19th ETH-Conference on Combustion Generated Nanoparticles

Soot Deposit Evolution and the Mechanism of Particle Emissions During Regeneration in Diesel Particulate Filters

A.G. Konstandopoulos[1,2],
A. Melas[1,2], P. Baltzopoulou[1]
N. Vlachos[1], M. Kostoglou[1,3],

[1]*Aerosol and Particle Technology Laboratory, CPERI/CERTH, P.O. Box 60361, Thermi 57001, Greece*
[2]*Department of Chemical Engineering, Aristotle University, Thessaloniki, Greece*
[3]*Department of Chemistry, Aristotle University, Thessaloniki , Greece*

CPERI Chemical Process & Energy Resources Institute

CERTH CENTRE FOR RESEARCH & TECHNOLOGY-HELLAS

Motivation

Soot Deposit Growth

- Soot deposit is major contributor to Diesel Particulate Filter ΔP
- Need reliable soot deposit microstructural properties for DPF Simulation
- Develop on-board soot sensing methods in conjunction with DPF management and control

Soot Deposit Oxidation

- Soot deposit burnout gives rise to nanoparticle emissions, that are not yet understood based on filtration theory
- Need mechanistic models of soot deposit oxidation for DPF Simulation
- Develop on-board soot sensing methods in conjunction with DPF management and control

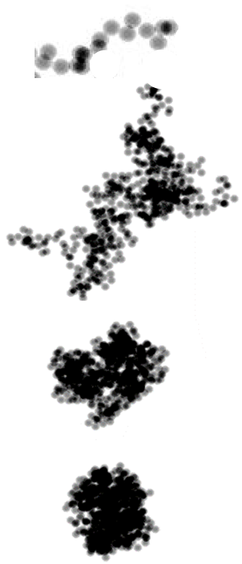
Diesel Soot Aggregate Morphology

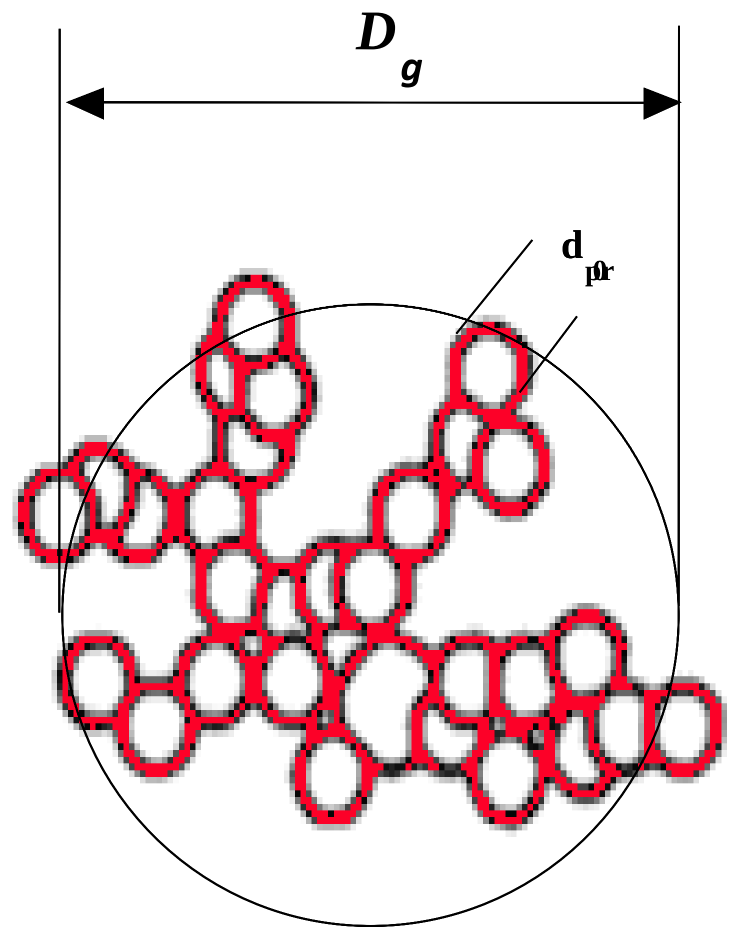
Soot fractal aggregate

Number of primary particles per aggregate

$$N_A = k_g \left[\frac{D_g}{d_{pr}} \right]^{D_f}$$

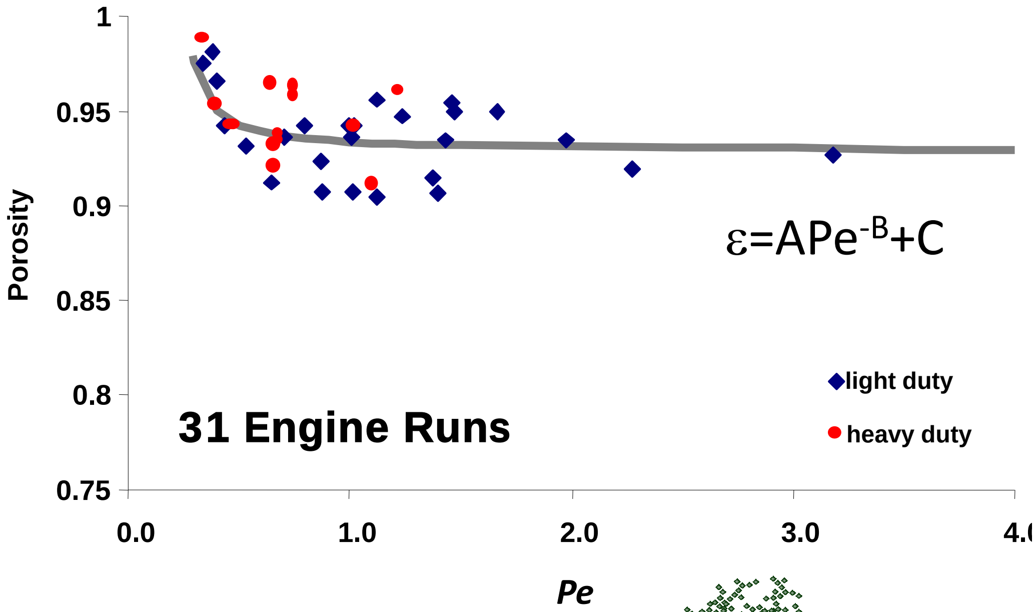
$$D_f = \begin{cases} 1 & \text{chains} \\ 1.8 & \text{CC-DLA} \\ 2.4 & \text{MC-DLA} \\ 3 & \text{compact} \end{cases}$$

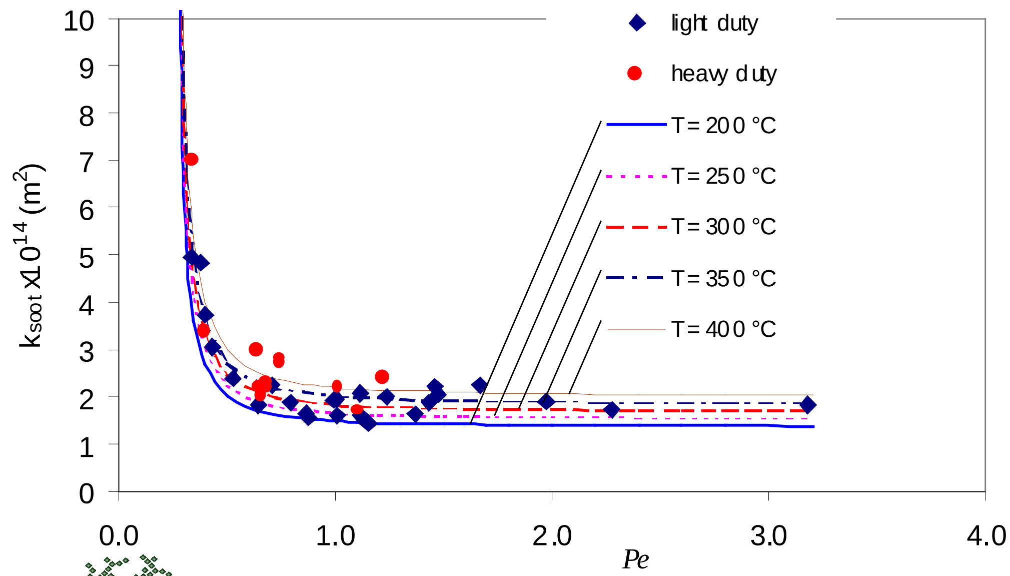


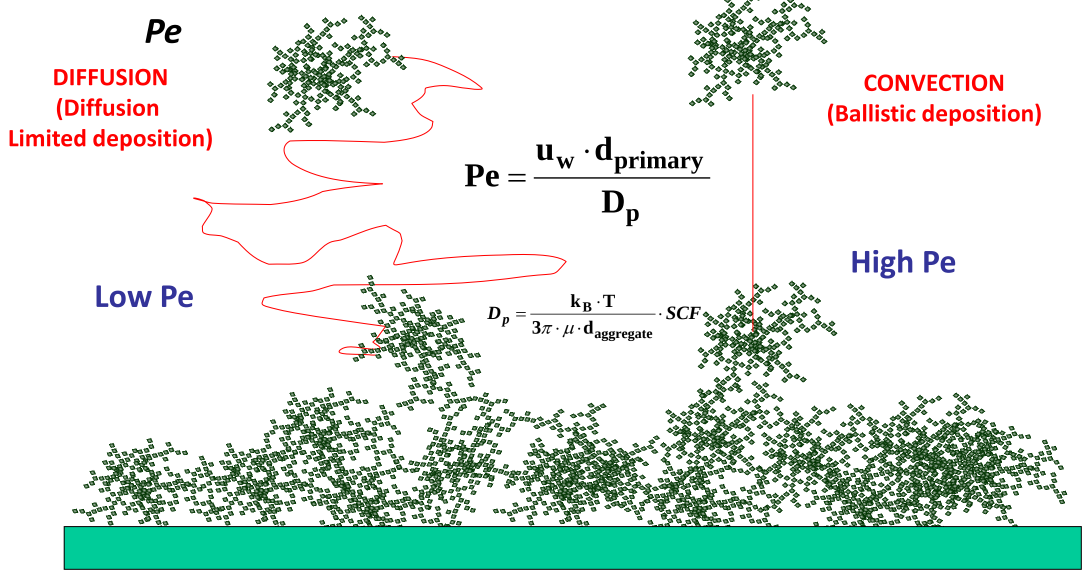


Soot deposit structure variation with Pe number

First ever experimental data were published in 2002





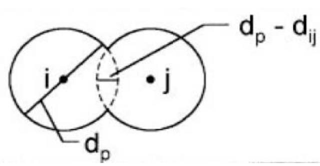


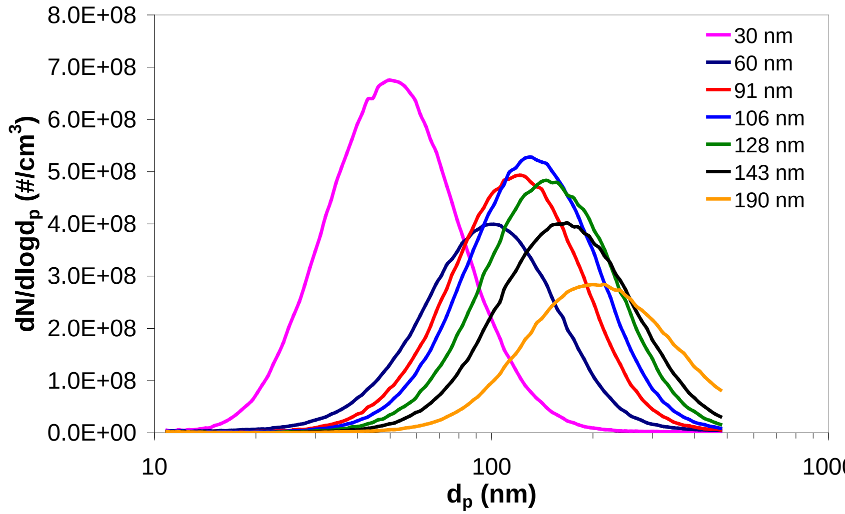
Konstandopoulos et al. (2002) SAE Tech. Paper No. 2002-01-1015, SAE Trans. 111 (J. Fuels & Lubricants), pp. 434-442.

