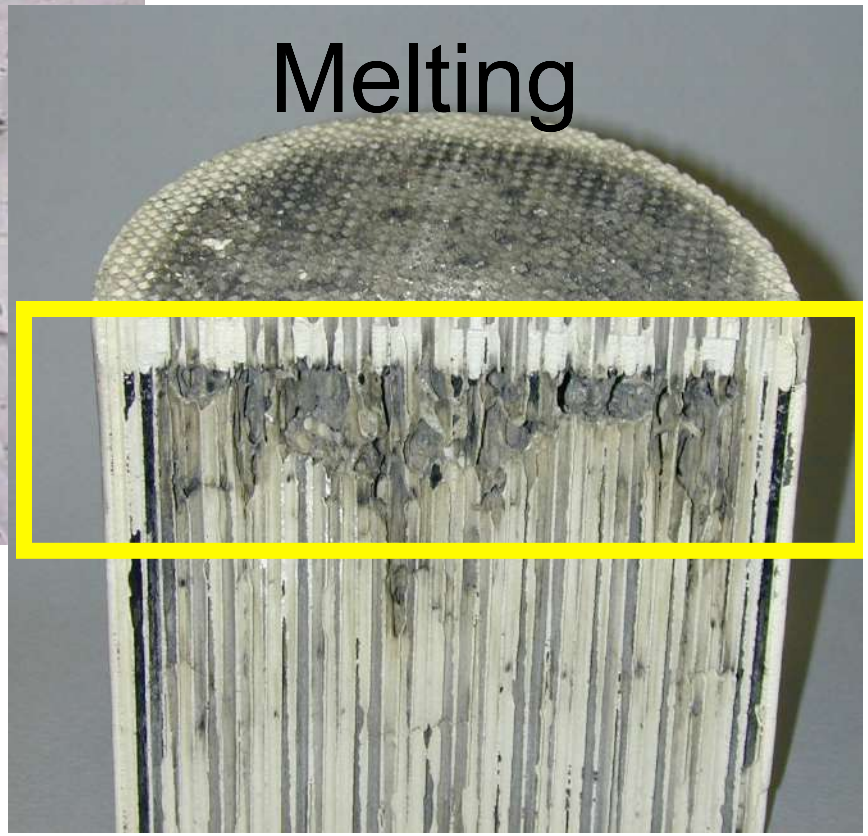
“Uncontrolled” Regeneration

- Hot filter, low exhaust flow rate, high oxygen concentration
- Catalysts and filters can get too hot (below) or experience too large of a temperature gradient (results in cracking)



Cutler & Merkel, SAE 2000-01-2844

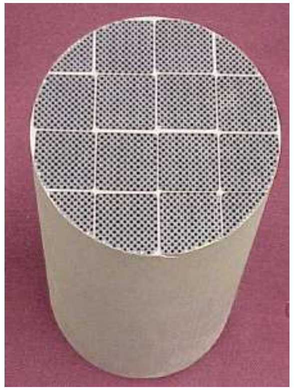
Uncontrolled Regeneration Survivability Issues



Filter requirements
Materials properties

- Thermal shock resistance
  - Low CTE
  - Low elastic modulus
  - High strength

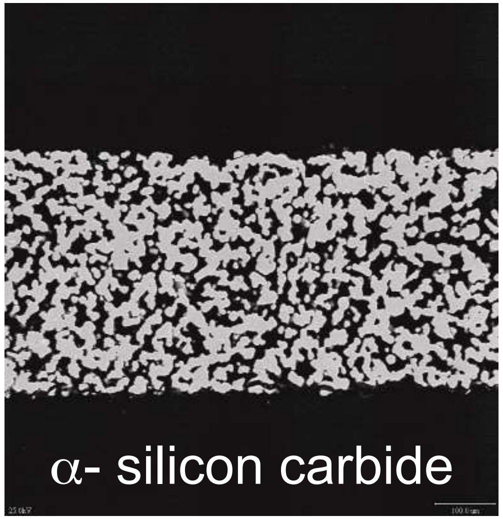
Enables monolithic filters as opposed to segmented



