CATERPILLAR®

Phosphorous Aging Model

Catalyst Deactivation due to Phosphorous in Oil

2011 DOE CLEERS Workshop

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April 20, 2011

Contents

Section I

Model formulation, inputs and assumptions

Phosphorous deactivation mechanism

- Non selective, surface phenomena
- Phosphorous compounds carried to surface of the catalyst, where they deactivate catalytic activity, primarily through physical masking of active sites
- Physical blockage of micro pores on catalyst also reduces total catalyst surface area
- Impact of phosphorous on catalyst performance is a function of aging temperature, concentration of phosphorous in exhaust gas and space velocity

Modeling of Phosphorus Poisoning Phenomena over Diesel Oxidation Catalysts	2010-01-0884 Published 04/12/2010

Makoto Nagata and Yasushi Tanaka
N E Chemcat Corp.

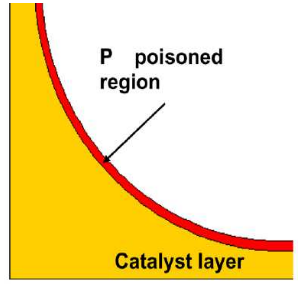


Fig.1. Schematic diagram of a general P concentration profile at the cross section of a P poisoned catalyst.

2009-01-0628

The Roles of Phosphorus and Soot on the Deactivation of Diesel Oxidation Catalysts

Scott J. Eaton, Bruce G. Bunting and Todd J. Toops
Oak Ridge National Laboratory

Ke Nguyen
University of Tennessee

Deactivation of Diesel Oxidation Catalysts by Oil-Derived Phosphorus

Scott J. Eaton and Ke Nguyen
Department of Mechanical, Aerospace and Biomedical Engineering
University of Tennessee

Bruce G. Bunting
Oak Ridge National Laboratory

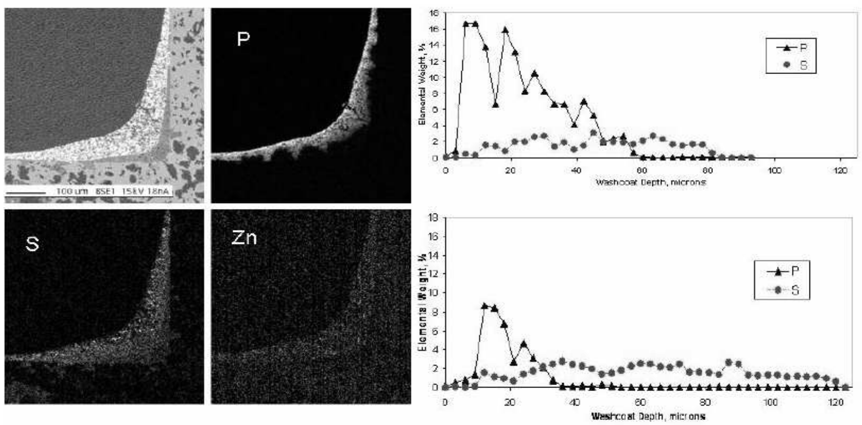


Figure 6: Elemental maps for ZDDP-doped fuel injection at 0.64 cm from inlet and line-scans 0.64 cm from DOC inlet and exit sections (Top – Front, Lower – Rear)

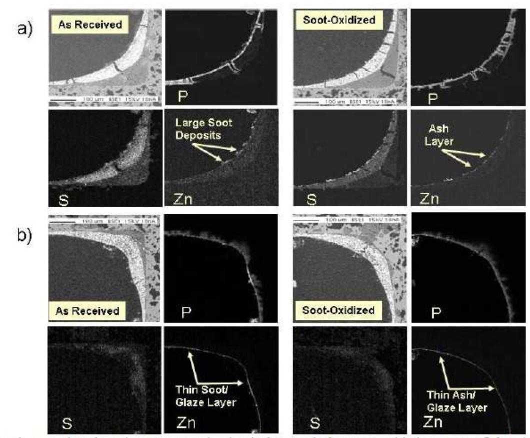
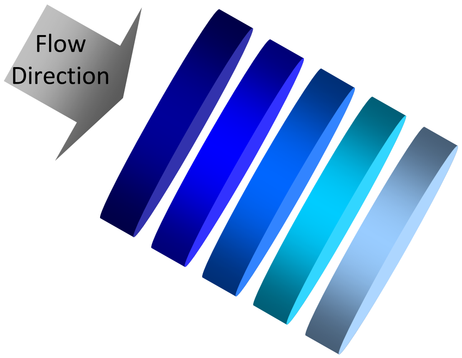
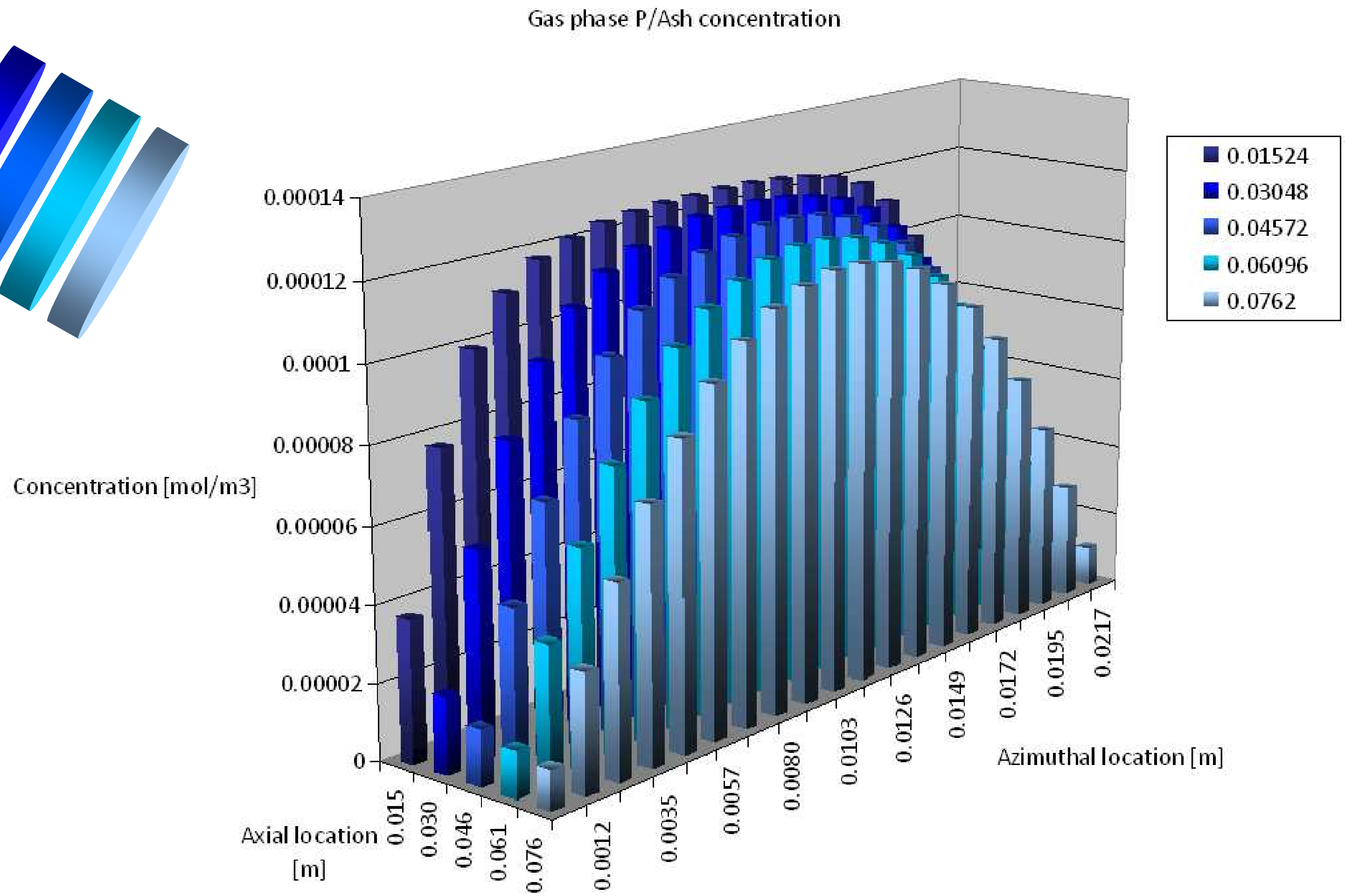


