

Urea Decomposition and SCR Performance at Low Temperature

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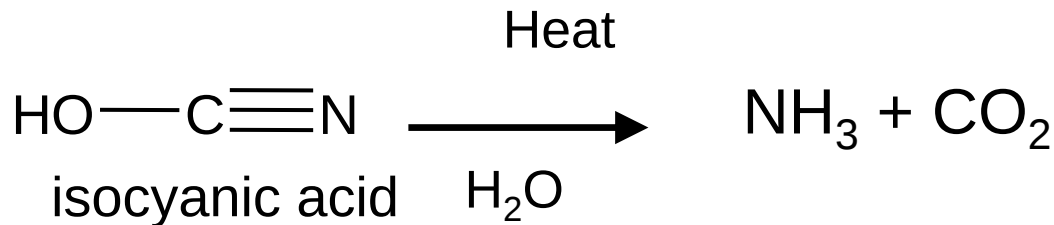
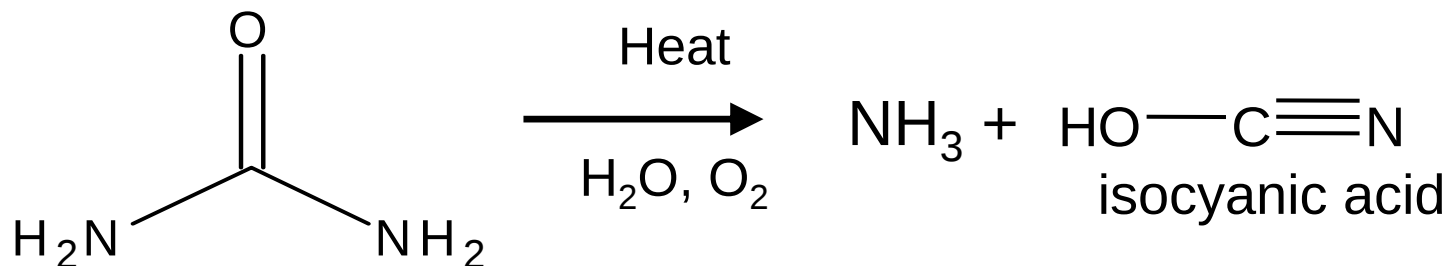
Sponsors: DOE-OFCVT, Steve Goguen and Kevin Stork

Why study urea decomposition?

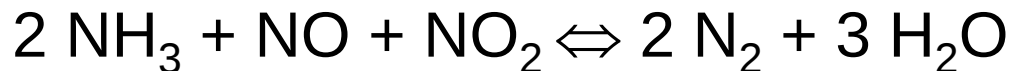
- Under light-duty conditions ($< 250\text{ }^{\circ}\text{C}$), there is negligible urea decomposition in the gas phase. Current models assume NH_3 as input to catalyst.
- It appears that urea decomposition kinetics on catalyst surfaces has to be understood. This will affect the length of the catalyst that is used for urea decomposition.

Urea/SCR Chemistry

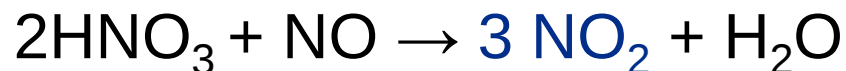
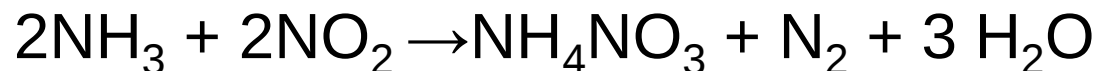
Ideally, injected urea decomposes to NH_3



then reacts with NO_x to form N_2 .



Unusual things can happen, such as ammonium nitrate formation and decomposition at $T < 200\text{ }^{\circ}\text{C}$.

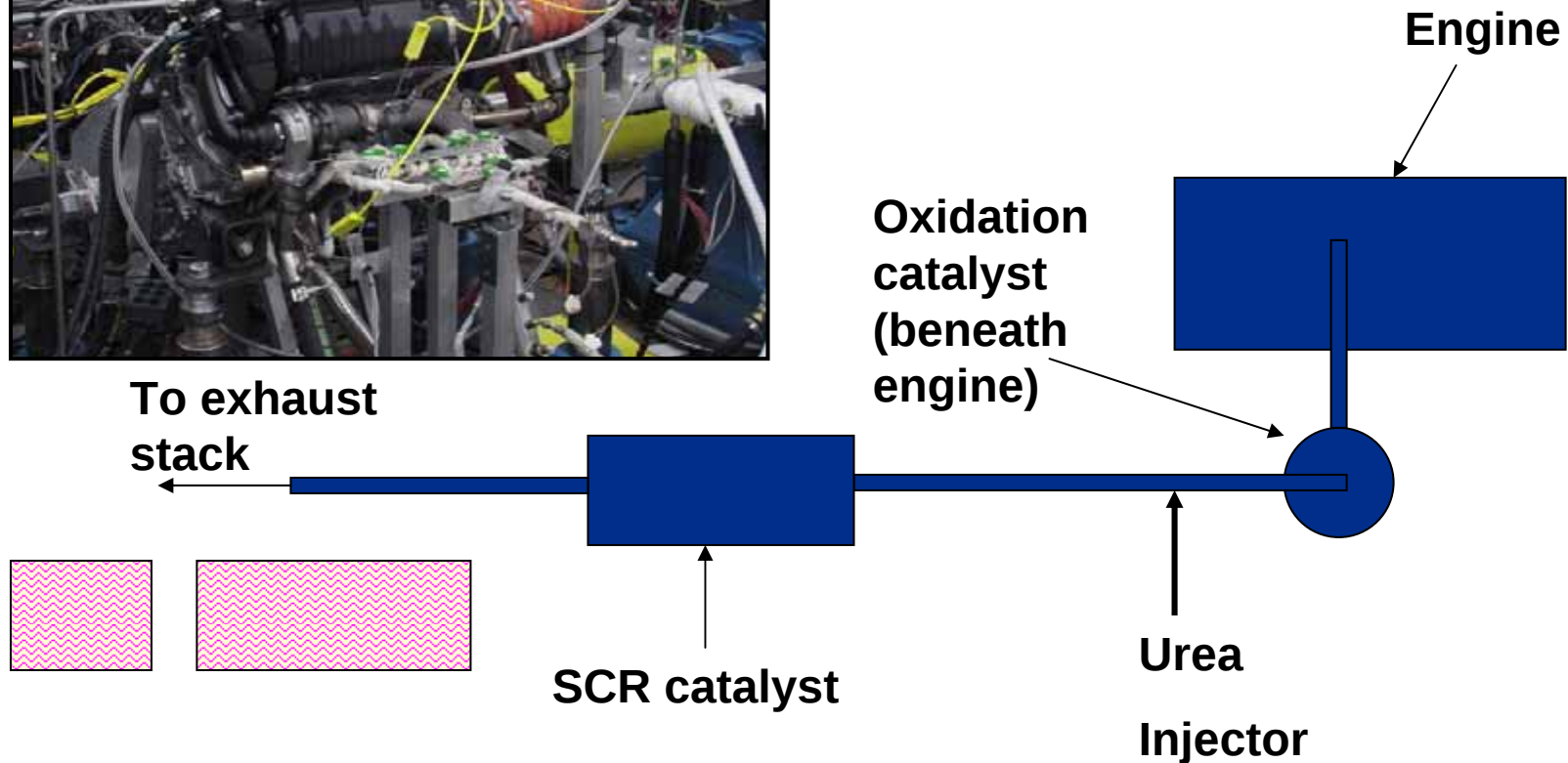
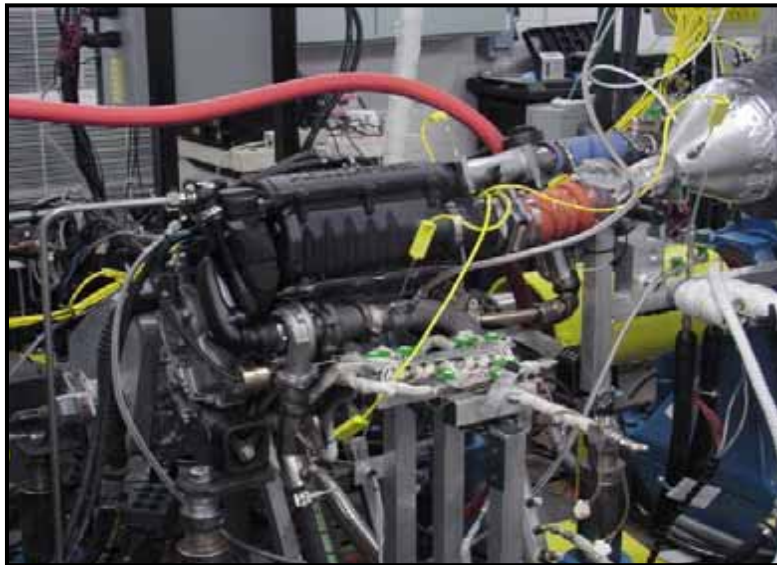


