Temperature and Concentration Gradients during NOX Storage and Reduction Cycling

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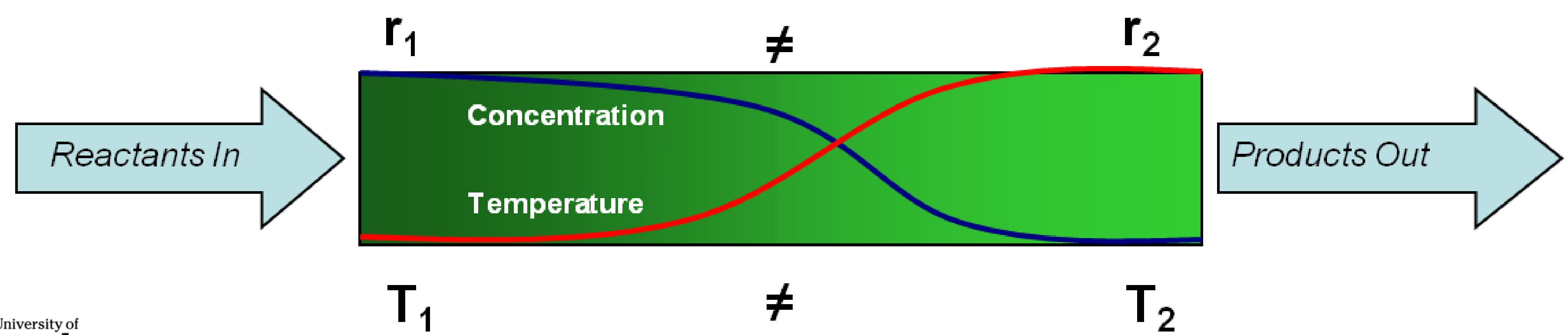
Introduction – gradients tied to emissions catalysts

- Resolved axial gradients in a catalyst bed or monolith are often described in models, but not always easily verified experimentally
- Methodology is being and has been developed to characterize the gradients existing in these reactor systems
  - SPACiMS – spatially resolved capillary-inlet mass spectrometry
  - Phosphor thermography
  - In-situ DRIFTS
  - Cutting samples into pieces
  - Not only validate models - novel understanding of chemistry



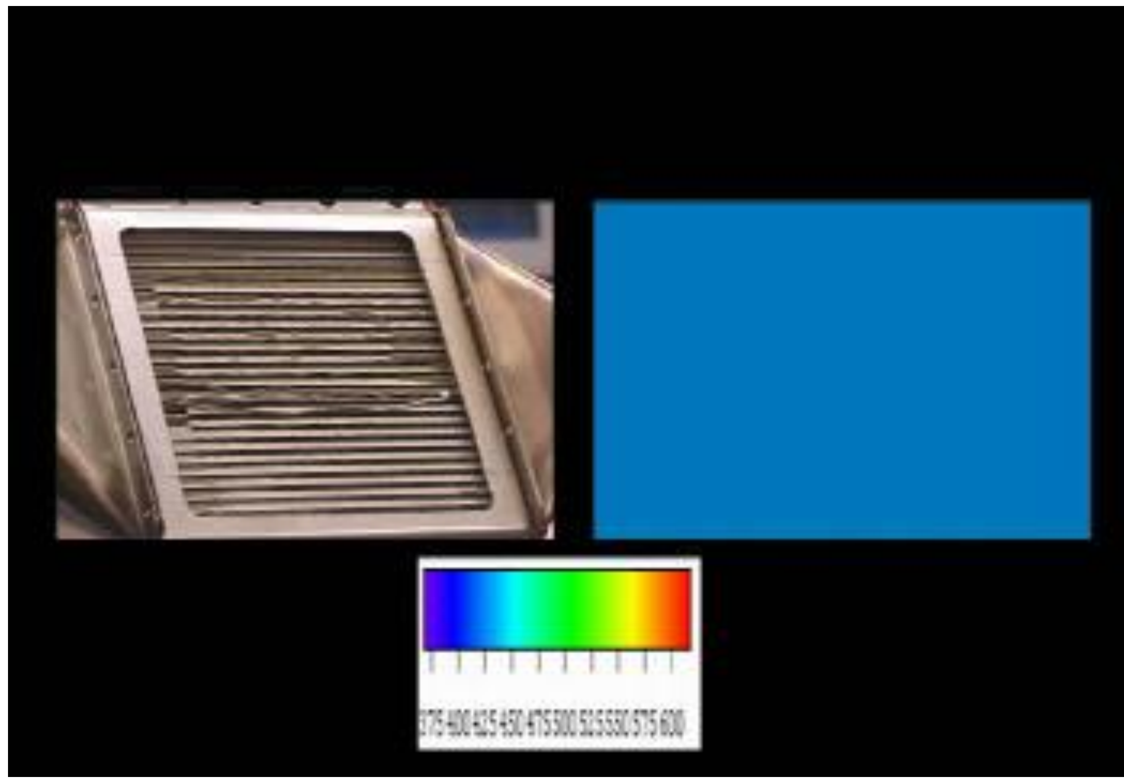
Introduction – measuring gradients (cont.)

IR thermography previously used in catalyst and reactor characterization applications

- Professors Luss, Wolf, Schmitz
- Provides spatial and temporal resolution of temperature gradients/changes

Soot filters

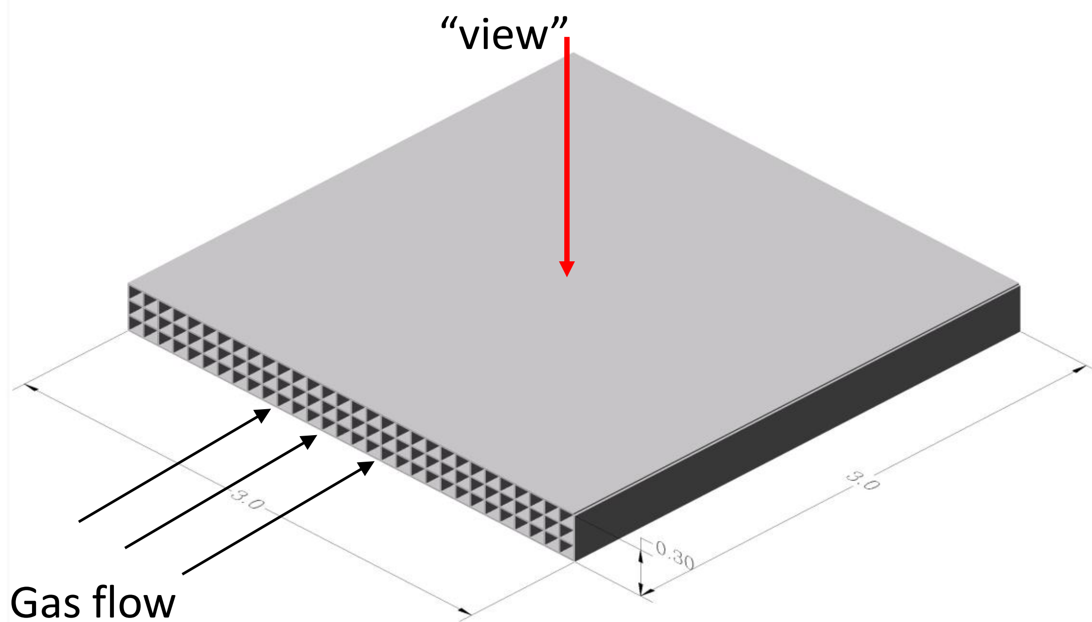
- Large exotherms,
- non-uniform reactant concentrations,
- non-uniform flow,
- non-uniform reaction