Figure 6: EPMA micrographs of washcoat contamination before and after soot oxidation at 500°C for a) a representative field-returned DOC (28656N-front) and b) AEA-Exhaust DOC taken at a location approximately 5mm from the device inlet.

Example output

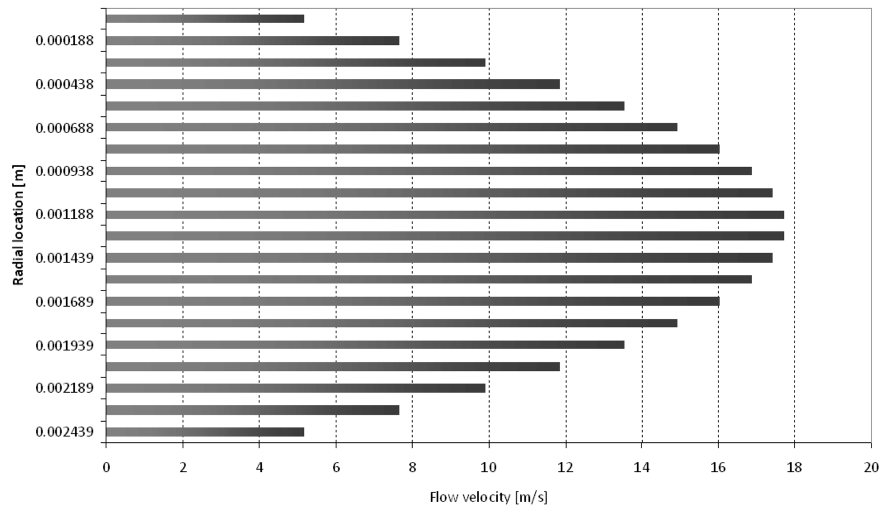
Gas phase Phosphorous profile



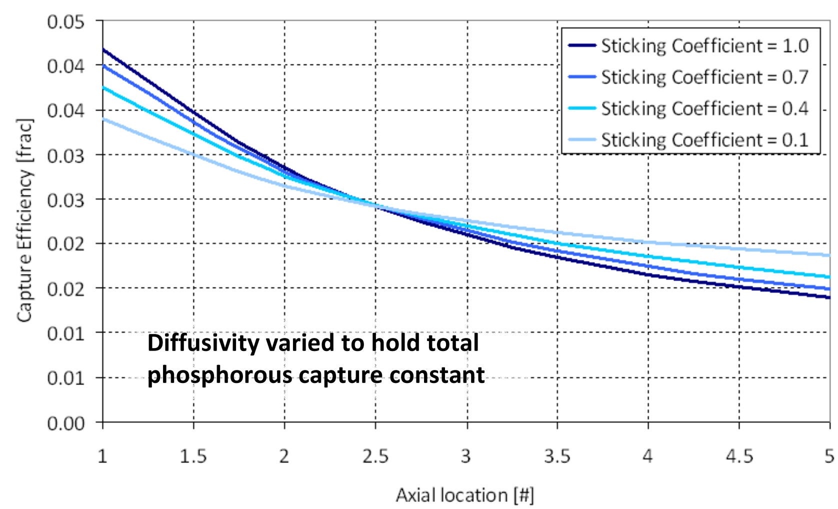


Model Inputs

- Flow velocity profile in catalyst channel
  - *Axially invariant, fully developed laminar flow velocity profile*
- Specific area of catalyst washcoat
  - *Input from supplier regarding BET surface area of washcoat for various technologies*
- Masking molecule
  - *Oil that is exposed to combustion conditions results in formation of oxides of phosphorous (P_2O_5, P_4O_{10})*
  - *Oxides of phosphorous are fairly strong dessicants, expected to hydrolyze to form phosphoric acids*



- Sticking coefficient of deactivating molecule
  - *Potential question over validity of a 100% sticking coefficient*
  - *Modified model to enable a non-perfect (less than 100%) sticking coefficient*
  - *Data on phosphorous deposition profile on catalyst appears to indicate close to 100% sticking coefficient – lower sticking coefficients result in flatter phosphorous distribution profiles*



Section II

Phosphorous distribution on Catalyst surfaces

Validation of model predictions

Phosphorous loading

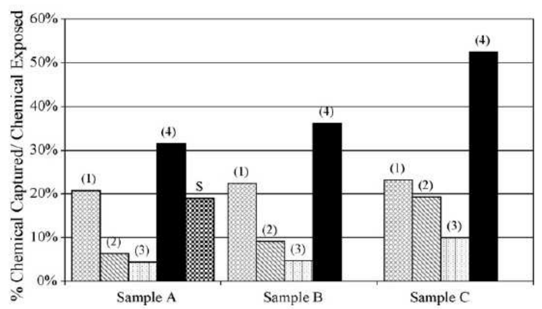


Fig. 1. Axial chemical profiles of P within the monolith channels of each sample, analyzed via XRF: (1) front third; (2) middle third; (3) rear third; (4) total for each monolith core. (S) is total sulfur captured by Sample A, determined via LECO sulfur analyzer. No sulfur analysis was performed for Sample C.