CAST: Combustion Aerosol Standard Characterization

Nominal, D (nm)	D_{me} (nm)	D_f	k_g	C_{ov}
190	*210*	2.25	3.95	0.36
143	*156*	2.27	3.69	0.34
128	*138*	2.14	4.28	0.40
106	*121*	2.13	6.69	0.52
91	*104*	2.03	5.25	0.48
60	*78*	2.15	4.97	0.44

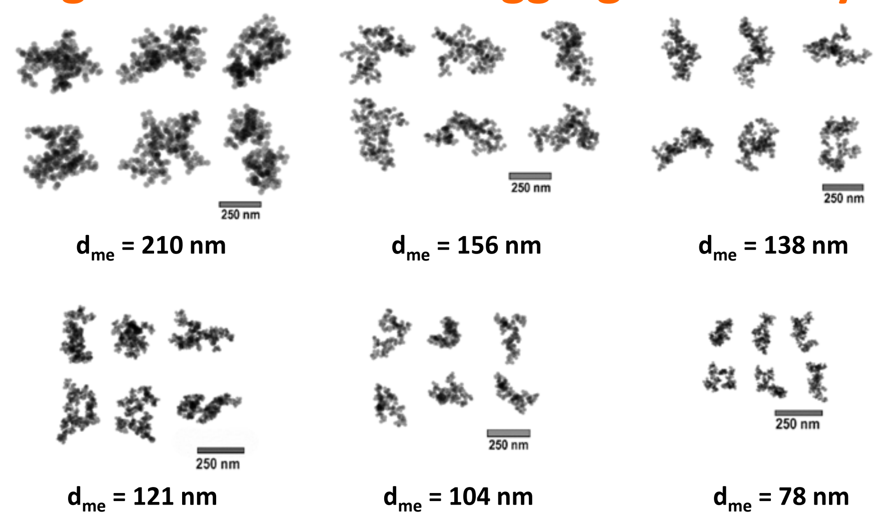
$$C_{ov} = \frac{d_p - d_{ij}}{d_p}$$





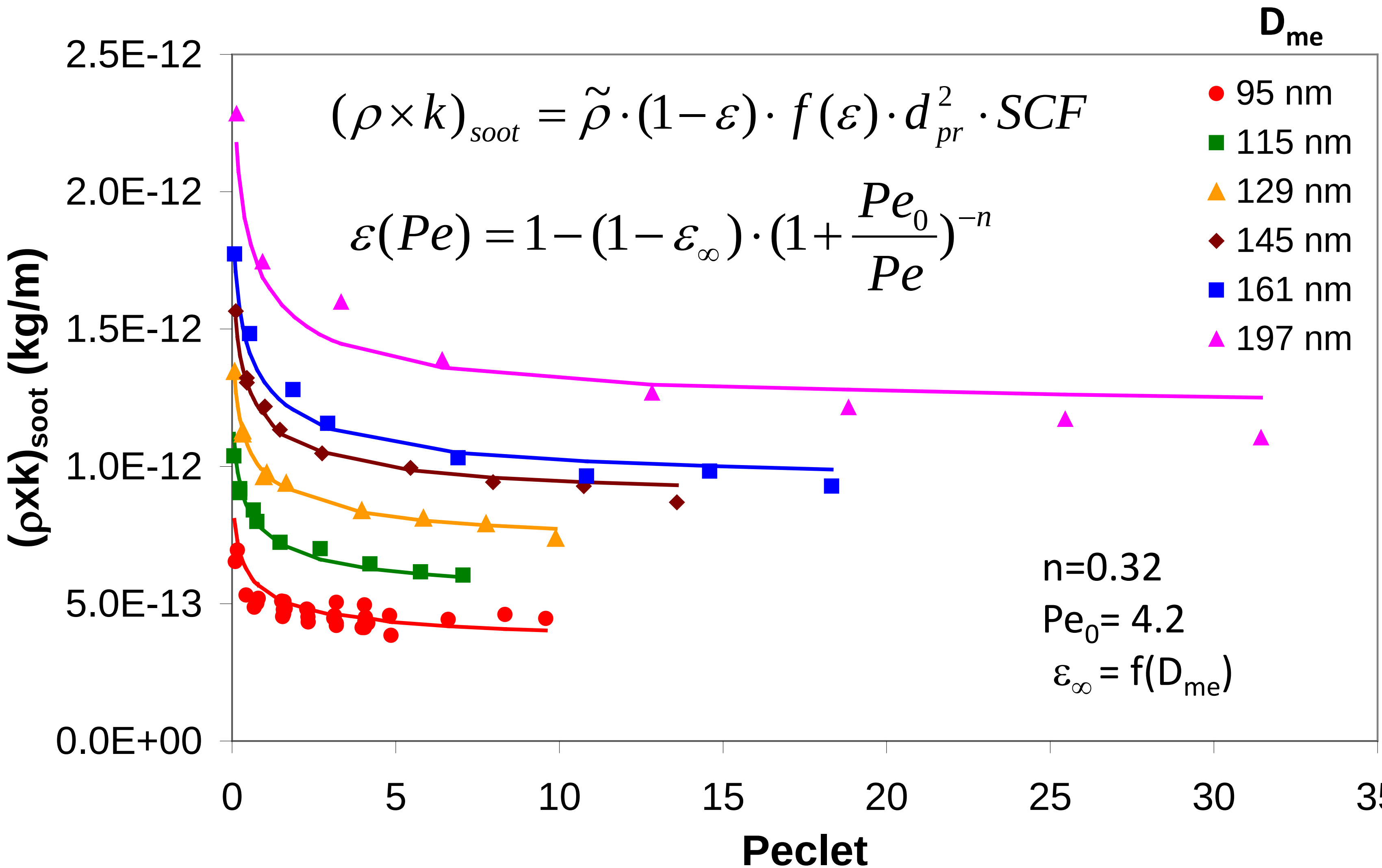
Mobility diameter

"Digital CAST" – Soot Aggregate Library



Konstandopoulos et al. ETH Conference 2010, extension of Filipov et. al, J. of Colloid & Interface Sci., 229, pp. 261-273, 2000

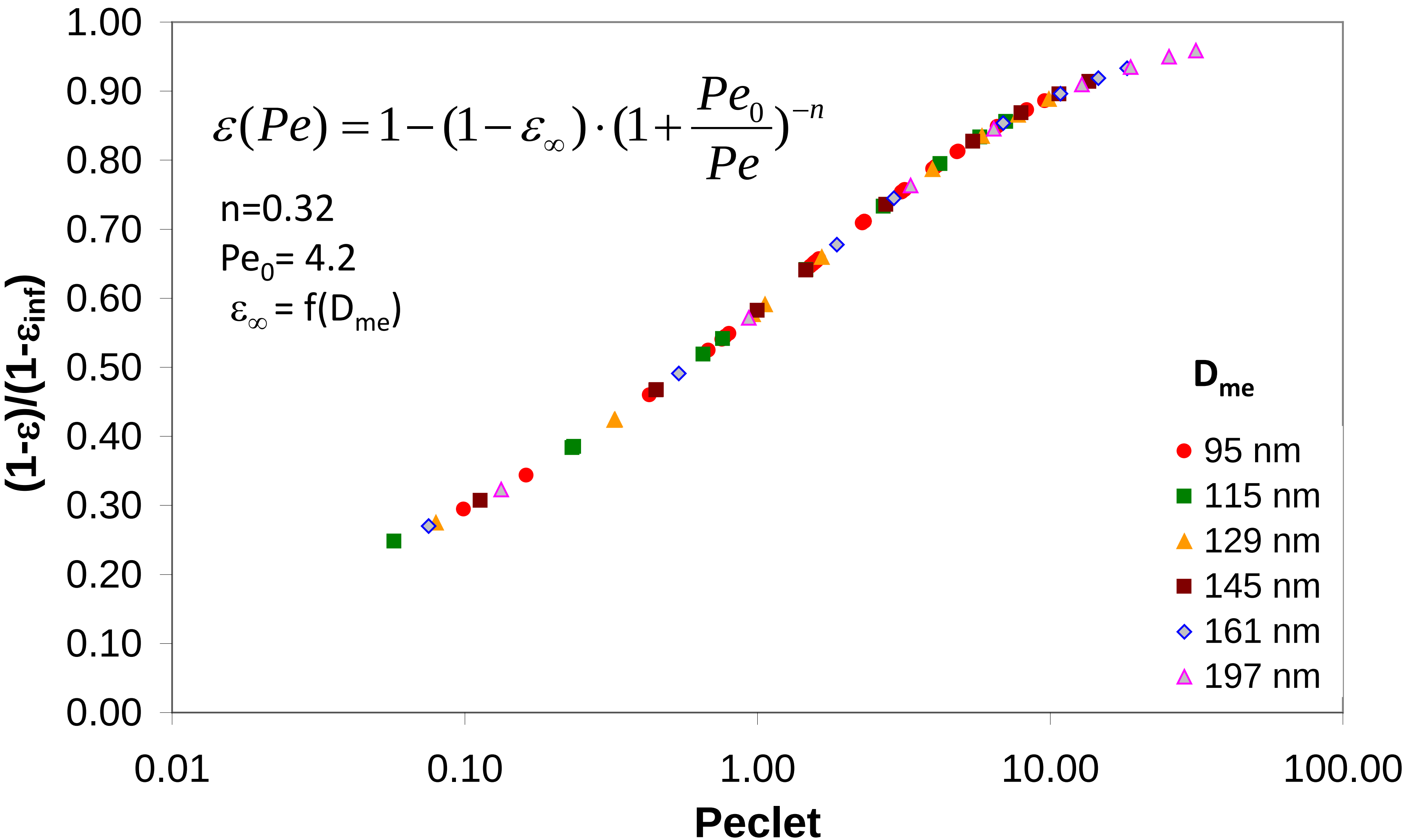
Flow resistance vs. Peclet number



Konstandopoulos et al. SAE Paper 2005-01-0946 (2005)

