

**Selective Catalytic Reduction (SCR)
With Urea Injection for NO_x Control on
Lean-Burn Gasoline Engines**

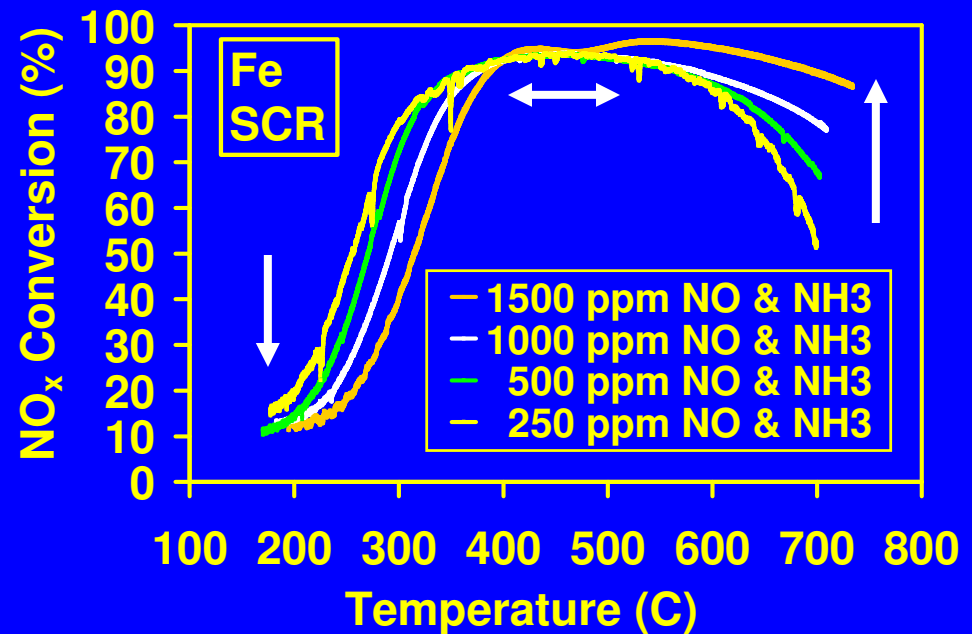
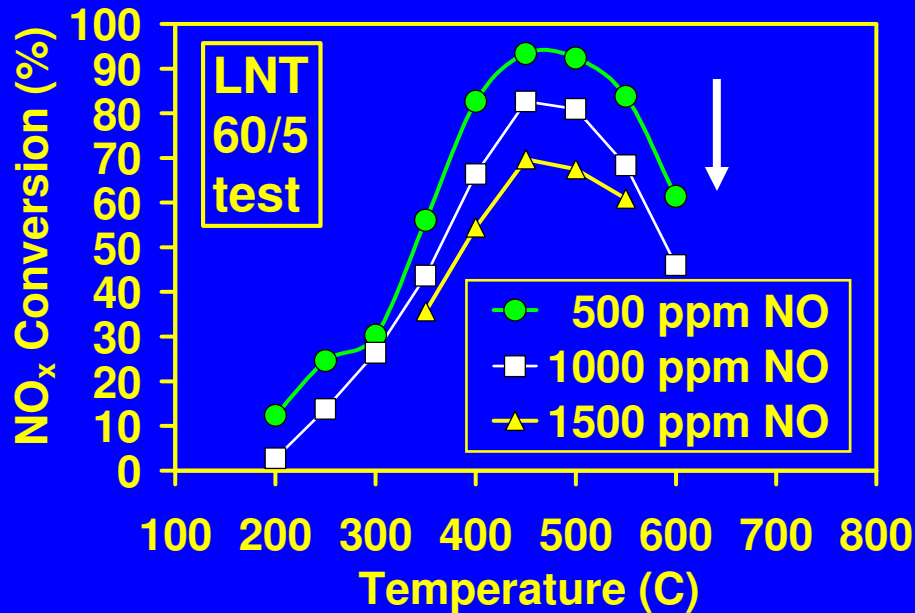
2008 CLEERS Conference