ScienceDirect

Catalysis Today 136 (2008) 28–33

A study of chemical aging effects on HDD Fe–zeolite SCR catalyst

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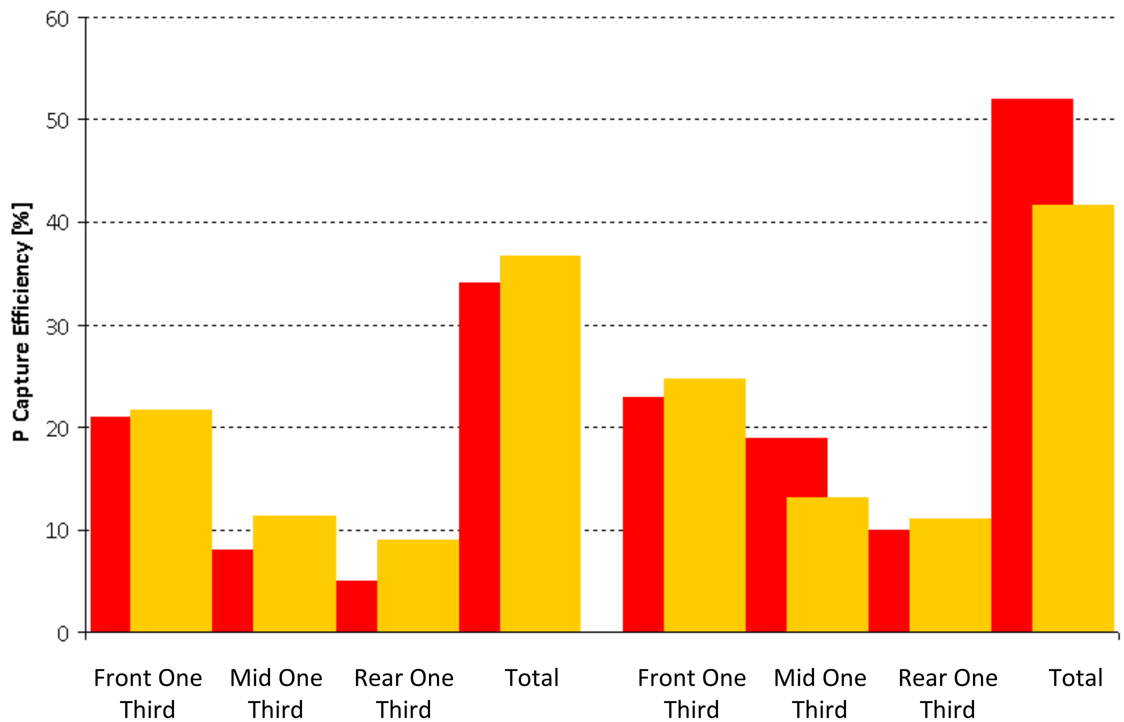
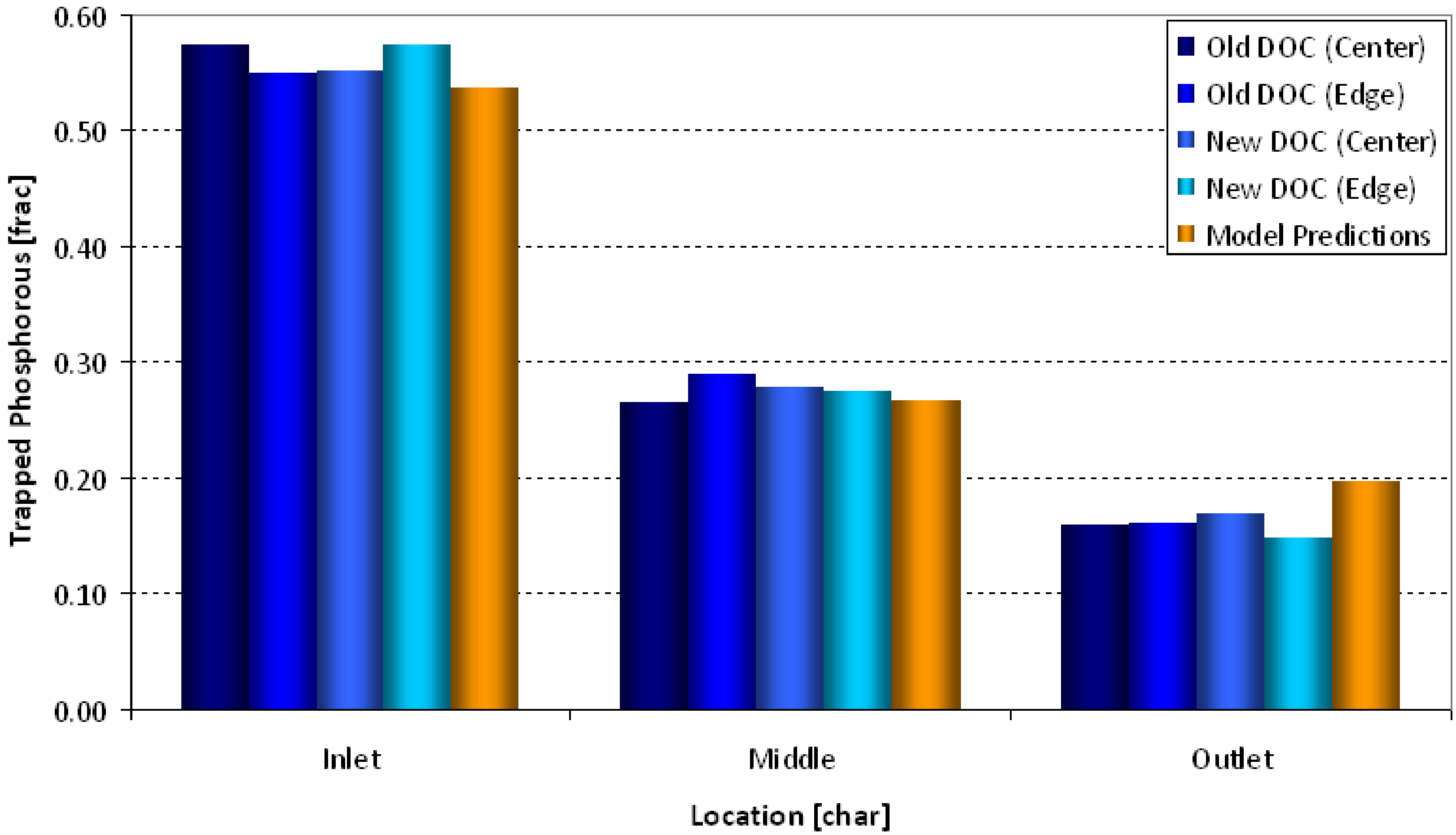
[b] Caterpillar Inc., Emissions Solutions, P.O. Box 610, Mossville, IL 61552, USA