M. Koebel *et al.* in *Ind.Eng.Chem.Res.*:
39,p. 4120; **40**, p. 52; **41**, p.4008; **42**, p.2093
Also in *Catal.Today*, **73**, p.239

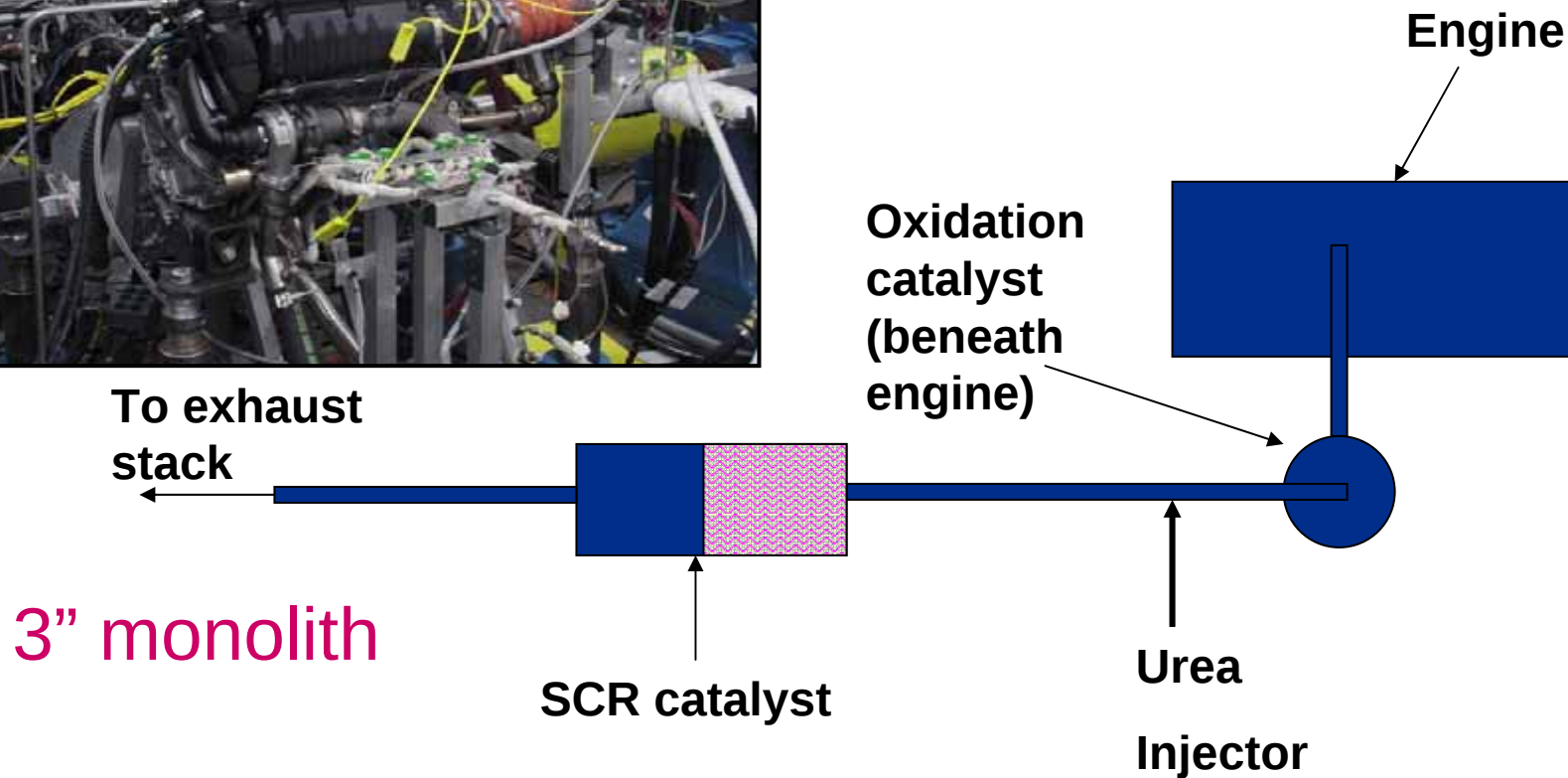
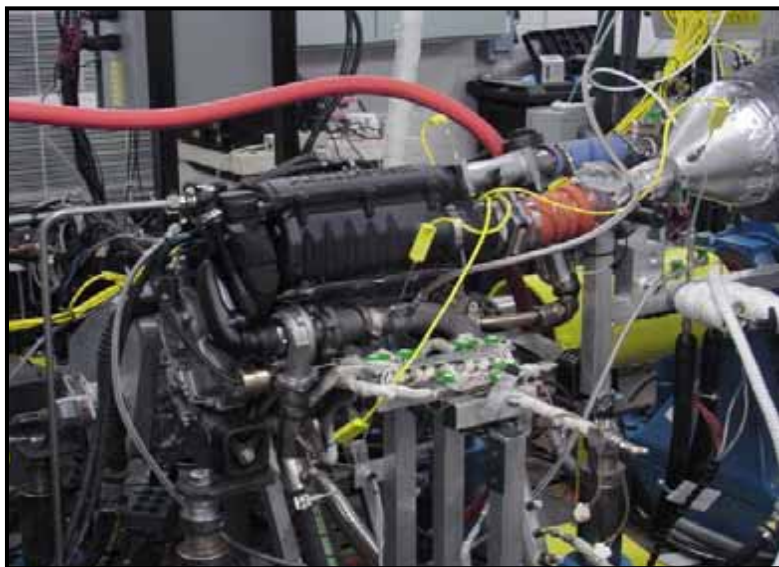
Experimental Approach

- Use engine controls to:
 - Vary temperature
 - Keep constant: NO_x and exhaust flow.
- Investigate urea decomposition (*if any*) upstream of SCR catalyst.
- Analyze exhaust products exiting undersized monoliths to elucidate urea decomposition
 - 3" and 6" monoliths = space velocities of 25K and 50K
 - const. urea residence time in the exhaust stream. (~0.1 sec)
 - From clean condition, begin injecting urea:
Wait 20 minutes (3" monolith) or,
40 minutes (6" monolith),
Then collect data and samples.