Rodriguez-Perez D., Castillo J. L., Antoranz J. C., Konstandopoulos A. G. and Vlachos N., EAC 2004, Budapest, Hungary, 6-10 Sep, 2004

Soot Deposit Normalized Porosity



Konstandopoulos et al. SAE Paper 2005-01-0946 (2005)

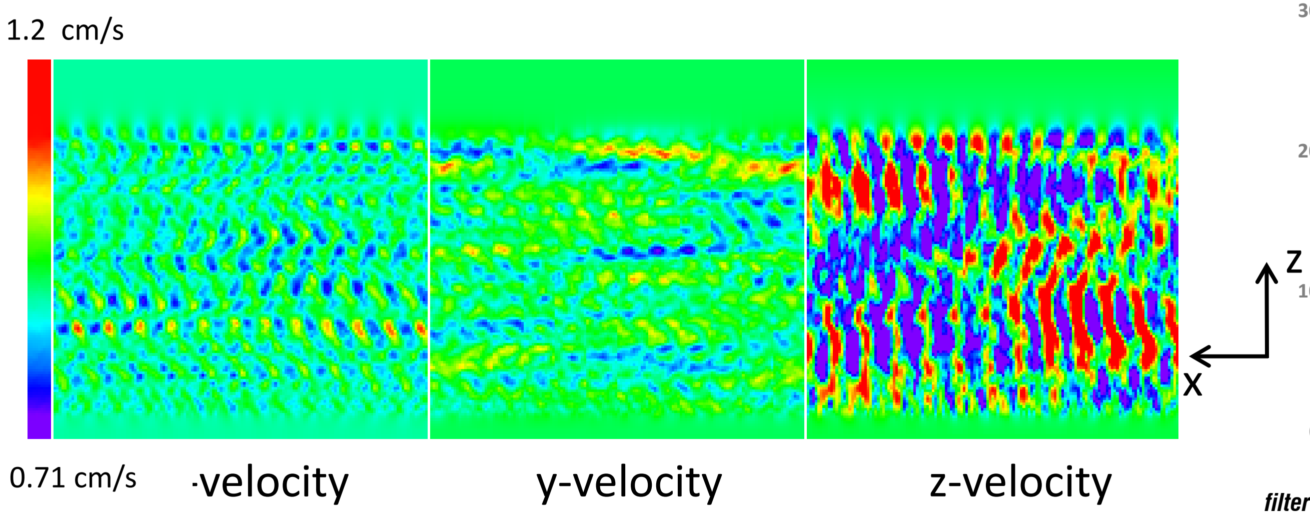
Rodriguez-Perez D., Castillo J. L., Antoranz J. C., Konstandopoulos A. G. and Vlachos N., EAC 2004, Budapest, Hungary, 6-10 Sep, 2004

Simulation of Soot Deposit Evolution

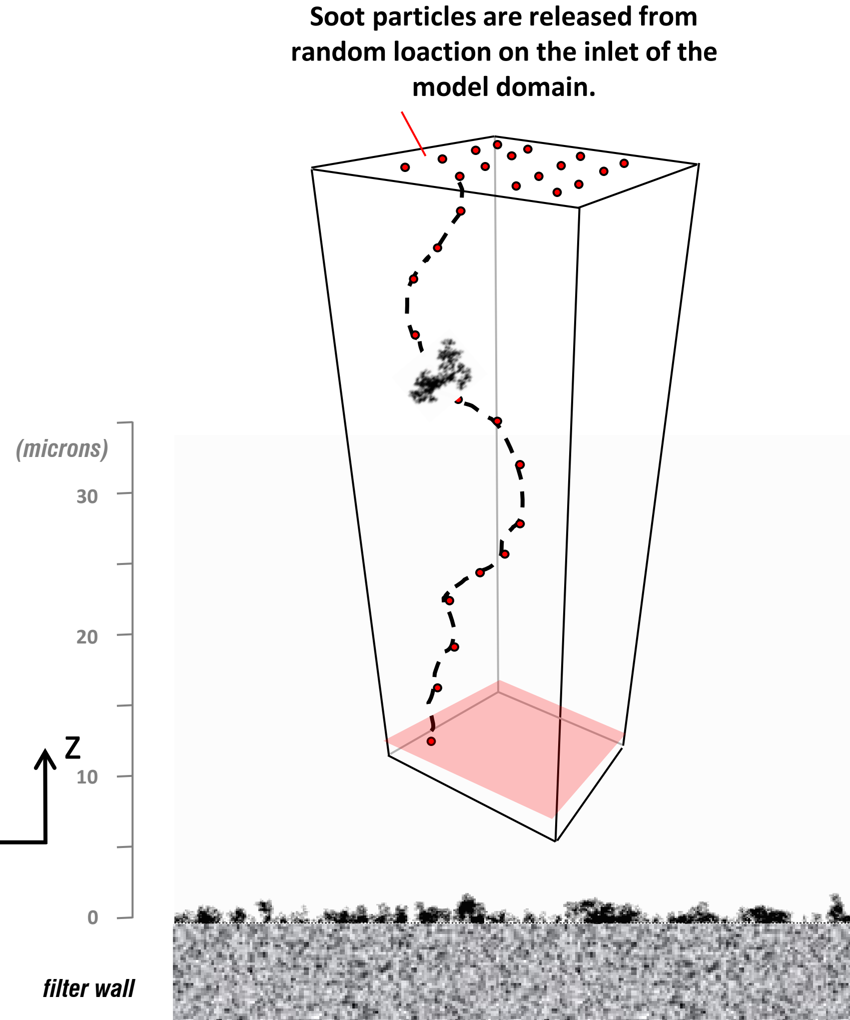
- Realistic soot aggregates (d_{pr}, D_{me}, D_f, k_g, C_{ov})
- Langevin dynamics for aggregates
- Evolving flow field from Microflow simulator*

*Vlachos N., Konstandopoulos A.G. (2006) SAE. 2006-01-0260, SAE Trans. (*Journal of Fuels & Lubricants*), 115, pp. 79-89.