5/13/08

Joe Theis & Bob McCabe, Ford Motor Company

Advantages of SCR vs LNT

I. More robust to feedgas NO level



II. No rich purges

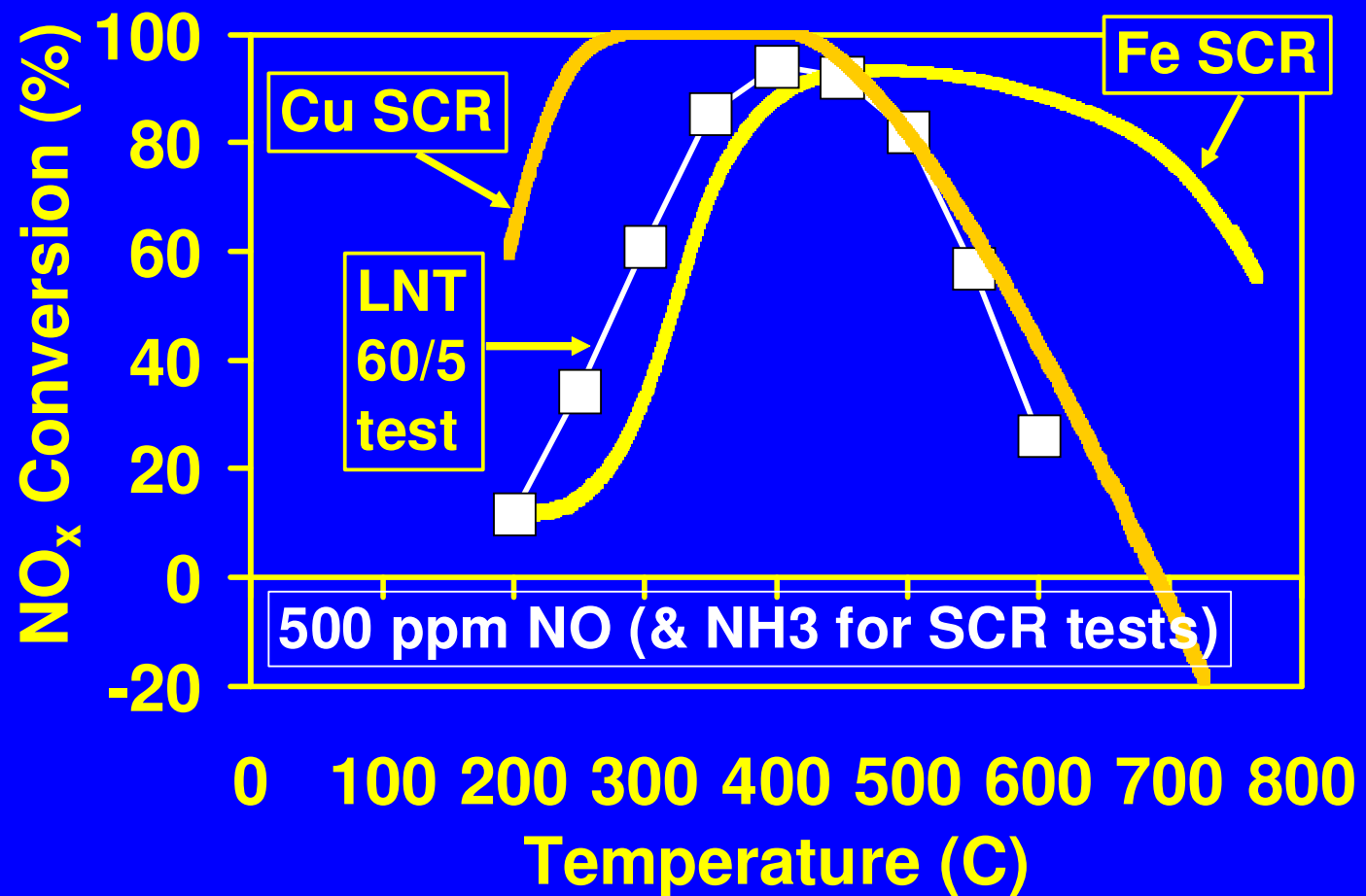
- Fuel economy benefit (1.5 to 2.0%)
- Eliminates purge NO_x release

SAE paper
2008-01-0810

Advantages of SCR vs LNT

III. SCR uses low cost base metals such as V, Cu, or Fe
- LNT uses high concentrations of PGM

IV. SCR can provide broader range of temperature



Issues with SCR

General Issues (Lean-Burn Gasoline & Diesel)

Second tank for urea

Urea injection system (\$\$)

