Urea Decomposition and Storage under Light-Duty Diesel Conditions

8th CLEERS Workshop
Dearborn, MI
May 19, 2005

John M. E. Storey*, **C. Scott Sluder, Samuel A. Lewis, Sr., and Linda A. Lewis**

Fuels, Engines and Emissions Research Center, Oak Ridge National Laboratory

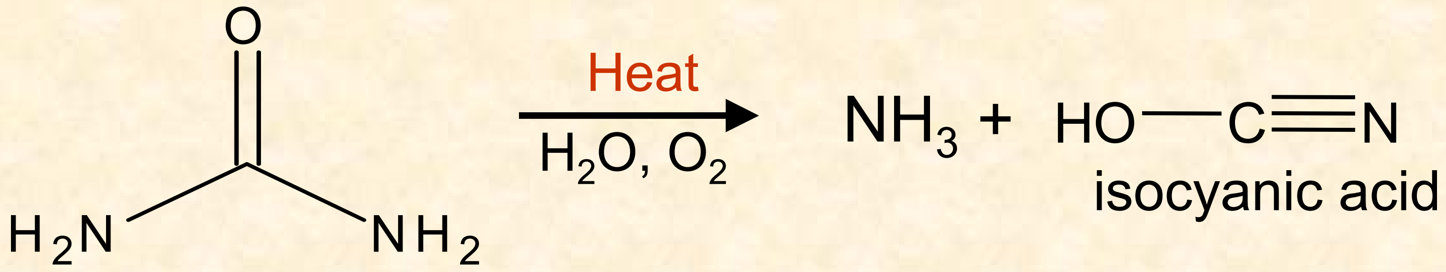
P.O. Box 2008, MS 6472, Oak Ridge, TN 37831-6472

***storeyjm@ornl.gov**

Background

- **Urea SCR offers viable alternative for diesel NOx control**
  - **NOx conversion is high; infrastructure issues being resolved**
- **Heavy-duty vehicles run at higher loads and temperatures >250 °C where urea decomposition is rapid on catalyst**
- **Light-duty temperatures (150 °C – 300 °C) require changes to traditional vanadia based. Zeolitic system provided by Umicore**

Ideally, urea decomposes to form ammonia, which then reduces NO_X to N_2.

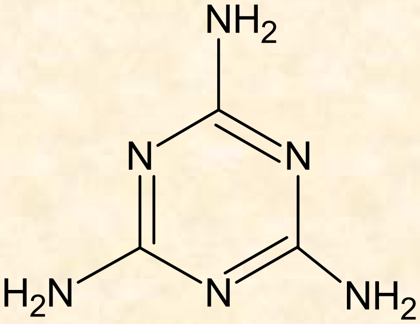


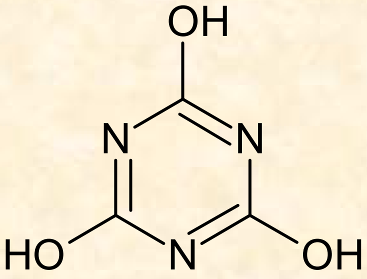
$$HO{-}C{\equiv}N \xrightarrow[H_2O]{\text{Heat}} NH_3 + CO_2$$

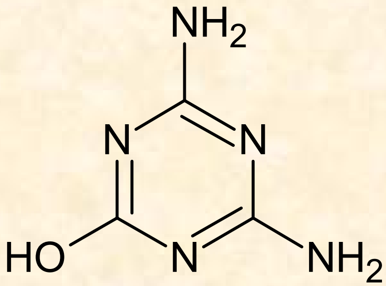
isocyanic acid

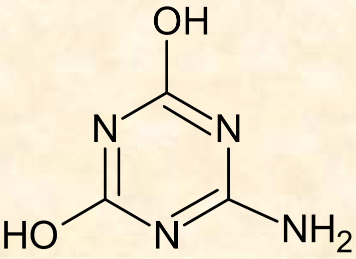
$$2\ NH_3 + NO + NO_2 \Leftrightarrow 2\ N_2 + 3\ H_2O$$

Urea decomposition can lead to the formation of several undesirable species.


melamine

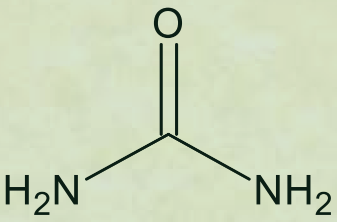

cyanuric acid


ammeline


ammelide

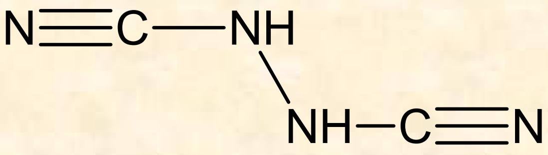
$H_2N{-}C{\equiv}N$

cyanamide


urea

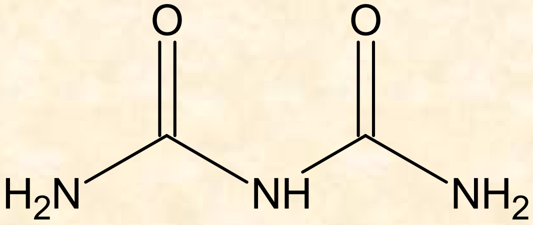
$HO{-}C{\equiv}N$

cyanic acid


dicyandiamide

NH_4NO_3

Ammonium nitrate


biuret

Several reaction pathways available for NH_3 and NOx…*f*(T), SV, NO:NO_2

$$2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + 3\ H_2O$$

$$NH_4NO_3 \rightarrow NH_3 + HNO_3$$

$$2HNO_3 + NO \rightarrow 3\ NO_2 + H_2O$$

Ammonium nitrate formation, decomposition, and subsequent reaction with nitric oxide.

Important when T< = 200 C.

$$6NH_3 + 8\ NO_2 \rightarrow 7\ N_2O + 9H_2O$$

$$4\ NH_3 + 4\ NO_2 + O_2 \rightarrow 4N_2O + 6\ H_2O$$

Conversion of NO_2 to N_2O.

