Non-uniform Aging on Super Duty Diesel Truck Aged Urea Cu/Zeolite SCR Catalysts

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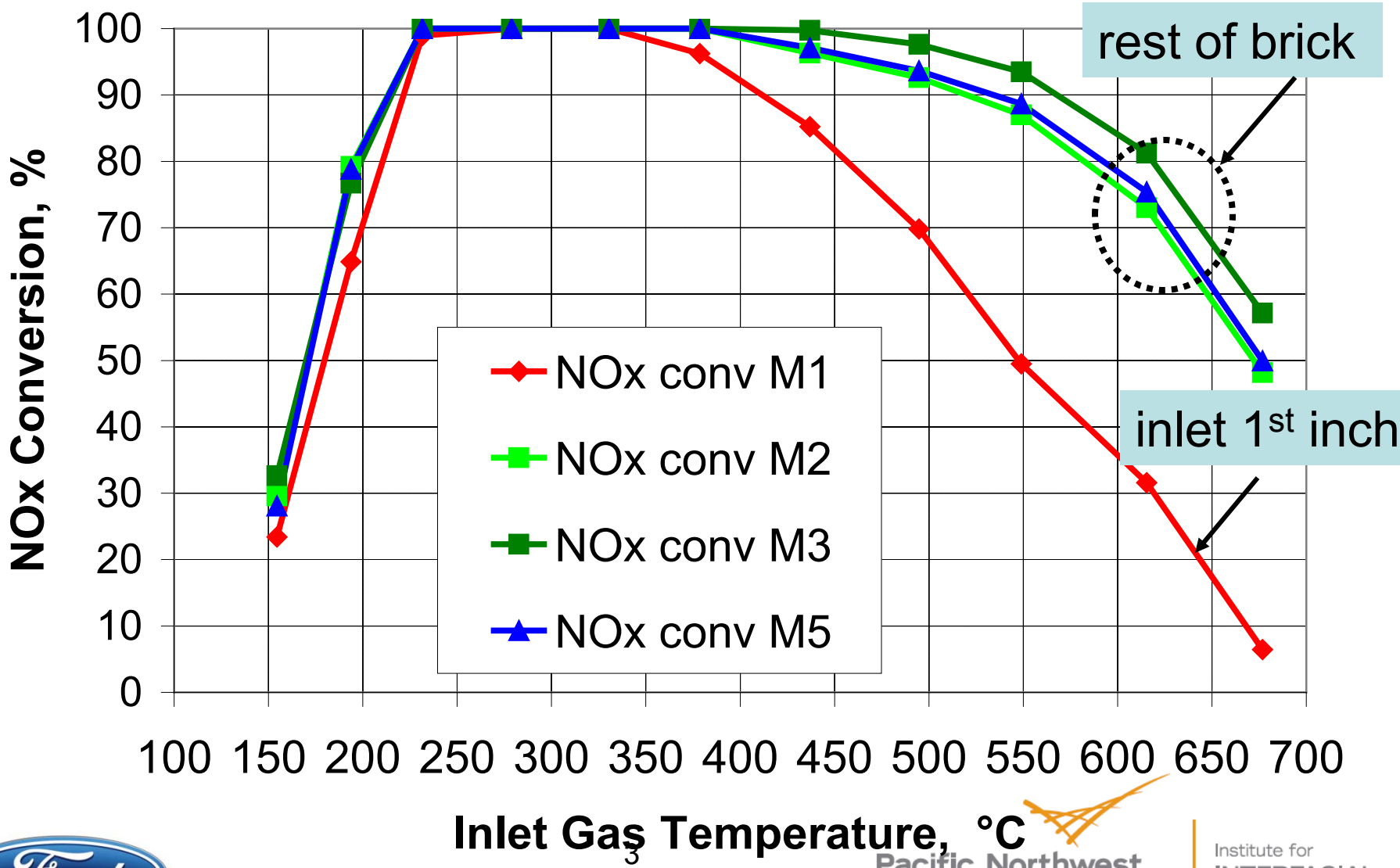
Background

- Previous studies
  - the deactivation of engine aged SCR catalysts is not uniform
  - the inlet section of the catalyst brick deactivating the most
- This study
  - to better understand this non uniform aging phenomena especially the inlet section
  - Cu/zeolite SCR catalysts aged for 50K miles on a Super Duty diesel truck
  - analyses including catalyst activity evaluation and catalyst characterization, such as BET surface area, TPR, XRF, XPS and TEM.