Urea infrastructure

Customer compliance

Urea freezing, mixing, decomposing into NH_3 at low T

Specific Issues for Lean-Burn Gasoline

No three-way activity at stoichiometry from SCR catalyst

- Requires larger TWC

High NO_x concentrations

- More frequent refills or larger urea tank

High exhaust temperatures

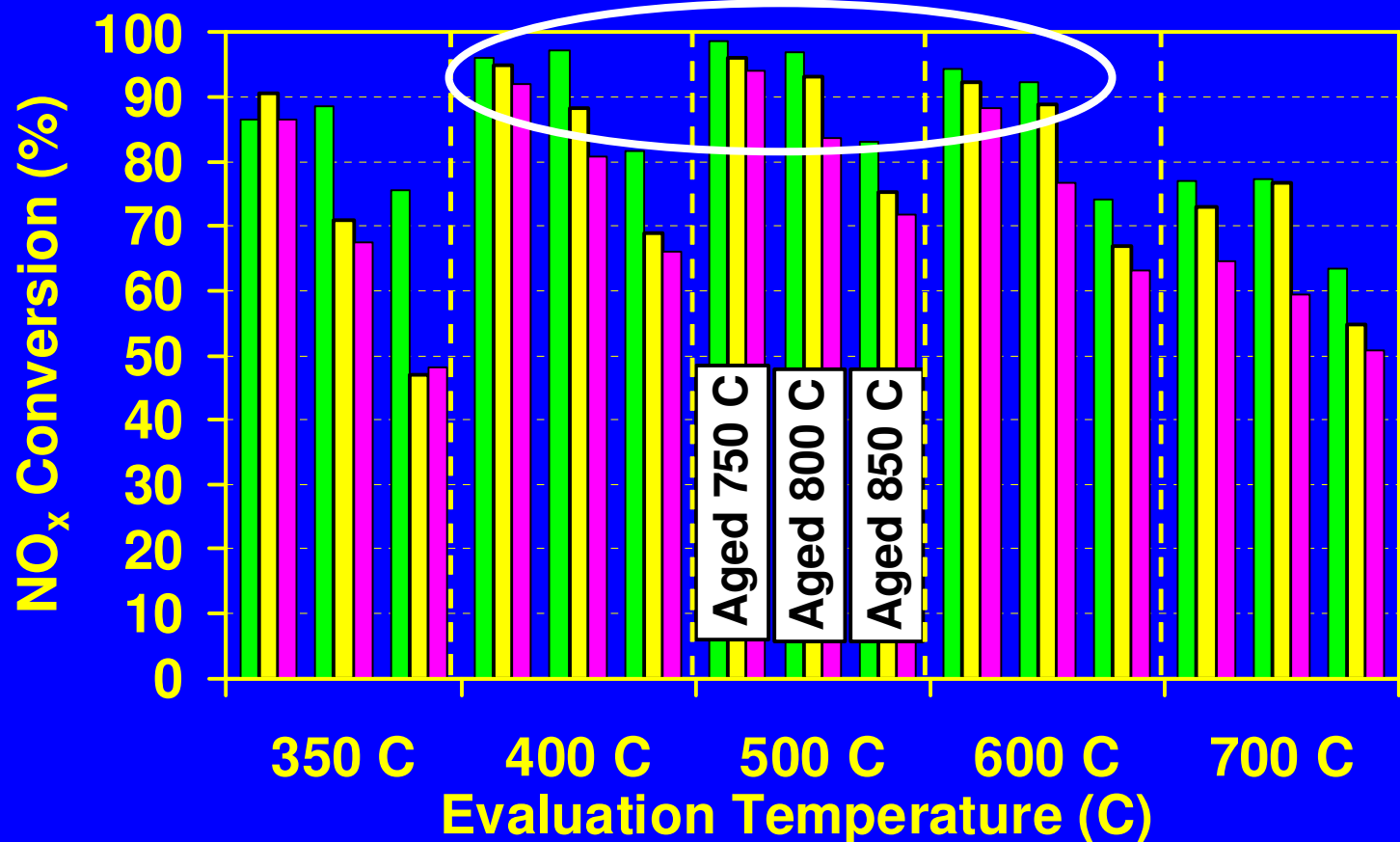
- SCR catalyst loses NH_3 storage capacity above 400°C
- Need to inject urea to match NO_x flux
- Challenge for control system during transient driving



Hot rich exhaust conditions

- Durability of zeolite-based SCR catalysts

Effect of A/F Ratio & Temperature during Aging Fe SCR Catalyst, Eval at 25K hr⁻¹, 500 ppm NO & NH₃



SAE paper
2008-01-0811

■ Aged lean ■ Aged stoich (2/3 time) ■ Aged rich (2/3 time)

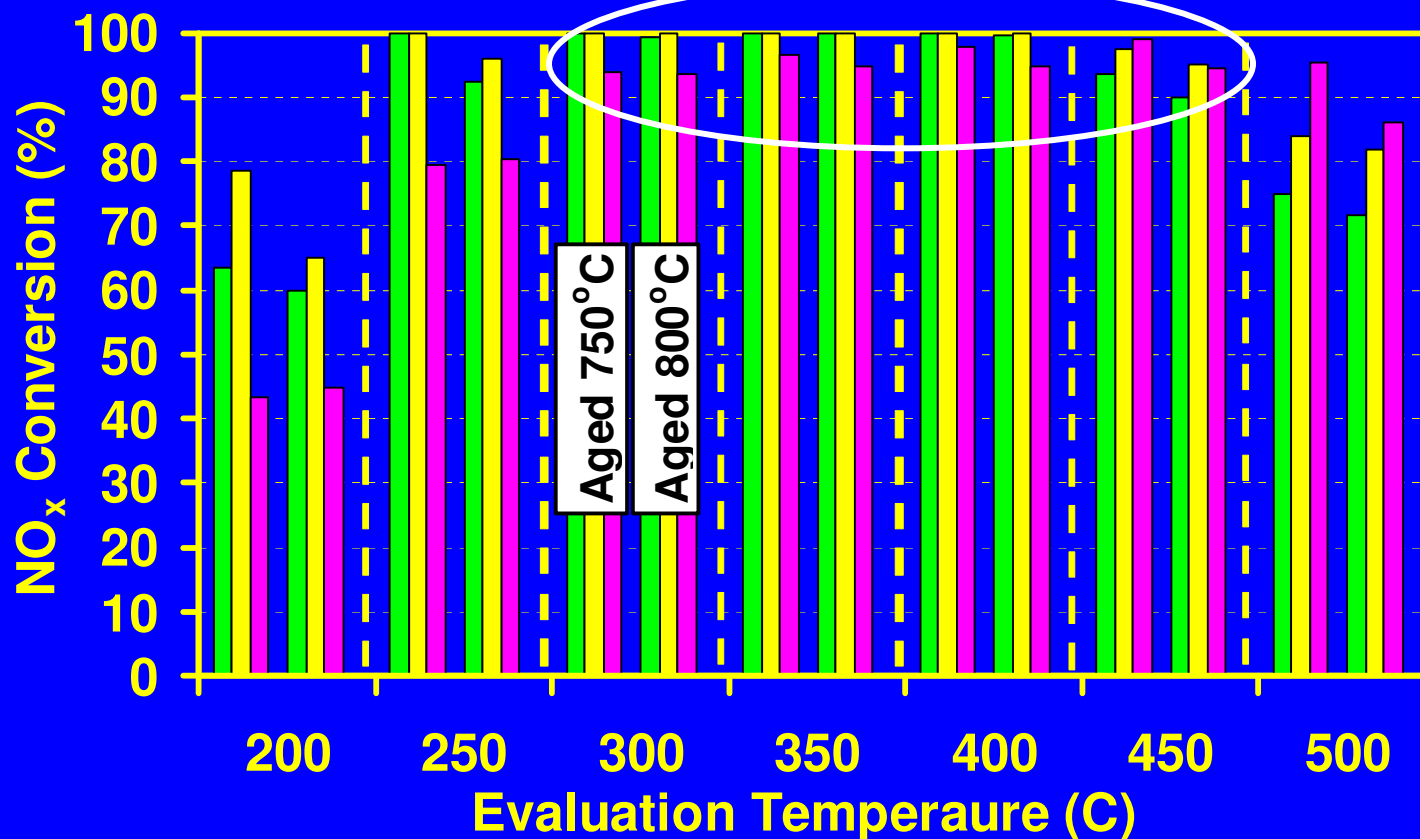
Stoich or lean aging at 800°C → 90%+ at 500°C