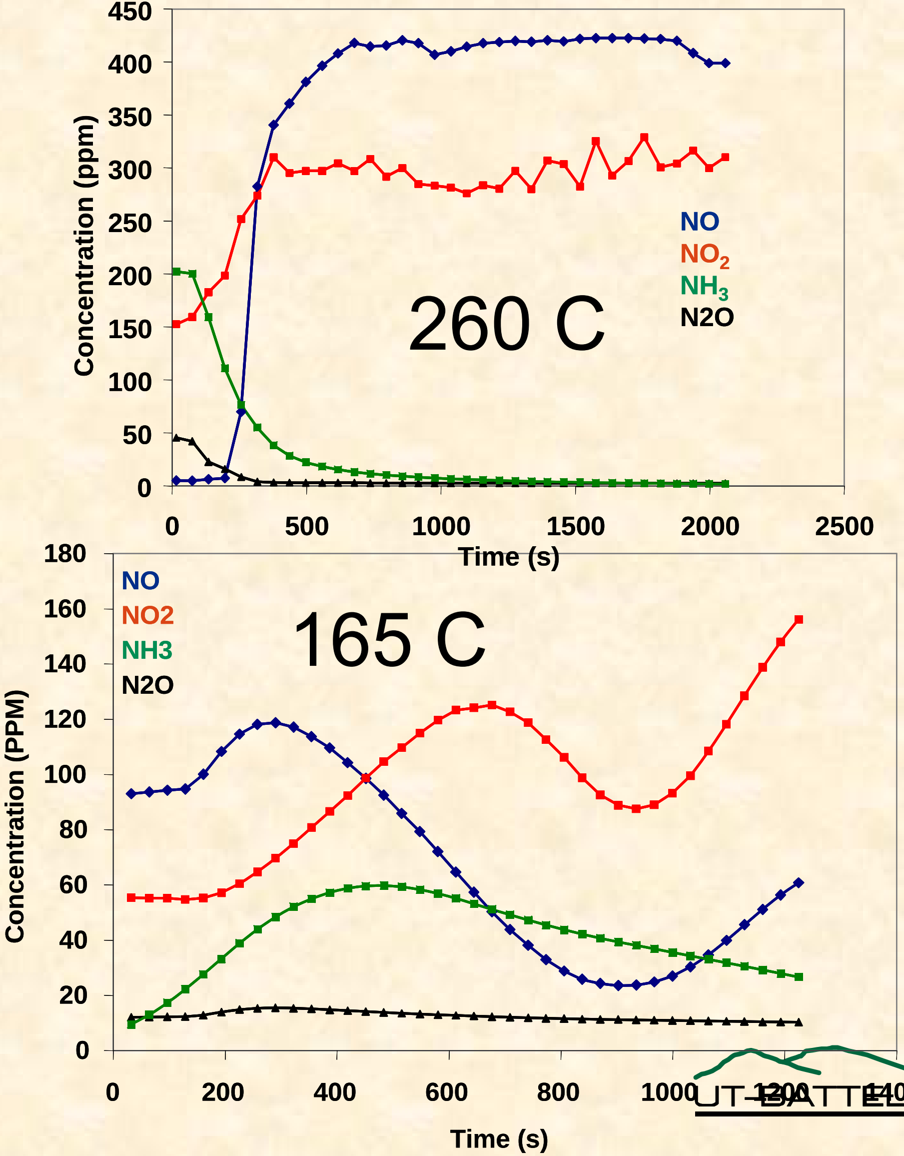
Important when NO_2 / NO > 1.

So… significant methods development research required to understand the sample and measurement techniques for urea decomposition products

Last year at CLEERS …"burn off" of urea found to be *f*(T), evidence of storage compound releasing NH_3

- **Hydrolysis kinetics on surfaces still need to be understood. Will affect the length of the catalyst that is used only for thermohydrolysis**
- **Understanding**

$NH_4NO_3 \Leftrightarrow NH_3 + HNO_3$ **and further decomposition of nitric acid is likely key to low T behavior**



Current study:
Understanding low-temperature urea behavior is key to developing effective and efficient SCR systems for light-duty vehicles.

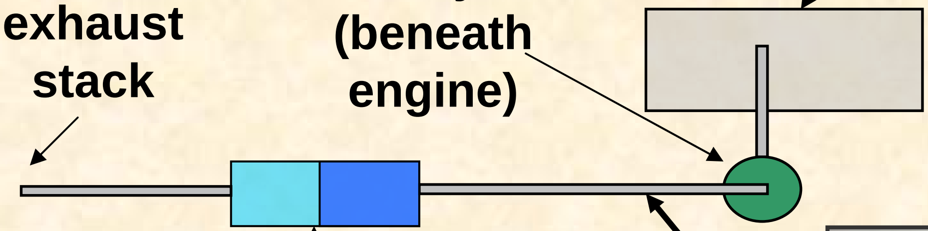
- **WHY?**
- **Most models and bench reactor studies assume complete urea decomposition upstream of the SCR catalyst.**
  - **ammonia used as reductant**
  - **May lead to inefficient sizing or urea injection strategies.**

- **Device models and model-based controls for SCR-systems need to account for many processes, including urea decomposition and storage.**
  - **Avoiding under/over injection of urea.**
  - **Sizing devices for specific applications.**

Experimental: emphasize light duty conditions

- SCR temperatures less than 300 °C.
- Stoichiometric urea injection *based on total NOx*
- 200 ppm NO_X at SCR inlet.
- Space Velocity of 25,000 hr^{-1} (based on 2.6 liter monolith).
- Investigate urea decomposition (*if any*) upstream of SCR catalyst.
- Analyze SCR performance and exhaust products exiting undersized monoliths to elucidate decomposition effects.

- Rinse Experiments: Expose clean monoliths until steady-state is reached ~30 min.
  - 205 °C and 180 °C experiments
  - Rinsed exposed monoliths with buffer solution
  - Analyzed with capillary electrophoresis
  - not quantitative



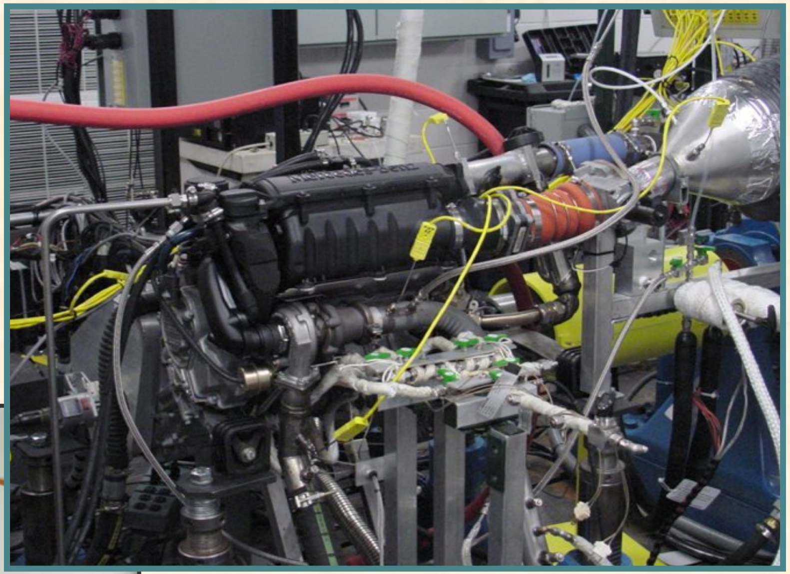
To exhaust stack

Oxidation catalyst (beneath engine)