Non-uniform NOx Conversion

NOx-NH3 SCR Steady State, SV=30K, 350ppm NO/350ppm NH3



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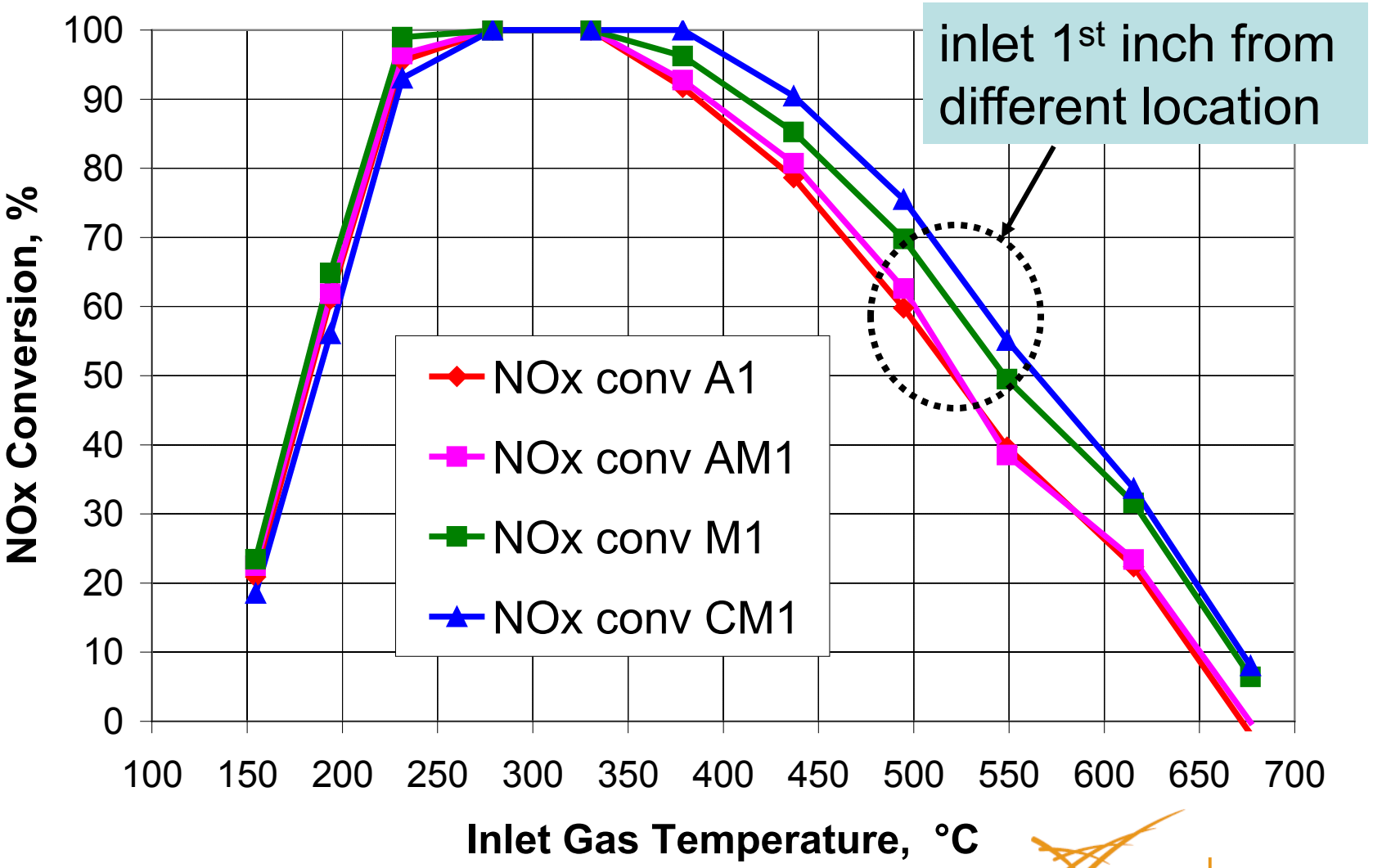
1st Inch Deactivated the Most