Rich aging at 750°C → 90%+ between 400-500°C

→ Fe SCR catalyst durable for lean gasoline applications

Effect of A/F Ratio & Temperature during Aging

Cu SCR Catalyst, Eval at 25K hr⁻¹, 500 ppm NO & NH₃

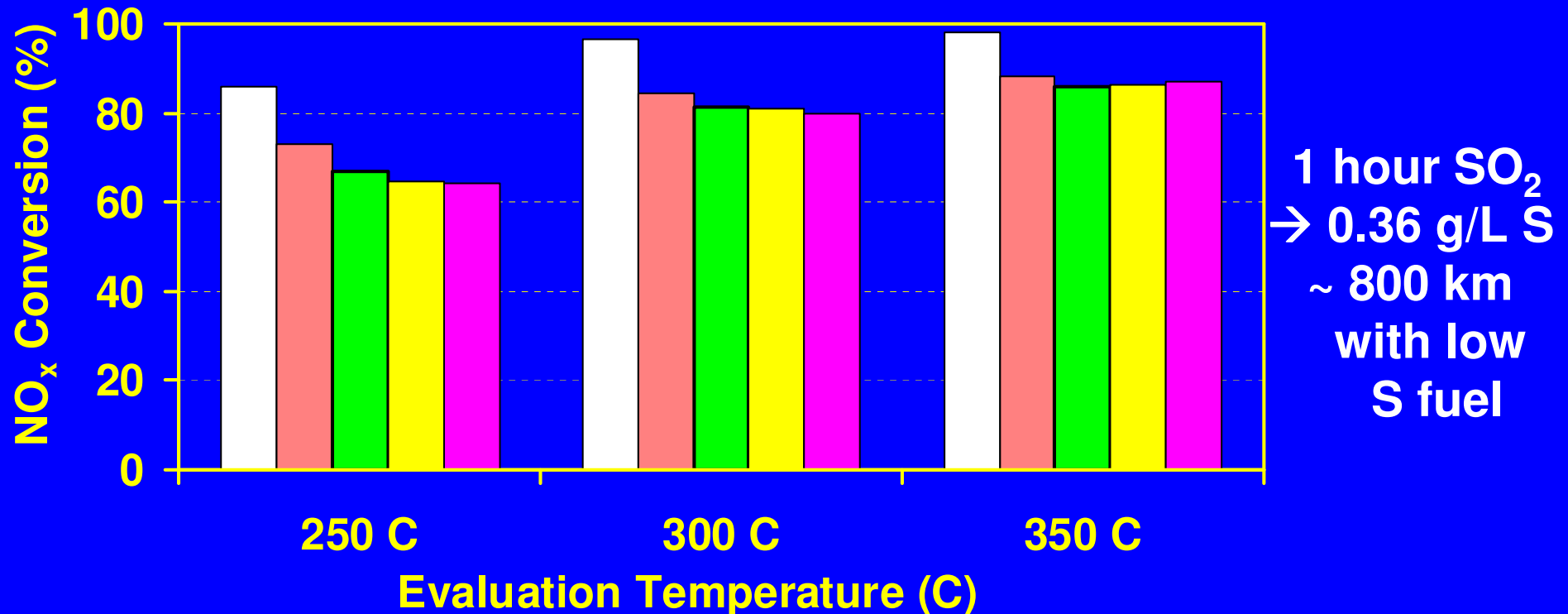


■ Aged lean ■ Aged stoich (2/3 time) ■ Aged rich (2/3 time)

≥ 90% conversion between 300-450°C for both aging temperatures and all 3 A/F ratio schedules
→ Cu SCR catalyst durable for lean gasoline applications