Courtesy of PNNL

Introduction – measuring gradients

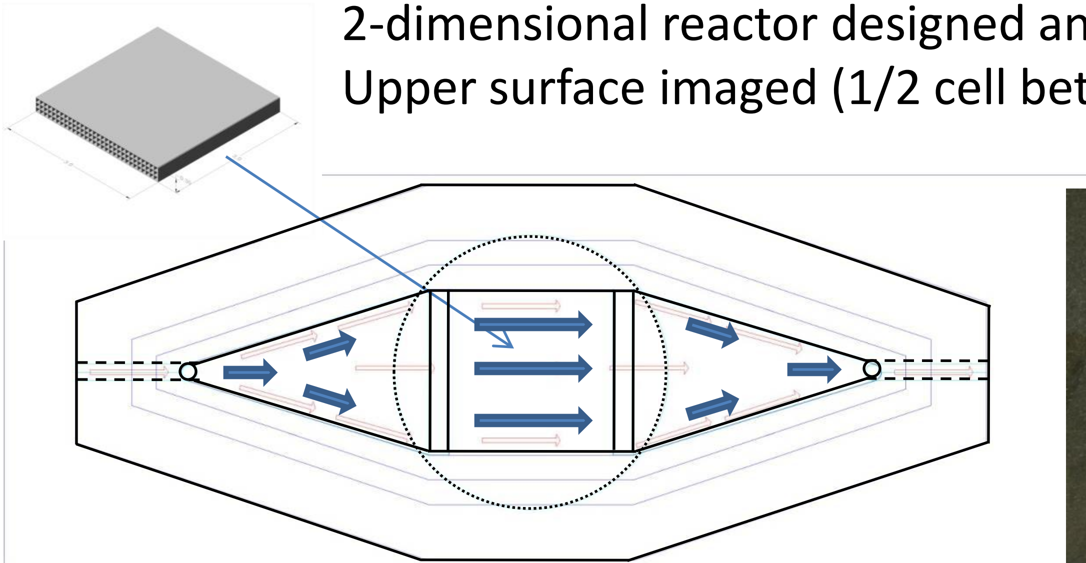
- To date focus has been on DOC and NOX trap catalysts

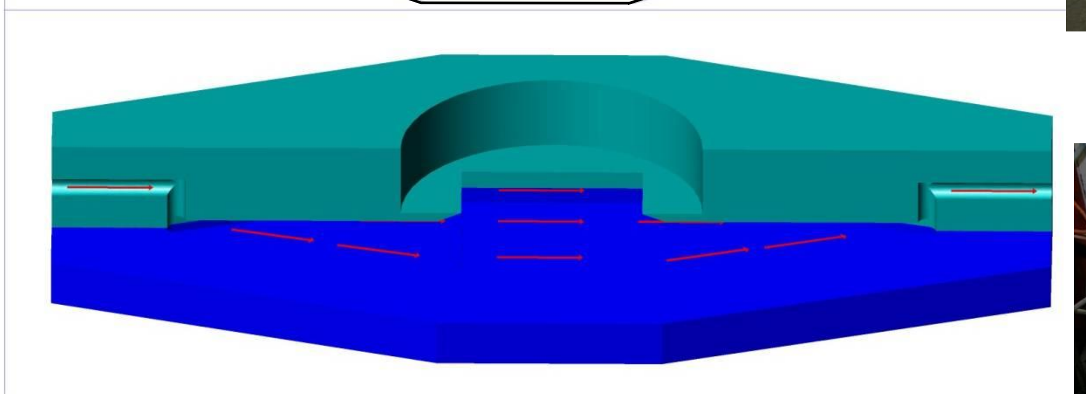


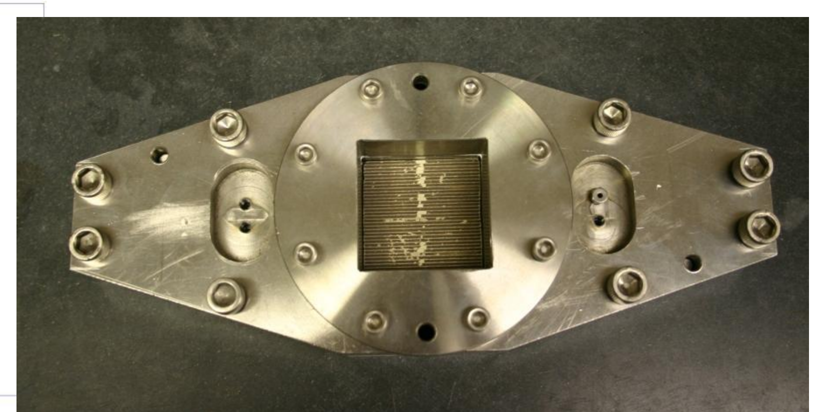
- To facilitate "viewing" – 2-D sample
  - Catalyst samples are 3" x 3" x 2 (or 3) cells high

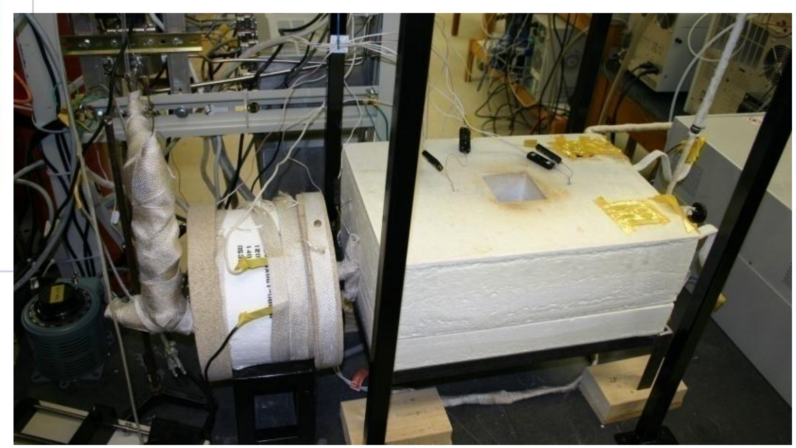
Introduction – IRT reactor

2-dimensional reactor designed and used for these experiments
Upper surface imaged (1/2 cell between surface and reactor top)









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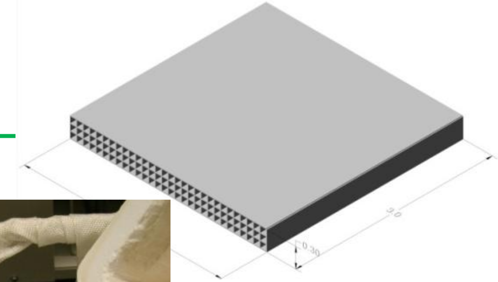
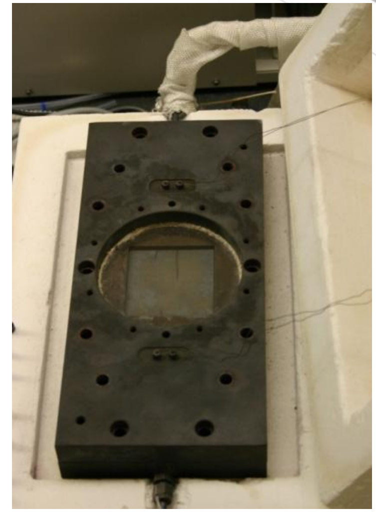
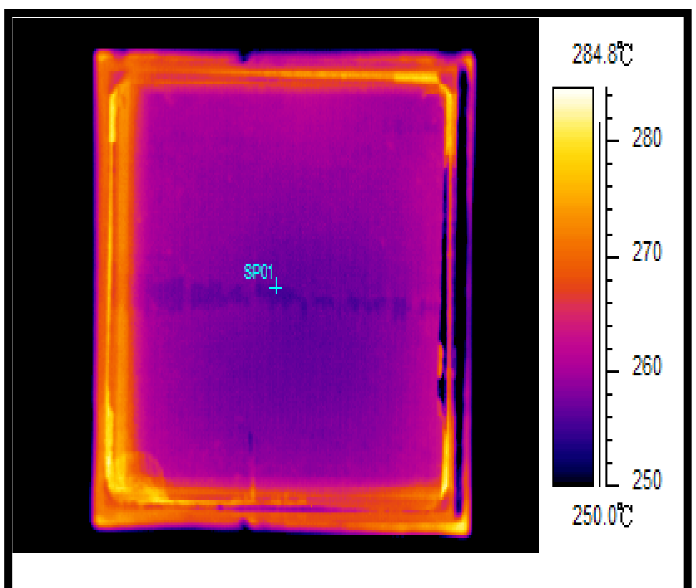
Introduction – experiment set-up