NOx-NH3 SCR Steady State, SV=30K, 350ppm NO/350ppm NH3



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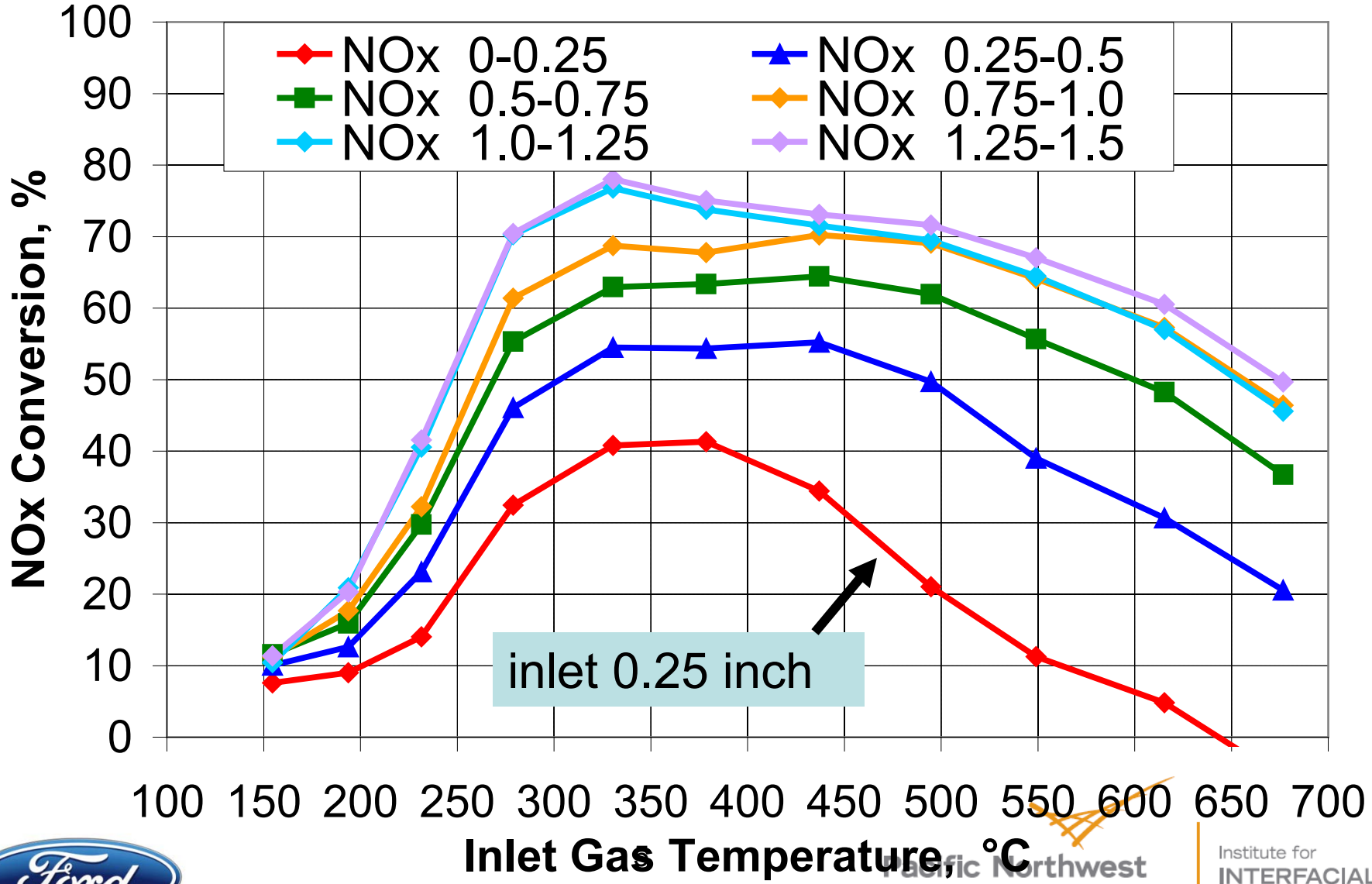
Inlet Section: Non-uniform NOx Conversion