Engine

SCR catalyst
76- or 152-mm length

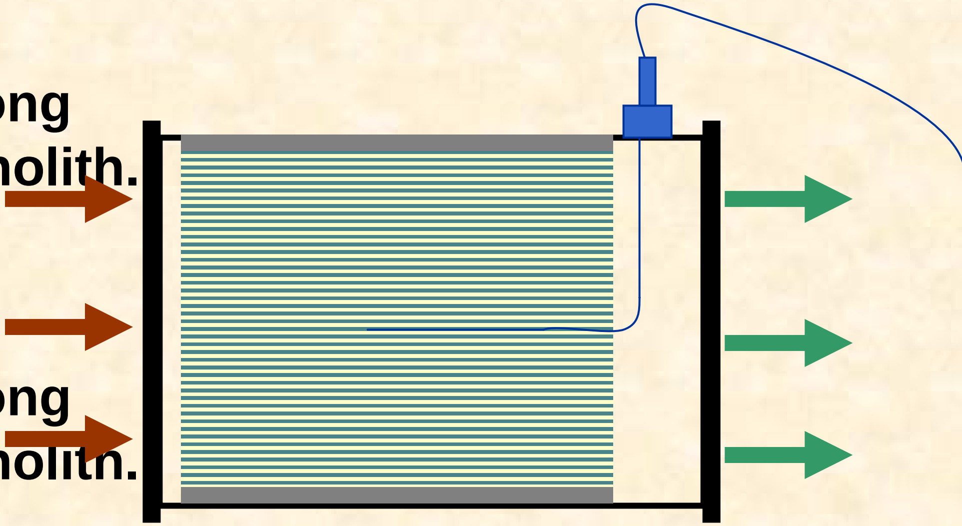
Urea Injector



Exhaust flow rate and NO_X concentration were held constant while varying exhaust temperature by manipulating the engine EGR rate, boost pressure, and fuel rate.

Full-size catalyst monoliths provided by an industry partner were utilized for this study.

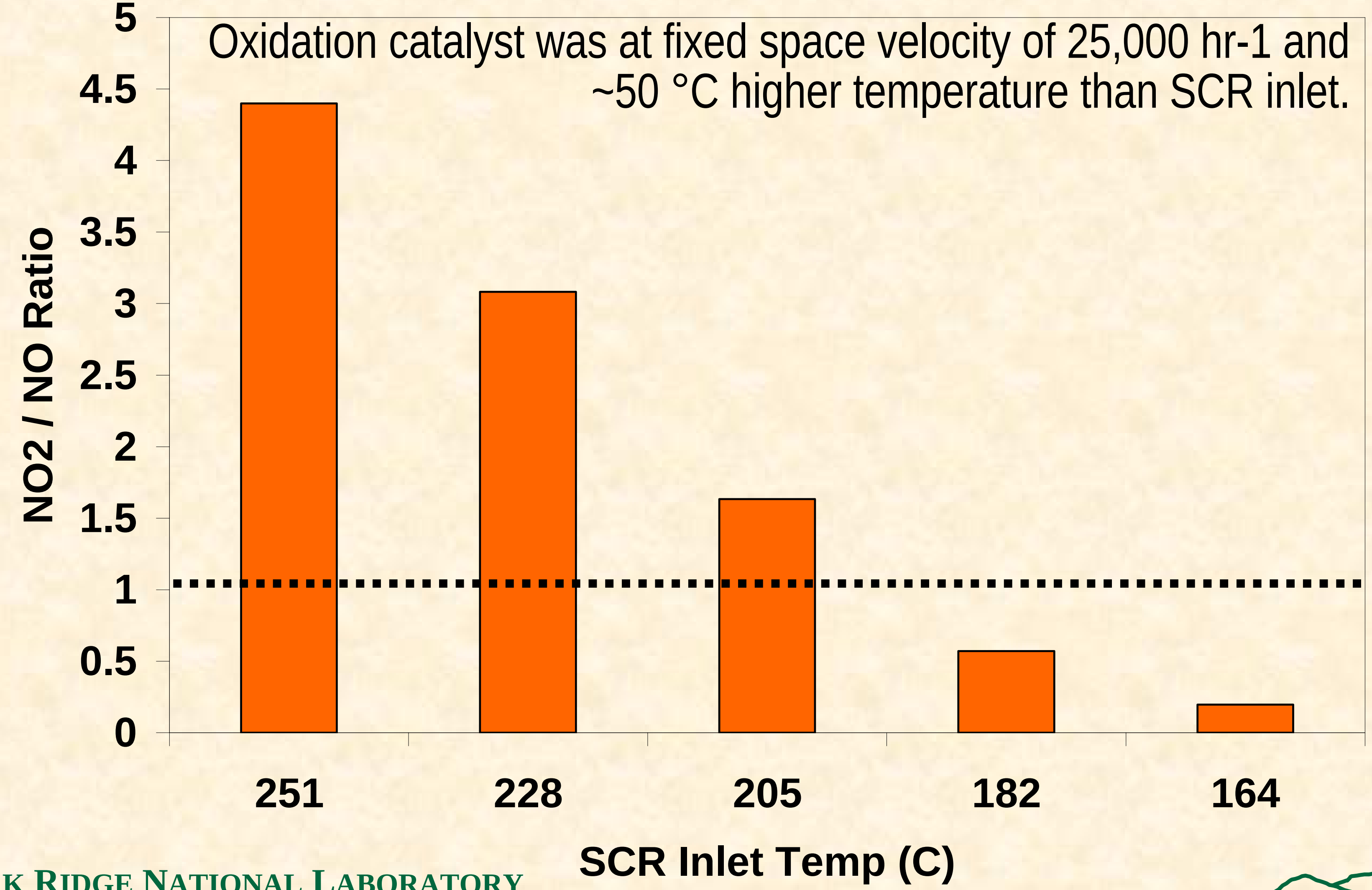
- **Pre-Oxidation Catalyst**
  - **144 mm diameter x 152 mm long (5.66” x 6.00”) cylindrical monolith.**



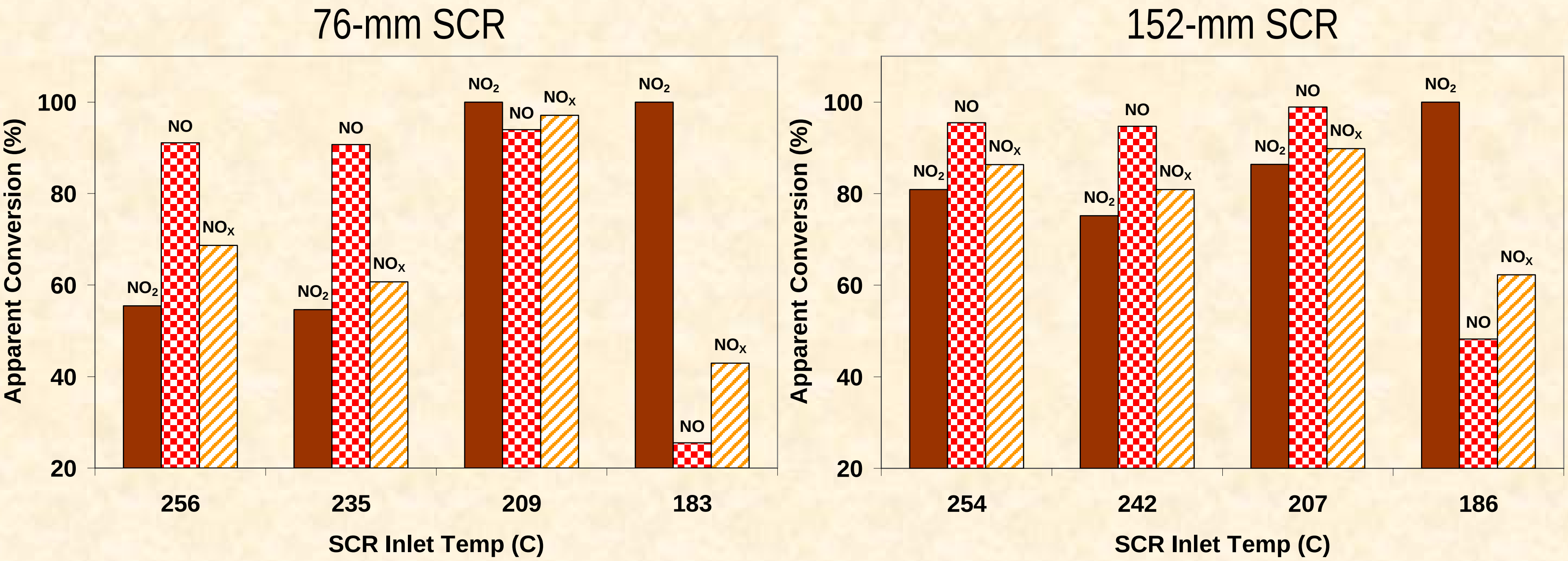
- **SCR Catalysts**
  - **144 mm diameter x 152 mm long (5.66” x 6.00”) cylindrical monolith.**
  - **144 mm diameter x 76 mm long (5.66” x 3.00”) cylindrical monolith.**
  - **Non-vanadium zeolite formulation.**
- **Canned for modular installation and measurement access to the rear of the monolith.**