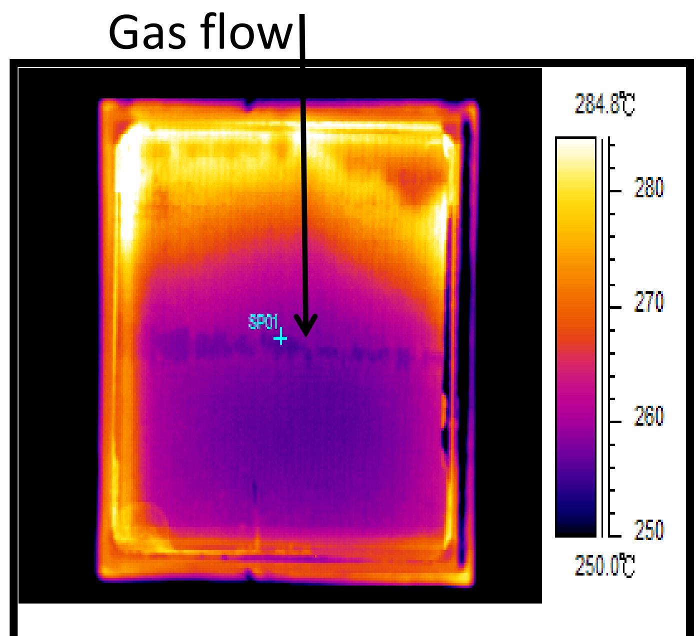


- “2-D” catalyst sample
- IR thermography
  - Temperature changes across the surface can be directly monitored
  - Therefore, __thermic reactions can be indirectly monitored
  - Spatially resolving the reaction



“screen-shot” style data





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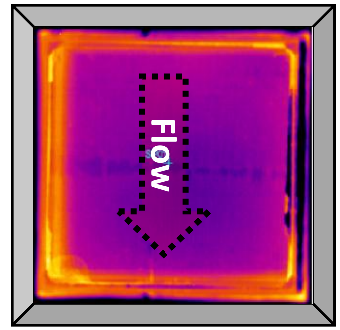
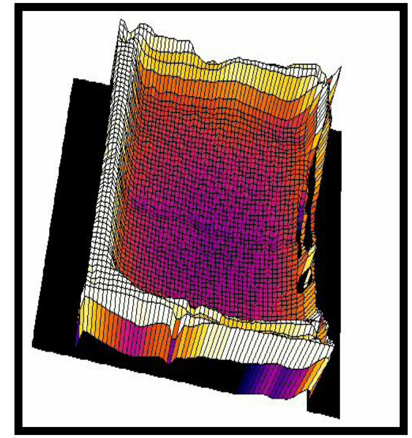
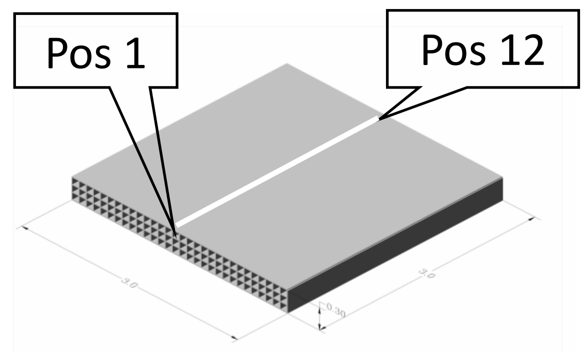
Introduction – data analysis

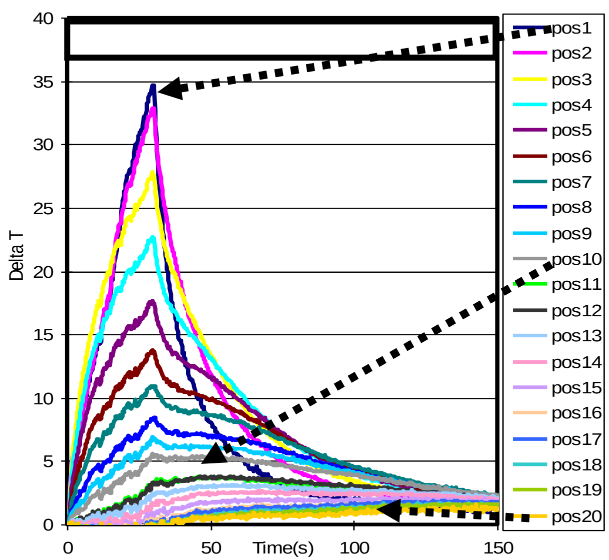
- Camera image of catalyst
- Color palette is converted to temperature
- Radially centered line, 12 points chosen
  - Change in T plotted







Sample for IR-thermography



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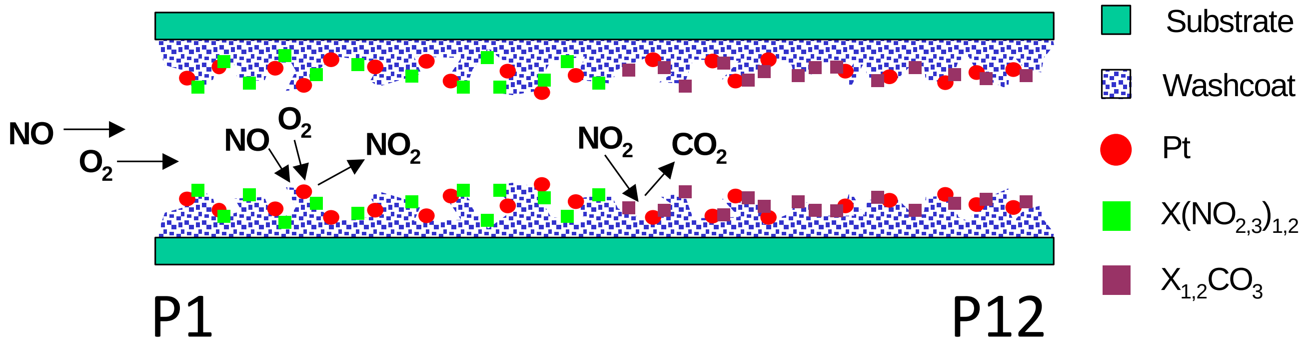
NSR – typical reaction scheme

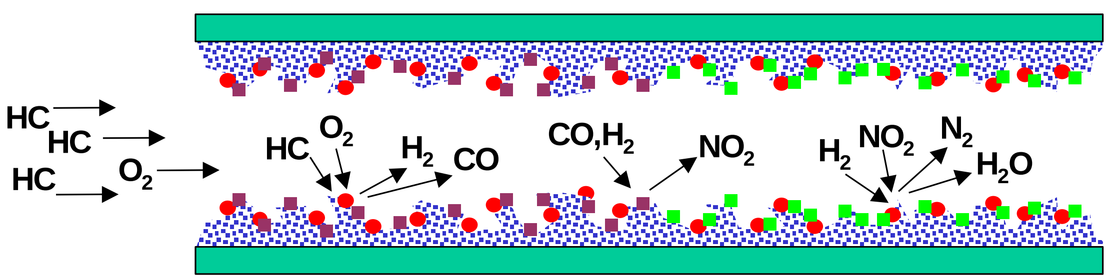
1. $NO \rightarrow NO_2$ — $NO \leftrightarrow NO_2$
2. NO_2 storage — $BaO + 2NO_2 + \{O\} \rightarrow Ba(NO_3)_2$

Sorption (Oxidizing Atmosphere)



3. Reductant evolution — (diesel, rich exhaust, reformed gas)
4. NO_X release from the storage site - — $Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + \{O\}$
   $Ba(NO_3)_2 + CO \rightarrow BaCO_3 + 2NO_2$
5. NO_X reduction to N_2 — $2NO_2 + 4CO \rightarrow N_2 + 4CO_2$

Regeneration (Reducing Atmosphere)