Effects of Sulfur Poisoning on Cu SCR Catalyst

Aged Cu SCR, Poison at 400°C w/ 9 ppm SO₂
Evaluated with 500 ppm NO & NH₃, 25K hr⁻¹



■ after purge ■ 1 hr SO₂ ■ 2 hr SO₂ ■ 4 hr SO₂ ■ 8 hr SO₂

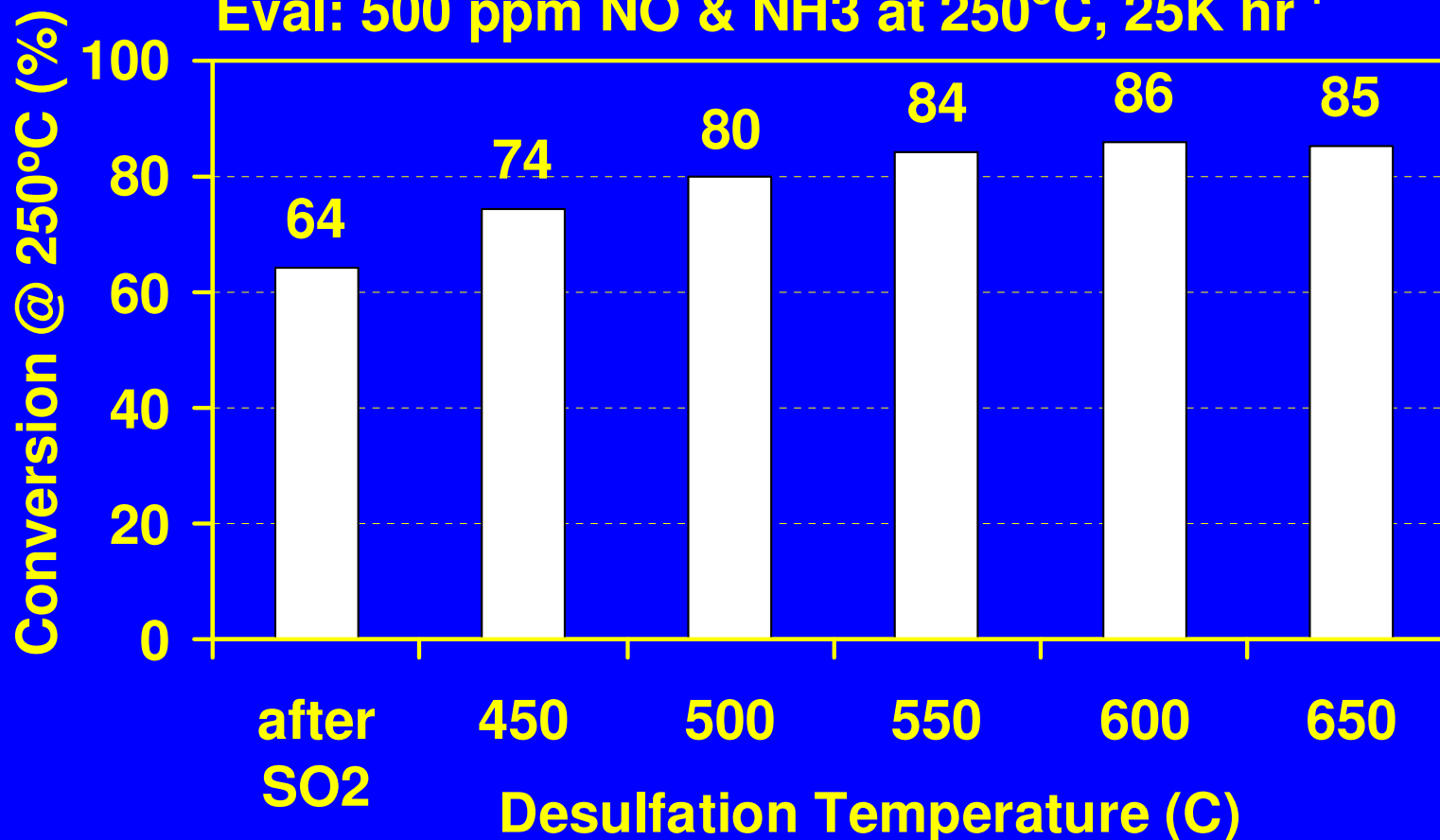
- Conversion decreased during first 2 hrs of poisoning
- Stable with continued SO₂ exposure
- Similar observation for Fe SCR catalyst