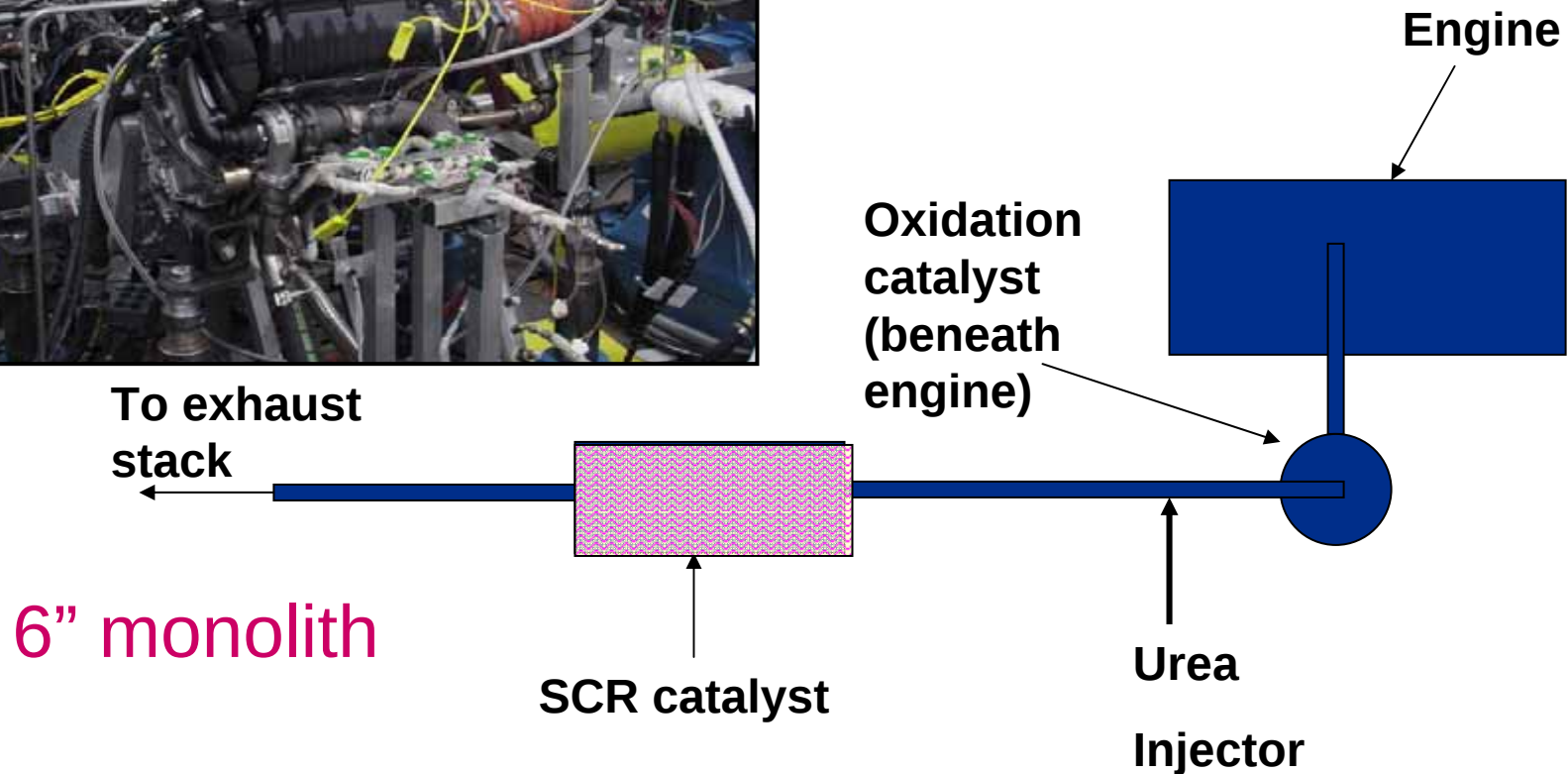
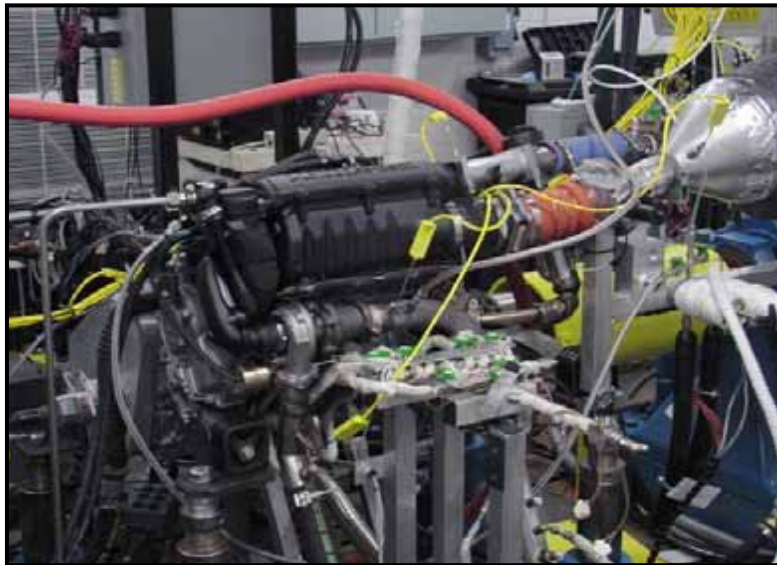
Experiments conducted at NTRC cell 4 using Mercedes engine and BP15 fuel.



Experiments conducted at NTRC using Mercedes engine and BP15 fuel.