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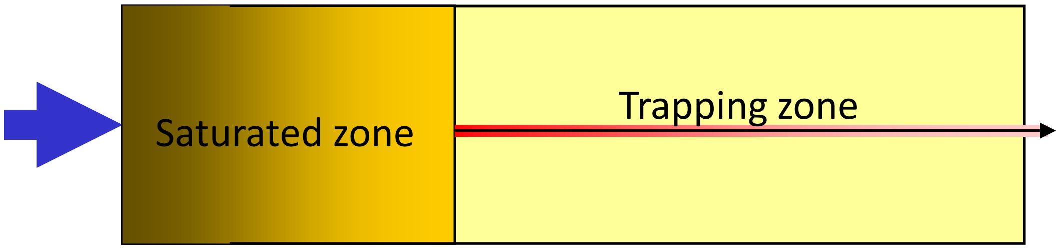
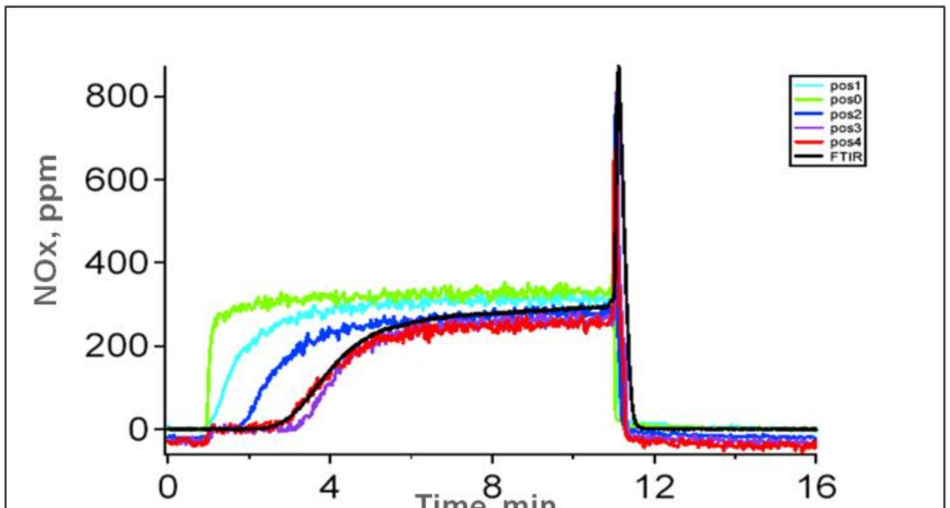
NSR – moving reaction “front”

Lean phase



Literature typically reports a relatively homogeneous moving front through NSR catalysts



Courtesy of Cummins Inc and Chalmers U

Spaci-MS work confirms saturation front

So, how much of the sample is really being used?

During regeneration, the same phenomenon occurs, just in reverse – reductant progresses through the sample, reducing nitrates

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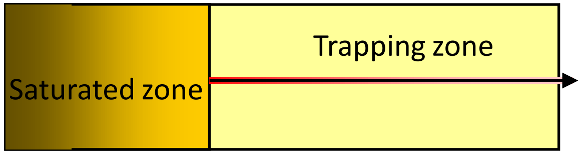
NSR – IR thermography application

Multiple reactions

- Lean – NO oxidation and NOX trapping
  - Exothermic
  - Spread over a long period of time
  - Low reactant amounts (100's ppm)



- Regeneration – nitrate reduction
  - Exothermic
  - Regeneration is typically short (~5 seconds)
  - Larger reactant amounts (concentrated nitrates on surface, larger % of reductant)

Therefore – during regeneration the heat evolved could be associated with nitrate reduction – telling us where NOX was trapped in the previous trapping phase

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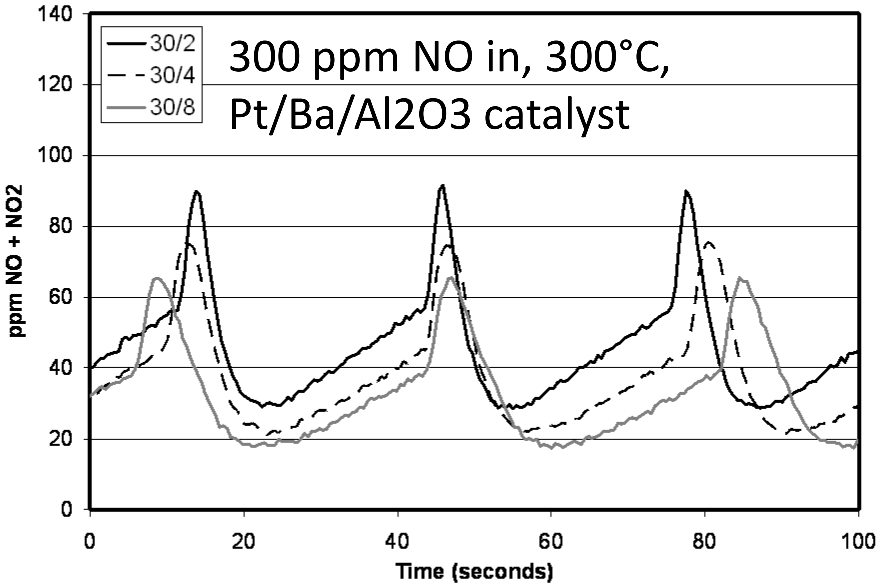
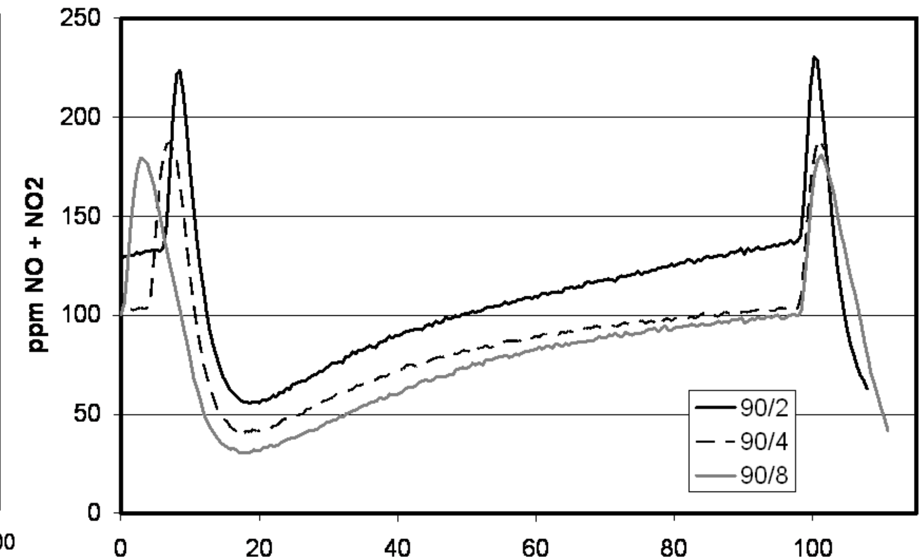
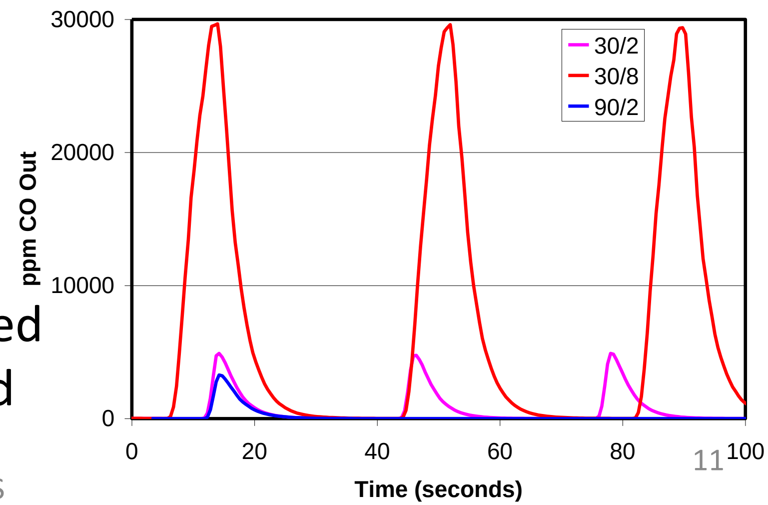
NSR – results, performance data