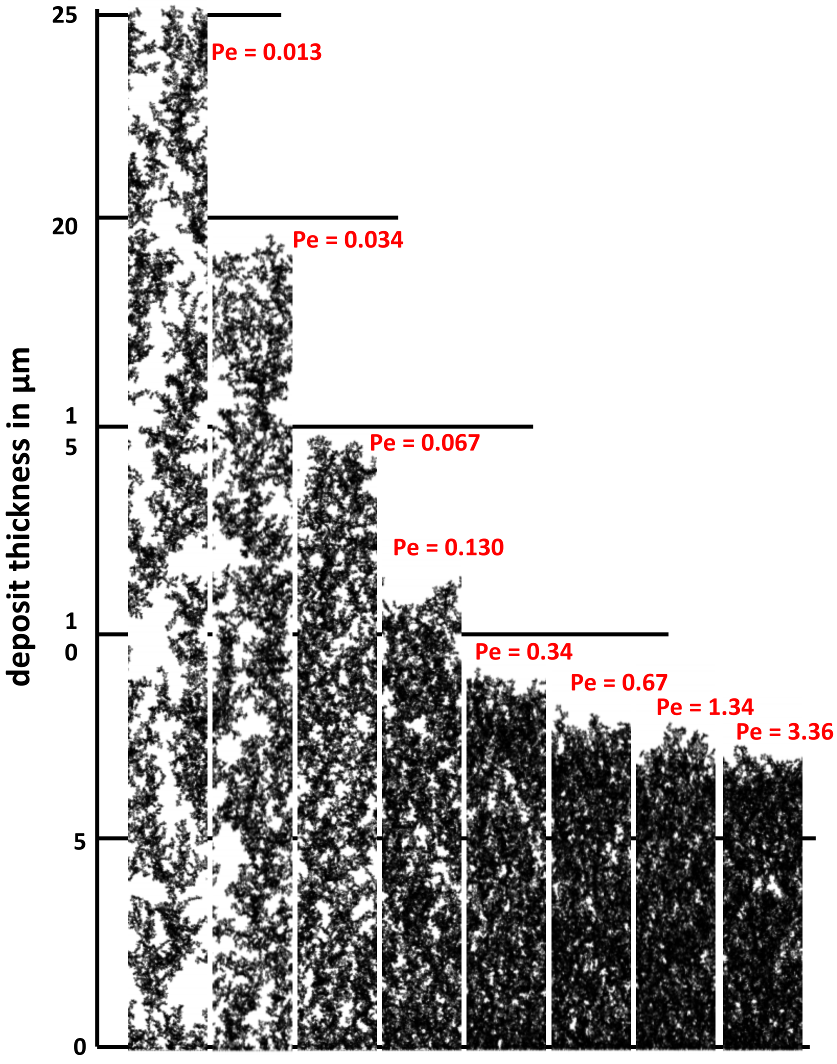
Pe = 0.067



3D Deposit Growth

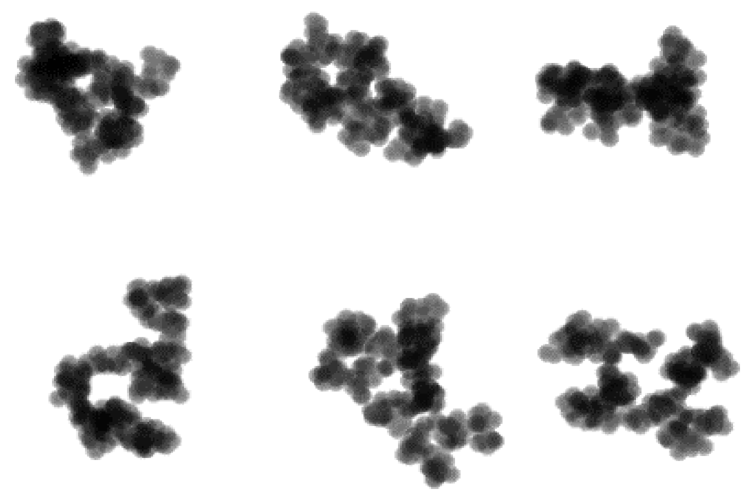


Soot Deposit Evolution vs. Pe

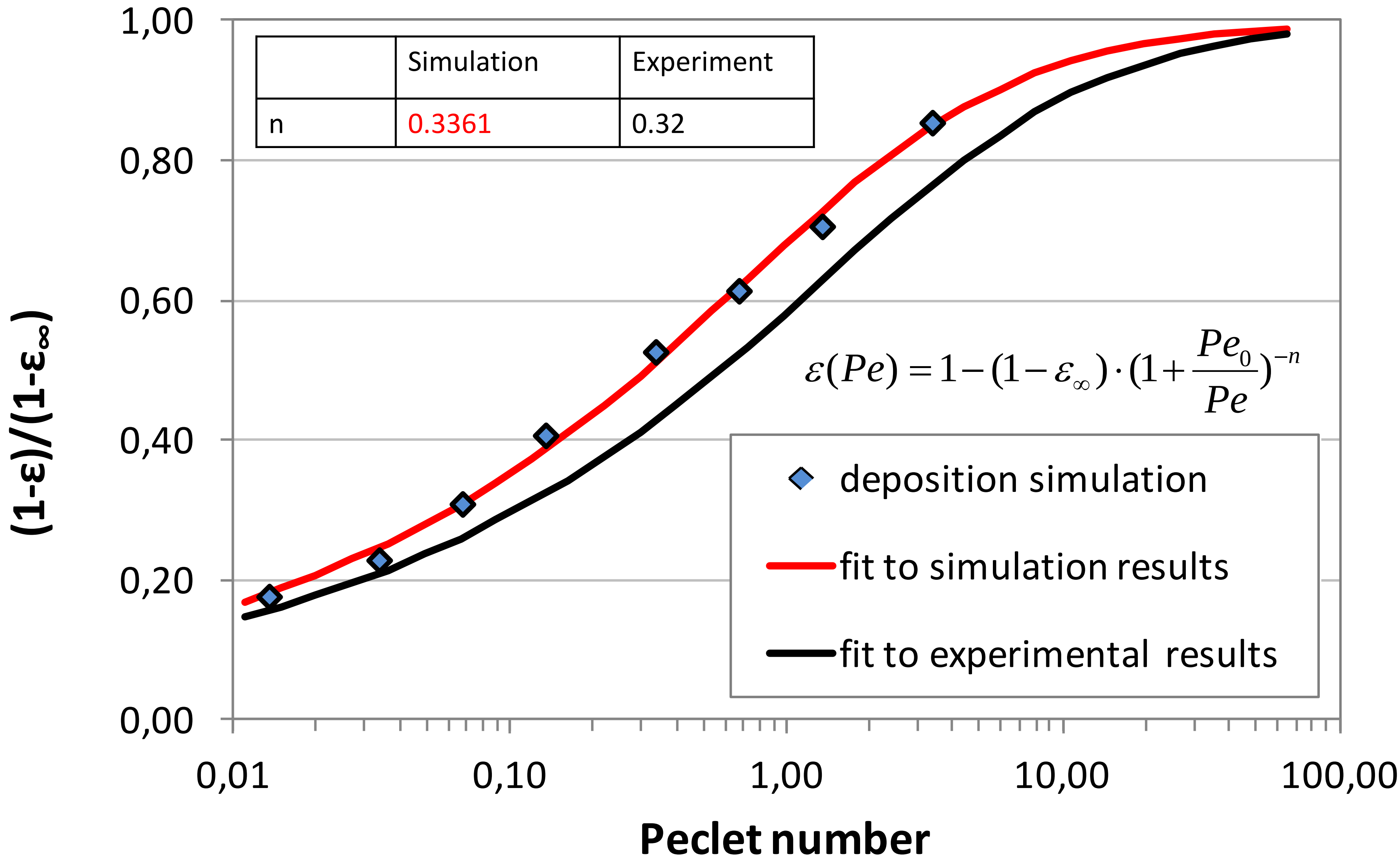


Simulation conditions

- challenge soot mass ≈ 0.02g/m²
- mobility diameter 78nm
- d_o = 17.8nm
- D_f = 2.15 k_g=4.2
- aggregate morphologies



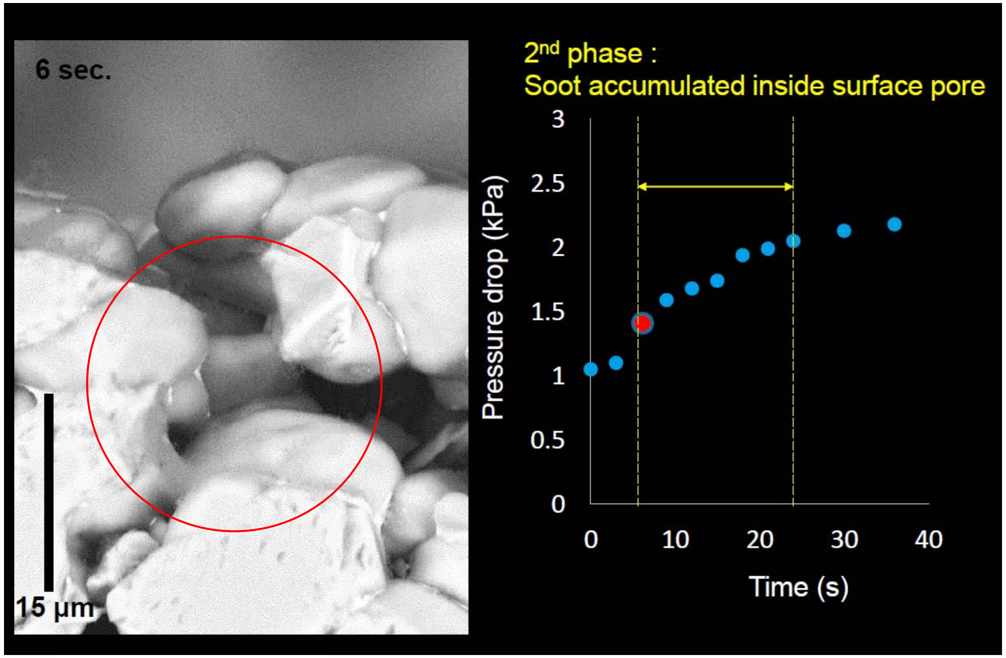
Soot Deposit Evolution vs. Pe



	Simulation	Experiment
n	0.3361	0.32

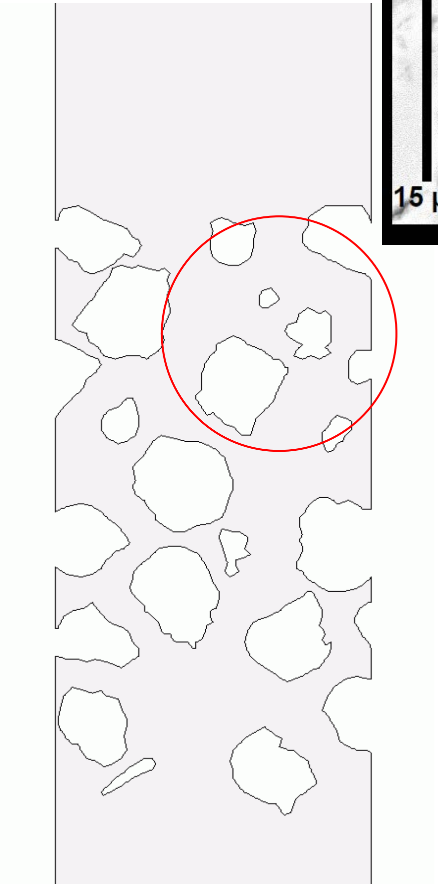
$$\varepsilon(Pe) = 1 - (1 - \varepsilon_\infty) \cdot (1 + \frac{Pe_0}{Pe})^{-n}$$

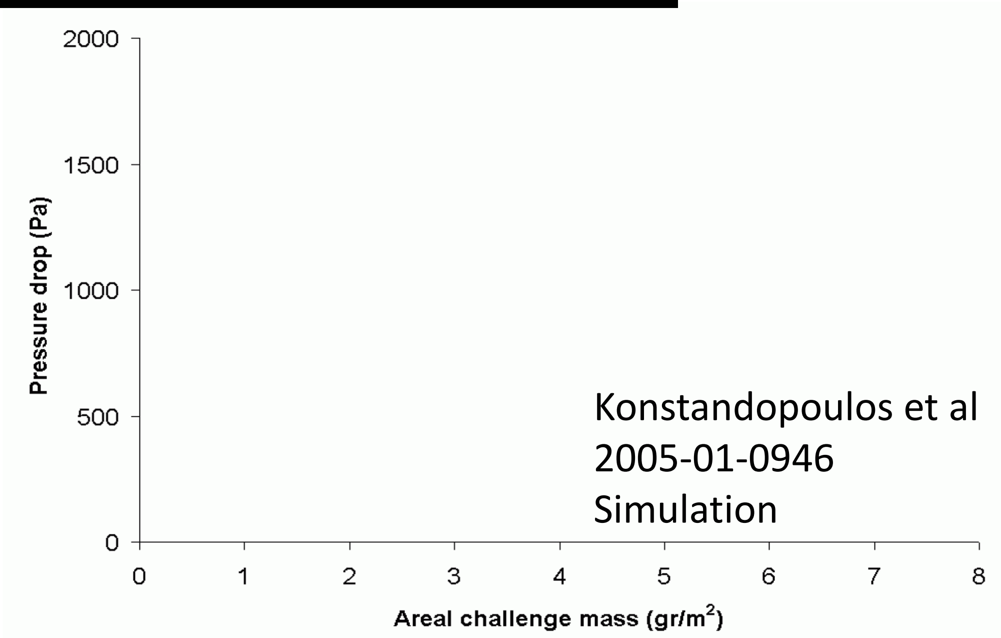
Microflow Deposition in Filter Wall



Hanamura et al
2015-01-1018

SEM video





Konstandopoulos et al
2005-01-0946
Simulation

Soot Deposit Oxidation

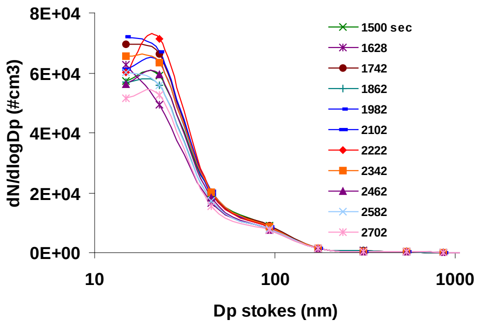
- Soot deposit mobility has been postulated within the two-layer model (Konstandopoulos and Kostoglou 1999) and has been confirmed optically by Hino Motors (2005) and Hanamura et al (2009).

- Oxidation occurs on the surface of the primary particles. Necks oxidize faster leading to loss of connectivity (oxidative fragmentation, Konstandopoulos and Kostoglou 2003).