Validation of model predictions

Phosphorous loading (Accelerated DOC aging)



Dual leg system, one fresh DOC ("new") and one 100 hr aged DOC ("old") (prior to being exposed to phosphorous aging)

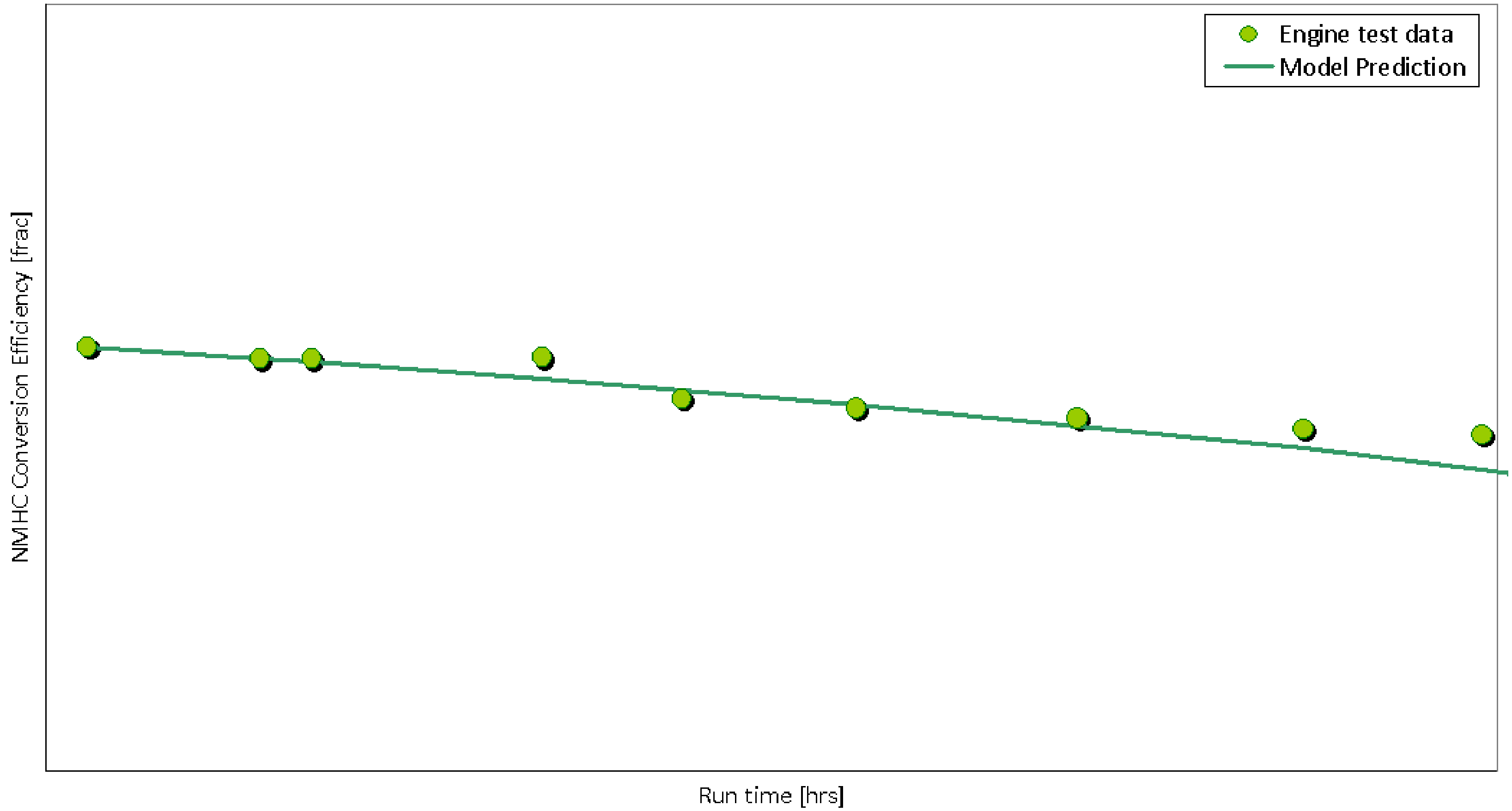
298 C average temperature, 831 kg/hr (per leg), Aging time: 2250 hrs

