Laboratory and Vehicle Demonstration of a "2nd-Generation" LNT+in-situ SCR Diesel NOx Emission Control Concept

L. Xu, M.A. Dearth, W.C. Ruona, and R.W. McCabe,

Ford Motor Company

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Contact: rmccabe@ford.com

2nd Generation LNT+ in-situ SCR

- *New system-level technology enabled by advanced LNT and urea-SCR type catalysts provided by Ford's catalyst suppliers.*

- Extends aged FTP NOx conversion efficiency to >93% vs 75-80% for LNT only system
- Opens door to sub-T2/B5 emissions for diesel applications
- Enables low-loaded LNT technology and improves cost-competitiveness with urea-SCR
- Potential common technology solution for Euro and U.S. LD diesel emissions
- Reduced fuel economy penalty compared to 1st Gen systems aimed at generating NH3

NH_3 in-situ mechanism

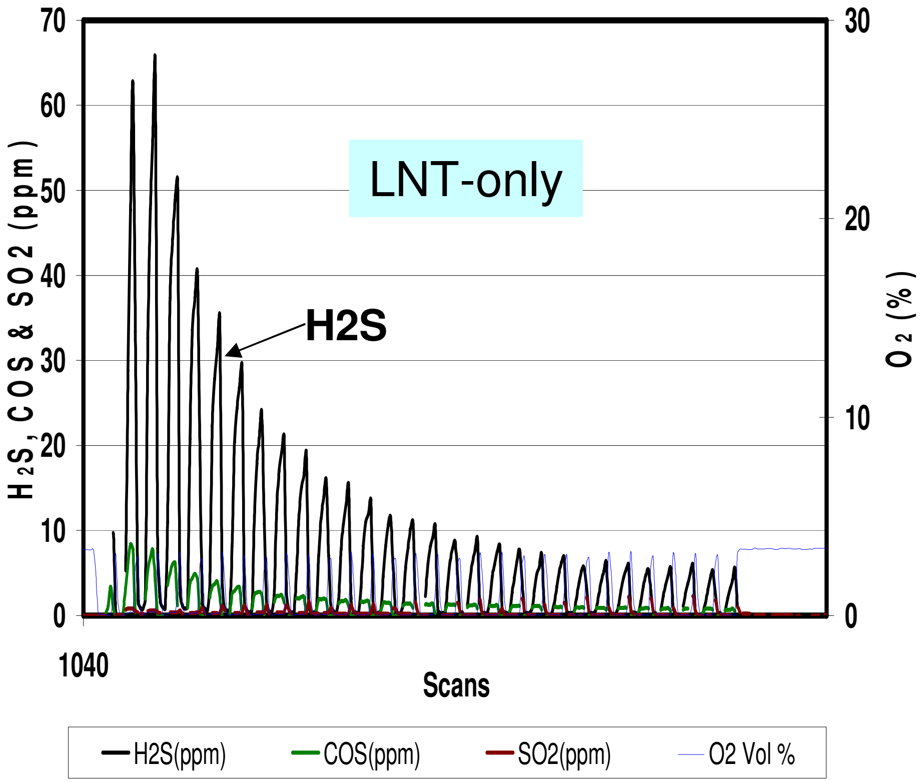
- "Classical" explanation:
  - LNT produces NH_3 during rich purges (similar to TWC under rich engine conditions)
  - NH_3 stores on downstream SCR catalyst
  - Stored NH_3 reacts with "breakthrough" NOx during lean operation
  - Similar to urea-SCR except that NH3 is generated "in-situ" or "passively" by the LNT
- NH_3 in-situ mechanism does not appear to fully explain 2nd-Gen LNT+SCR data