Desulfation of Cu SCR Catalyst After SO₂ Poisoning

Aged Cu SCR, Poisoned 8 hrs with 9 ppm SO₂

Desulfated with 5 minute Lean Periods

Eval: 500 ppm NO & NH₃ at 250°C, 25K hr⁻¹



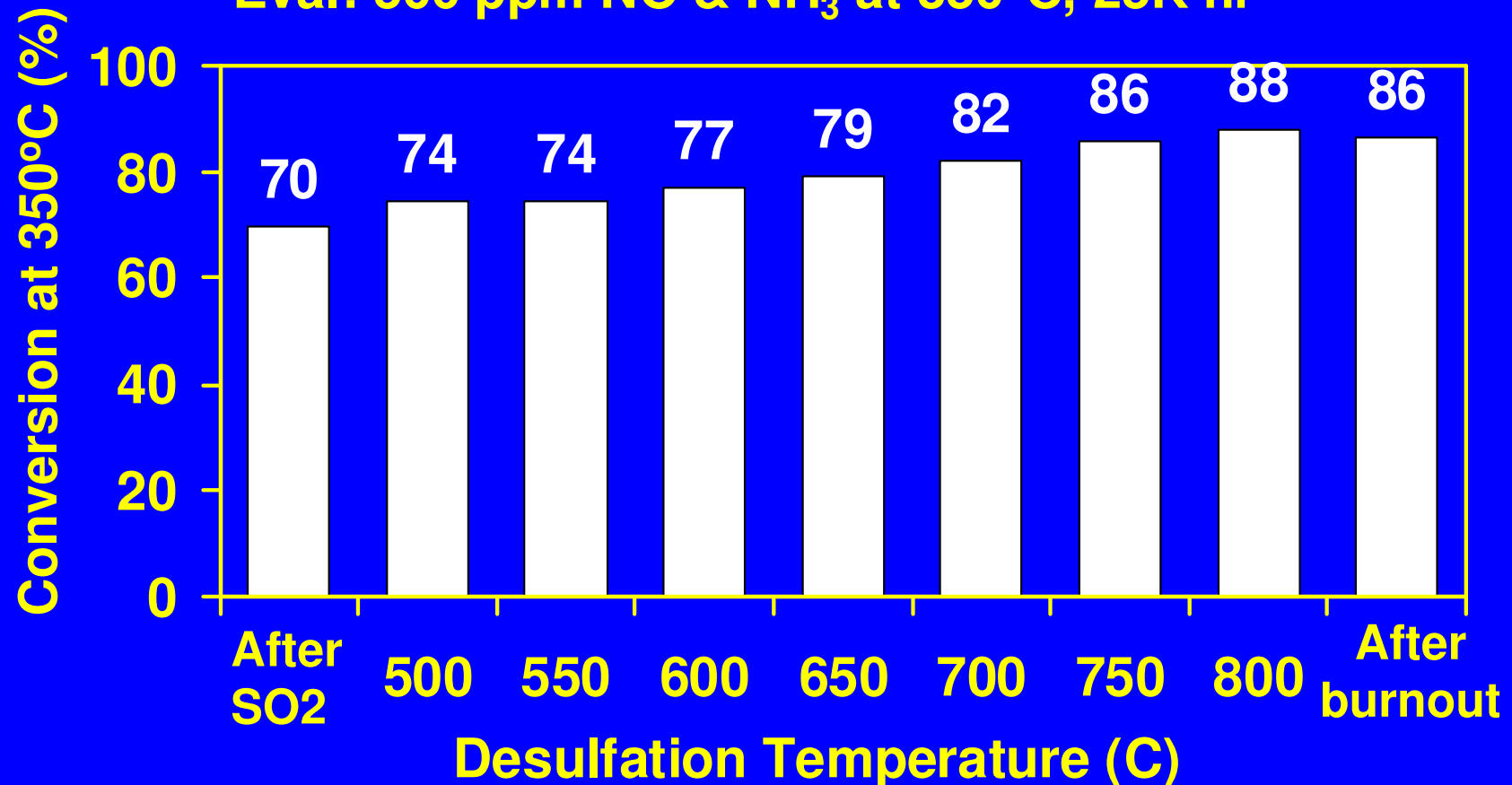
Poisoned Cu SCR catalyst recovered its maximum performance after lean exposure at 600°C