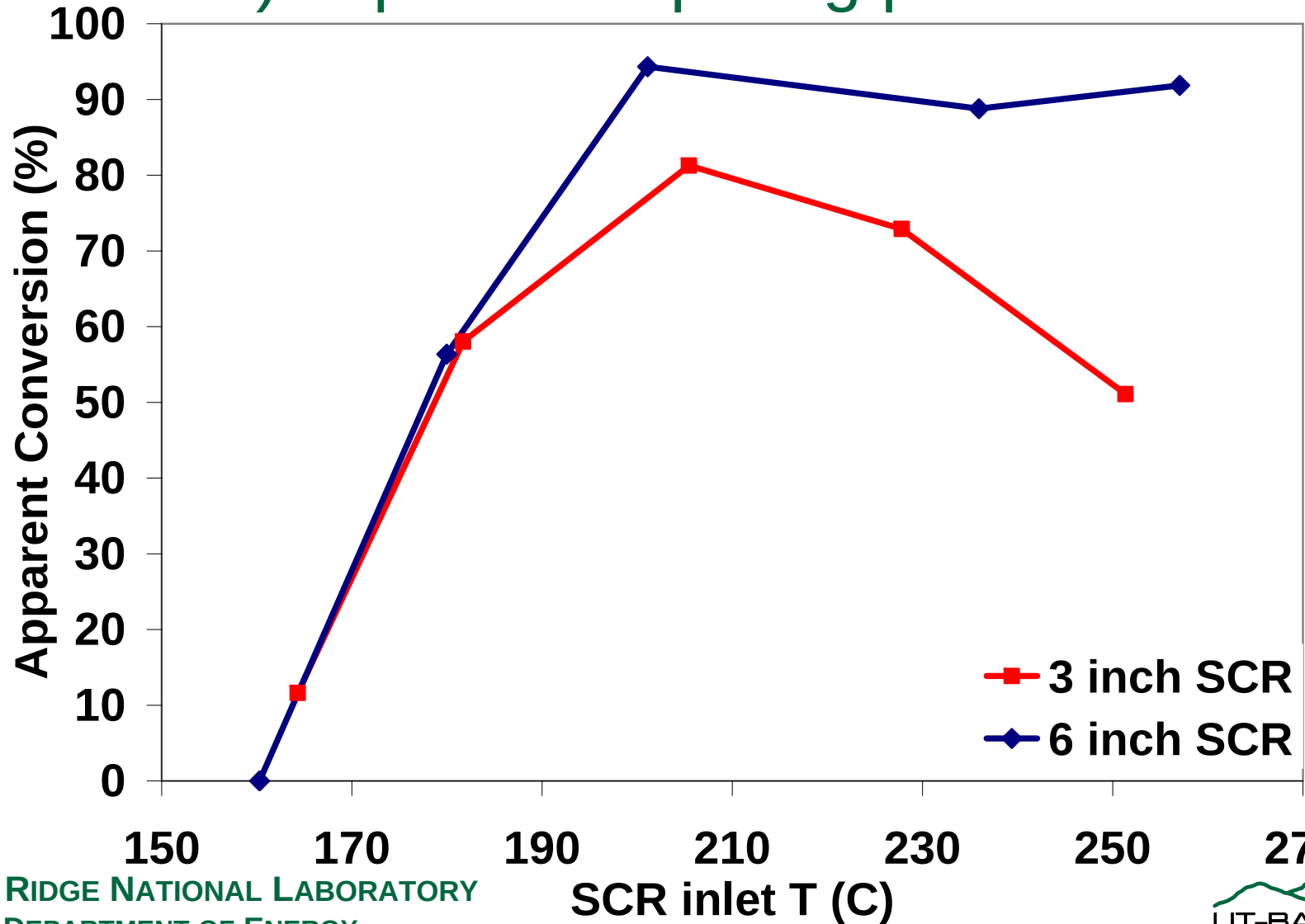
Experiments conducted at NTRC cell 4 using Mercedes engine and BP15 fuel.



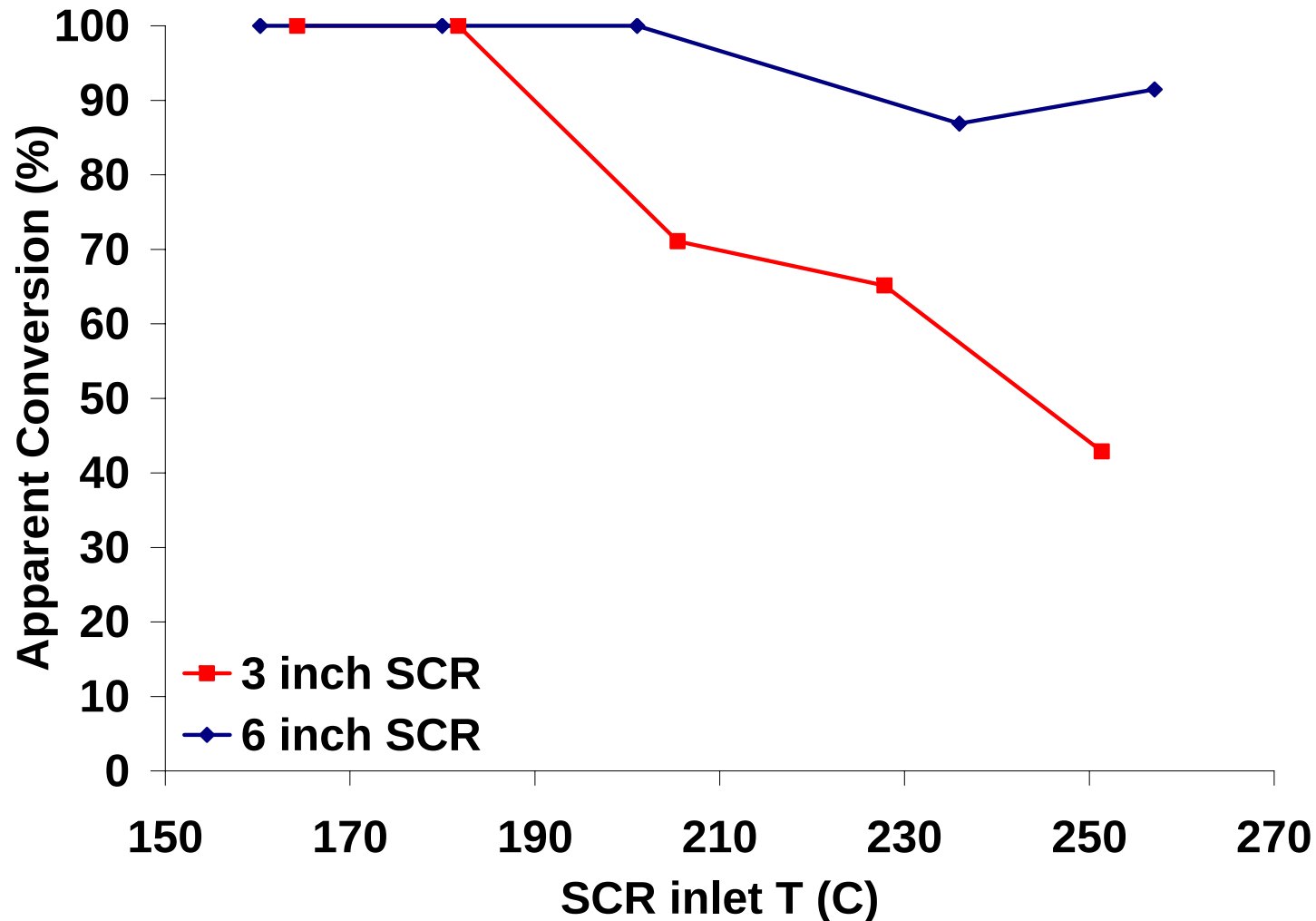
Measurement of actual NH_3 in the presence of urea and isocyanic acid is difficult.

- Problematic if making measurements of urea decomposition products.
- Short experiments showed that urea decomposed (to ammonia) on instrument filter at T as low as 80 °C.
- Filters are required for sampling PM-laden exhaust gas.
- Instrument filter T is typically > 100 °C to prevent condensation and loss of water soluble NH_3
- Using 60 °C filter allows measurement of NH_3 without decomposition of precursors, but precludes same stream from being used for HC measurements.