- **Catalysts were de-greened in exhaust for several hours prior to use, but should not be considered aged significantly.**

SCR-inlet NO_2/NO ratios showed an over-oxidized condition at temperatures over 200 °C.



Apparent NO_X conversions were high given the relatively small size of the SCRs.

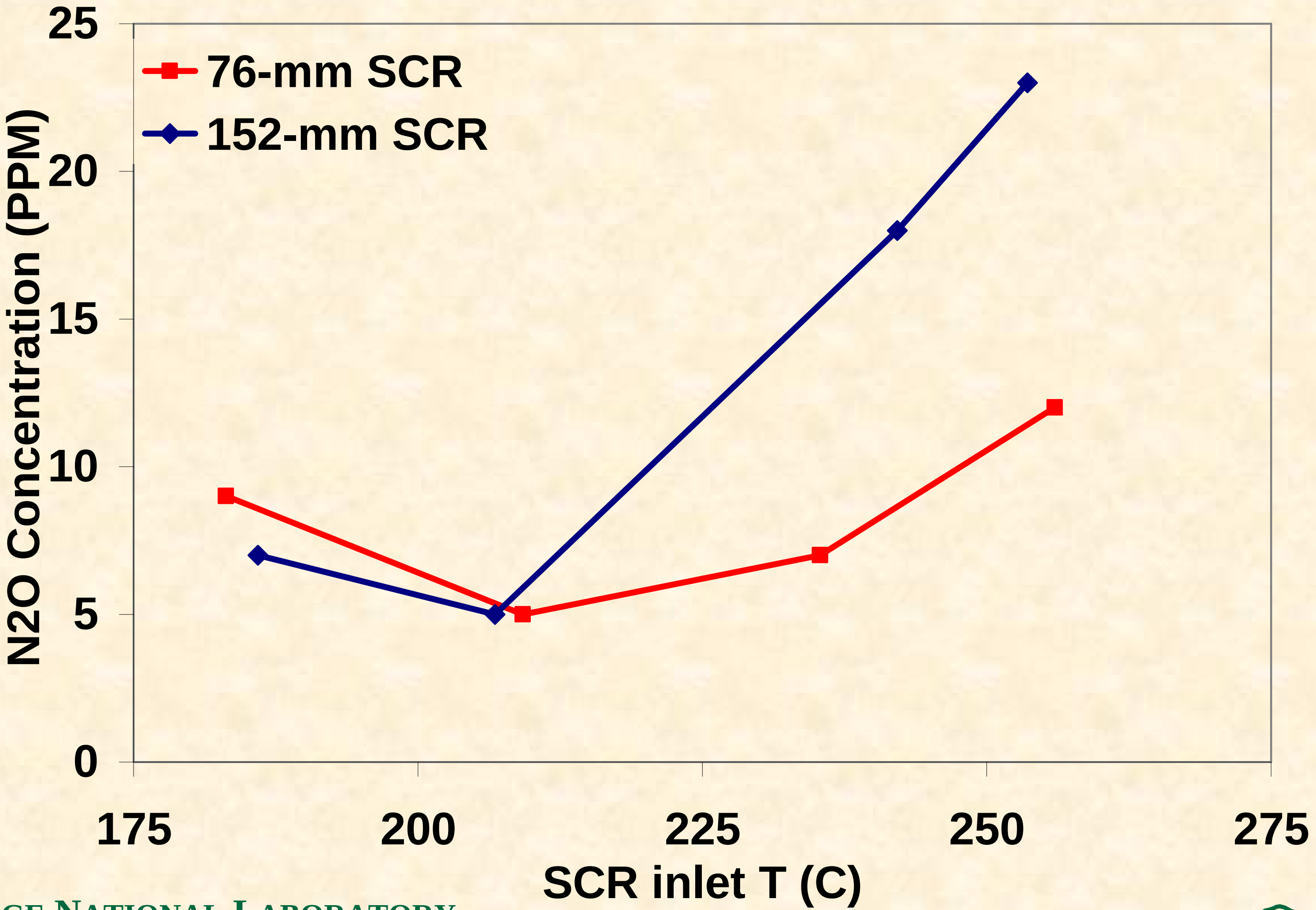


- Highest conversion was for the species of lower concentration. (Dominated by fast reaction.)*
- Highest overall conversion occurred when NO_2 / NO ~1, despite low temperature.
- Longer SCR shows improved conversion of the species of lower concentration.
- * Below 200 °C NO_2 reduction is favored for both SCRs. This is caused by ammonium nitrate formation.