Desulfation of Fe SCR Catalyst After SO₂ Poisoning

Aged Fe SCR, Poisoned 8 hrs with 9 ppm SO₂

Desulfated with 5 minute Lean Periods

Eval: 500 ppm NO & NH₃ at 350°C, 25K hr⁻¹

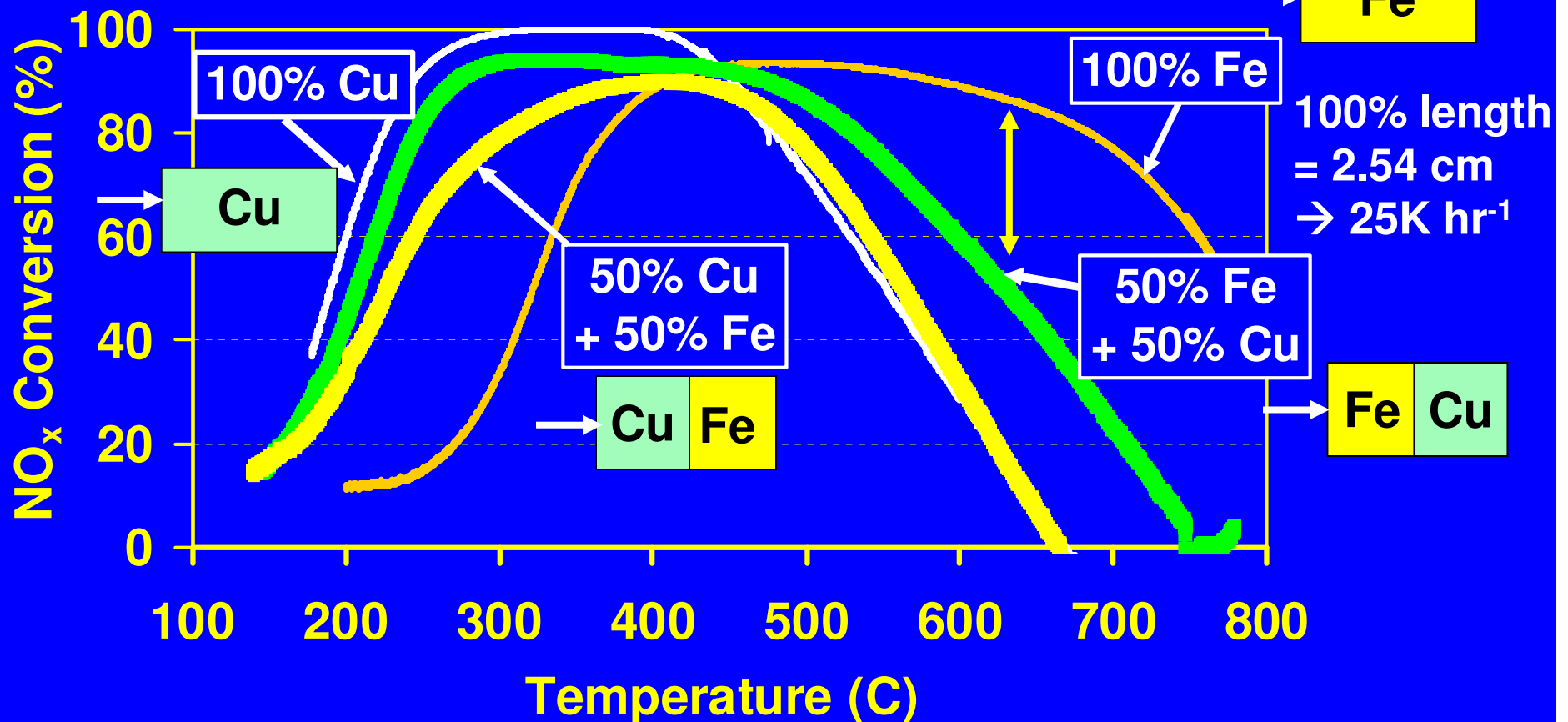


Poisoned Fe SCR catalyst required ~750°C under lean conditions to recover maximum performance