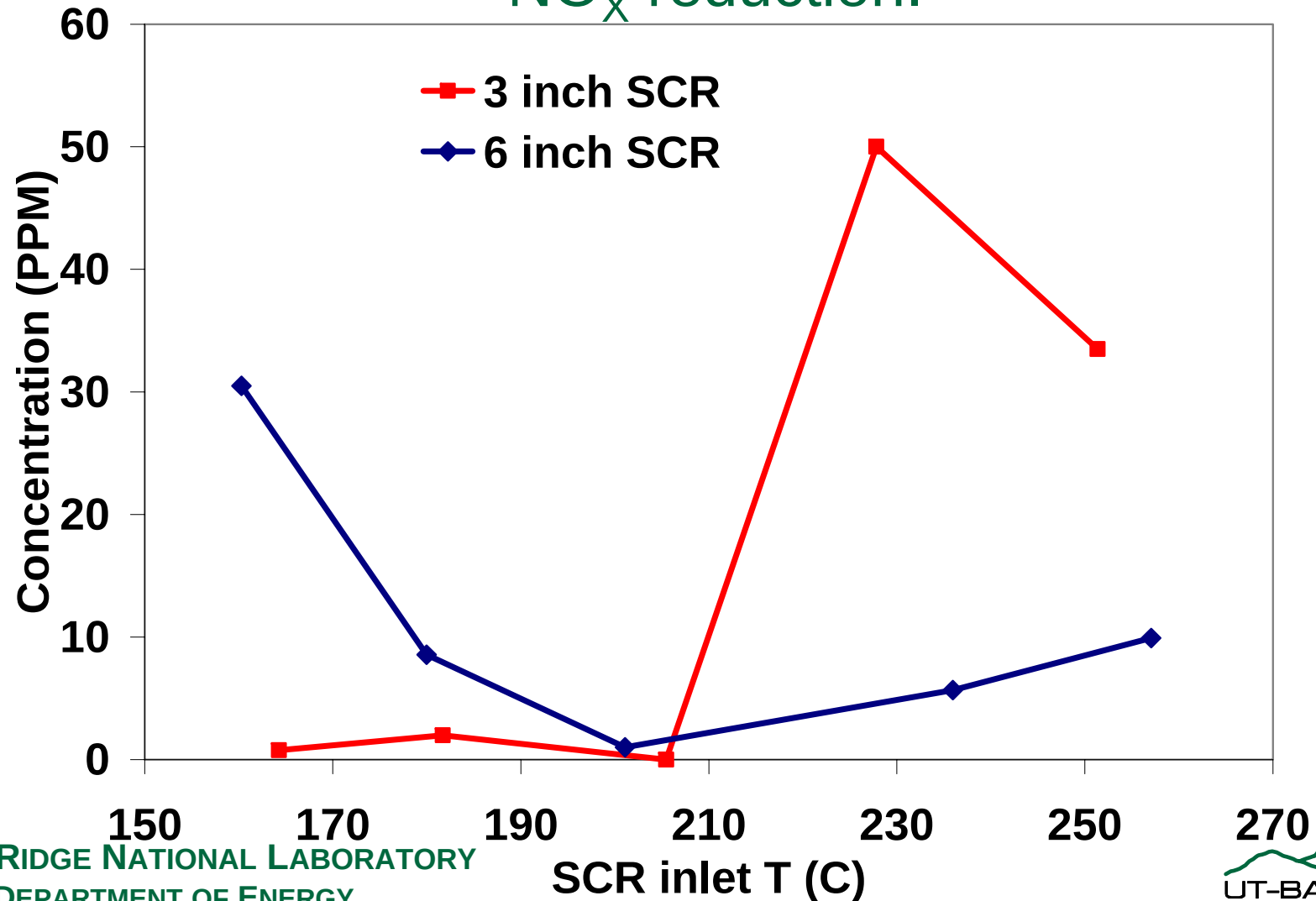
Higher T decrease in NOX conversion (for 3" brick) implies competing processes....



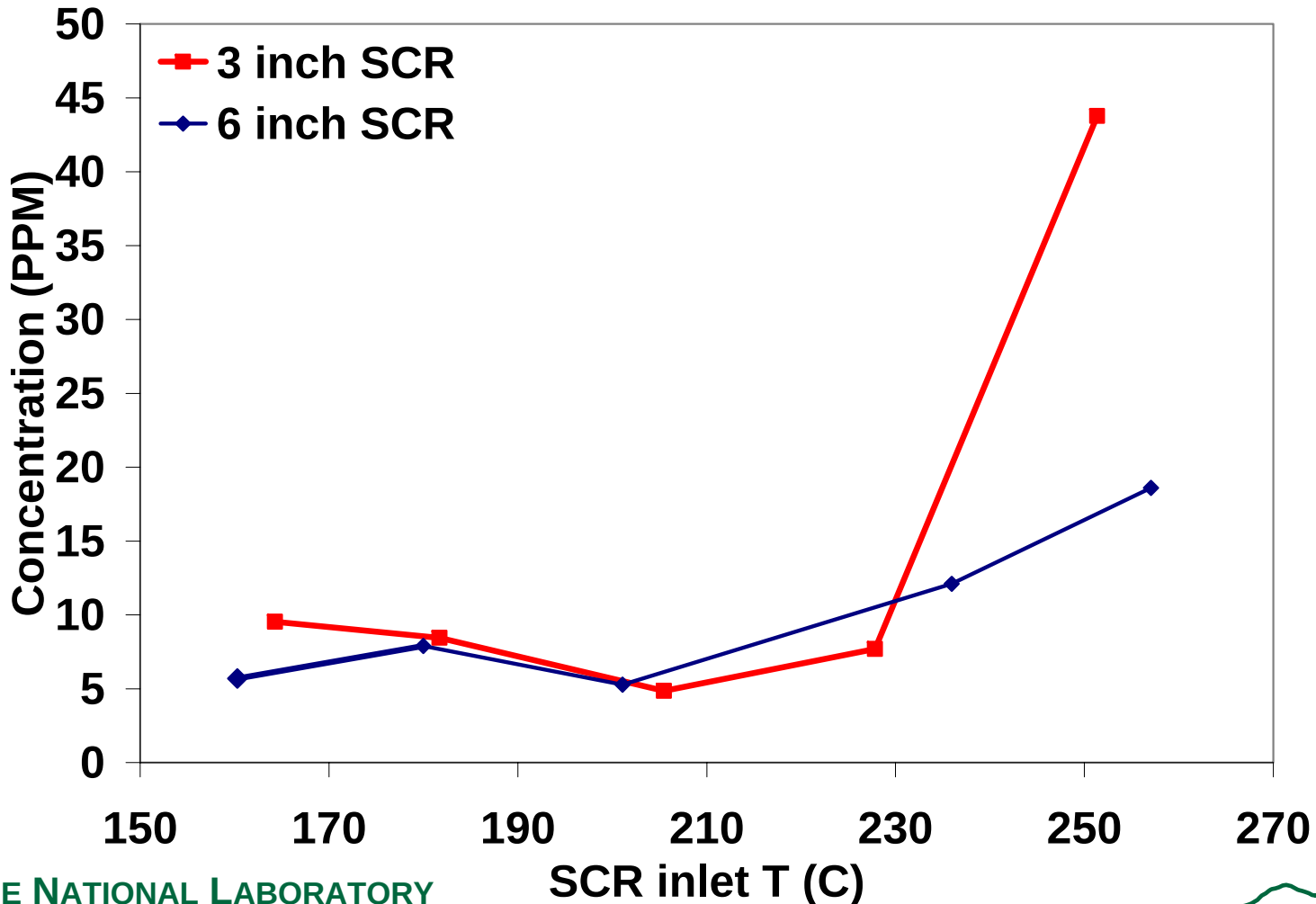
The lower conversion of NO_x is due at high temperature is due to lower NO_2 conversion.