NOx-NH3 SCR Steady State, SV=120K, 350ppm NO/350ppm NH3



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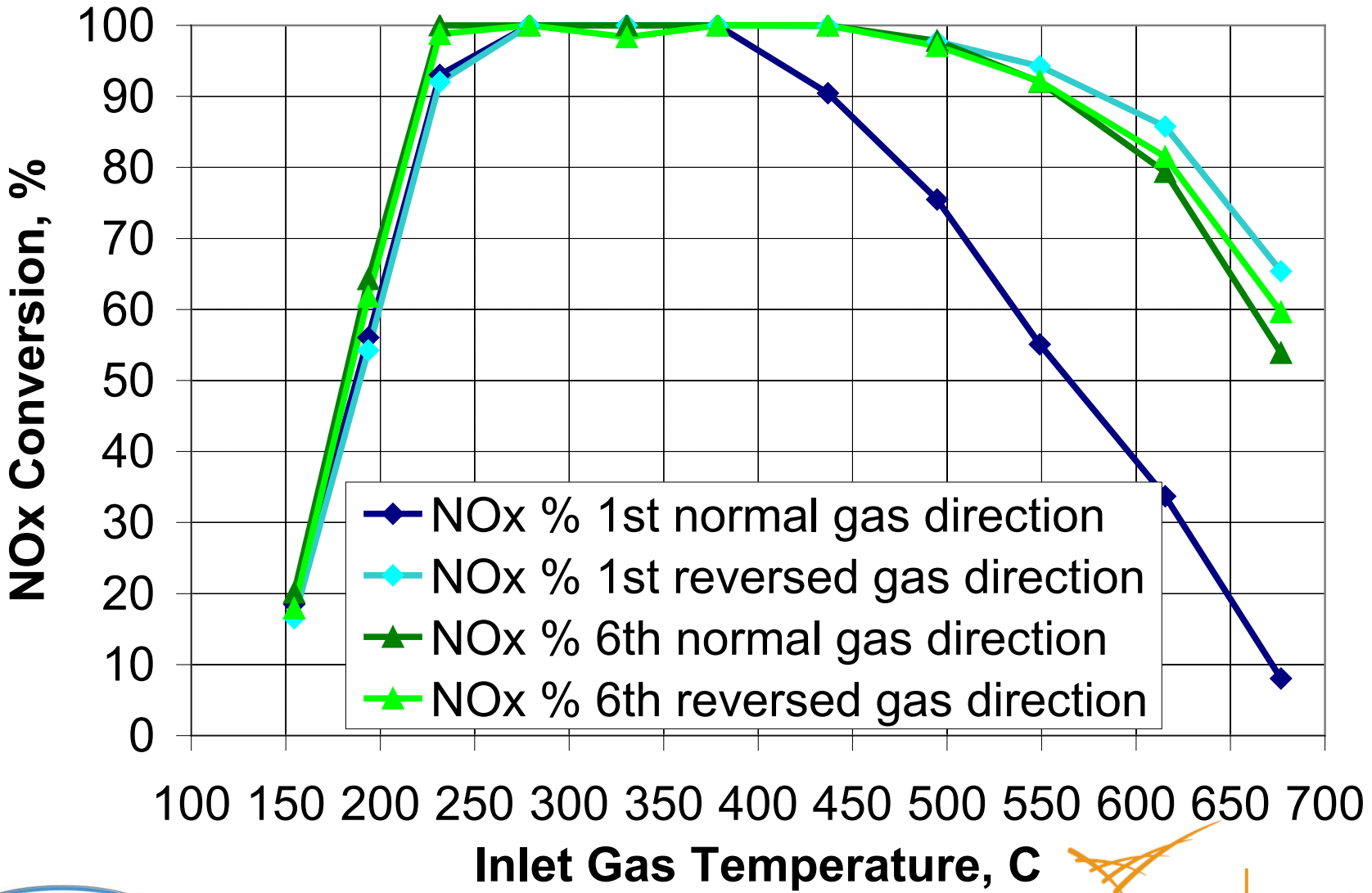
1st inch deactivation – the deterioration of NOx conversion on the 1st inch disappears after reversing the gas flow direction.