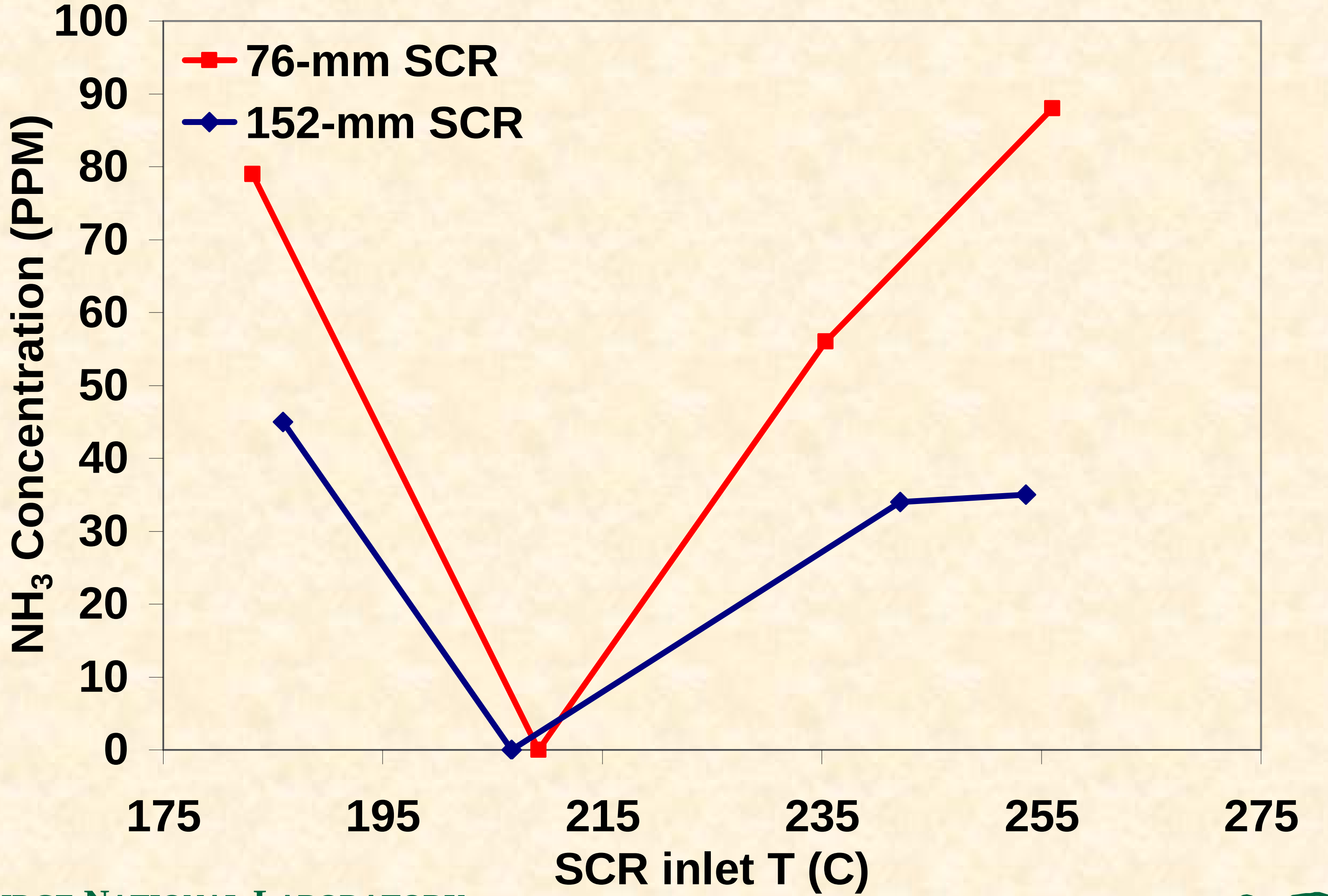
Urea and urea decomposition products were difficult to find in the exhaust

- **FTIR measurements of NH_3 required reducing filter temperature to 60 °C to avoid false-positives upstream of SCRs.**
- **NH_3 measurements upstream of the SCRs showed very low urea decomposition in the exhaust stream.**
- **Quantification of urea decomposition products downstream of the SCRs was limited to NH_3.**
  - **Several impinger-collection and analysis methods were explored.**
  - **Difficulty is isolating species and preventing subsequent reactions.**
  - **No reliable detections of urea or isocyanic acid.**

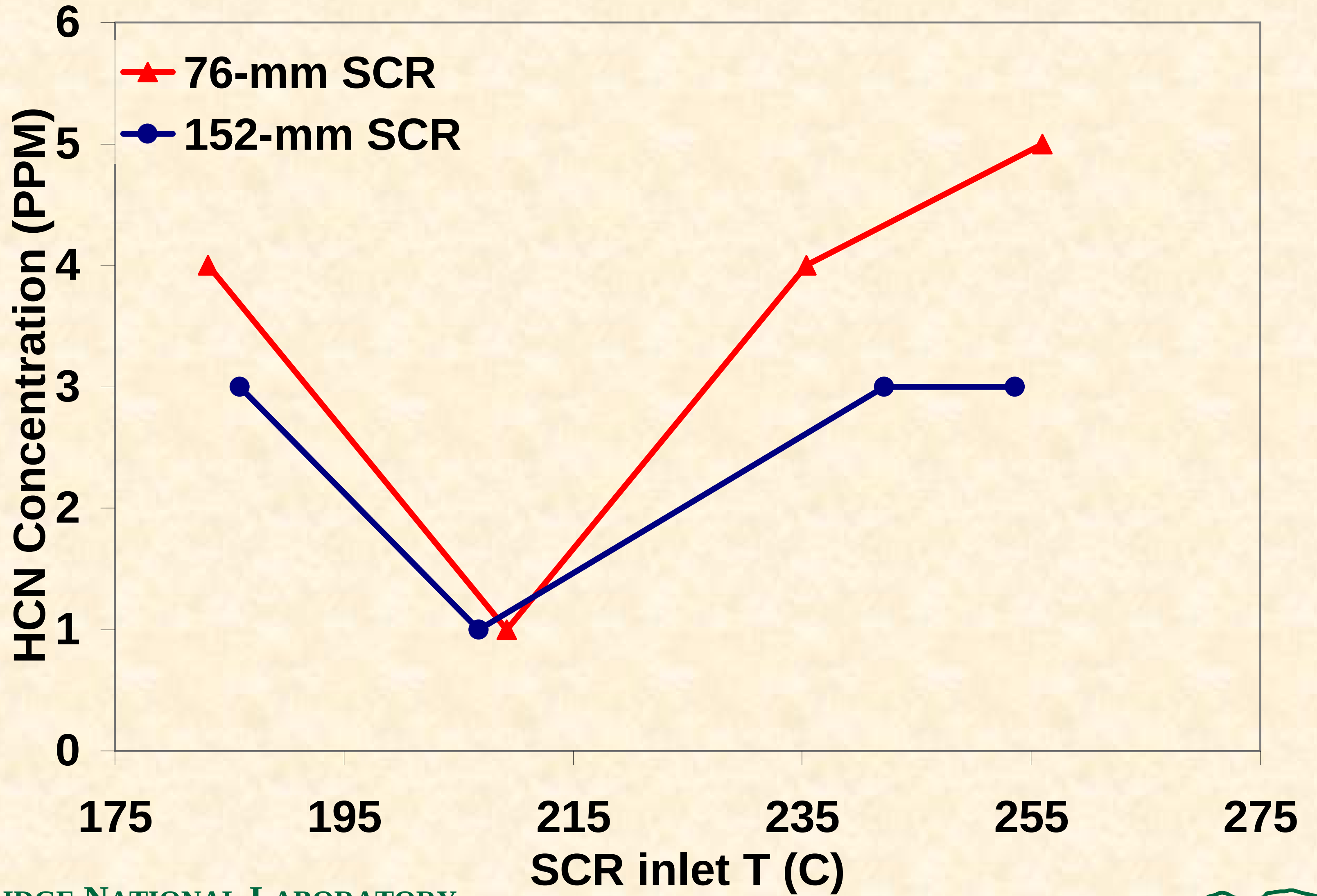
Steady-state temperature sweeps showed that the 152-mm SCR produced more N_2O above 200 °C.