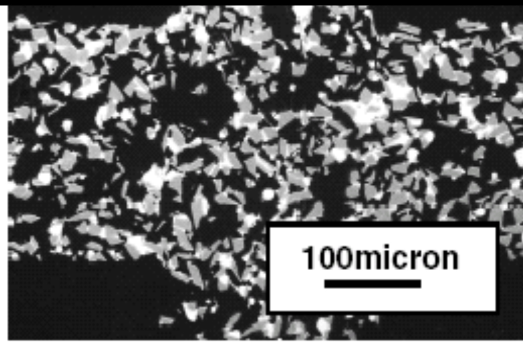
- Engineered pore structure
  - Porosity and pore size and distribution
  - Filtration efficiency
  - Pressure drop – Fuel penalty – CO_2 emissions
  - Strength
- High melting temperature

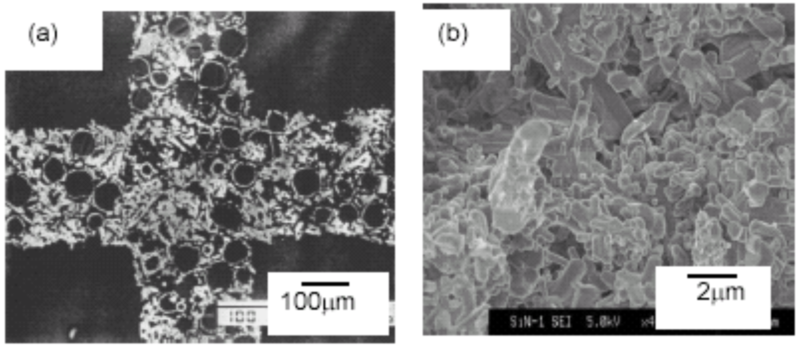
High Heat Capacity

Porosity engineering in non-oxide ceramics

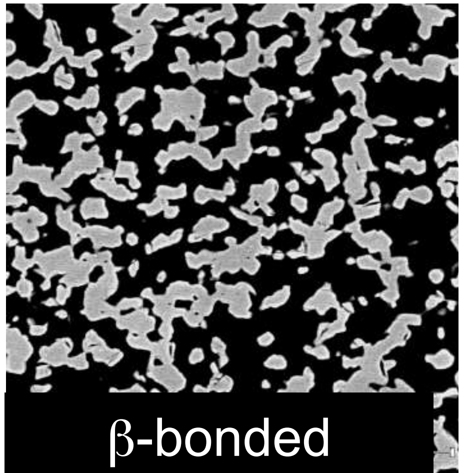


Si-bonded
α-silicon carbide





silicon nitride



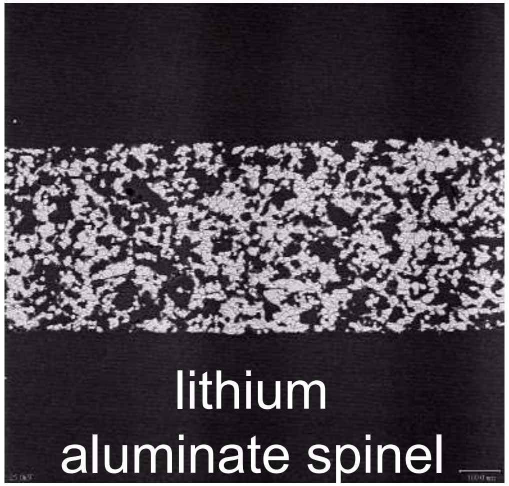
β-bonded
α-silicon carbide

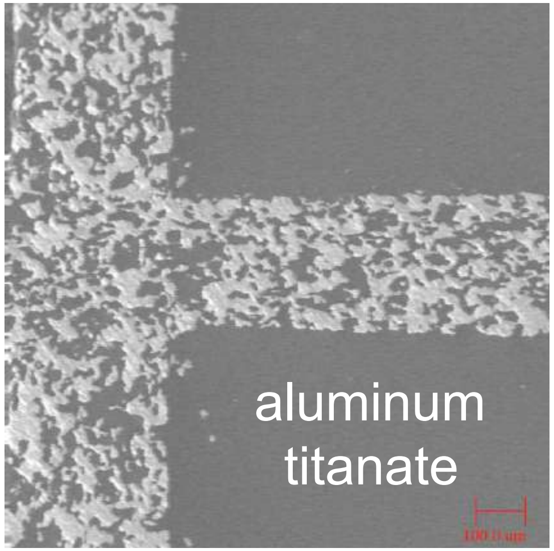
High heat capacity porous ceramics generally exhibit "high" thermal expansion…