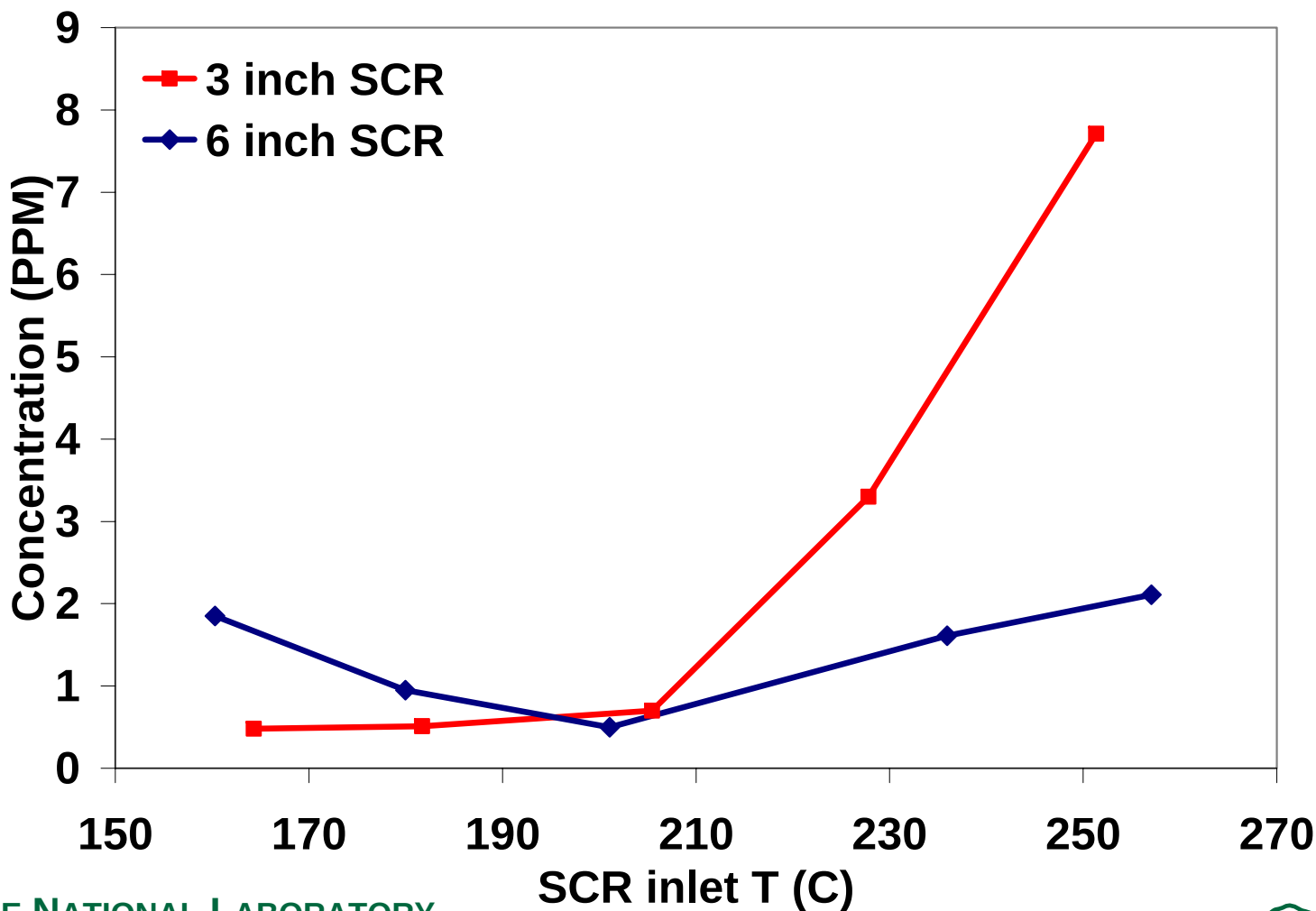
Undersized SCRs slipped some NH_3 at all conditions, indicating ample reductant available for NO_x reduction.



N₂O slip indicates incomplete reduction in the shorter catalyst



HCN was also formed as an intermediate at low concentrations at the temperatures studied.