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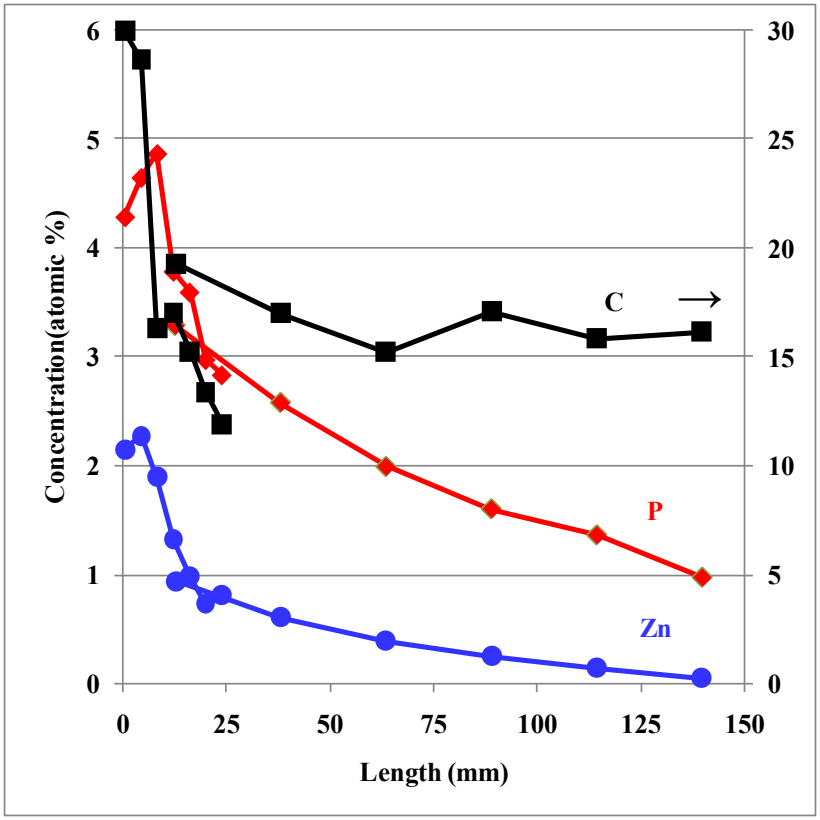
Surface Area

Sample	Surface area (m^2/g)*
Fresh	**161**
Lab aged	**152**
Engine aged	
1st	**109**
	110[1]
2nd	**123**
3rd	**133**
4th	**131**
5th	**124**
6th	**122**

***Catalyst + support mixture**
[1] after calcine at 550°C 2h

- Surface area decreased but the adsorption profiles are very similar → deactivation doesn't arise from structural degradation.
- Exactly same surface area even after 1st section calcined at 550°C → deactivation likely not due to carbon deposition.
- Some surface area decrease likely arises from loss of the catalytic component by attrition.
- Deactivation is not related to changes in zeolite structure.

1st inch XPS&XRF – C, S, P, Zn



- Significant carbon deposition of front side(~ 7 % for fresh sample and ~ 1 % for lab aged sample).
- Carbon deposition may account for some activity loss, especially 1st run.
- P and Zn deposition on the inlet end of the monolith.
- Practically no sulfur in the samples.

XRF	1st	2nd	3rd	4th	5th	6th
P	0.043	0.020	0.015	0.010	0.009	0.006
S	0.006	0.006	0.005	0.005	0.005	0.004
Zn	0.008	0.003	0.003	0.002	0.002	0.002