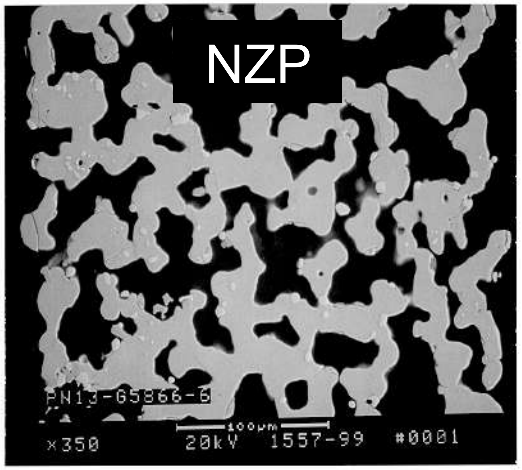
Porous Material	T_{melt} (°C)	T_{max} (°C) Est. use in air	CTE_c ($x10^{-7}$/°C)	Intrinsic Density (g/cm^3)	Specific Heat @ 500°C (J/g°C)	Thermal Conductivity @ 500°C (W/m K)
Alumina (Al_2O_3)	2050	1900	88	3.97	0.88	~8
Cordierite ($Mg_2Al_4Si_5O_{18}$)	1460	1350	6	2.51	1.11	~1
Mullite ($Al_6Si_2O_{13}$)	1810	1600	53	2.50	1.15	~2
Aluminum Titanate (TiO_2-Al_2O_3)	1600	1500	10	3.40	1.06	~1
NZP ($XZr_4P_6O_{24}$, X=alkaline earth)	1900	1800	5	3.44	0.75	~1
α- Silicon Carbide (SiC)	2400	1350	45	3.24	1.12	~20
β-bonded α- Silicon Carbide (SiC)	2400	1350	45	3.24	1.11	~12
Si-bonded α- Silicon Carbide (Si-SiC)	1400	1350	43	3.19	1.12	~10
Silicon Nitride (Si_3N_4)	1900	1350	30	3.0	1.15	~5

W.A. Cutler, Ceram. Eng. SCi. Proc., 25[3] 421-430, 2004

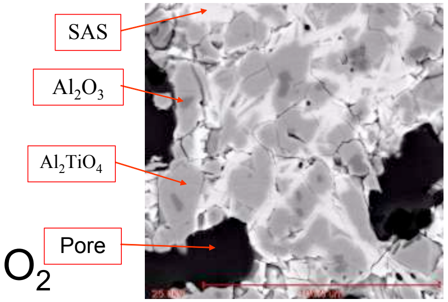
High heat capacity low expansion oxides for monolithic filters