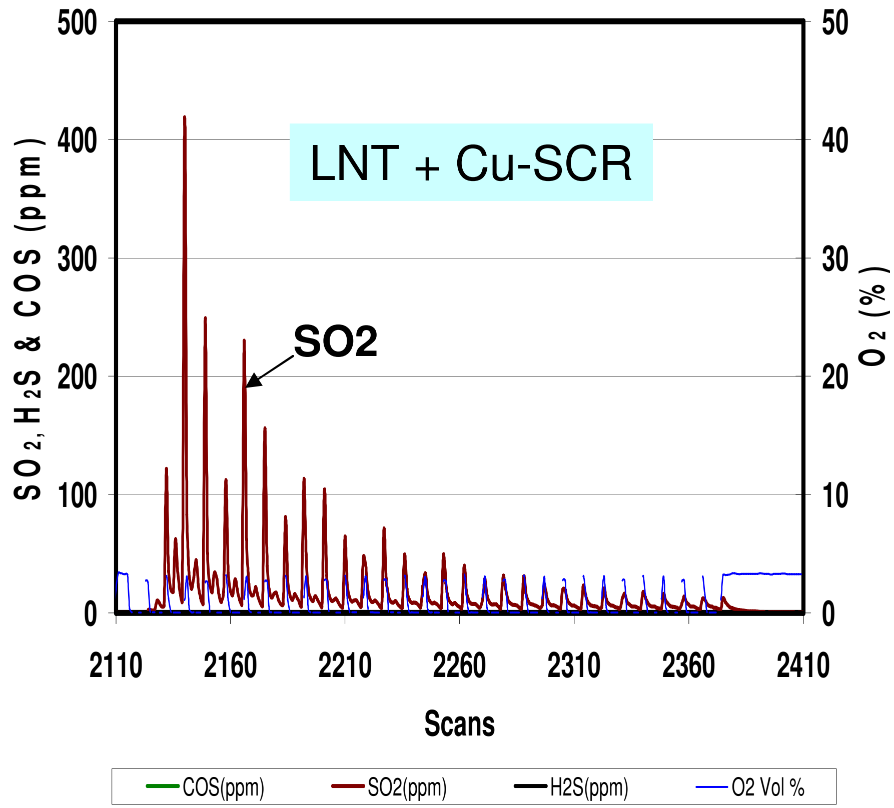
2^{nd} Gen LNT + SCR

- Key points:
  - enabled by advances to <u>both</u> LNT catalyst technology and SCR catalyst technology
  - relies (to some extent) on a non-ammonia NOx reduction mechanism
  - LNT purge parameters are critical (rich λ, O_2 content, HC type & amount, NOx storage levels, LNT temps, etc.)
  - suppresses H_2S emissions during LNT desulfation (see next slide)