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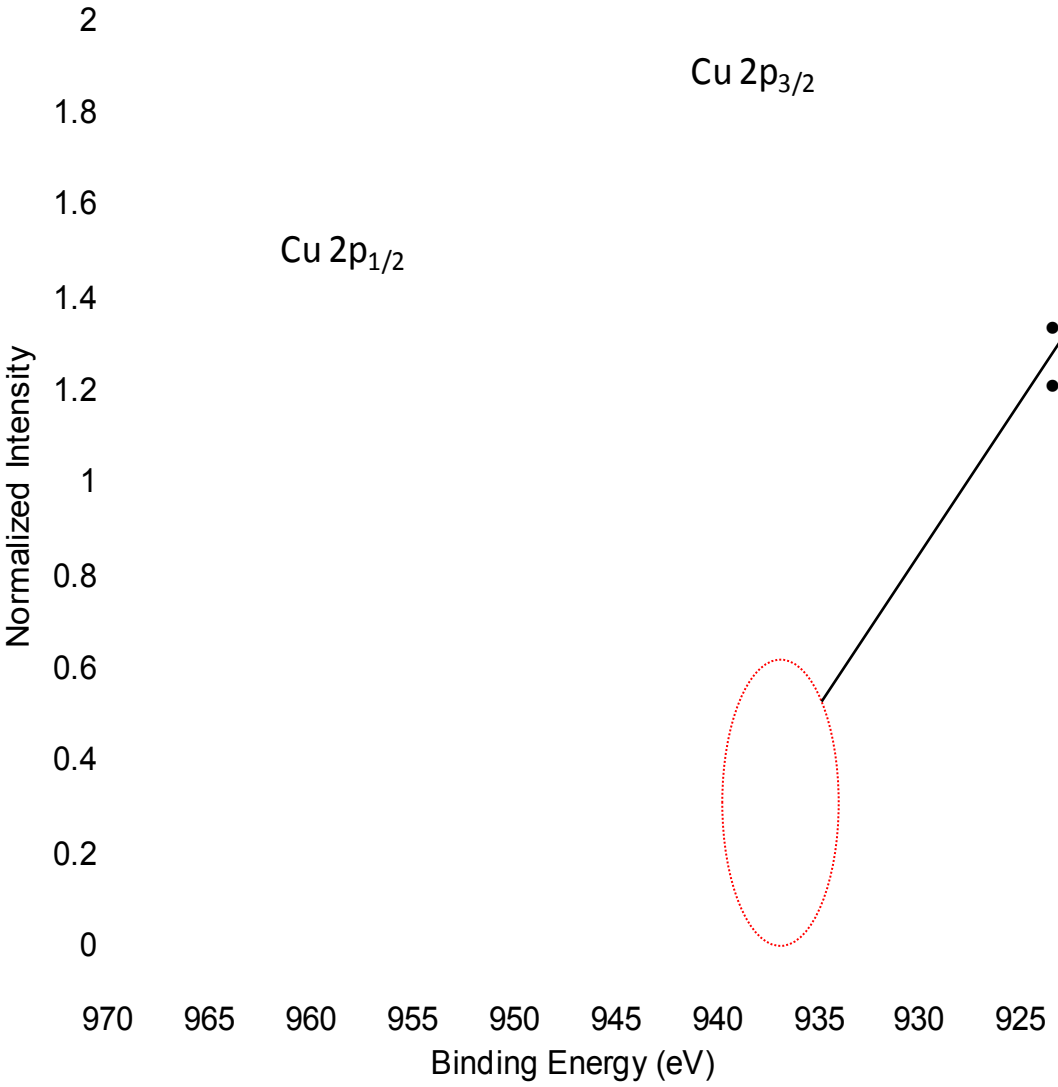
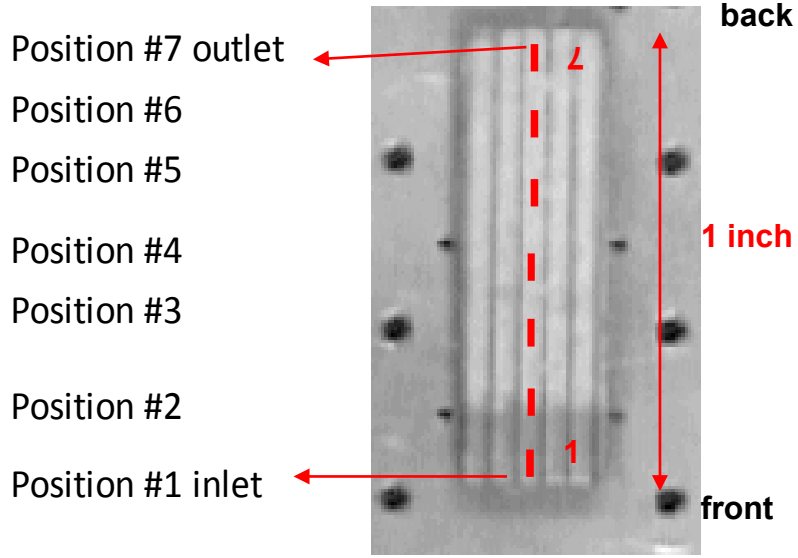
1st inch XPS - Cu



- Very front part of monolith shows a very small Cu^{2+} peak related with Cu sintering(?)