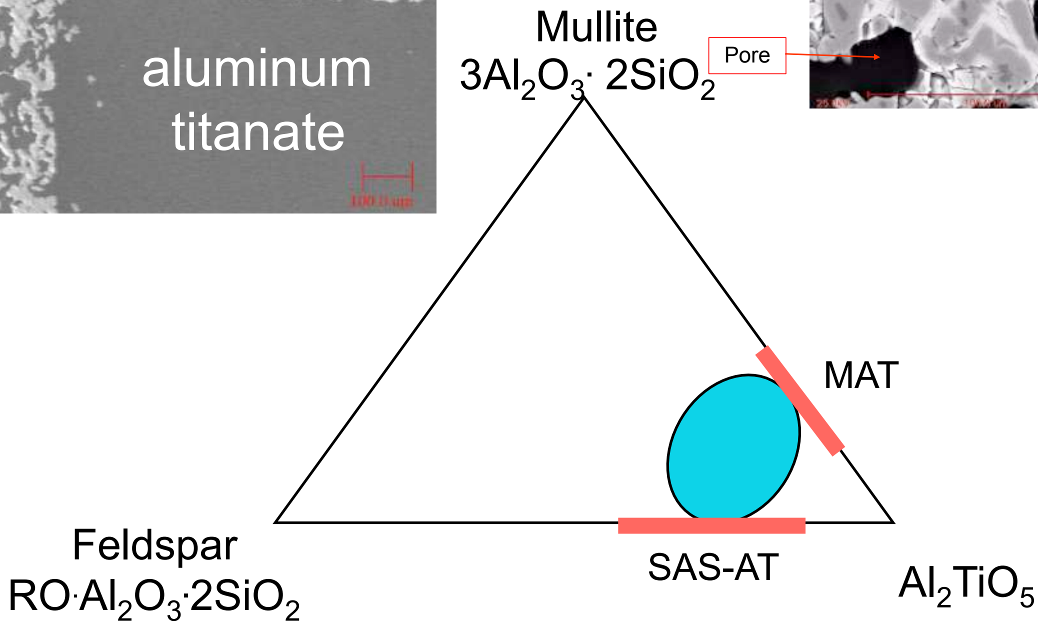






DuraTrap® AT
Phase Assemblage

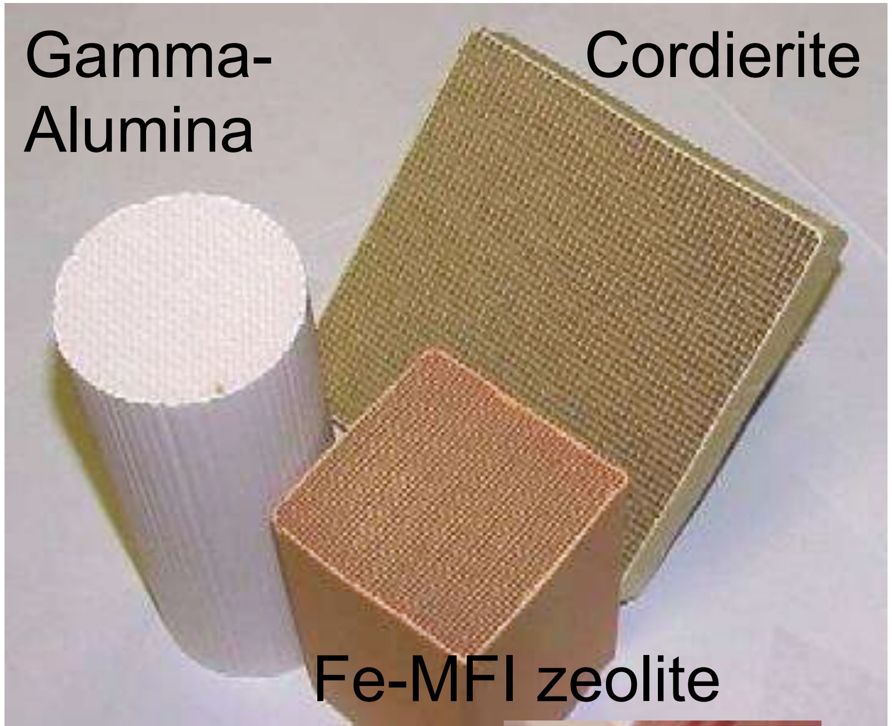




Ogunwumi et al., 28th Int. Cocoa Beach conference on Advanced Ceramics and Composites, 2004

Extruded High surface area catalysts

- Extruded Vanadia Titania for SCR deNOx
- Zeolites
  - Extruded substrates
  - Membranes
- Extruded iron oxide catalysts
- Extruded γ-alumina
  - Catalyst support