- Shorter trapping – better conversion
- Longer regeneration – better conversion







CO (and NH3) breakthrough observed during regen – not reductant limited

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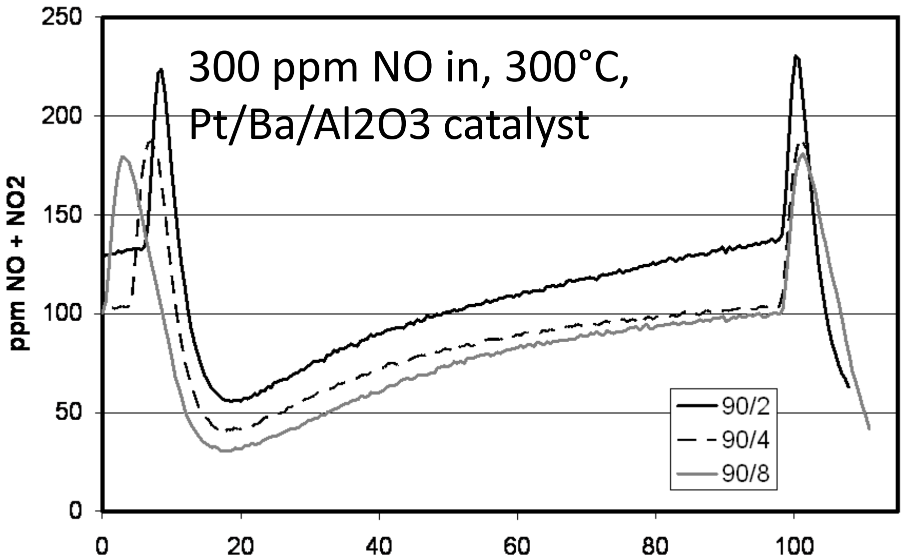
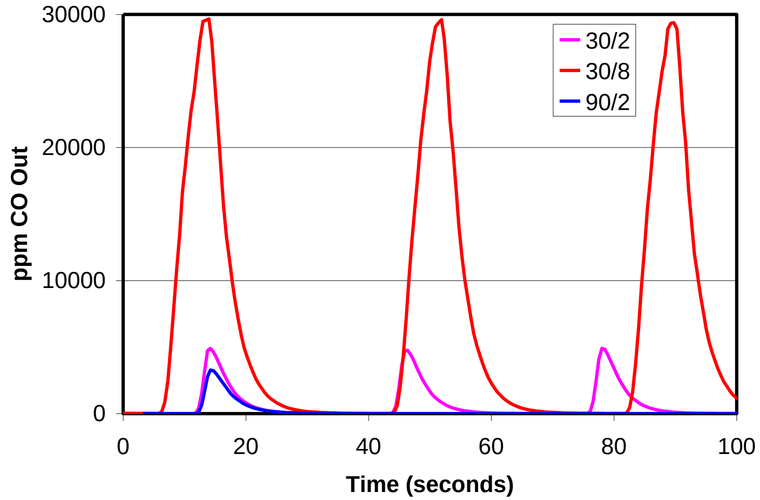
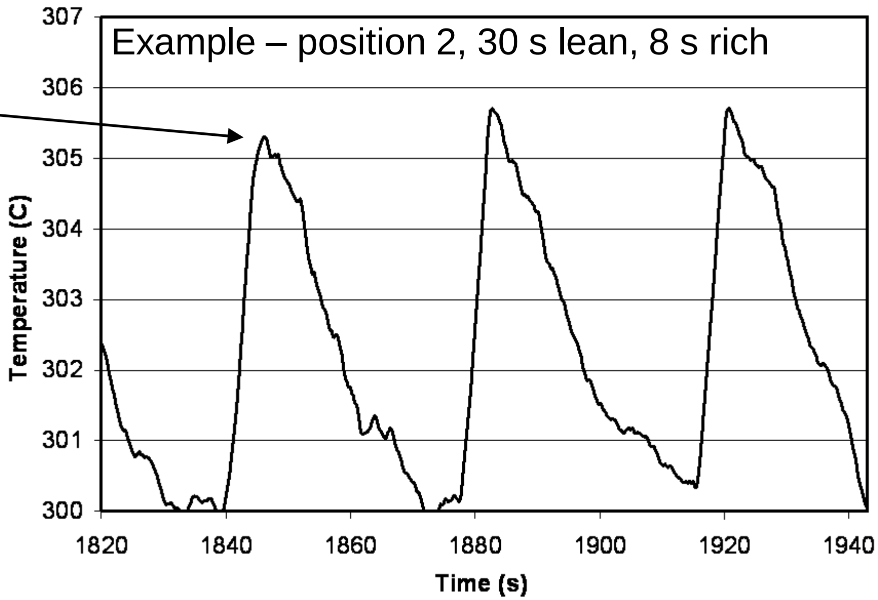
NSR – results, performance data





For the following data – plotting maximum temperature difference observed for each cycle, at the different positions



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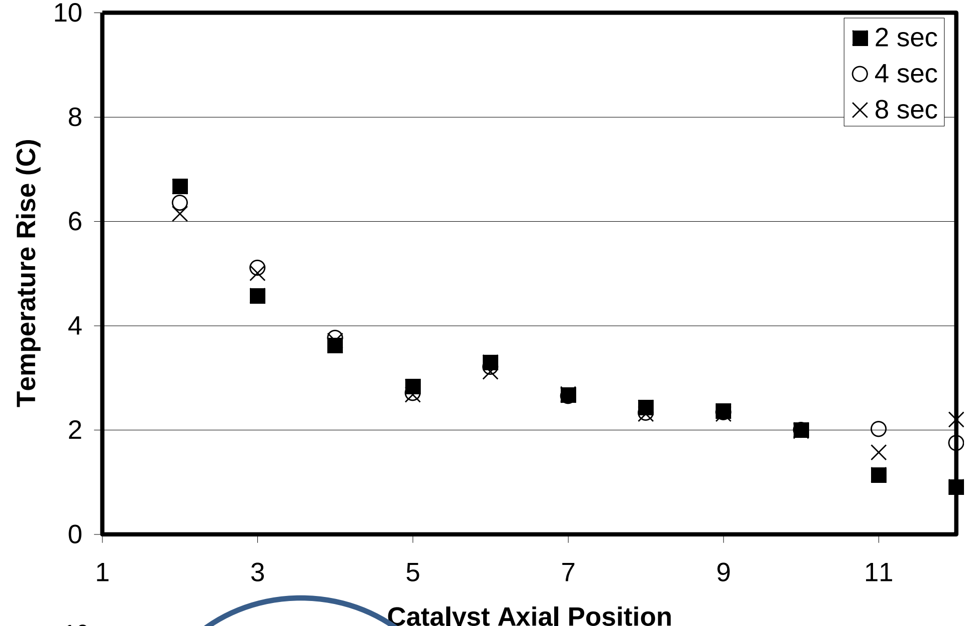
NSR – temperature data

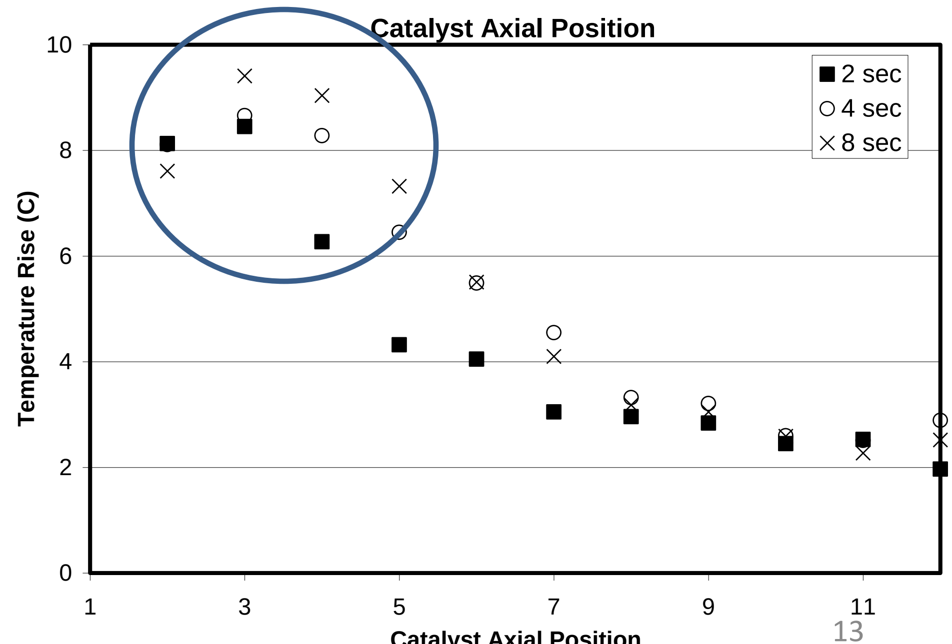
Shorter lean time (30s)

- Front-to-back saturation observed
- Not much effect of regeneration time
  - 1.41, 1.47 and 1.51 cm^3 of NOX trapped



Longer lean time (90s)

- Larger temperature rise indicates more was trapped
  - 3.4, 3.7, and 3.9 cm^3 trapped
- Effect of regeneration observed (more trapped with longer regen)
- Not front-to-back monotonic temperature rise