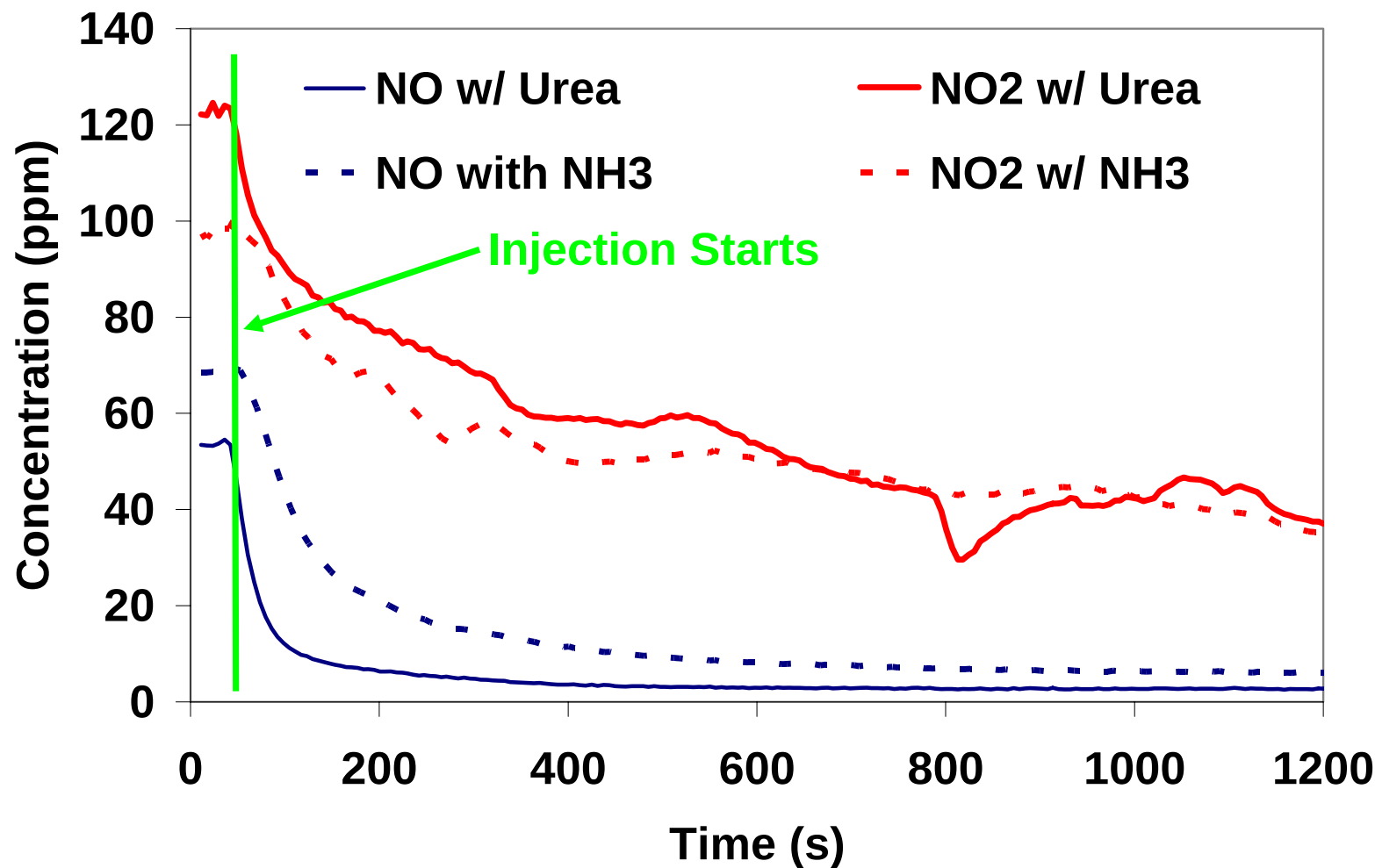


Steady-state data suggest urea decomposition competes with NOX reduction processes.

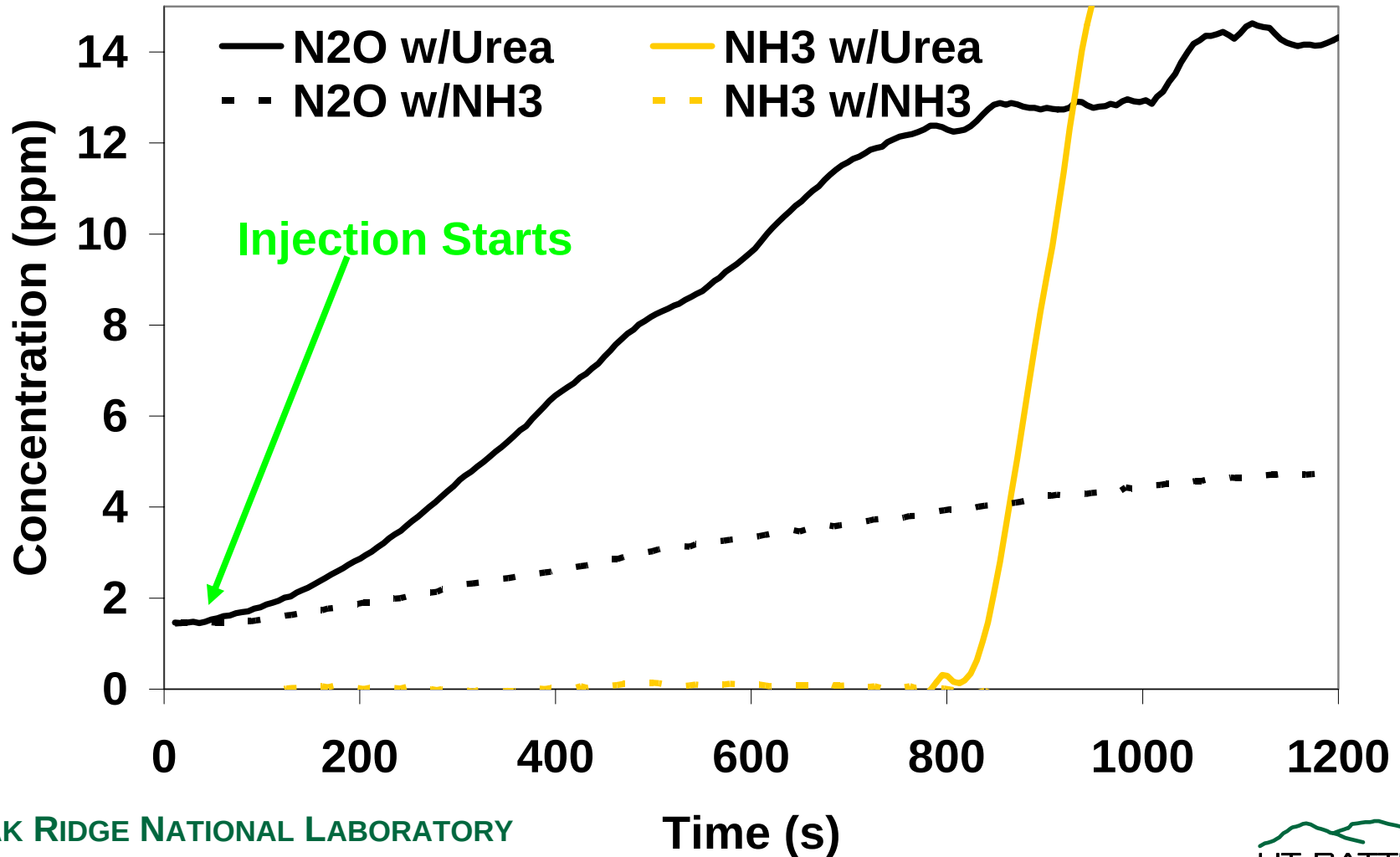
- NO₂ not converted as efficiently at high temperatures with the 3" SCR.
- High concentration of intermediate N₂O in the 3" SCR could account for most NOX disappearance.
- Concentrations of intermediates drop with longer catalyst.
- NH₃ slip indicates available reductant.
- Temperature gradients associated with urea decomposition and NOX reduction were too small to measure.