- **#1 located 0.5 mm from front end**
- **Each spot spaced by 4 mm**



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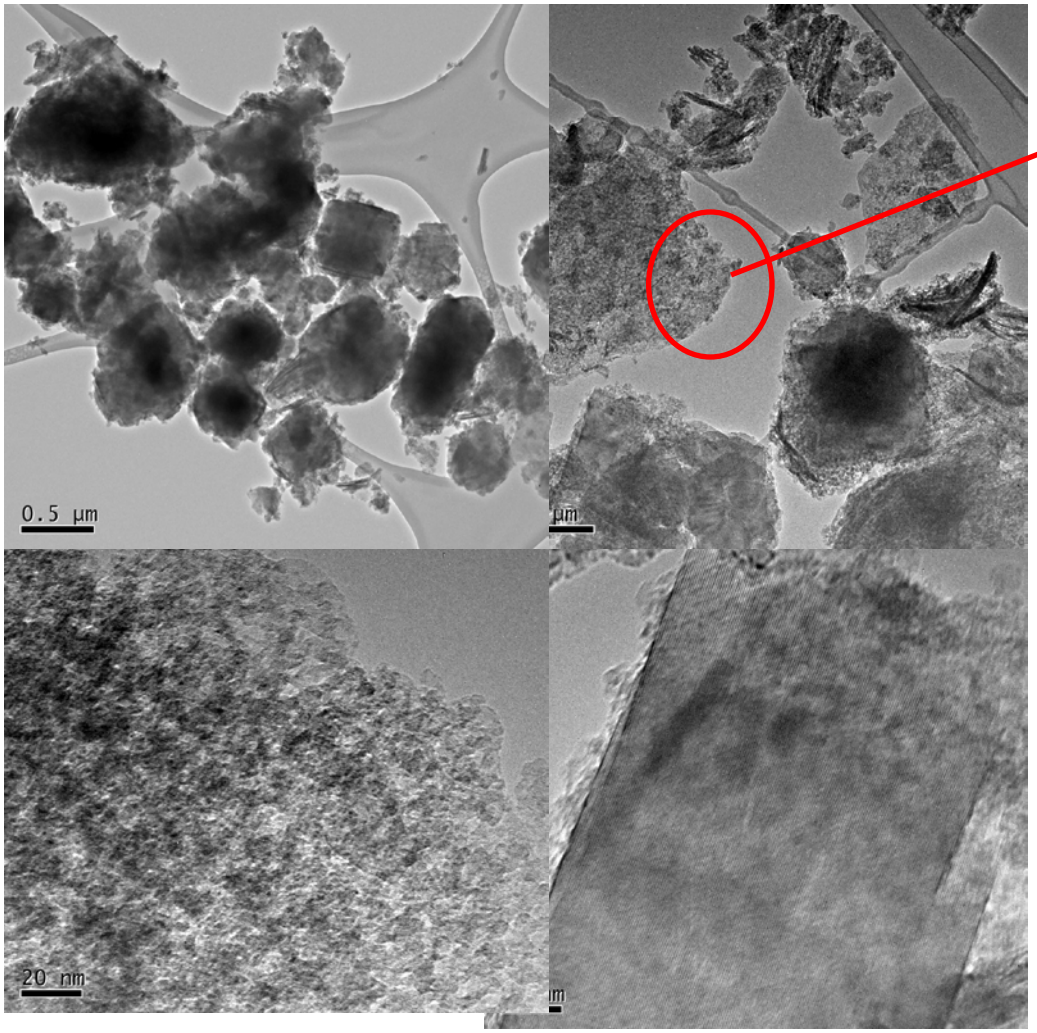
1st inch – TEM



- Morphology shows little change after engine aging other than perhaps including somewhat increased amorphous (or mixture with support(?)) areas.