Desulfation Comparison: LNT-only vs LNT+SCR

Laboratory Data



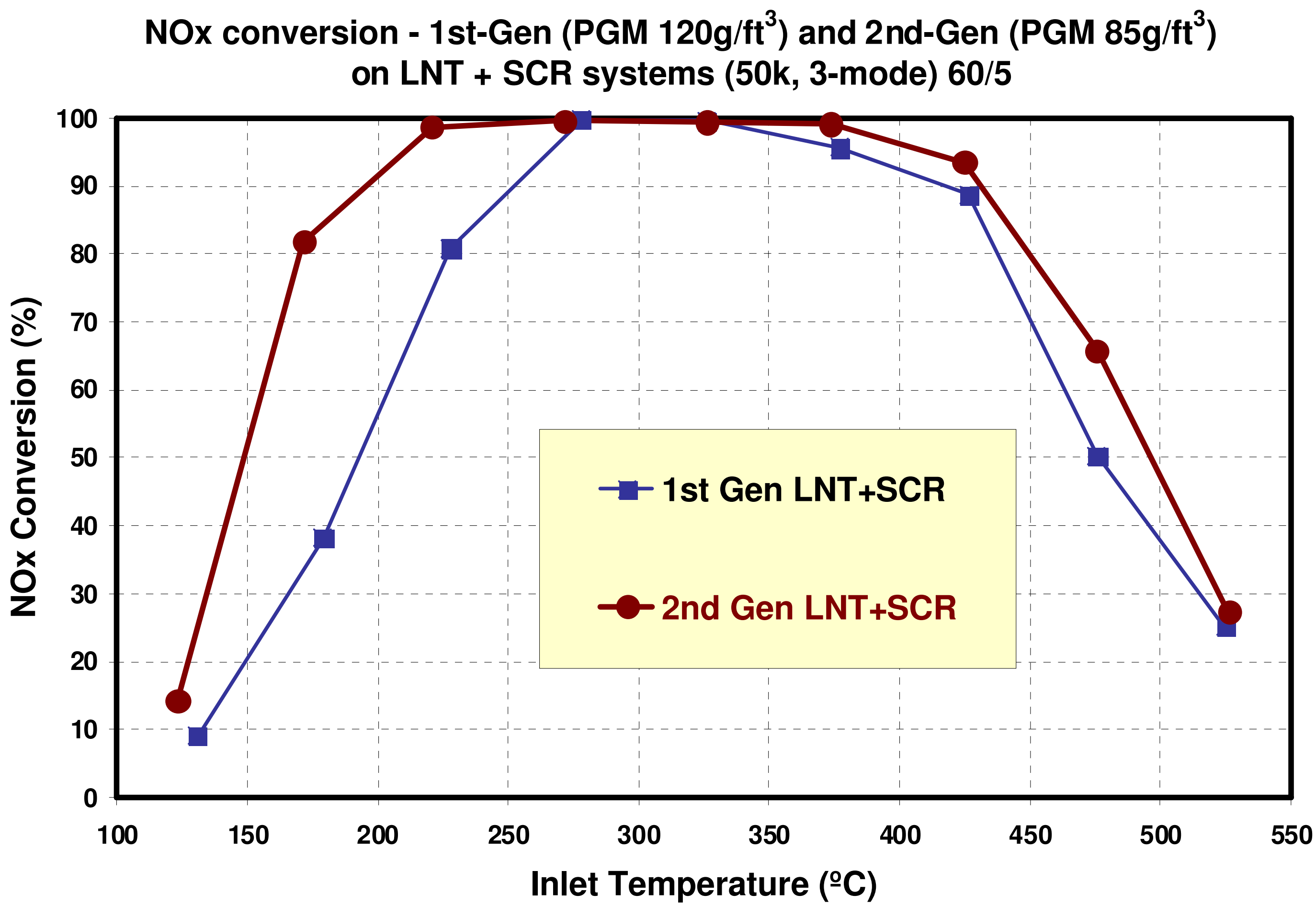


New Cu-SCR catalyst virtually eliminates H2S emissions produced by LNT during rich high-temperature desulfation (H2S from LNT converted to SO2) – more detail in SAE 2009-01-0285 (L. Xu et al.)

Catalysts: New LNTs

- Suppliers are providing LNTs with lower PGM loadings and lower De-SOx temperatures.
  - De-SOx temperatures reduced from 750-800C to 680-745C
  - PGM loadings decreased by 30-40%
  - Reference: Xu, et al., SAE 2009-01-0285
- Lower De-SOx temperatures improve durability & may allow synergistic De-SOx & DPF regeneration.
- Lower PGM loadings & volumes improve cost competiveness of LNT+SCR with urea-SCR.

Lab data showing improved NOx efficiency of 2nd-Gen LNT+SCR with lowered PGM loading



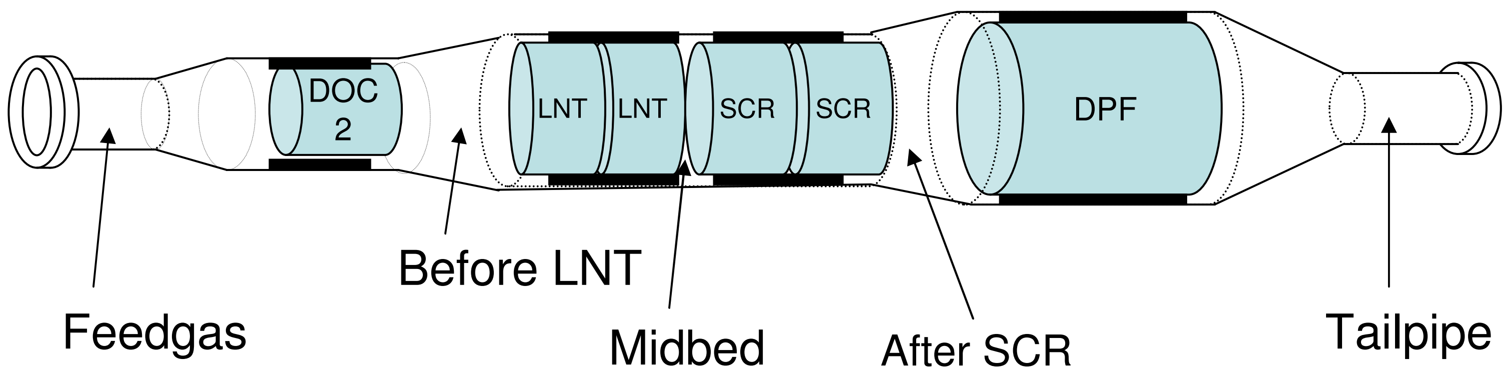
Catalysts: New SCRs

- 2nd-Gen urea-SCR formulations (HC poison resistant, low N2O yield) work well for LNT-SCR.
    - both Cu and Fe zeolite technologies effective
    - 2nd-Gen SCR formulations show good durability under rich aging conditions
- Several suppliers capable of providing SCR technology.