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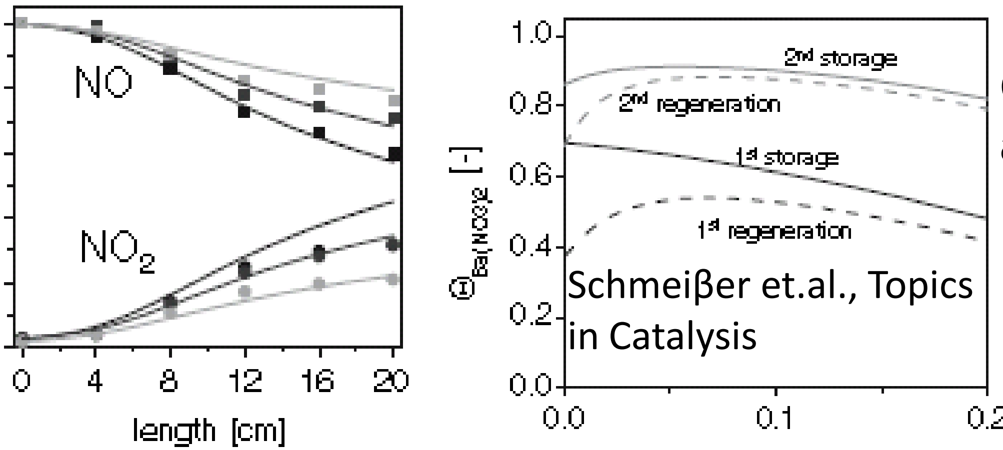
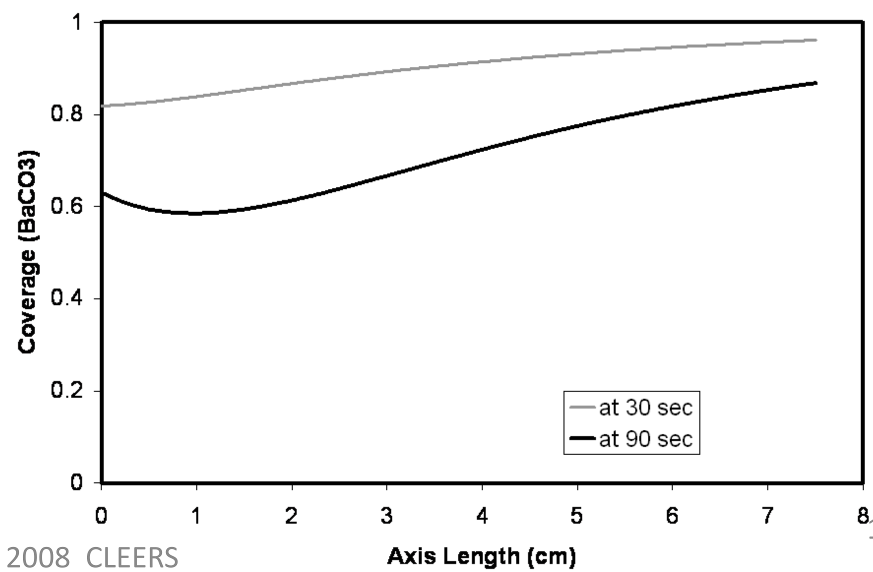
NSR – model predictions

There is some justification for seeing a non-monotonic profile, intuitively, NO oxidation might limit



Coverage of $Ba(NO_3)_2$ along catalyst

Separate model[1] has been <u>adapted</u> to fit cycling and saturation data



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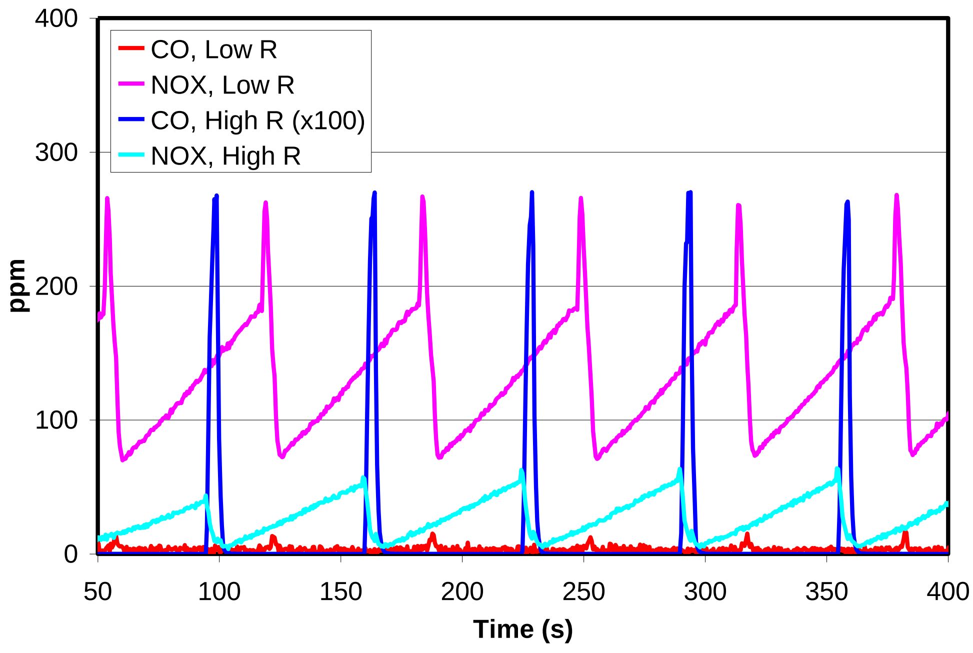
[1]Guthenke et.al. Chem. Eng. Sci. 62(2007)5357

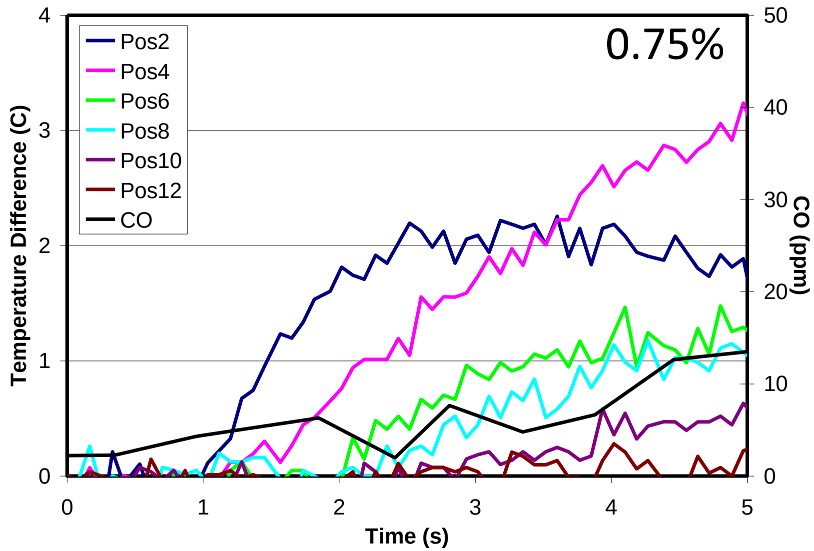
NSR – cycling data

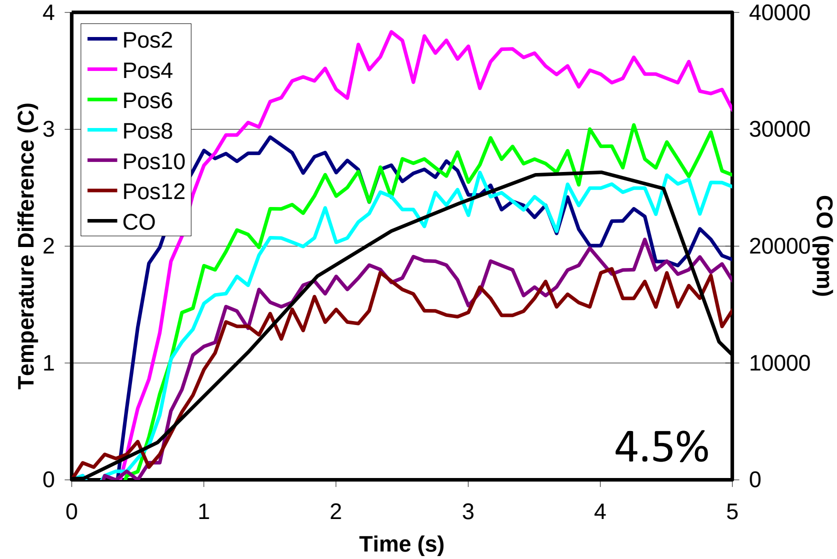
- Standard cycling experiments again (aged sample)
- 2 reductant levels, one below OSC (0.75%) one well above (4.5%)