Section III

Impact of Phosphorous on Catalytic Activity

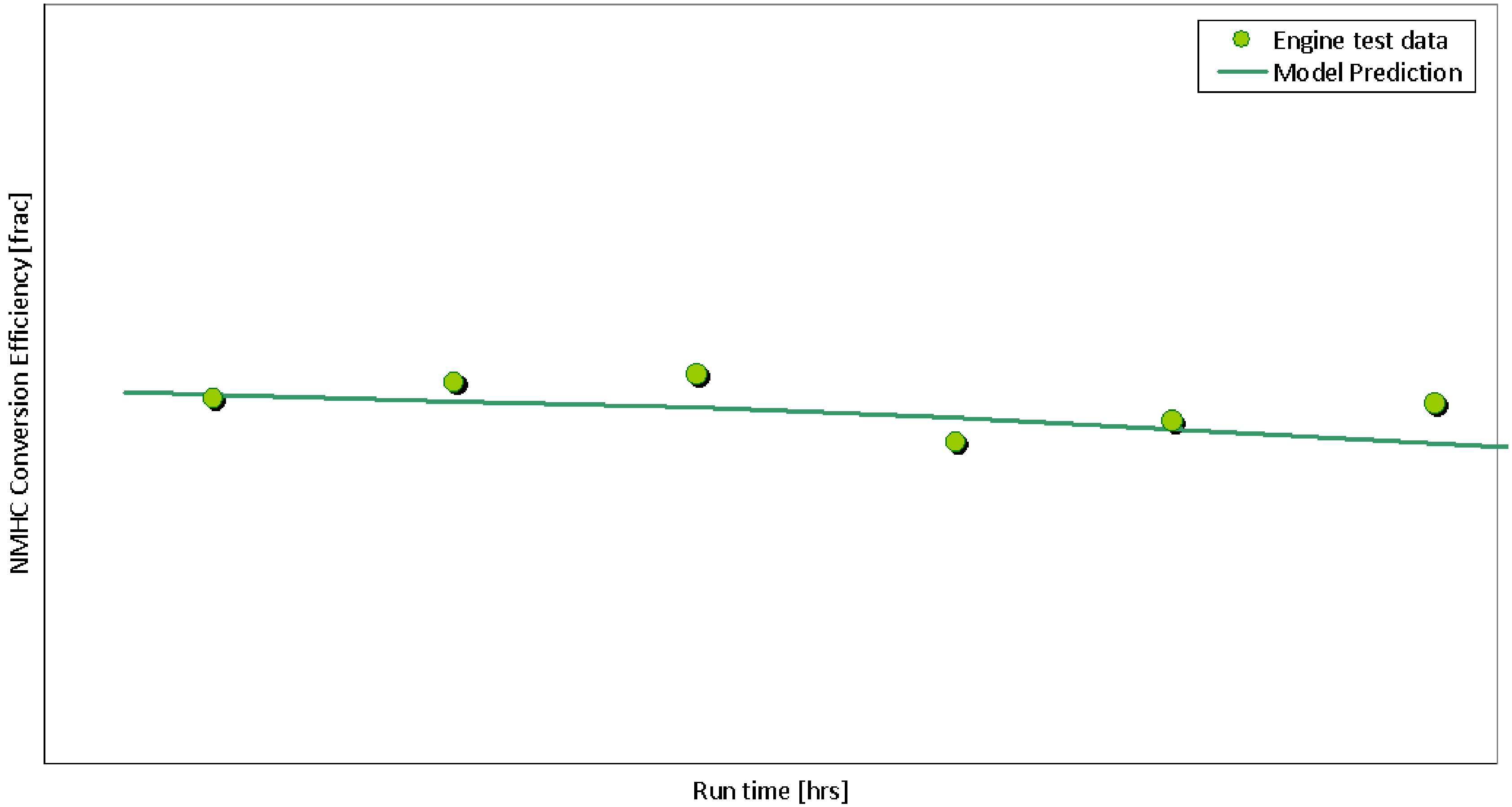
Caterpillar® Engine Test 1

DOC NMHC Oxidation



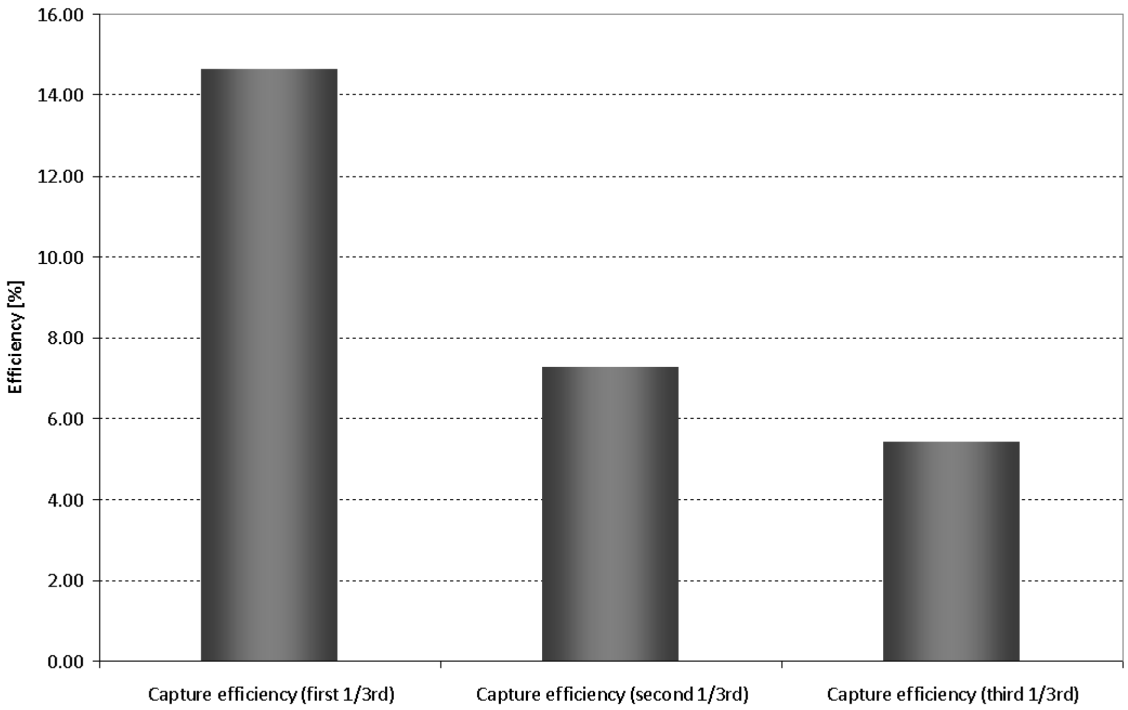
Caterpillar® Engine Test 2

DOC NMHC Oxidation



Caterpillar® Engine Test 2

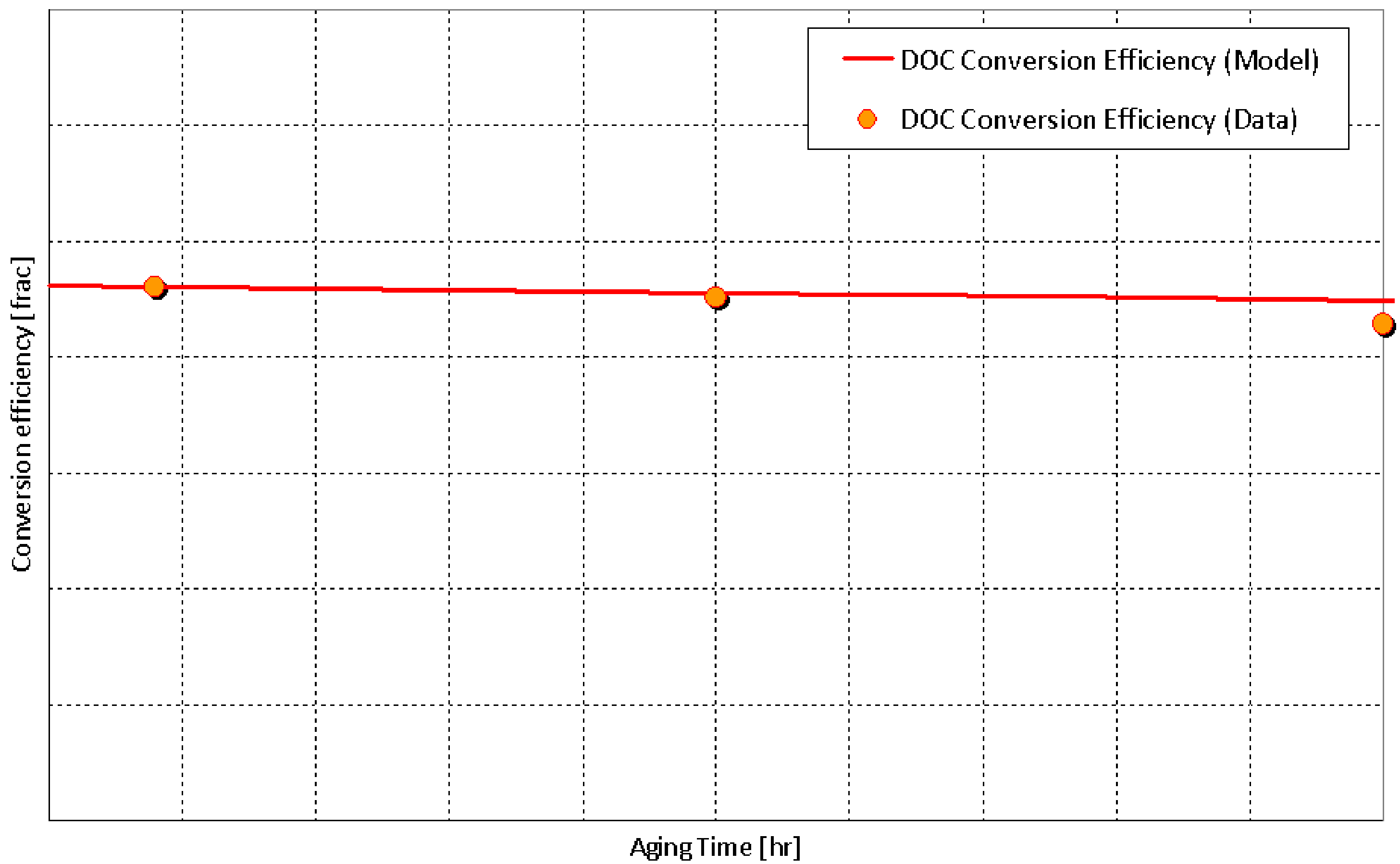
DOC NMHC Oxidation