Vehicle Evaluations

- **Vehicle 1**: Land Rover LR3 Euro Stage 3 vehicle (~ 50k miles on the test vehicle)
  - Calibrated for 2005-level LNT and SCR catalyst technology
  - 2.7L engine tested at an inertial weight of 3780 lb
- **Vehicle 2**: Mock-up on Light-Duty pick-up truck
  - Tested at 5750 lb inertial weight
- All testing carried out in Ford's VERL facility

2nd Gen LNT+SCR system – LR3

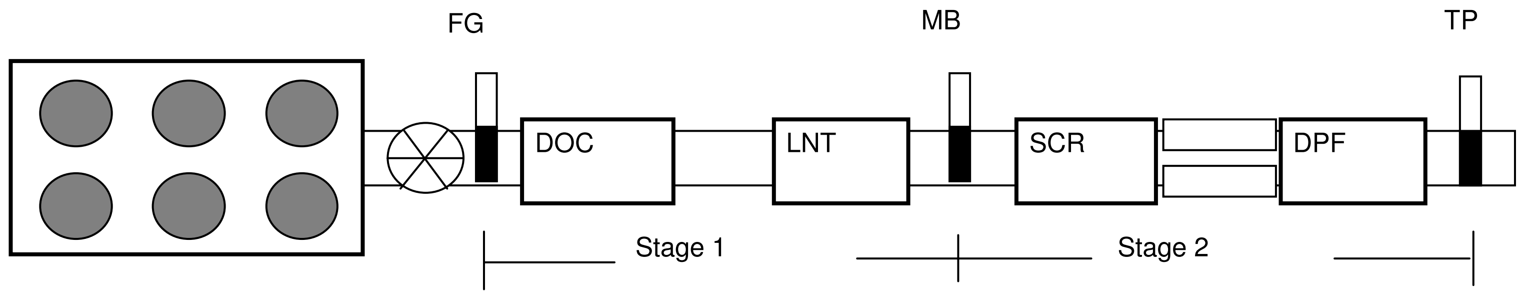


Component	Load	Dia. X Length (in)	Calc. Vol (L)	Engine Swept V	Material	Cell CPSI / Wall
DOC 2*	70g/ft3	4.66" x 3"	0.84	31%	Ceramic	400 / 6 mil
LNT**	85g/ft3	2 – 5.66"*3.5	2.88	107%	Ceramic	400 / 6 mil
SCR	-	2 – 5.66"*3.5	2.88	107%	Ceramic	400 / 6 mil
cDPF	20g/ft3	7.5" x 8 "	6.0	222%	SiC	200 / 15mil

- * There is a small metallic DOC 1 upstream
- **The LNT and SCR were hydrothermally aged (120k)

Note low loading (85 g/ft3) and volume (~1xESV) of LNT 2-brick system

FTP75 Emissions Results (Experimental LNT + SCR Systems for LR3 and Pick-up Truck)



Vehicle	Emissions	Before DOC FG g/mi	After LNT MB g/mi	Tailpipe TP g/mi	Stage #1 FG-MB Efficiency (%)	Stage #2 MB-TP Efficiency (%)	Overall FG-TP Efficiency (%)
LR3 120k mile (hydrothermal)	NMHC	3.42	0.25	0.10	92%	60%	97%
	CO	7.53	0.24	0.21	96.77%	12%	97%
	NOx	0.76	0.1	0.03	86.87%	66%	96%
Pick-up (mockup) * 120k mile (hydrothermal)	NMHC	2.10	0.08	0.050	96%	38%	98%
	CO	8.08	0.157	0.20	98%	-27%	98%
	NOx	0.52	0.07	0.023	86.5%	67%	96%

< T2/B3 (0.055NMOG, 2.1CO & 0.03 NOx)

* Pick-up LNT volume is 80% of the engine displacement

High-Load Testing (US06)

US06 traditionally a problem area for LNT systems because of decreased NOx storage at high temperatures

LR3 – Purge strategy not active at highest temperatures of US06 (83.5% overall NOx conversion nonetheless)