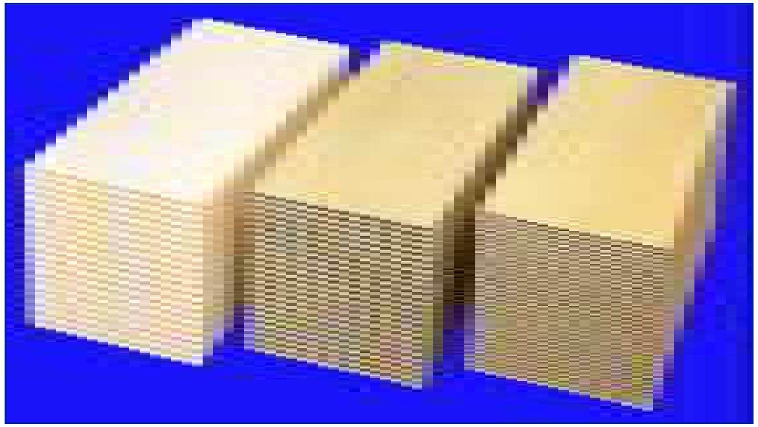
Promoted Fe_2O_3

Stationary Emissions Control - DeNOx

- Monolithic V_2O_5/TiO_2 catalysts are the standard in today's largest fixed bed catalyst application – SCR reactors
  - Main active component is V_2O_5
  - WO_3 increases thermal stability
  - Reactor volumes from $500\ m^3$ - $1200\ m^3$
  - Selective catalytic reduction of NOx

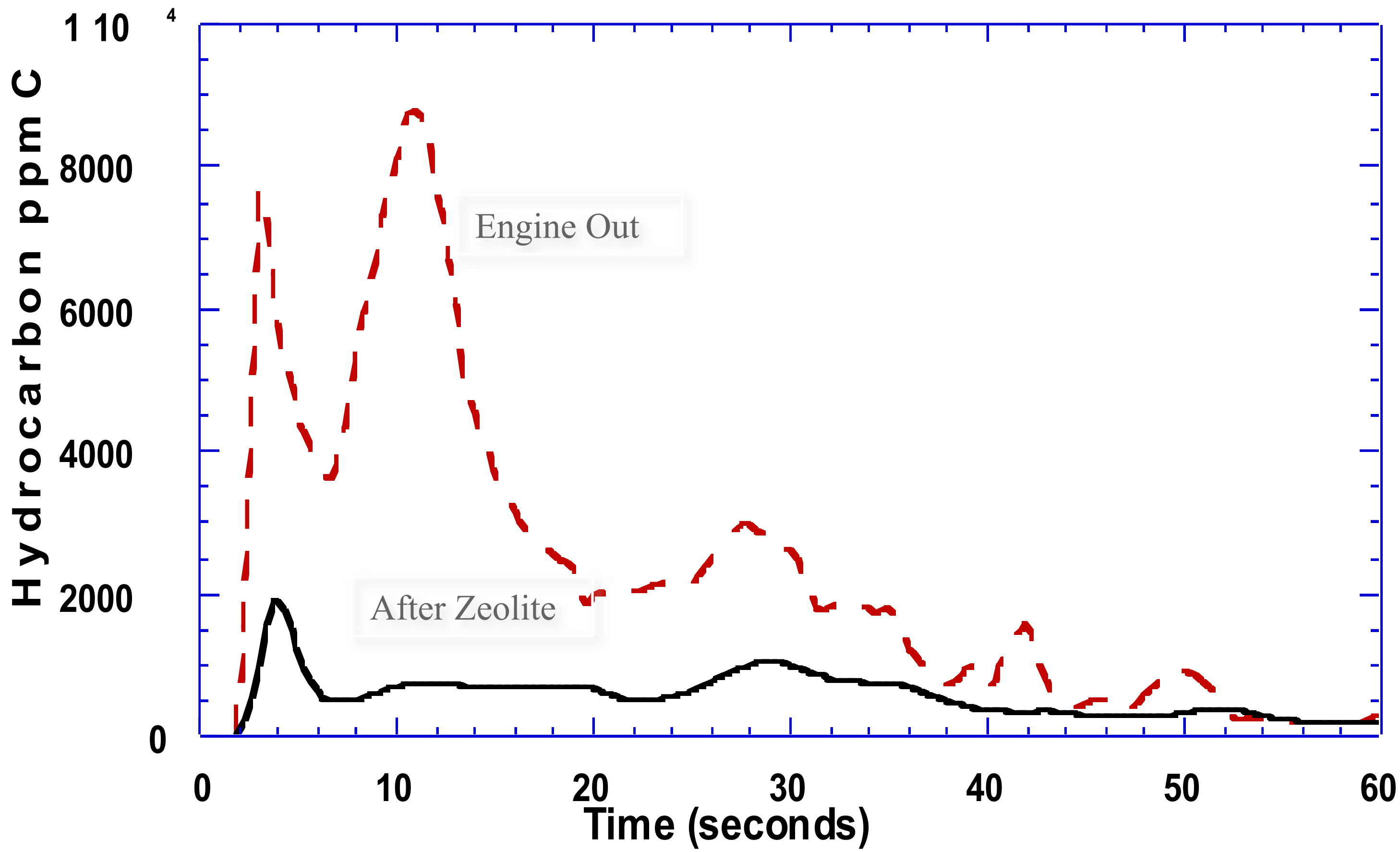
    $4NH_3 + 4NO + O_2 \text{ ---> } 4N_2 + 6H_2O$