NH_3 emissions were observed since NO_X reduction was not complete for either SCR.



HCN emissions were observed to be proportional to NH_3 emissions.



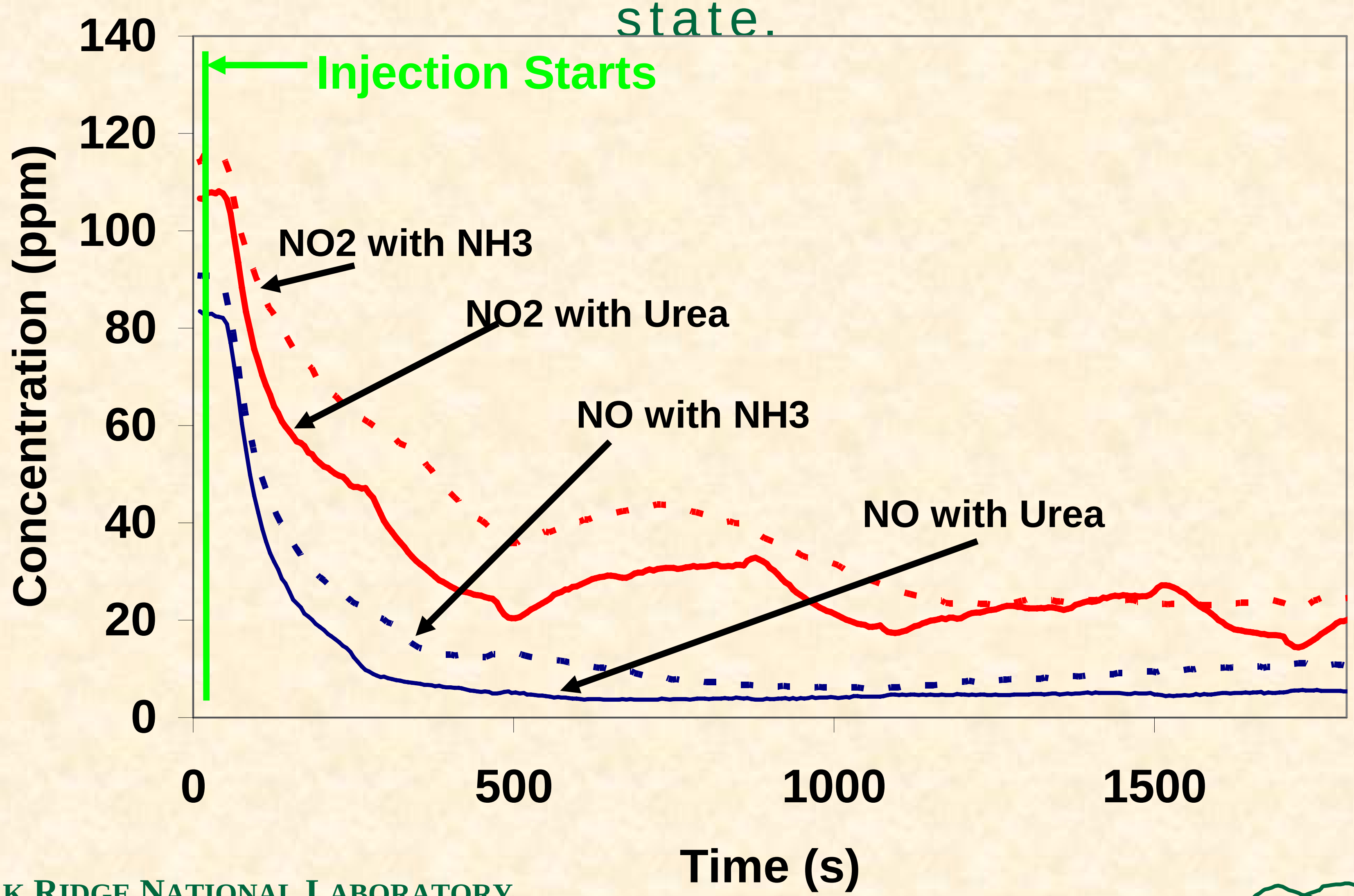
Transient Studies with Clean Catalyst

205 C

FTIR started when urea injection starts

Experiments with urea and NH_3

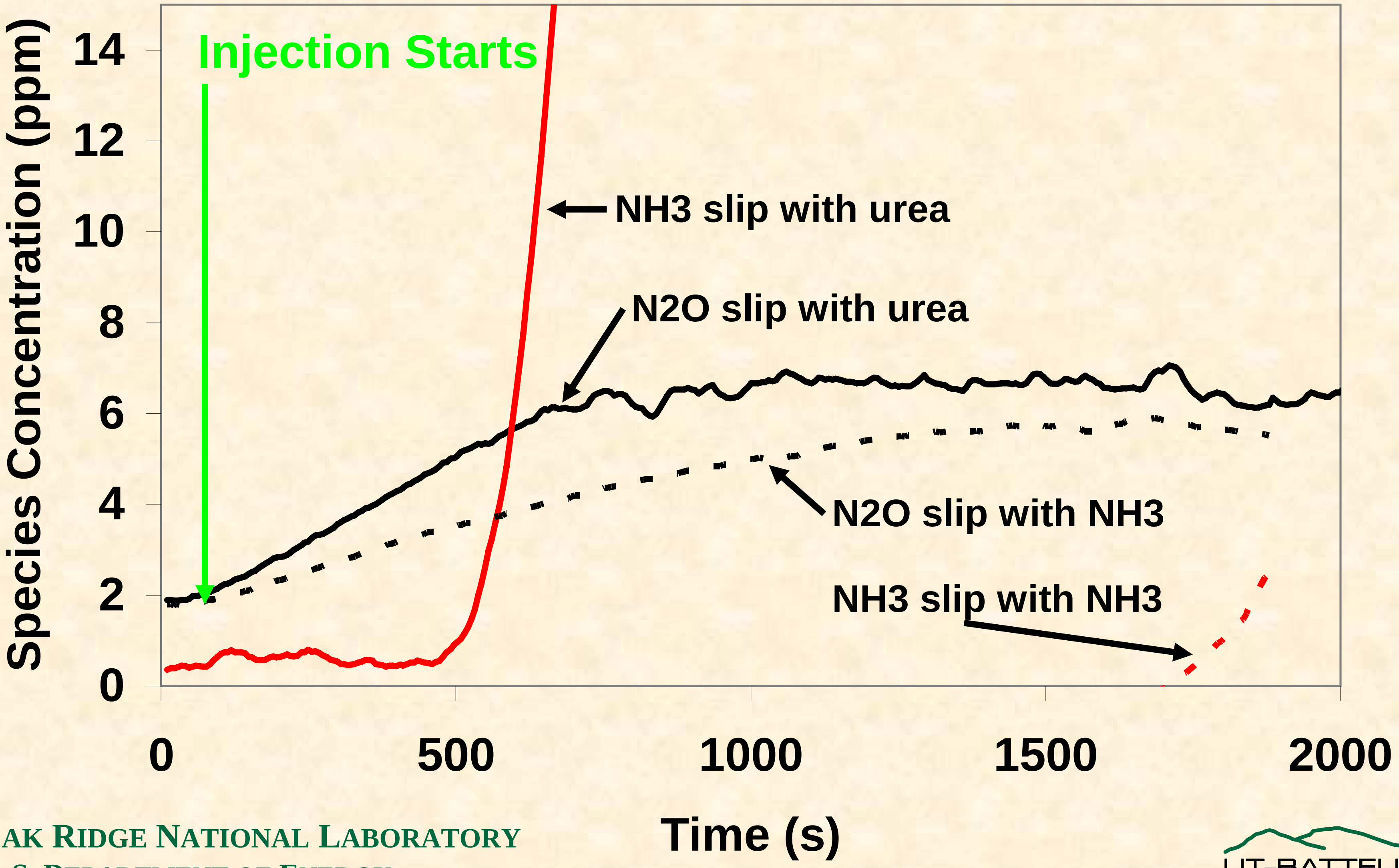
Transient experiments with both urea and NH_3 injection show relatively long period to reach steady-state.