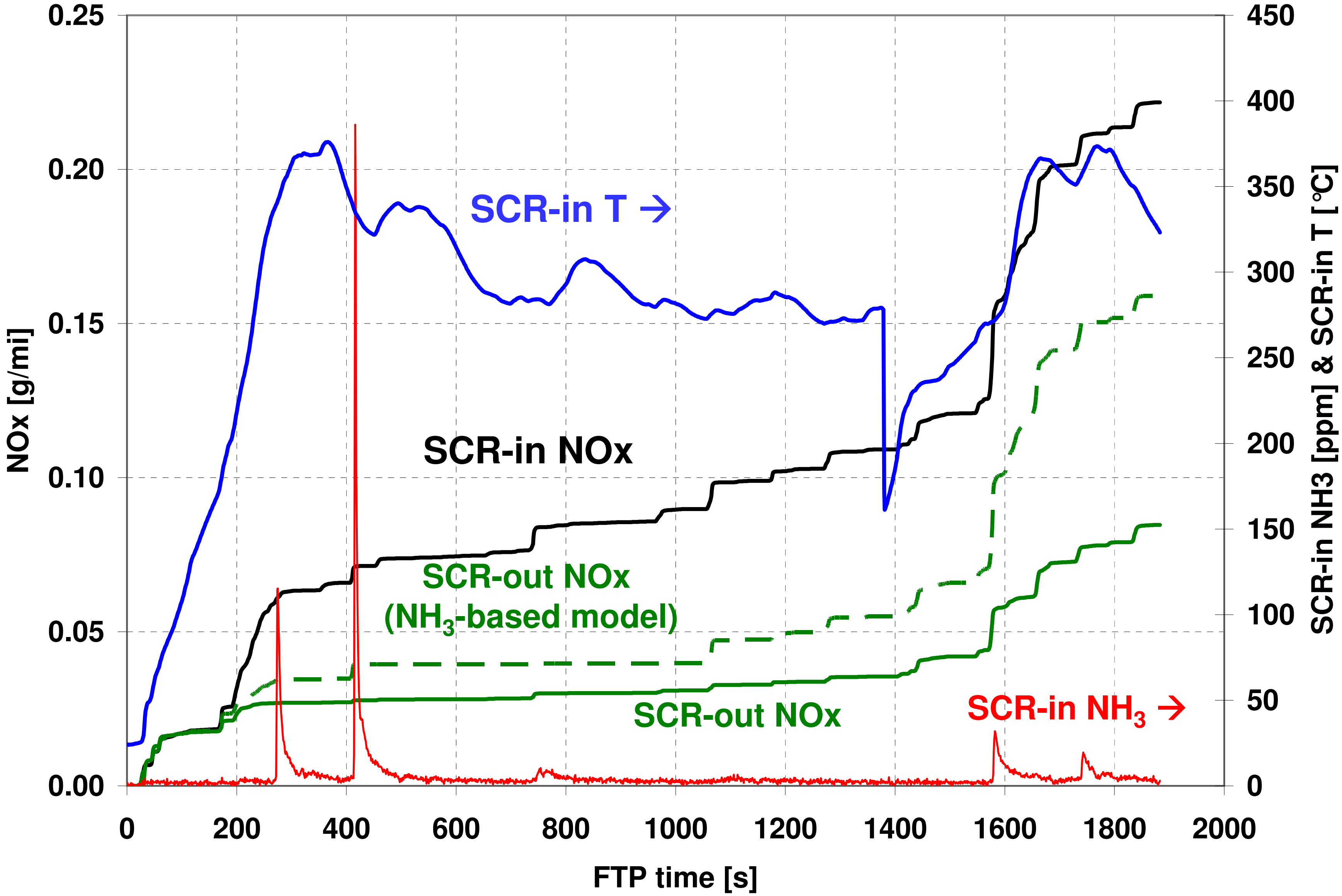
2.0L Mondeo* – TP NOx of 0.11 g/mi achieved with a FG NOx of 0.85 g/mi (87% efficiency) using 75K km dyno aged LNT and de-greened SCR catalyst (Max SCR temp = 400℃)

* Mondeo tests conducted at Ford's FFA laboratory in Aachen, Germany

How important is NH_3?