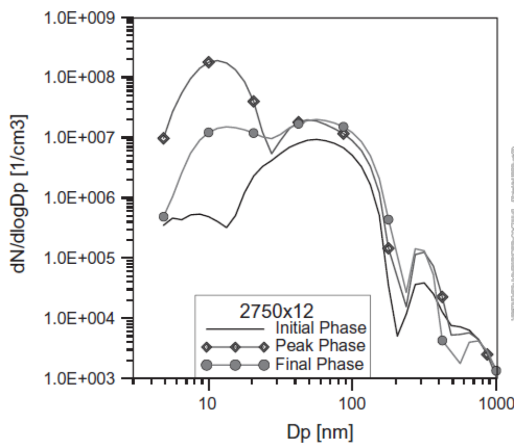
- Solid nanoparticle (~10 nm) emissions from DPF during regeneration cannot be explained based on filtration theory. Various observations:
  - ✓ Konstandopoulos et al (2002) ETH 2002
  - ✓ Cauda et al. Topics in Catalysis (2007) Vols. 42–43 253
  - ✓ Dwyer et al.(2010), Journal of Aerosol Science 4, 541–552
  - ✓ Beatrice et al.(2012) Experimental Thermal and Fluid Science 39, 45–53

Solid nanoparticle emissions during Regeneration

Konstandopoulos et al (2002) ETH 2002



Beatrice et al.(2012) Experimental Thermal and Fluid Science 39, 45–53



Dwyer et al.(2010), Journal of Aerosol Science 4, 541–552

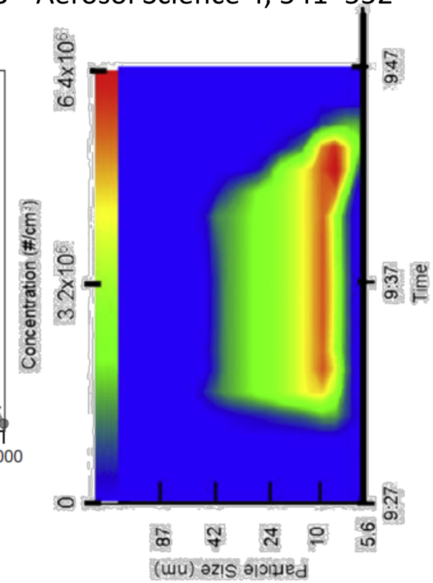


Fig. 3. EEPS particle concentration and size distribution during the first regeneration event.

Cauda et al. Topics in Catalysis (2007) Vols. 42–43 253

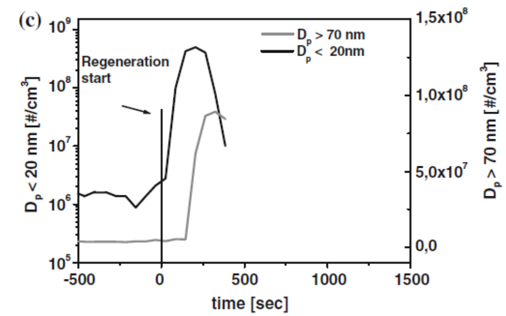
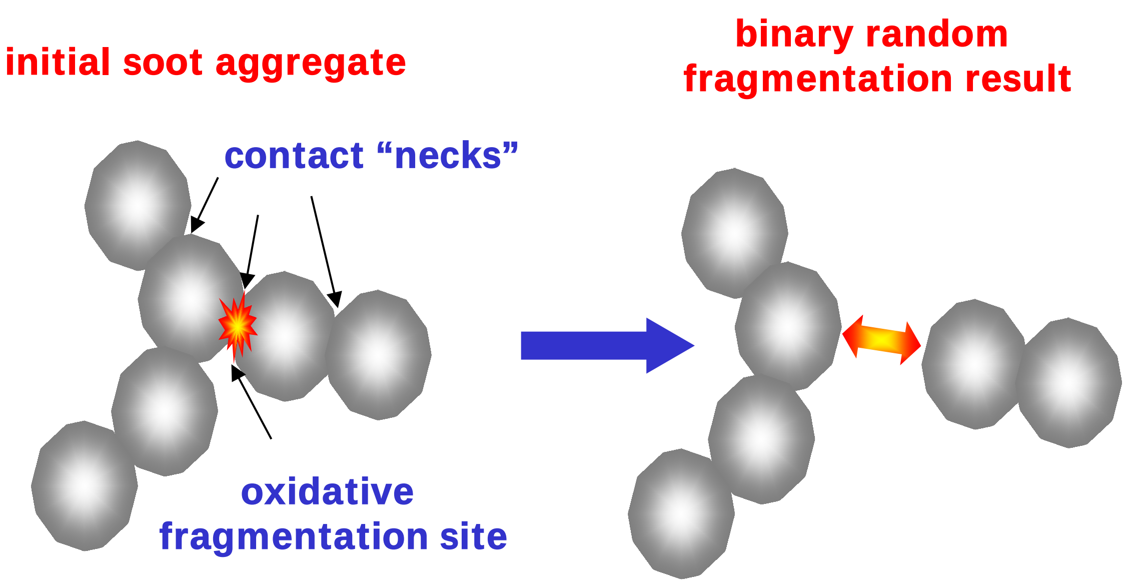
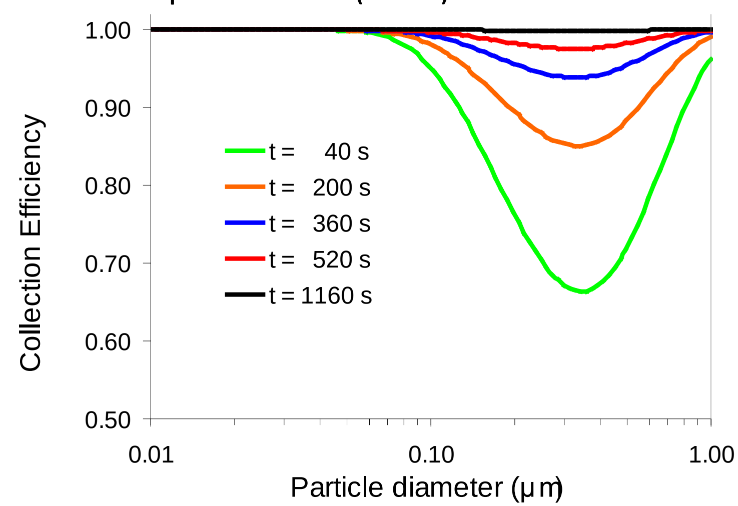


Figure 2. SMPS results obtained during the bench tests: (a) virgin trap; (b) $LiCrO_2$-catalysed trap; (c) $CoCr_2O_4$-catalysed trap. Same operating conditions as in figure 1. Dilution temperature: 25 °C. Dilution ratio: 10.