- 60/5 cycle, 400°C
- <10 ppm CO slip for low R testing



NSR – cycling data





With lower R

- longer delay before delta T (longer to titrate OSC)
- Delay between each position – titration of nitrates
- Only cleaning front 6-8 positions (and P2 not even at max T)

With higher R

- Some delay between positions
- Even at 400°C – some nitrates left behind after 5 seconds (only P1 T dropping)

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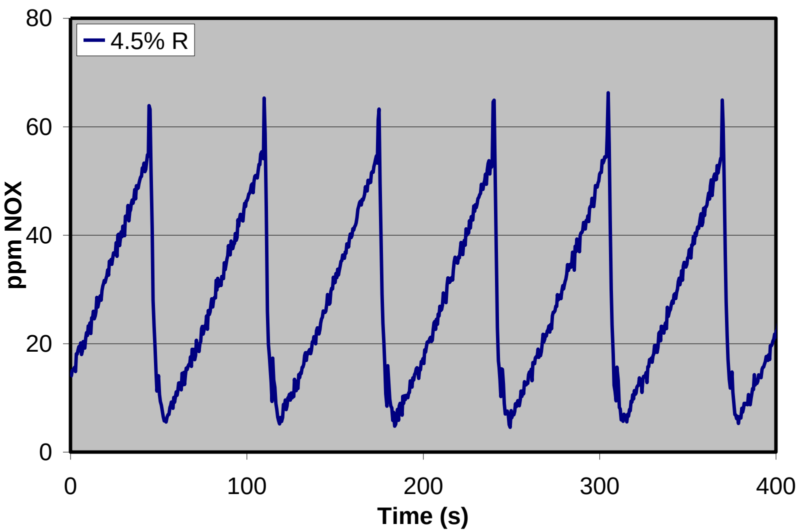
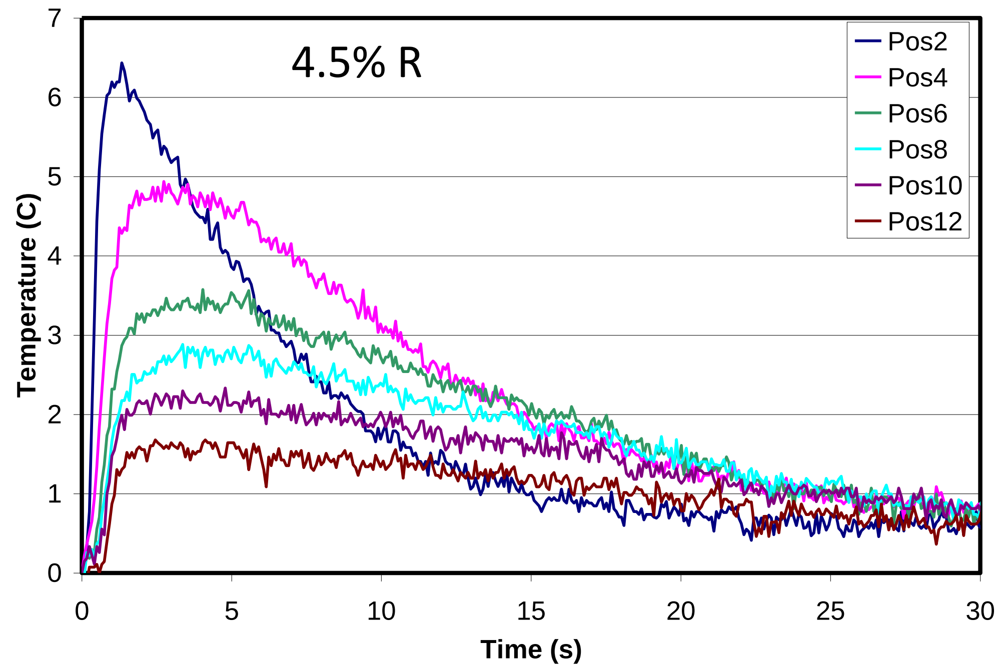
NSR – catalyst use

Experiment – cycle until steady performance (data above), then long regen

Long regen after cycling shows where the leftover nitrates are along the catalyst





With "enough" reductant – most NOX is trapped at front

Again – monotonically decreases down length

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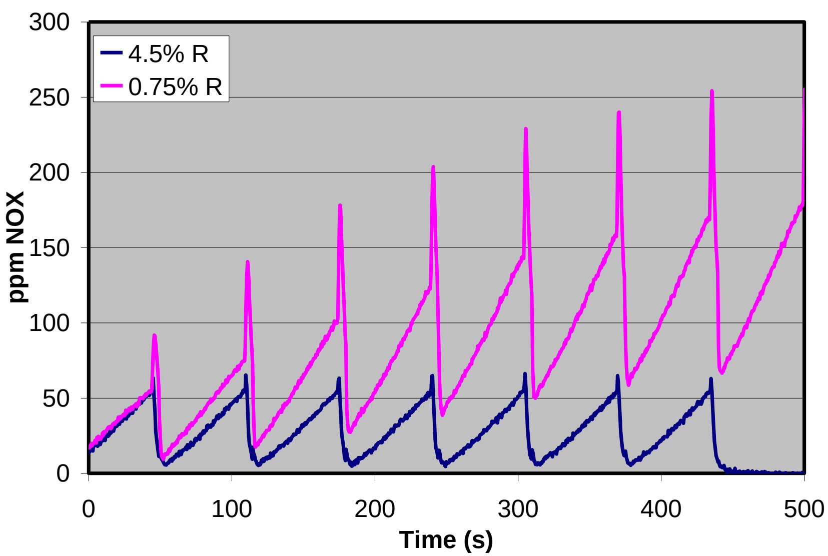
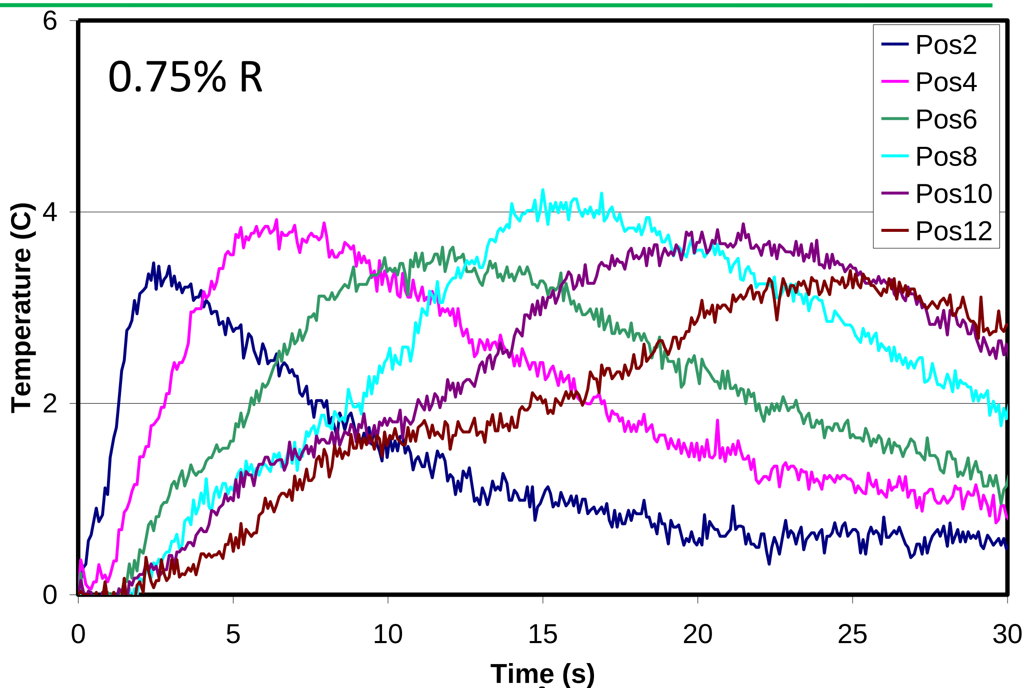
NSR – catalyst use





- With "not enough" reductant – NOX is trapped throughout catalyst – the front is being regenerated and used, the back fills up until steady cycle-to-cycle
- T rise is slightly less (6°C in previous plot)
- Not monotonic