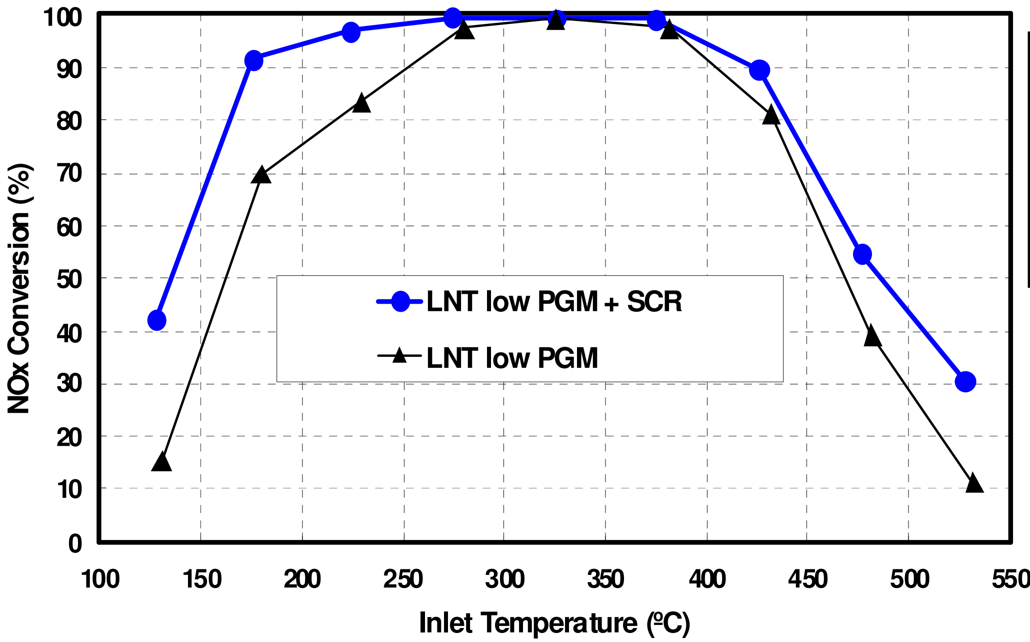
- Ford R&A Cat Modeling Team (Santhoji Katare) has conducted a detailed quantitative assessment of test procedures and theoretical NH_3 contribution to observed NOx conversion.
- This is a preliminary step toward developing models to aid in LNT+SCR system design and optimal operation.
- Results confirm presence of a significant non-NH_3 mechanism (see following slide).

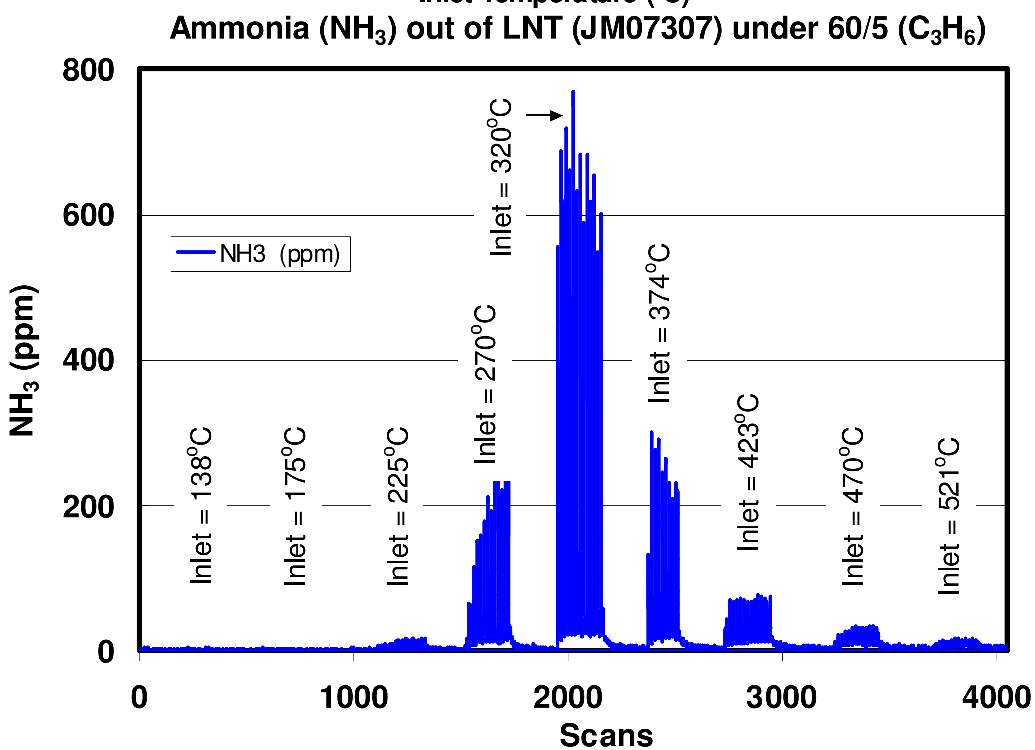
Performance across a typical FTP: Modeling analyses (S. Katare)