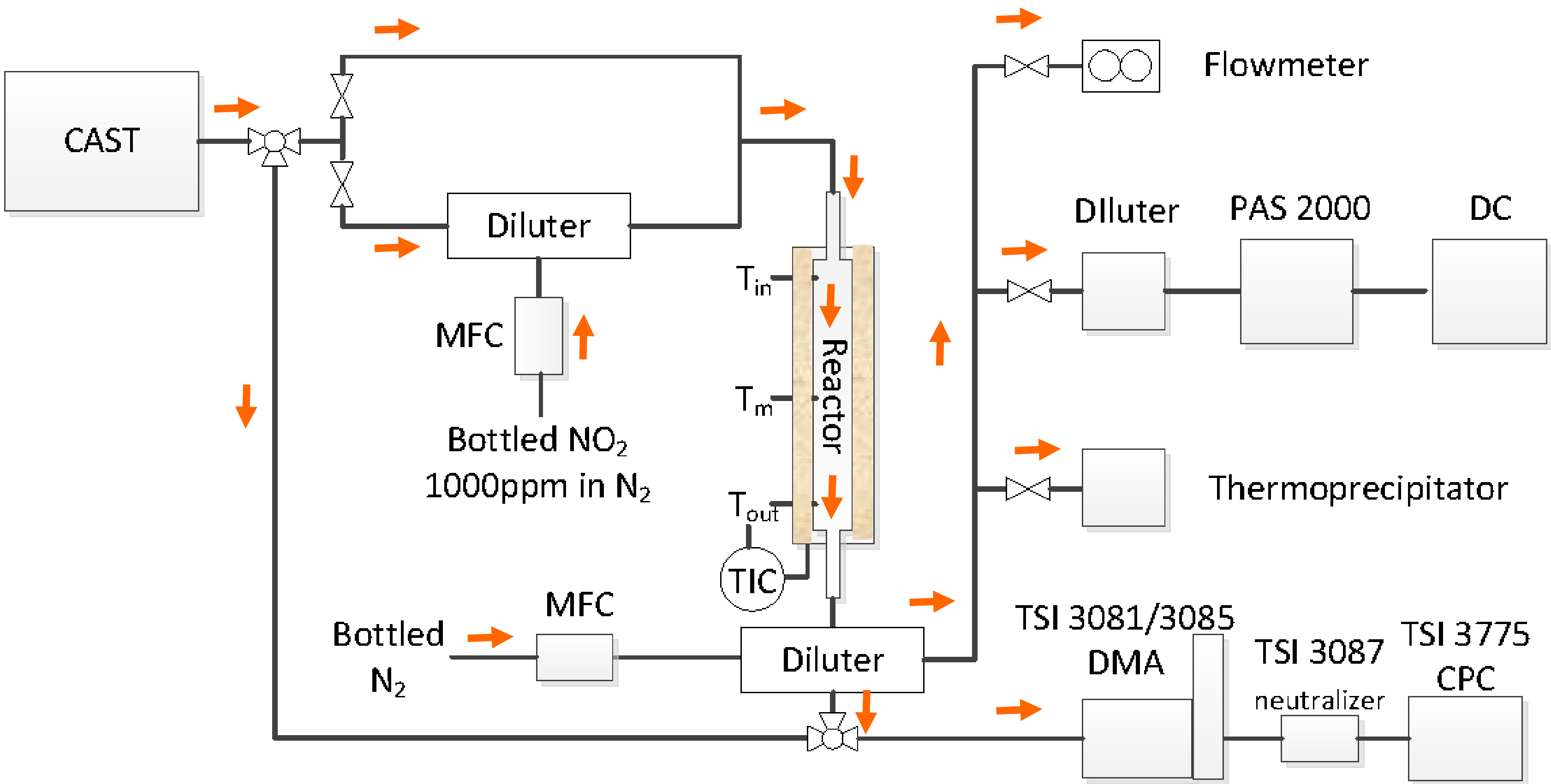
Konstandopoulos and Kostoglou ETH 2003



Konstandopoulos et al (2000) SAE 2000-01-1016

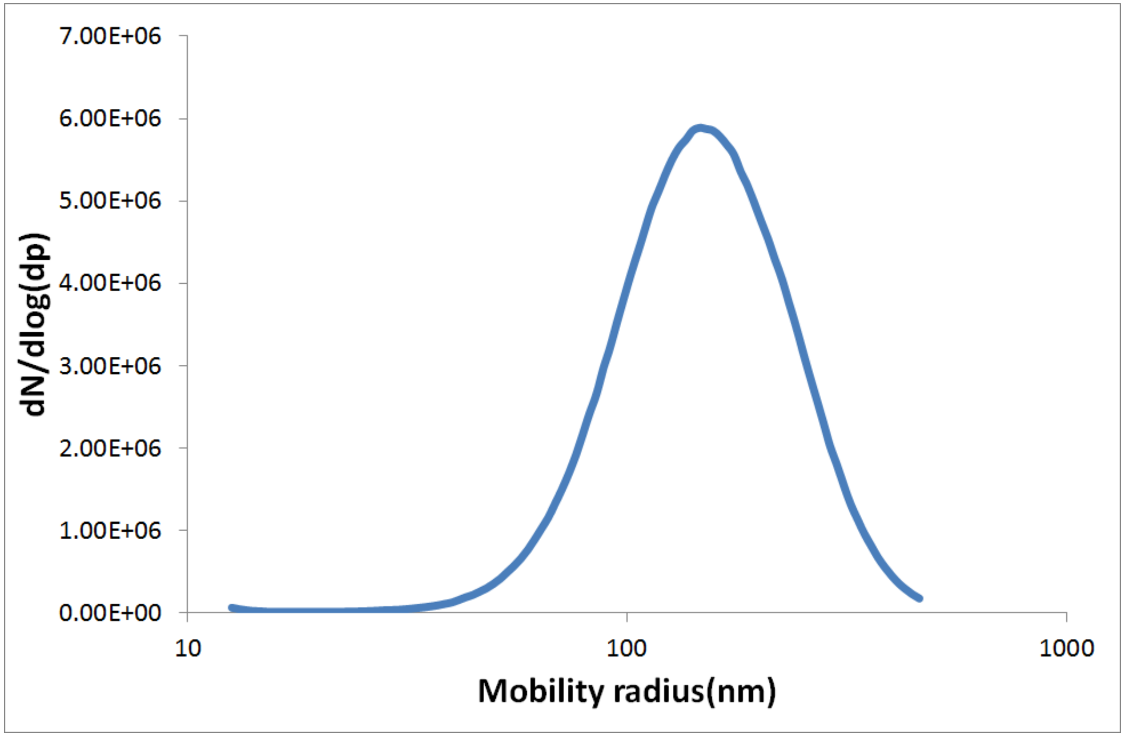


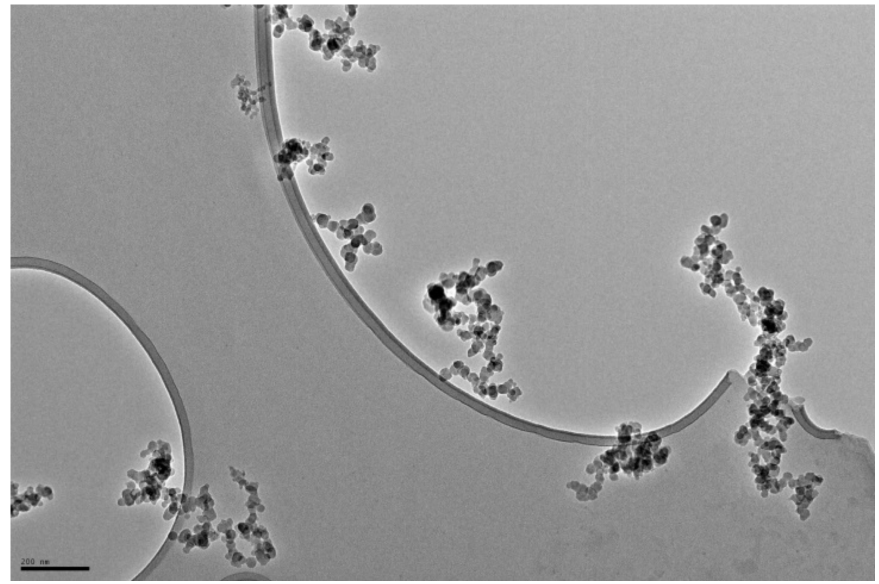
Experimental setup to study soot aggregate oxidative fragmentation



- Soot particle generation with a CAST
- Measurements with SMPS, TEM
- 2 different oxidants: 20% O_2 (oxA), 10% O_2 and 500 ppm NO_2 (oxB)

Inlet Soot Aggregate Size Distribution (CAST)

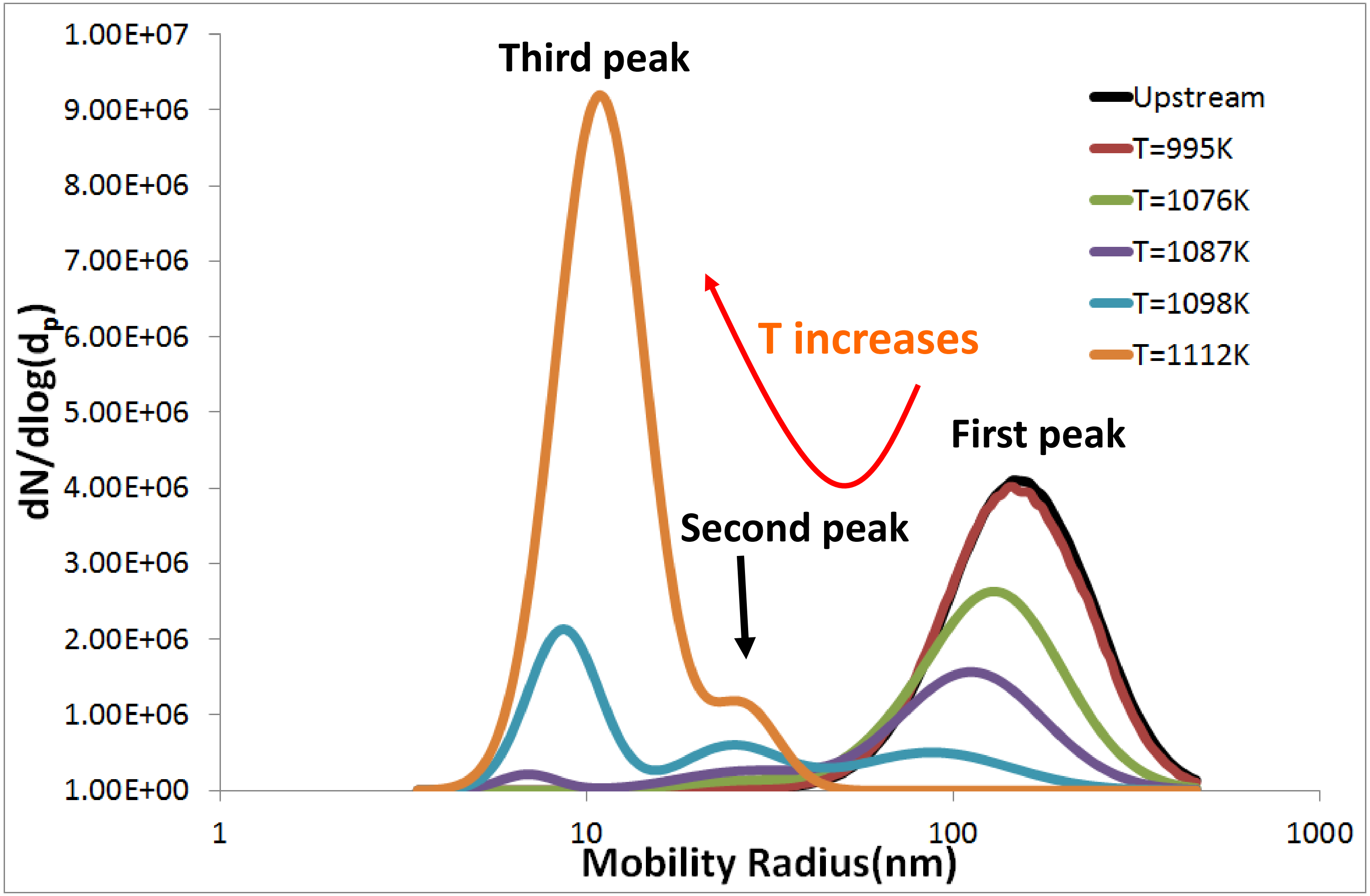




- Soot aggregates with a unimodal, stable, and repeatable size distribution
- No SOF is contained

Size distribution (oxA)

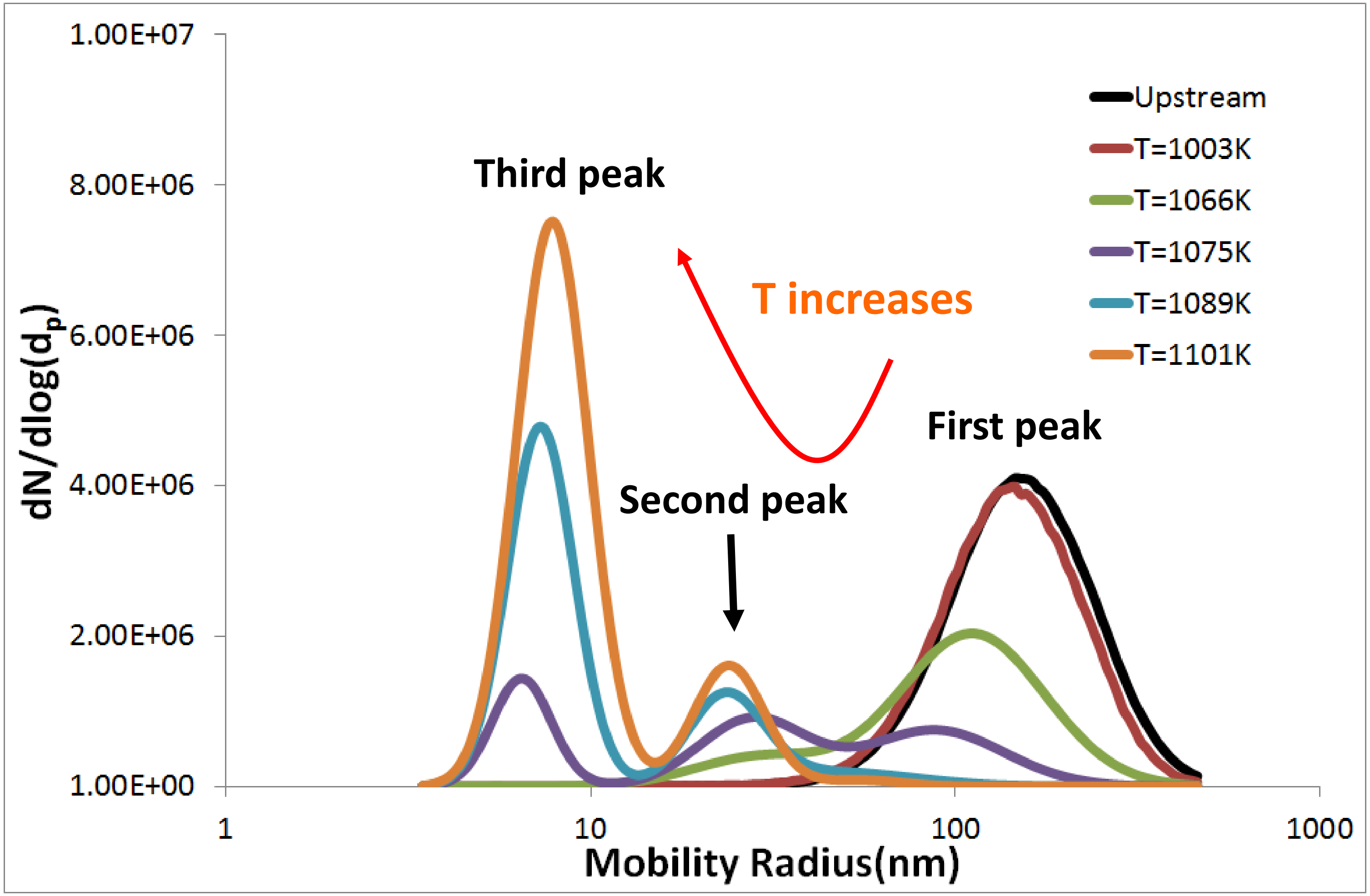
O_2 oxidation



- A second and a third peak are observed at 25nm and 7-11nm respectively as temperature is increased