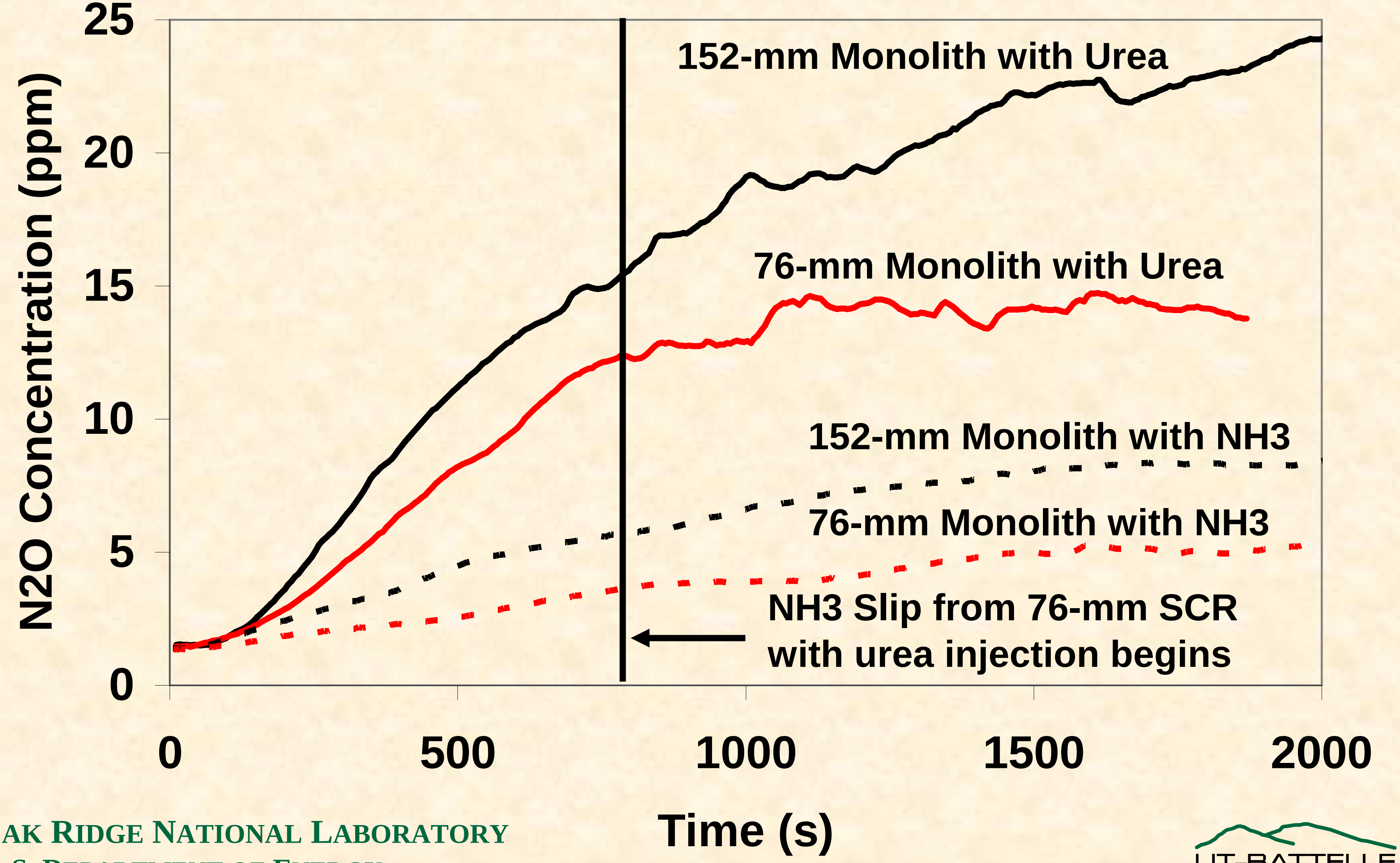
OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT-BATTELLE