Results from onset of injection

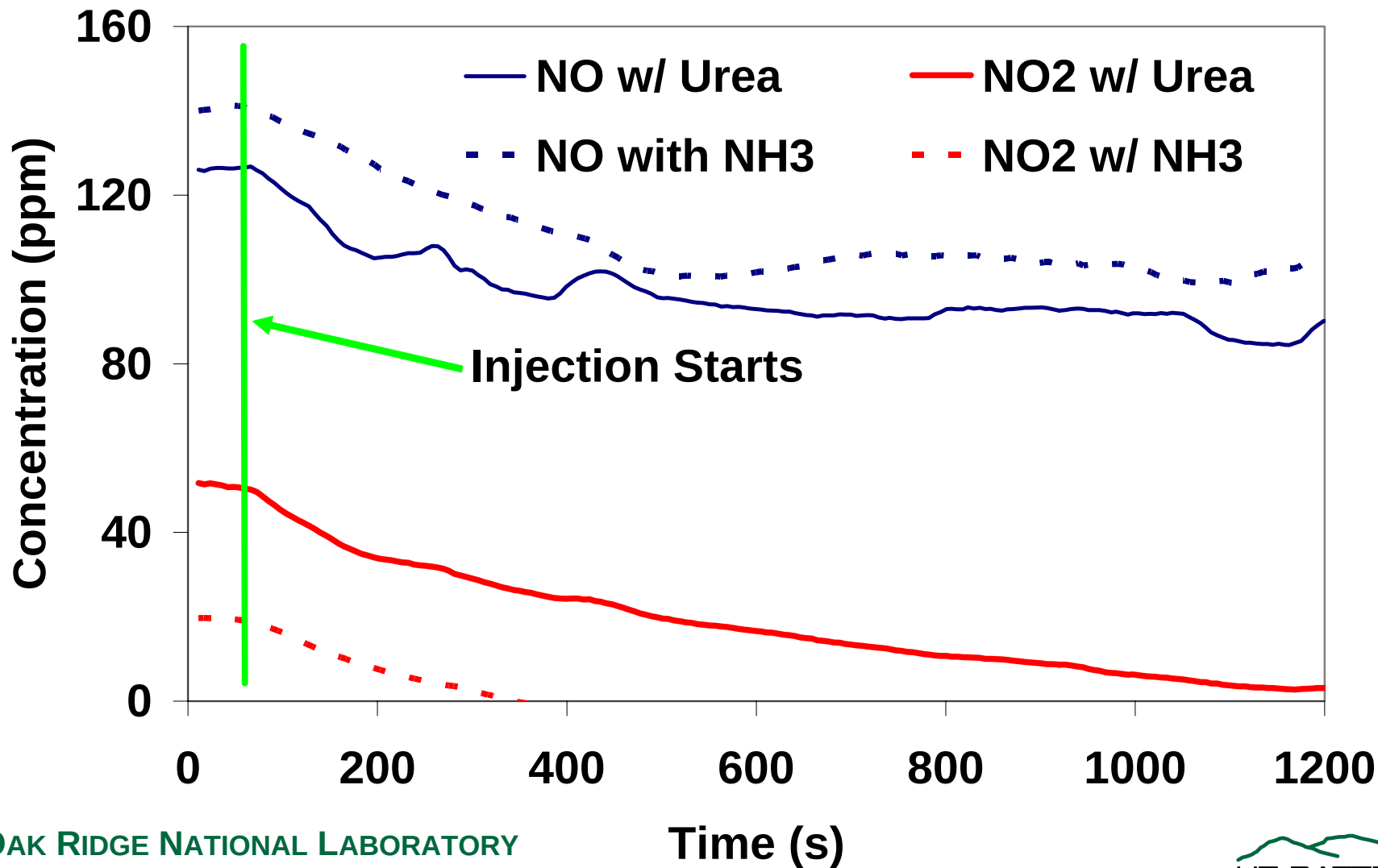
NO, NO₂ disappearance at 250 °C using urea and ammonia as reductants suggests similarity of reduction processes.



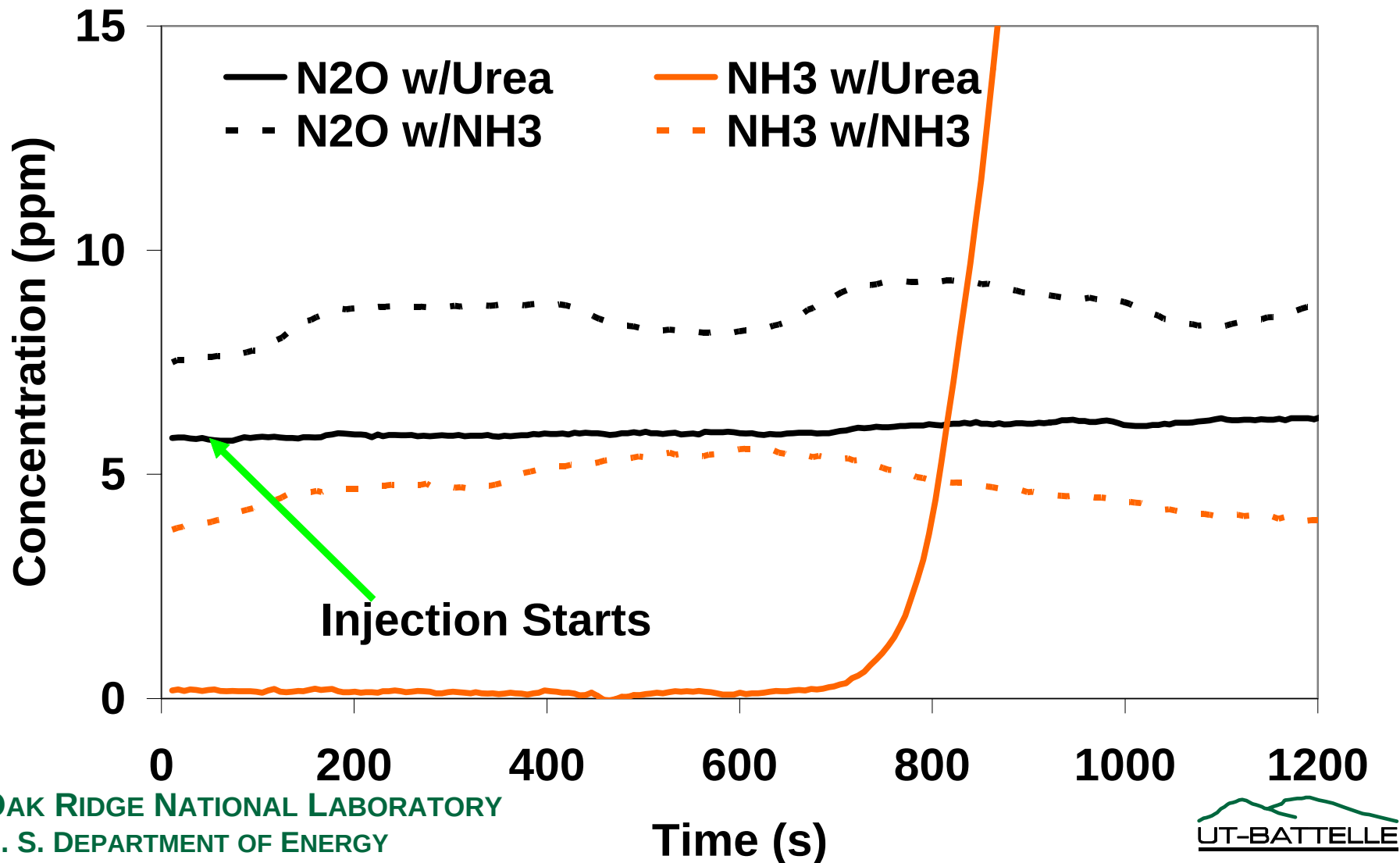
Onset of N₂O slip and NH₃ slip at 250 °C is due to competition of urea decomposition process



NO and NO₂ disappearance similar at 180 °C when using urea and ammonia as reductants.



Large NH_3 slip again occurs much sooner with urea injection than with ammonia injection.



Urea decomposition hampers NOX reduction in at least the first 3" of SCR catalyst.

- Steady state data showed presence of NH₃, intermediates downstream of 3" and 6" SCR.
- Transient data showed that NO, NO₂ disappearance were similar using both NH₃ and urea as reductants.
- Ammonia injection data showed intermediates (HCN, N₂O) at ~1/3 of concentration vs. urea
- Ammonia injection data showed longer NH₃ storage times before slip (~2X) than when urea was used.

Further investigation of the dynamics of urea decomposition is planned.

- Confirmatory, direct measurements of urea, isocyanic acid downstream of SCR are forthcoming.
- Study 3"+6" SCRs together (as a 9") to determine whether same trends are observed in rear 3" of 6" monolith.
- Comparisons of urea and ammonia injection at other conditions to confirm