- No evidence for Cu sintering

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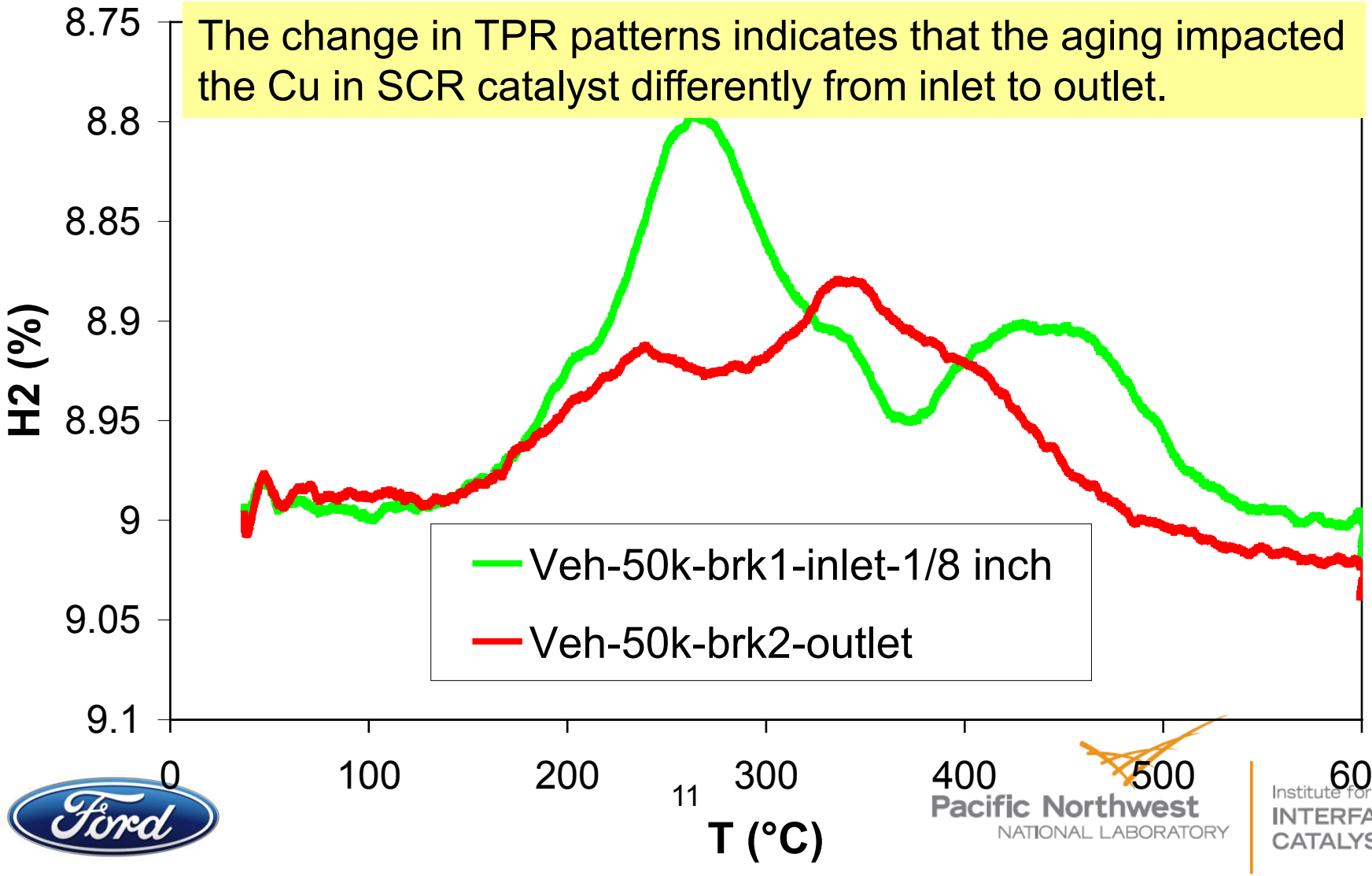
1st inch – TPR

TPR with 10°C/min to 600°C using 9%H2/Ar

The change in TPR patterns indicates that the aging impacted the Cu in SCR catalyst differently from inlet to outlet.



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Summary

- The inlet section of SCR catalyst was deactivated the most. The performance of the majority of SCR catalyst was uniform and as expected due to thermal aging.
  - Overall surface area drops due to loose the active component.
  - XPS results shows very small amount of 935.9eV band which will be related with no evidence for Cu sintering in TEM. But, the change in TPR patterns clearly indicates that the different Cu states in the inlet section.
  - Significant C, P and Zn in very front region of engine aged brick.
  - The deterioration of NOx conversion on the 1st inch disappeared after reversing the gas flow direction.

- Changes of Cu state and high levels of C, P and Zn impurities in the very front region (**no more than 1 inch**) might explain the more severe deactivation of the inlet section of the SCR catalyst.

- The above results suggest that the inlet section of the brick experienced all the aging factors in the most severe way, and that this section deactivates in a more complicated manner than the rest of the brick.

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