Bags 1 & 3 NOx conversion unaccounted for by NH_3-based model suggests non-NH_3 mechanism

Lab data also suggest a non-NH3 reduction mechanism

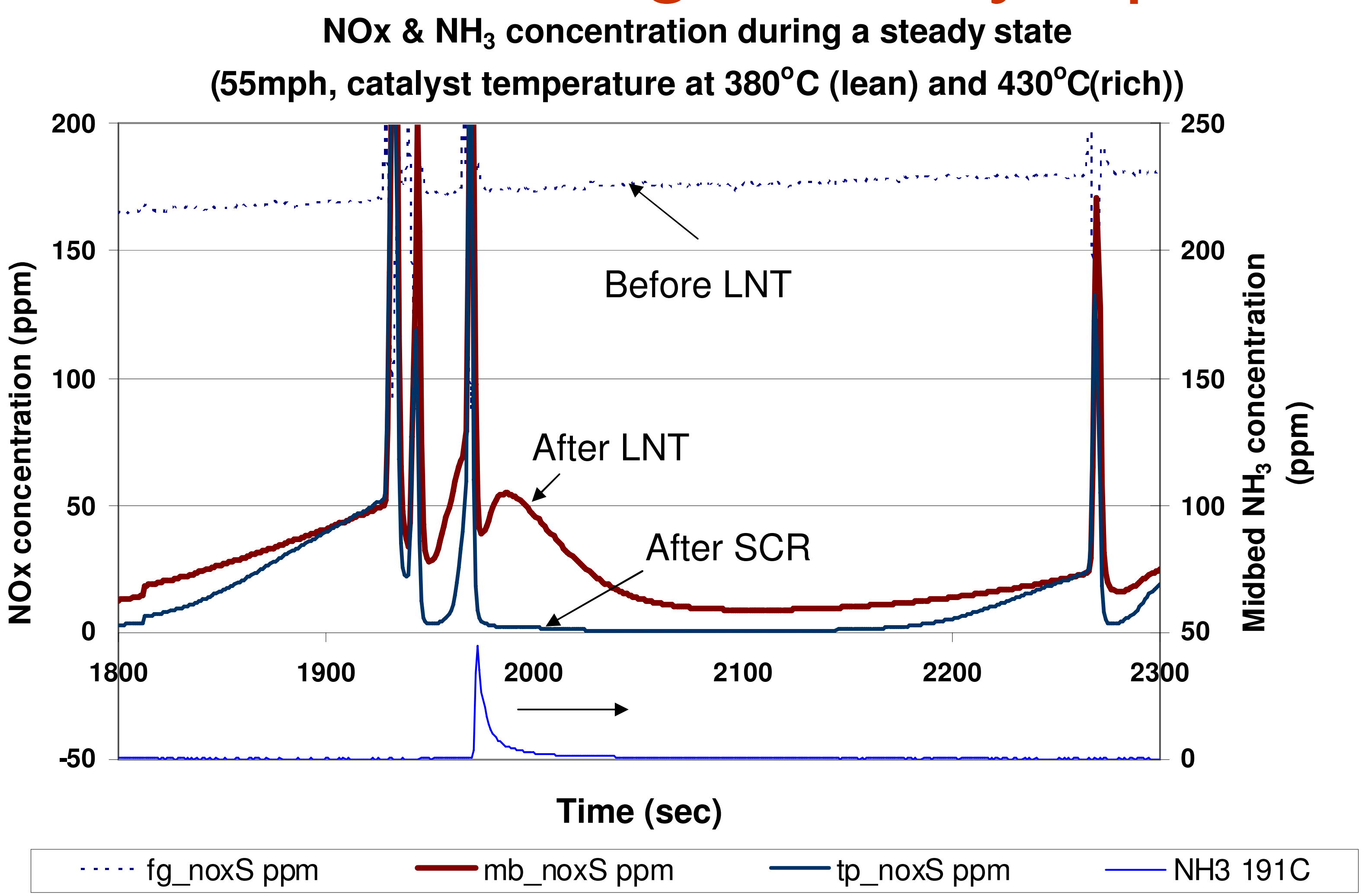




- Note enhanced conversion from SCR cat at temps below 225C and above 450C (where little or no NH3 is formed or expected to store on the SCR cat)
- Data suggest an additional non-ammonia NOx conversion mechanism over the SCR catalyst.