SCR Catalyst for Coal, Oil and Gas Applications



EPA/EPRI Symp. On Stationary Combustion NOx Control (1995)

Zeolite honeycomb
Hydrocarbon Adsorption During Engine Start



Significant amount (>80%) of cold start HC is adsorbed on Zeolite honeycomb

Patil, Williams et al. SAE 960348

Potassium Promoted Iron Oxide

- Catalyst used for the dehydrogenation of Ethylbenzene to Styrene

100cpsi 200cpsi 400cpsi

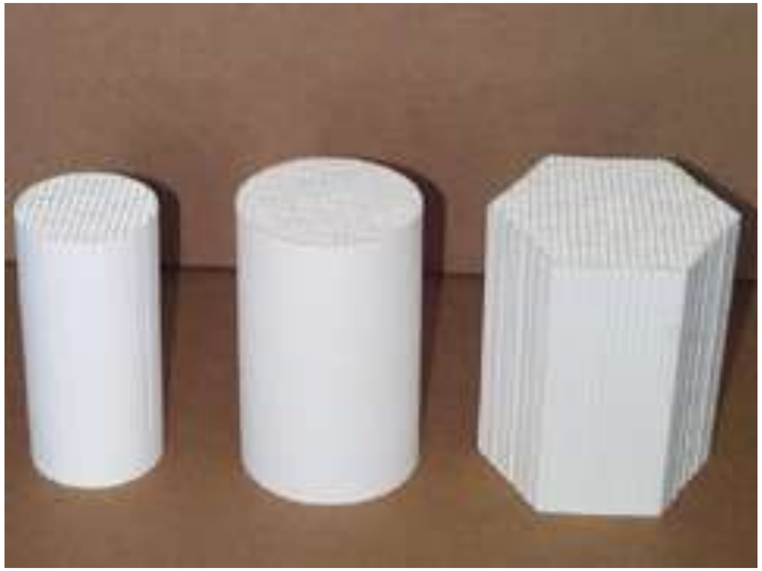
Ø 1"

- When suitable colloidal polymers are used to adjust the batch rheology it can be extruded to monoliths
  - Surface Area 3-4m2/g
  - Porosity 50-60%
  - Pore Size 330-400nm
  - Crush Strength >1300psi

Addiego et al, Catal. Today, 69(2001) 25

Extruded γ-Alumina with engineered porosity

- Cell density, surface area, and porosity tailored to the application



- Example properties

Sample	Surface Area (m^2/g)	% Porosity	%Pore Size >1000Å
A	240	64	2
B	228	64	12
C	190	68	31

Addiego et al., 28th Int. Cocoa Beach conference on Advanced Ceramics and Composites, 2004

Conclusions

- Extruded synthetic Cordierite with low CTE has been successfully used as macro-cellular body for exhaust catalyst support during the last 30 years
- Ceramic filters have successfully been applied to Diesel Particulate Filters with active regeneration for 20 years and extensively during the last 10 years
  - Challenges to use oxide ceramics for this particular demanding application have been overcome
- The use of oxide cellular ceramics honeycombs as high surface area extruded catalyst remains an active area of research with many promising applications in the future for remediation of both mobile and stationary emissions as well as for use as structured catalyst in the chemical processing industry

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