Phosphorous Distribution			
	Phosphorous Exposure	[g/L]	10.24
	Capture efficiency (first 1/3rd)	[%]	14.64
	Capture efficiency (second 1/3rd)	[%]	7.26
	Capture efficiency (third 1/3rd)	[%]	5.43
	Capture efficiency (total)	[%]	25.14

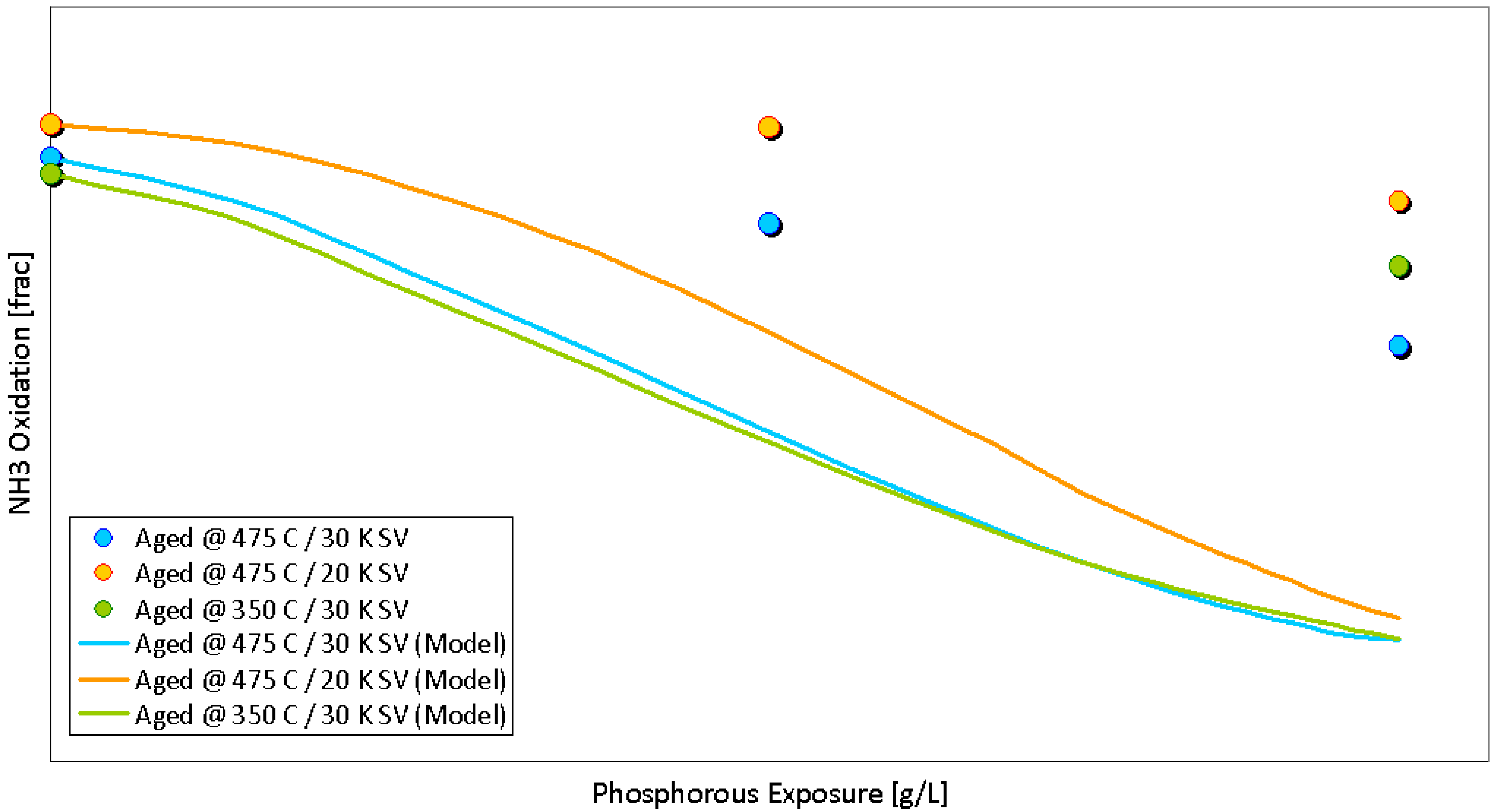
Caterpillar® Engine test

Model predictions versus test data (DOC HC conversion)