Lab data: 70K simulated 3-mode Lab aging; 60sL/5sR eval. cycles

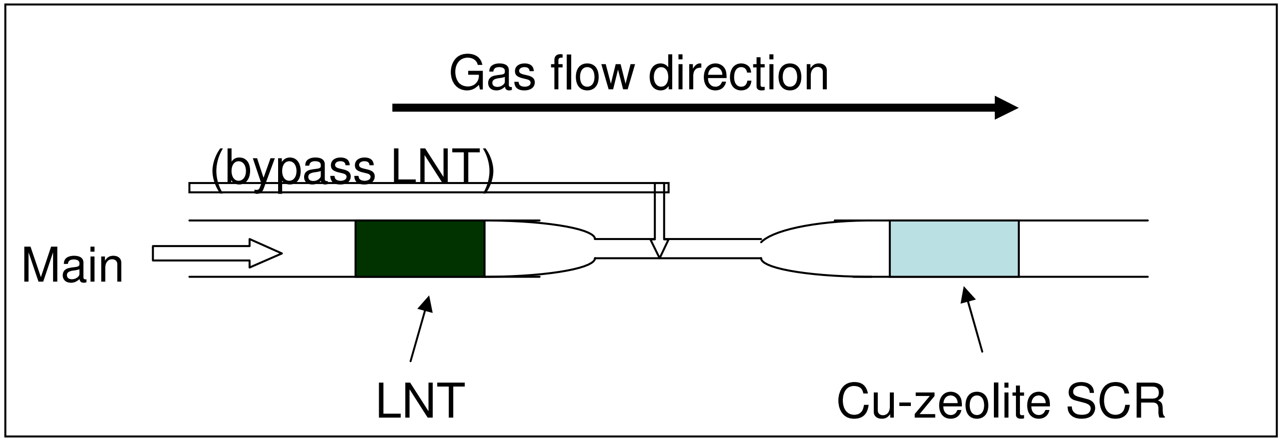
Vehicle Testing: Steady-Speed



Note: NH3 produced cannot explain extra NOx conversion by SCR cat

Mechanistic Considerations

Non-Ammonia NOx Reduction



NO, NO2, HC "main" & "bypass" experiments

- NO, NO2 and HC reductant all need to pass through the LNT upstream of the SCR to obtain enhanced conversion (suggests formation of an organo-nitrogen compound over the LNT & storage on the SCR cat).
- No evidence for NO2 + Aldehyde reaction at zeolite as with cold plasma research.
- Various species (such as nitromethane) ruled out (not observed with FTIR & V&F mass spectrometer).
- HCNO (isocyanic acid) observed via mass spec and FTIR in lab experiments with ethylene as the HC species

Working-level hypothesis of a literature-based non-NH3 LNT mechanism

$$C_2H_4 + O_2 \xrightarrow[PM]{LNT} HCCO + H_20 + H \qquad (1)$$

$$HCCO + NO_2 \xrightarrow[PM]{LNT} HCNO_{(g)} + CO_2 \qquad (2)$$

$$HCNO_{(ads)} + H_20 \xrightarrow[\text{Acid site}]{\text{SCR Lewis}} NH_3 + CO_2 \qquad (3)$$

(1) Ethylene partially oxidized across the LNT to form HCCO - the ketenyl radical.

(2) HCCO reacts over the precious metals with NO2 (released from Ba storage sites)

(3) HCNO is stable in the gas phase and is transported to the SCR where it is adsorbed by a Lewis acid site and is decomposed by reaction with H2O, to form NH3 (which can subsequently oxidize to N2 or react with breakthrough NOx from the LNT).

Summary

- Experimental results show low-emissions potential - possibly T2/B2 (SULEV) NOx with low-emitting engines and system optimization. NMOG may be the greatest challenge.
- Preliminary data suggest minimal FE penalty.
- All results obtained with production worthy LNT and SCR supplier catalyst formulations.
- SFTP-compatible (especially US06).
- Low PGM loadings/volumes improve cost-competitiveness with urea-SCR.

LNT+in-situ SCR: early stages of development but potentially an enabler of affordable, clean, fuel-efficient LD diesel vehicles.

R&D Needs

- Continued work on understanding the NOx reduction mechanisms.
- Further catalyst optimization.
- Catalyst system architecture including opportunities for integrated catalyst elements.
- Combustion optimization (LTC vs conventional)
- Controls! (cold-start; purge; de-SOx; DPF regen; sensors; diagnostics, etc.)

DOE grant with UH, UK, & BASF to explore these aspects