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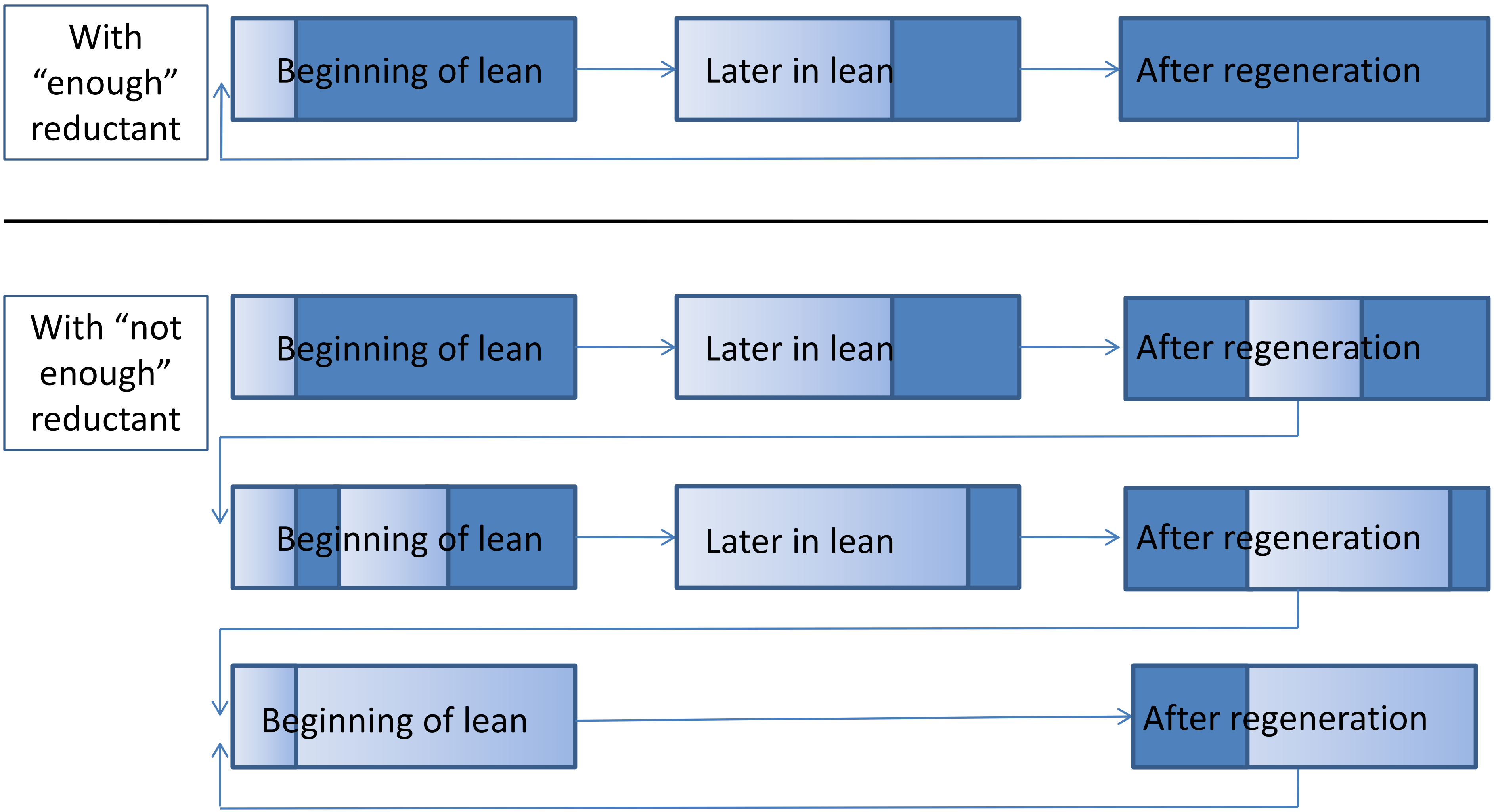
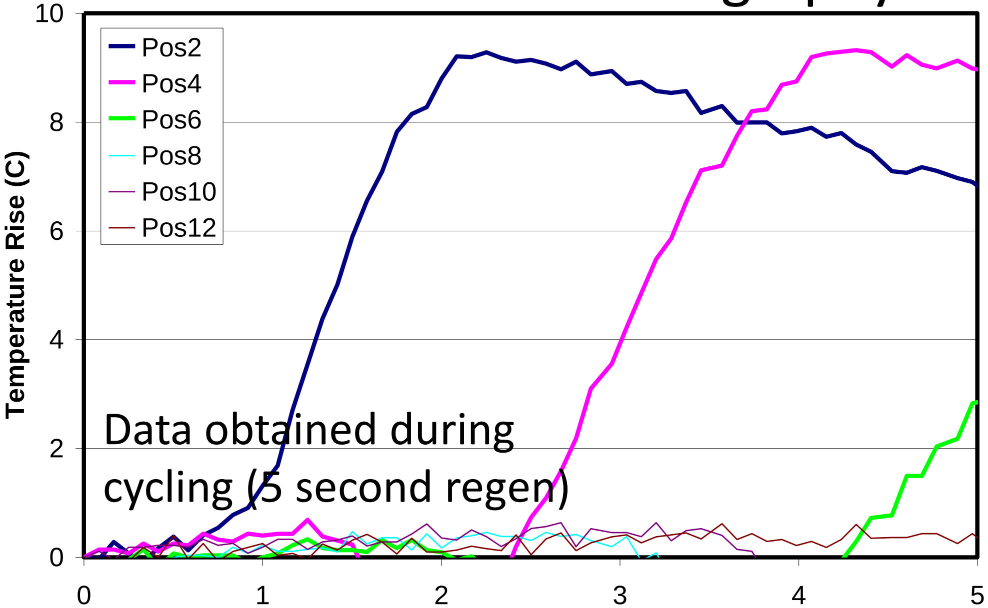
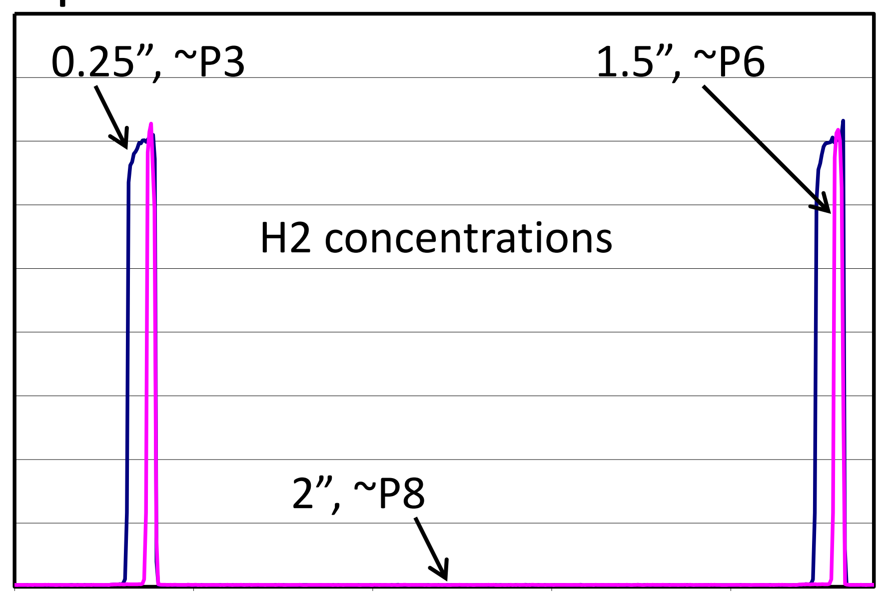
NSR – leftover trapped NOX



NSR – leftover nitrates

Combined thermography and “poor man’s” SPACiMS





- Low reductant amount to resolve temperature profiles
- Half of the catalyst being regenerated and therefore used

- Capillary probe positioned at rough estimates of camera positions
- Data taken after steady cycle-to cycle and moved after several cycles

Temperature increases match presence of H_2 – no H_2, no T increase

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NSR Summary

- Characterization of NSR catalysts shows
  - Short trapping times leads to monotonic saturation style gradient
  - Longer trapping times (more trapped) leads to a maximum in amount trapped slightly downstream of the inlet

- IR thermography clearly shows portion of catalyst being used during cycling
  - Thermography data is validated by SPACi

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Acknowledgements

People who did the work

Alan Shaw

Khurram Aftab

Frank Cheuk

People who paid for the work

National Sciences and Engineering Research Council of Canada

Cummins Inc

Johnson Matthey for catalysts