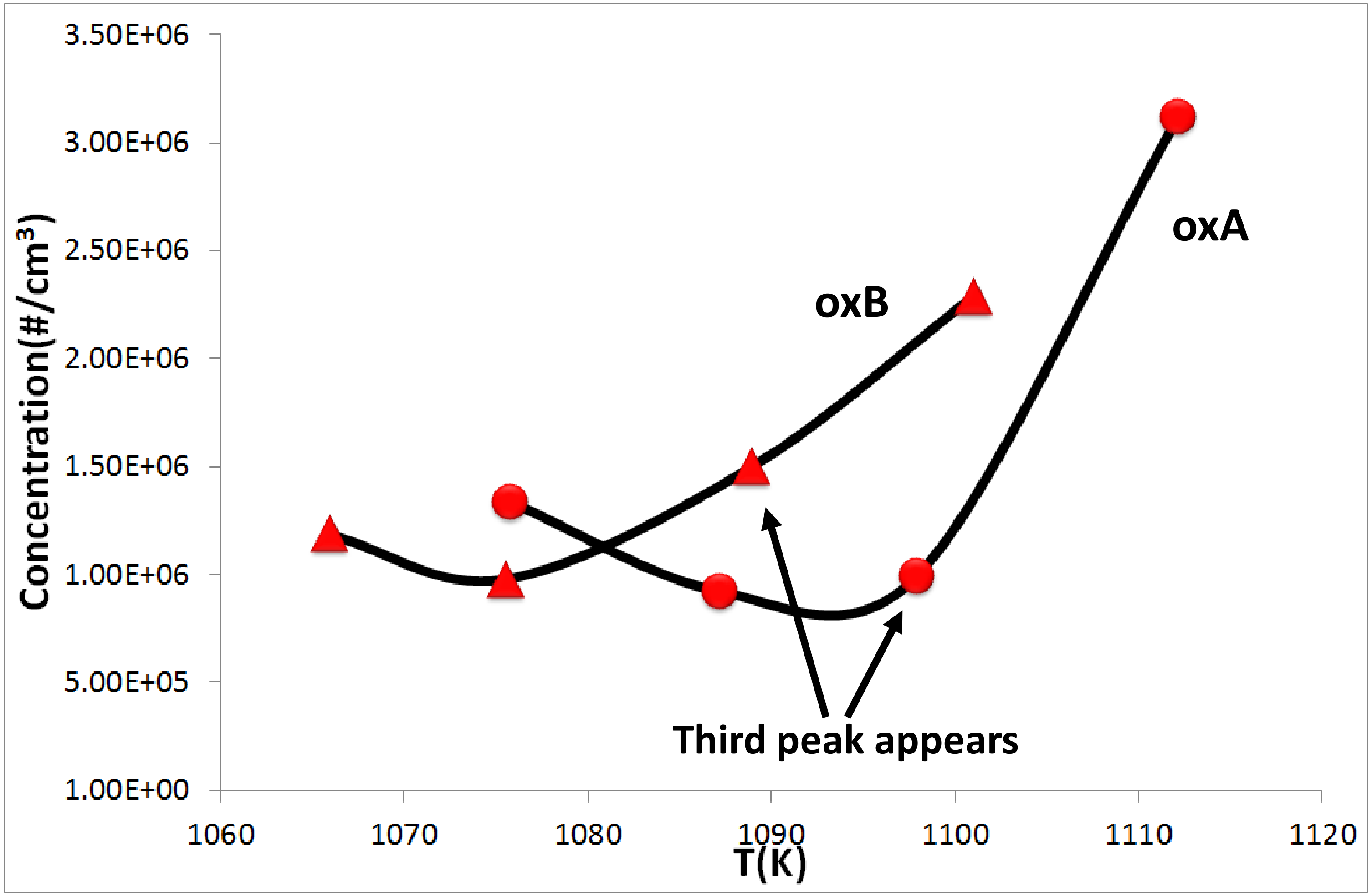
Size distribution (oxB)

$O_2 + NO_2$ oxidation



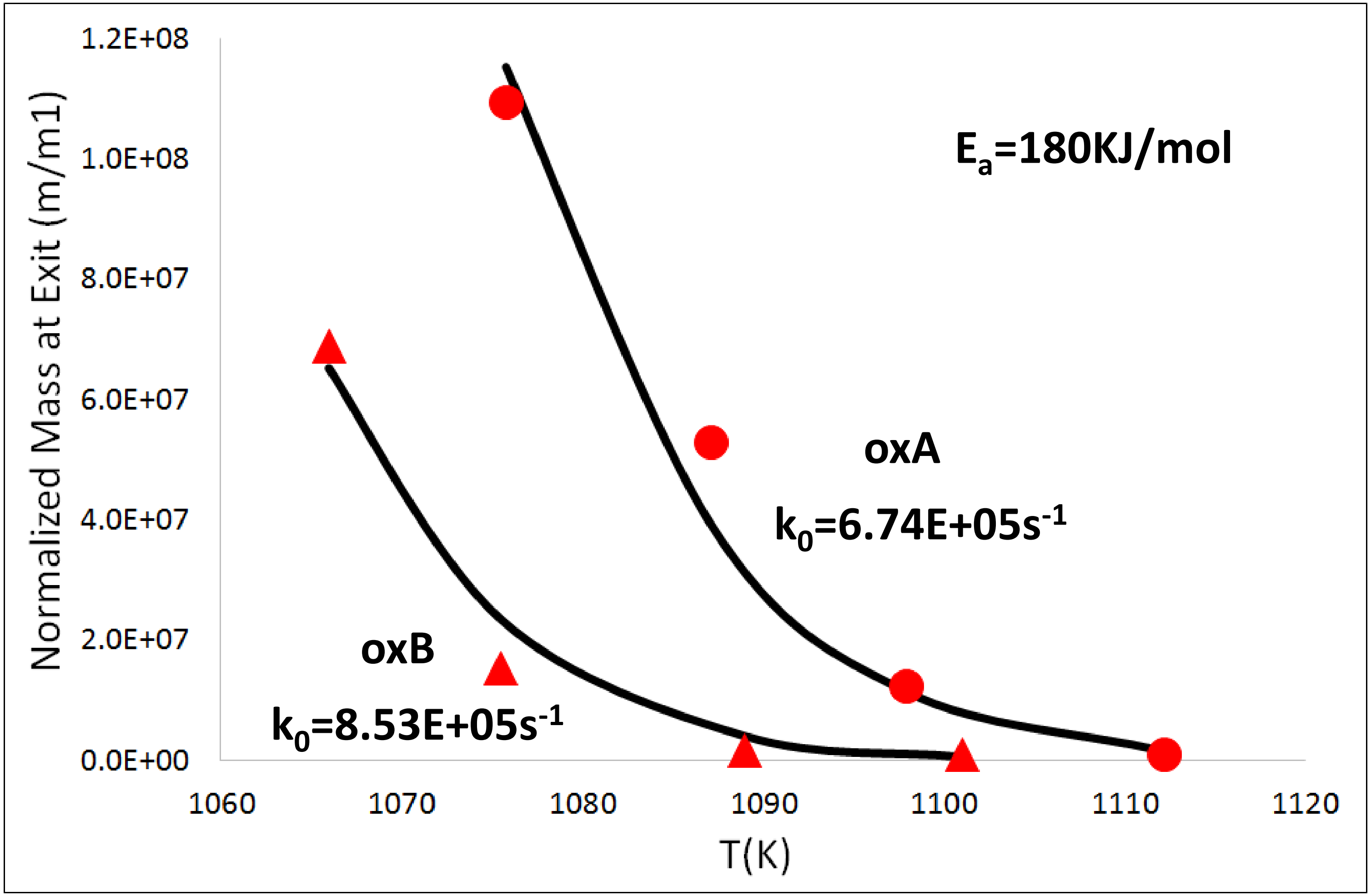
- The size distribution is similar with oxA but the temperatures that the phenomenon occurs are smaller