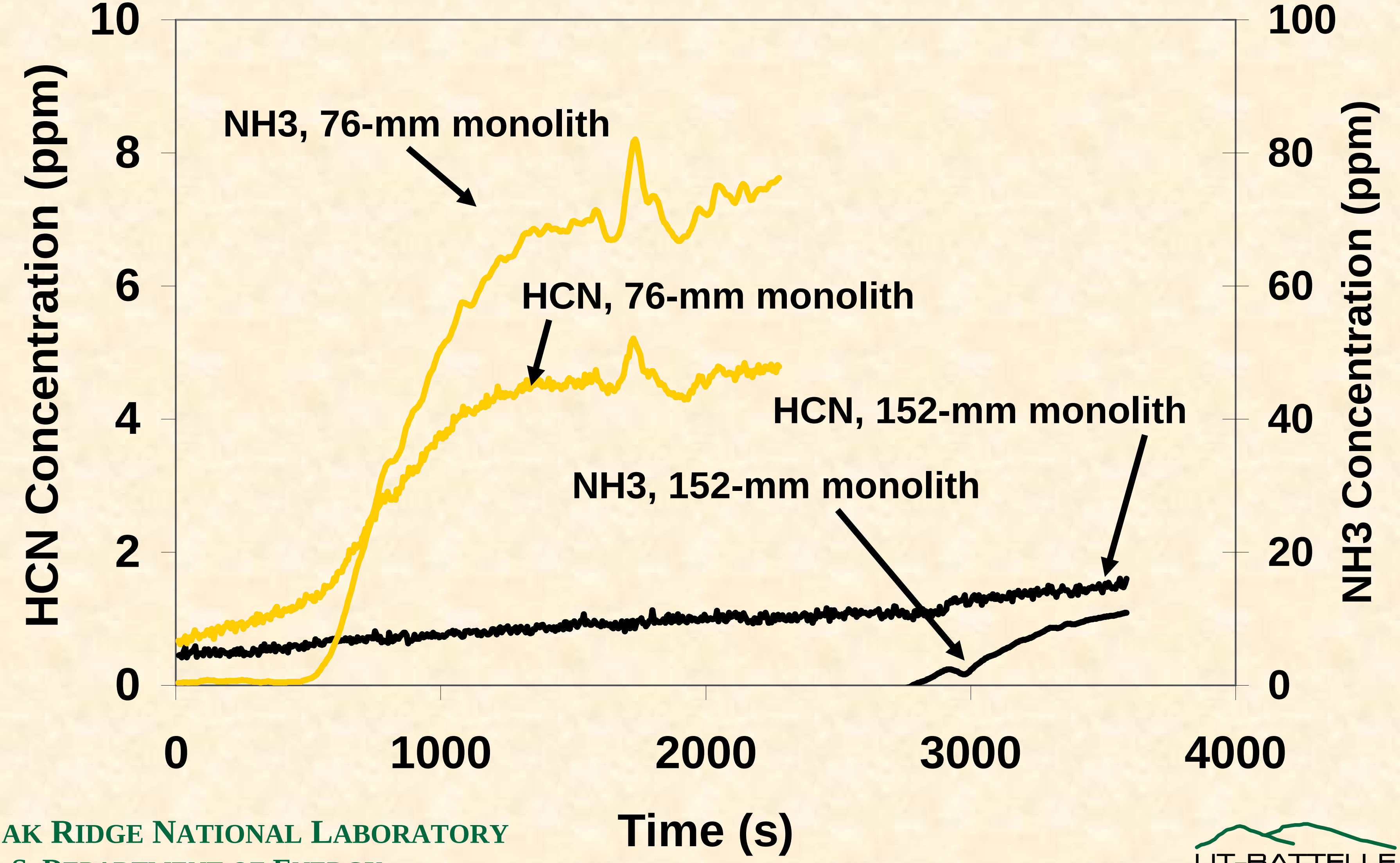
NH_3 slip was observed to occur sooner when urea was injected than when NH_3 was injected.



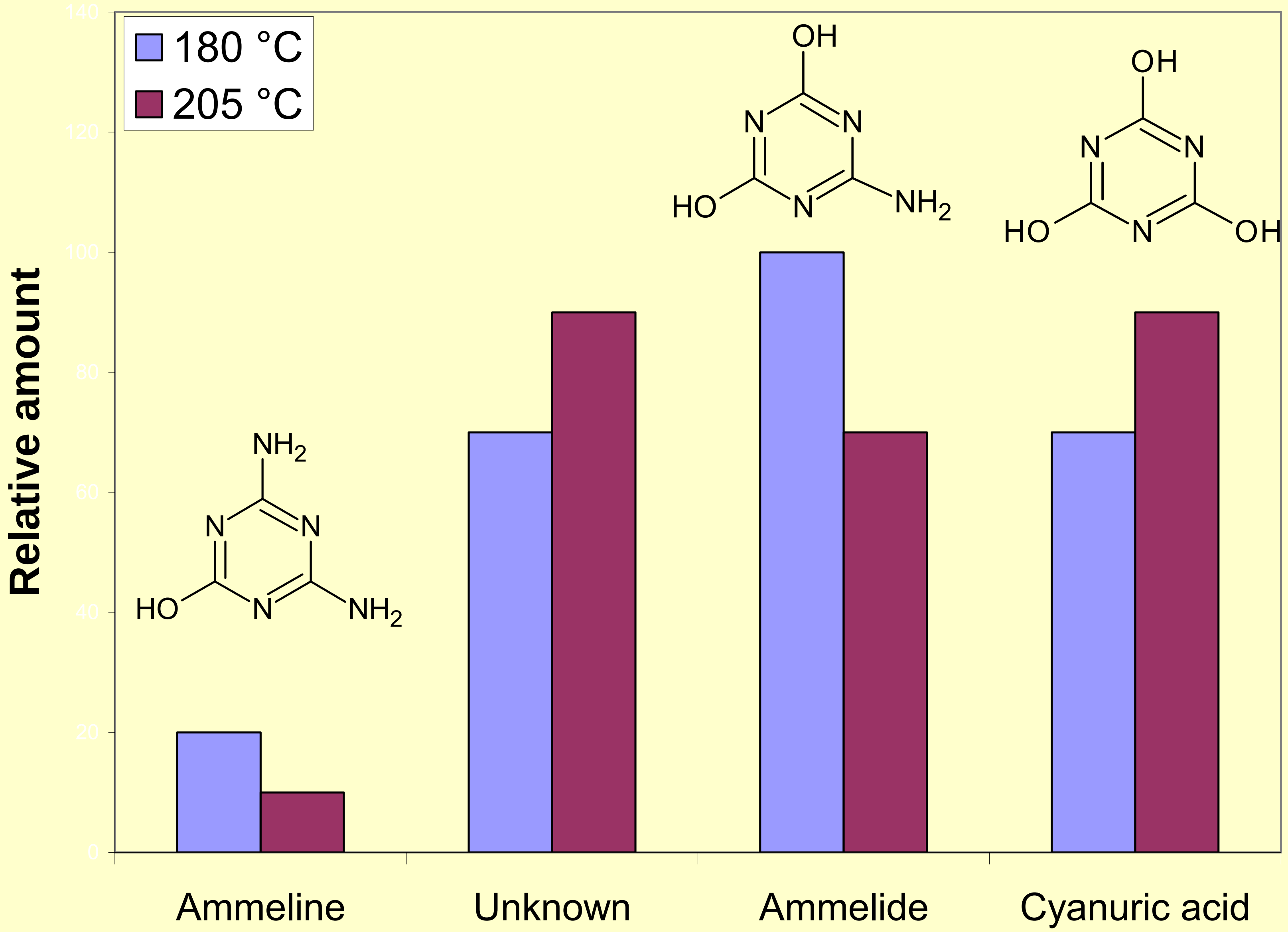
N_2O emissions were higher with urea injection than with NH_3 injection.



HCN emissions were proportional to and simultaneous with NH_3 emissions.



Urea decomposition products act as storage on the catalyst monolith



he results of the study support several conclusions.

- Urea decomposition on the catalyst surface causes:
  - **Lower NH_3 storage for first 76-mm compared with the next 76-mm of monolith.**
  - **Higher selectivity to N_2O in overoxidized conditions for both the first and second 76-mm of monolith.**
  - **Higher emissions of HCN during NH3-slip conditions.**

- Very small volume SCRs can have very high NO_X conversion if some issues could be overcome:
  - **Urea decomposition upstream of SCR.**
  - **NO_2 / NO ratio control close to optimum value.**
  - **Improved models / controls for urea dosing rate.**

Conclusions, continued

- Implications of catalyst rinsing experiment very important
  - **very little slip of decompostion products detected**
  - **Shift at higher temperature to cyanuric interesting**
    - **cyanuric is an SCR reagent!**
  - **Unknown likely an amino compound**
  - **the wrong amount of reduction can lead to refractory complexes – like melamine:cyanurate**
  - **modeling these reactions will be important to reduce size and prolong life.**