Caterpillar® accelerated bench aging

Zeolite SCR

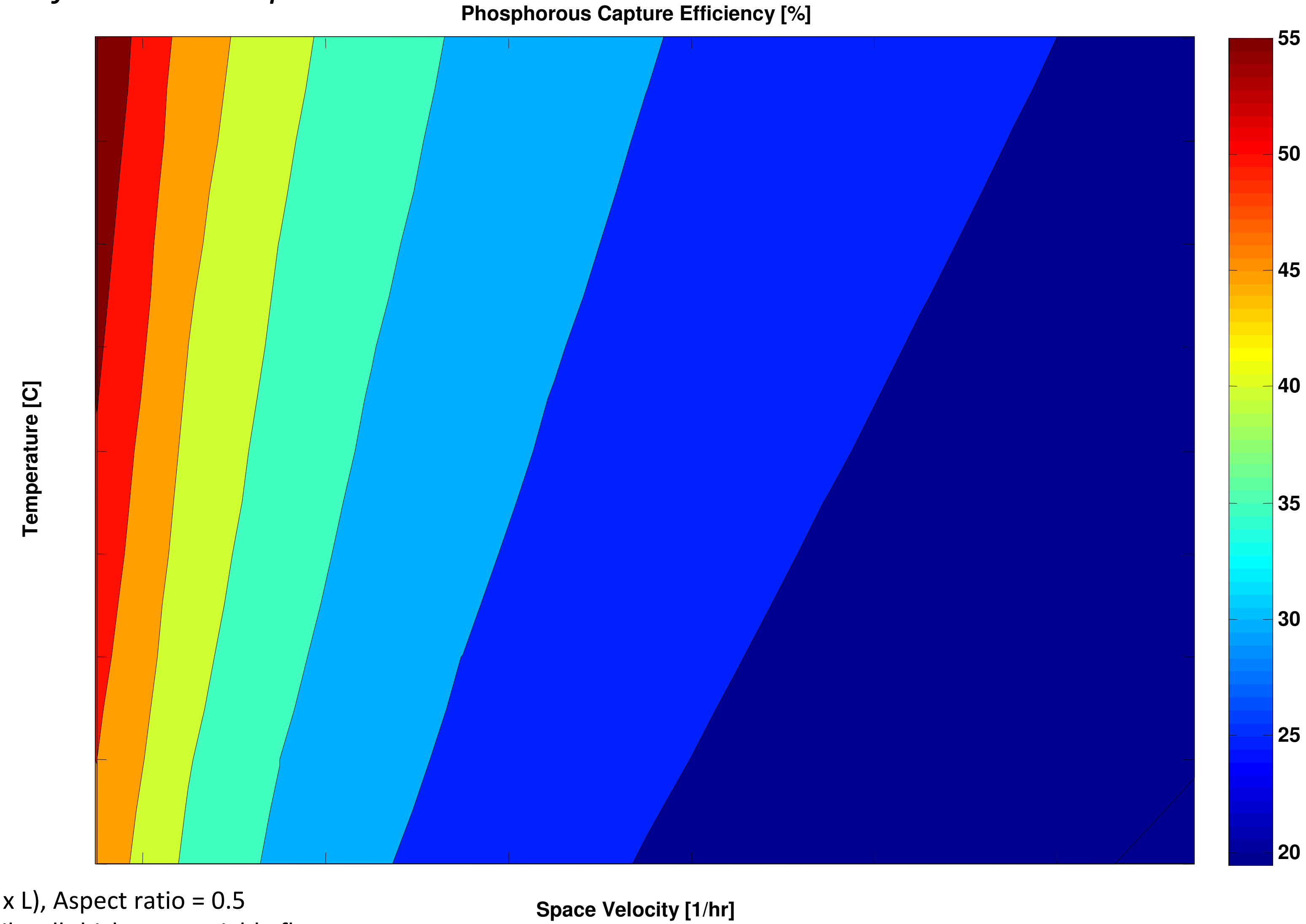


Section IV

Parametric study of catalyst deactivation

Phosphorous Capture Efficiency

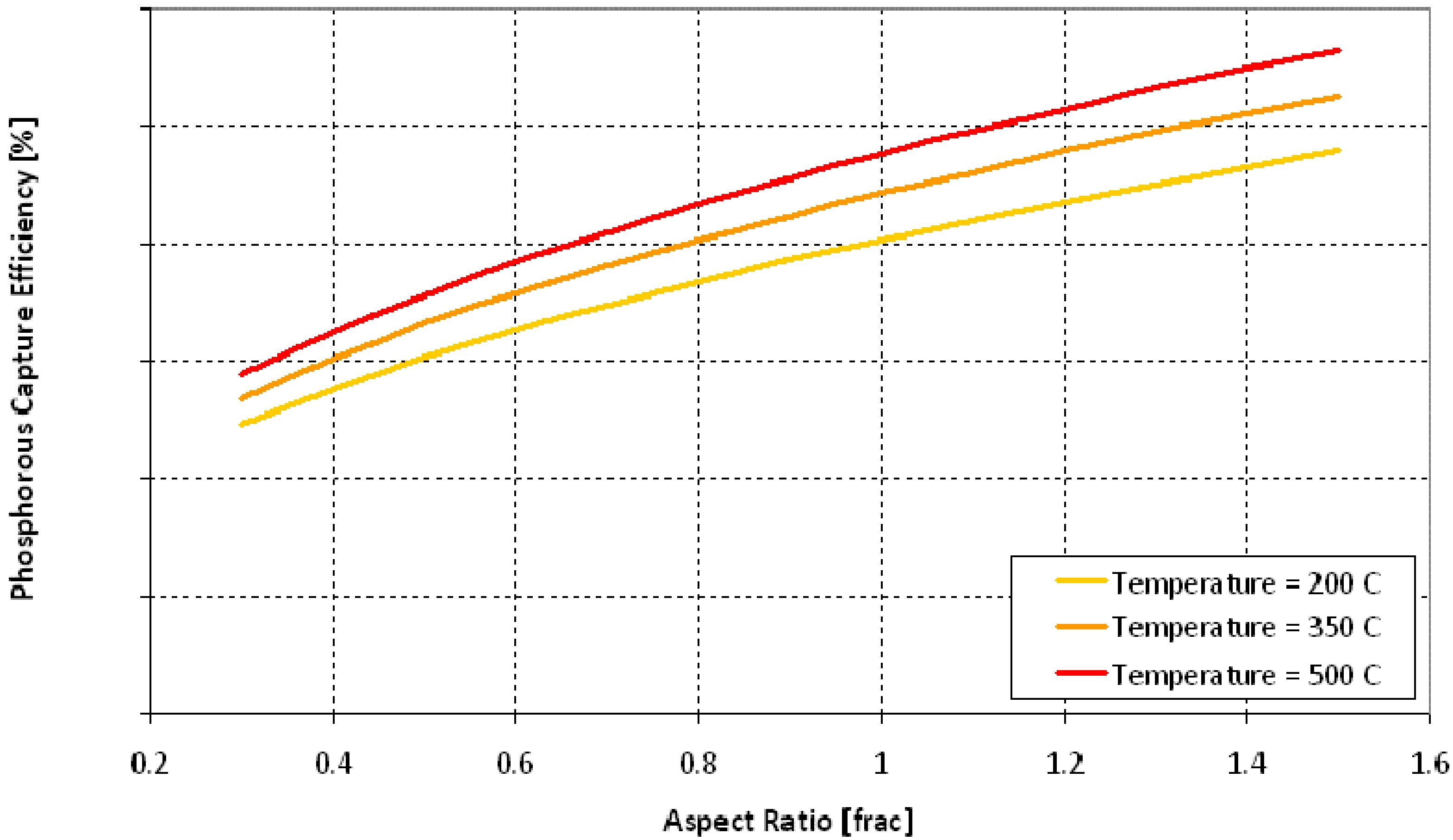
Impact of SV and Temperature



13” x 6.5” (D x L), Aspect ratio = 0.5
400 cpsi, 5 mil wall thickness, variable flow rate

Phosphorous Capture Efficiency

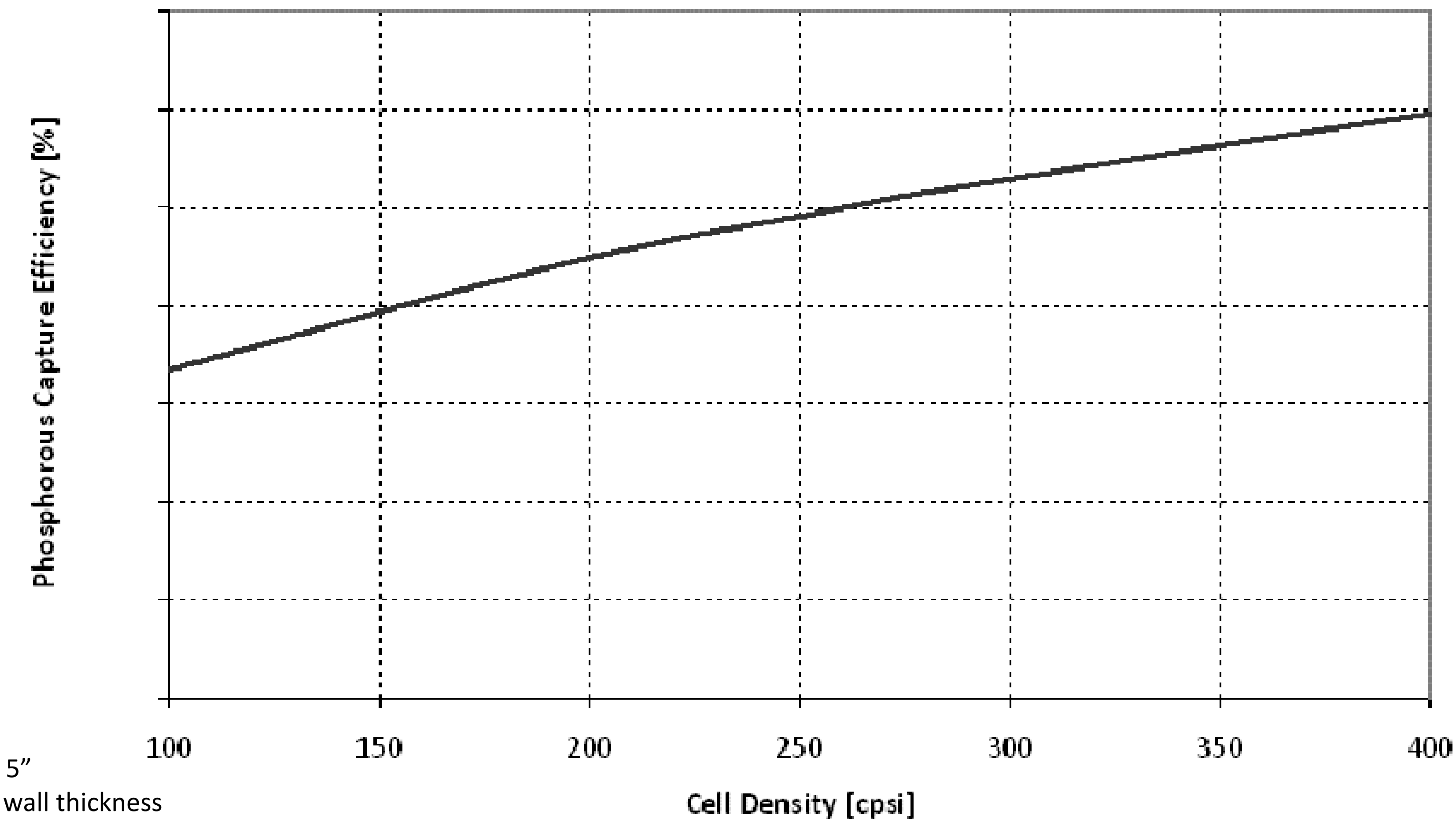
Impact of Catalyst Aspect Ratio



13” x 5”
400 cpsi, 5 mil wall thickness
60,000 1/hr SV

Phosphorous Capture Efficiency

Impact of Cell Density



13” x 5”
5 mil wall thickness
60,000 1/hr SV

Note: Net washcoat loading is held constant

Summary

- Model predictions agree well with test data for distribution of phosphorous within catalysts for both oxidation catalysts and SCR
- Model predictions agree with available DOC performance data, will continue to validate against any data that will become available
- Model predictions for zeolite SCR over predict deactivation compared to accelerated bench aging data
  - Method of aging? P doping of fuel to accelerate aging?
  - Aging mechanism for zeolite
  - Temperature profile on bench
  - Other reasons?

Backup Slides

Domain Discretization