Number concentration



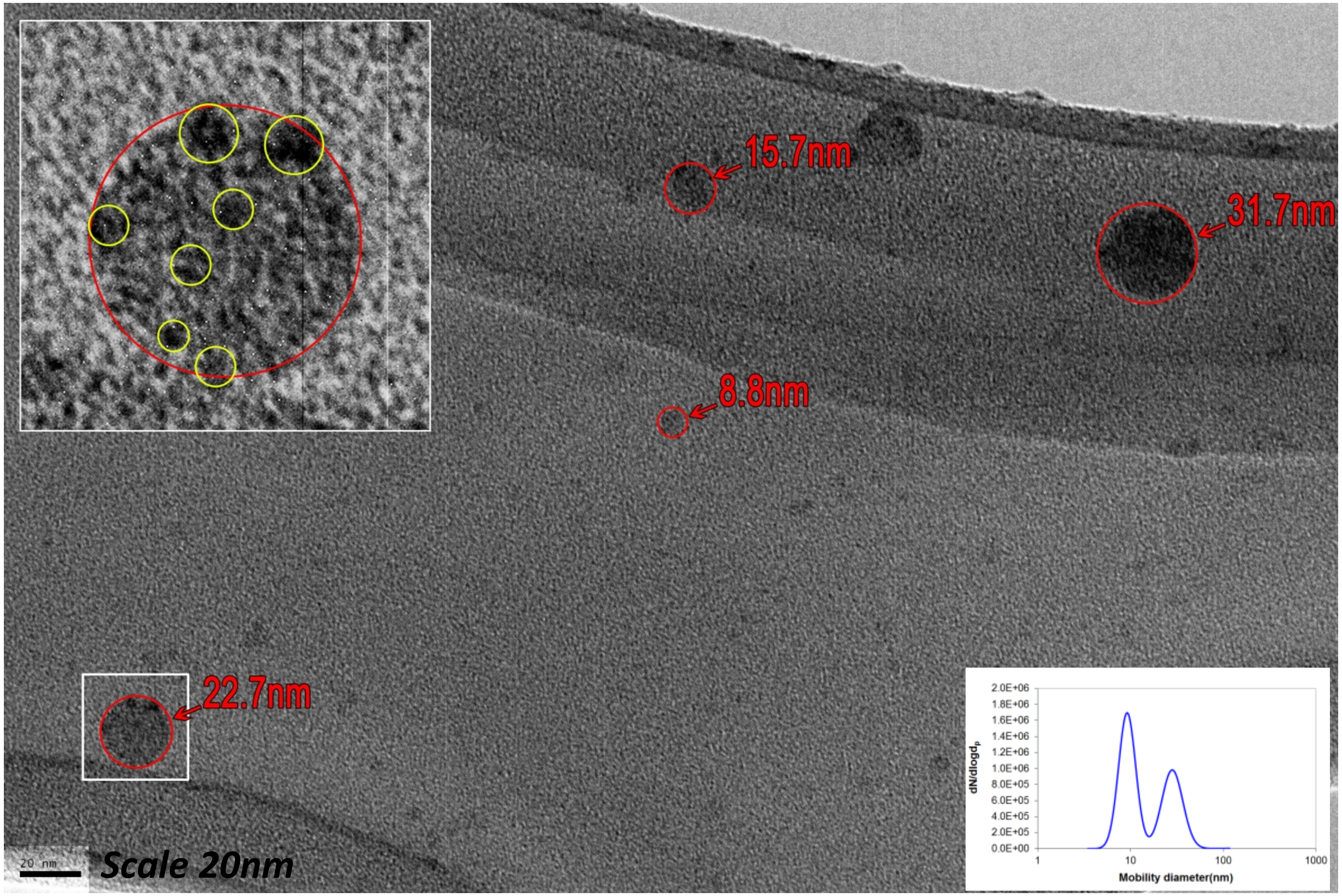
- When the third peak appears, the number concentration starts increasing for both oxA and oxB showing that fragmentation occurs

Activation Energy



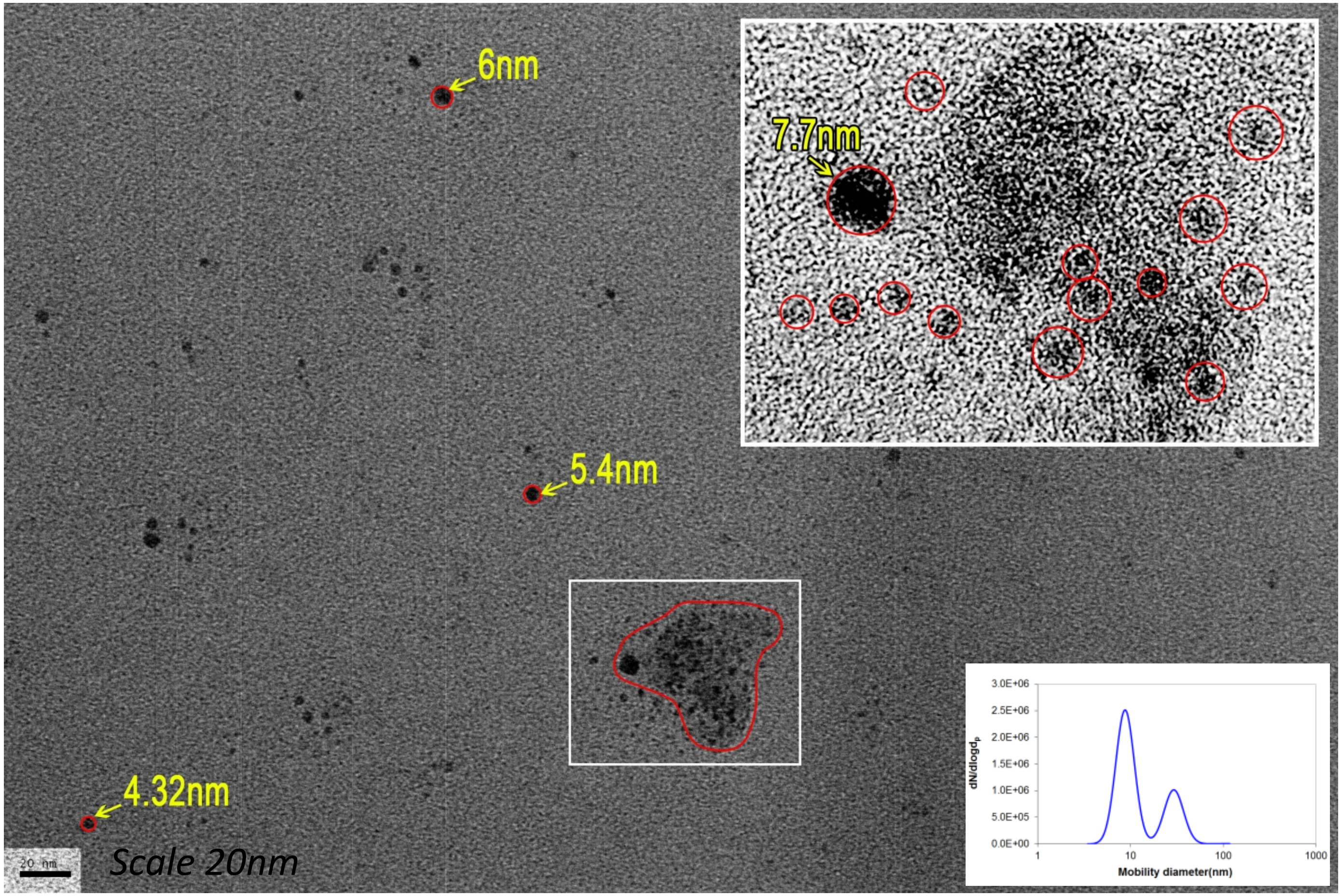
- The pre-exponential factor is 27% larger for oxB

TEM Images-oxA



- Particles with d=7-11nm appear that correspond to the third peak
- Larger spherical particles with d~25nm that correspond to the second peak with an internal mass distribution

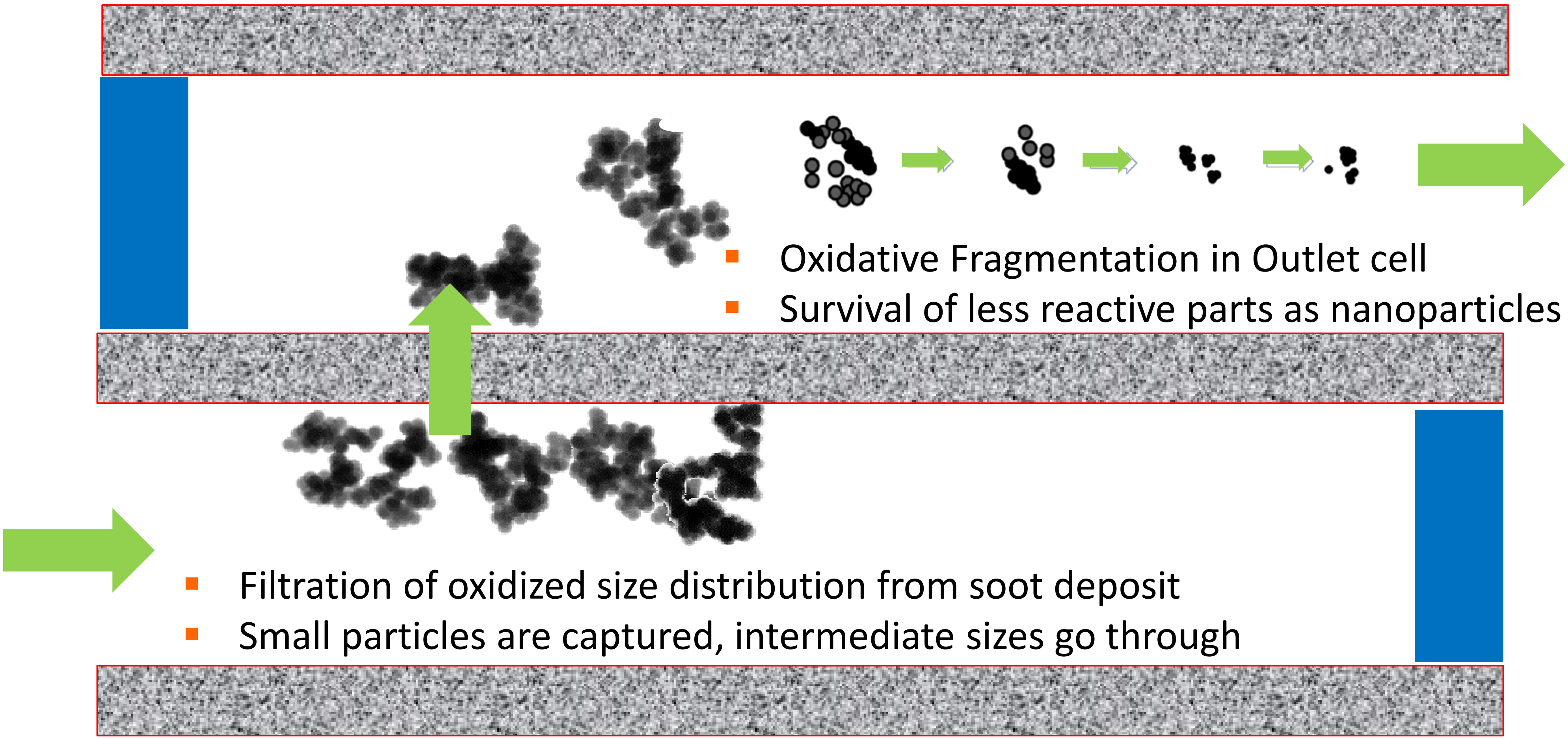
TEM Images-oxB



- Similar to oxA particles with d=7-11nm appear that correspond to the third peak
- Larger particles with d~25nm are not all spherical

Mechanism of Solid nanoparticle emissions during Regeneration

Convolution of (Residence Time Distribution*(Oxidation of Oligomer*(Oxidative Fragmentation of Agggregate*(Filtration*(Oxidative Fragmentation of Deposit)))))



Conclusions

- Soot deposit structure in the "fresh" state depends on the Pe under which deposition occurred.
- Deposition simulations employing aggregate particle morphologies and microflow computations have the potential to reproduce what is observed in the experiments.
- Soot aggregates are oxidized by a percolative fragmentation mechanism acting at the necks. Oxidation of the resulting (oligomer) fragments occurs in two steps, first of the more reactive part, releasing a multitude of nanoparticles around 9 nm.
- Solid nanoparticles emitted during regeneration of DPFs are generated by the in-flight percolative fragmentation of aggregates that are able to pass through the wall (the more penetrating size) according to filtration theory. On going work models the convoluted PSD and incorporates the mechanism into DPF simulators.

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Thank you for your attention!

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agk@cperi.certh.gr
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