Maximizing Temperature Window

Zoning of Aged Cu & Fe SCR Catalysts

Eval: 500 ppm NO & NH₃ at 25K hr⁻¹

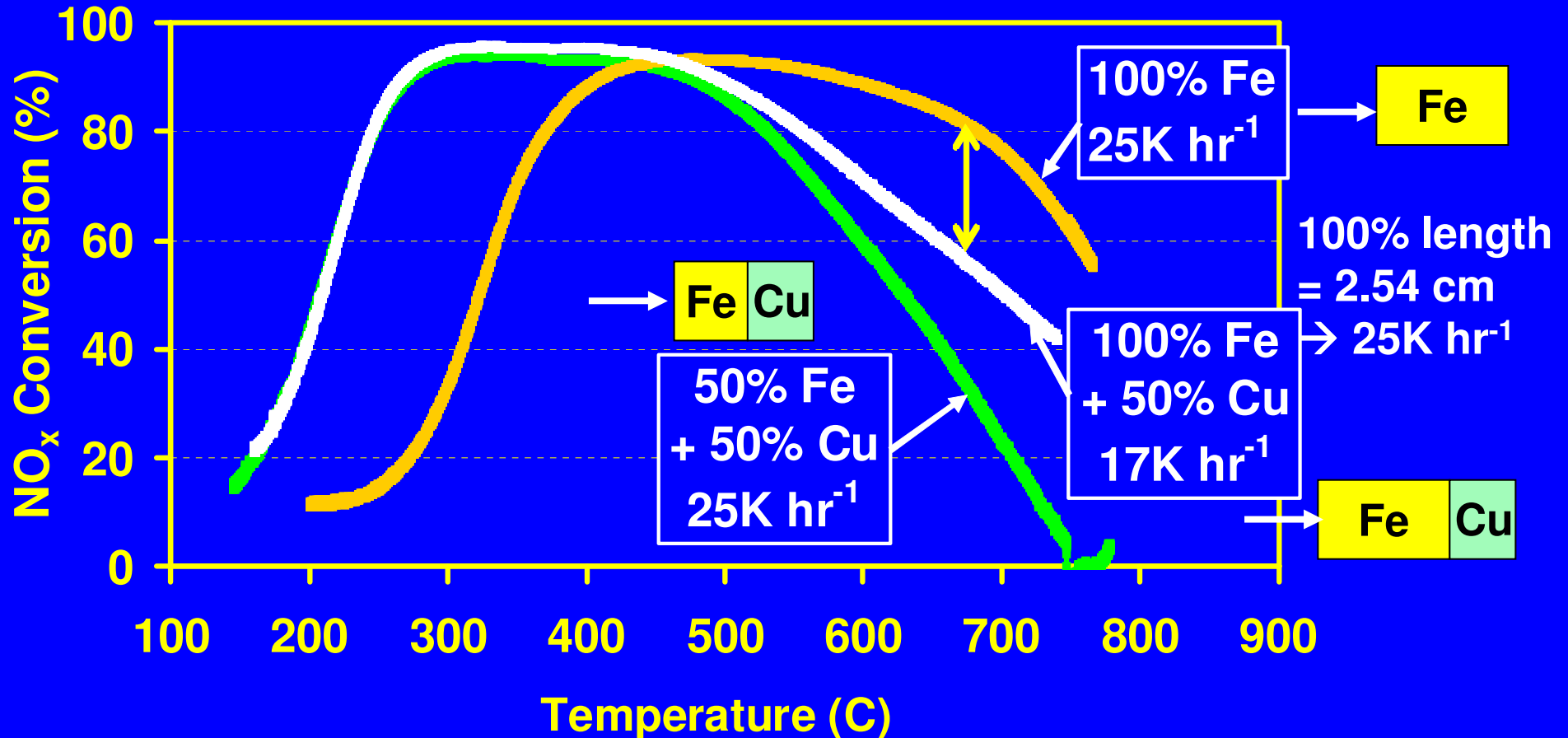


Fe SCR catalyst needs to be in front of Cu SCR catalyst

- Protects Cu SCR during aging, preserves activity at low T
- Fe SCR can use NH₃ for NO_x conversion at high T

Maximizing Temperature Window

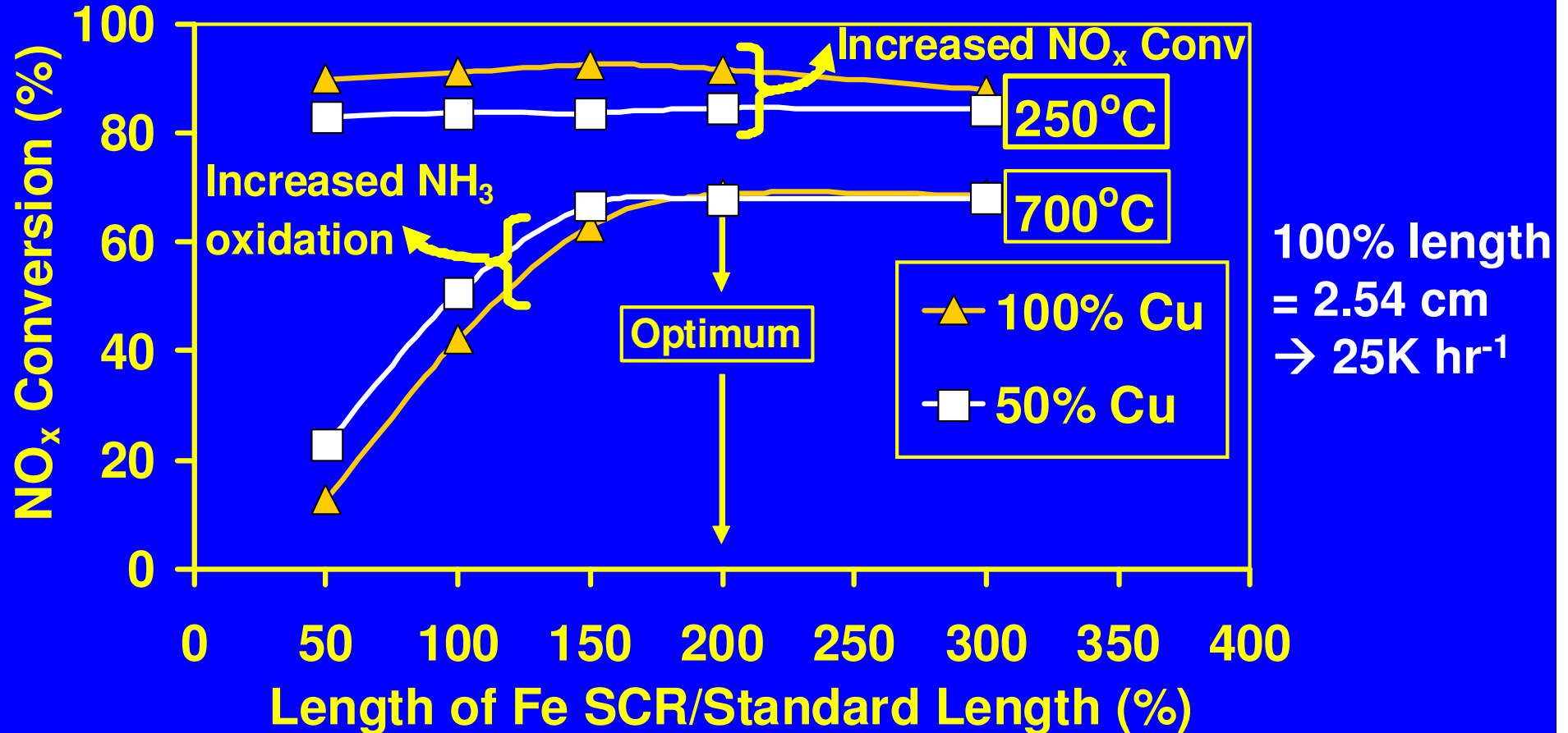
Combinations of Aged Cu and Fe SCR
Evaluated with 500 ppm NO & NH₃



NH₃ slip from Fe SCR oxidized to NO by Cu SCR at high T
→ Need larger Fe section to use NH₃ for NO_x conversion

Maximizing Temperature Window

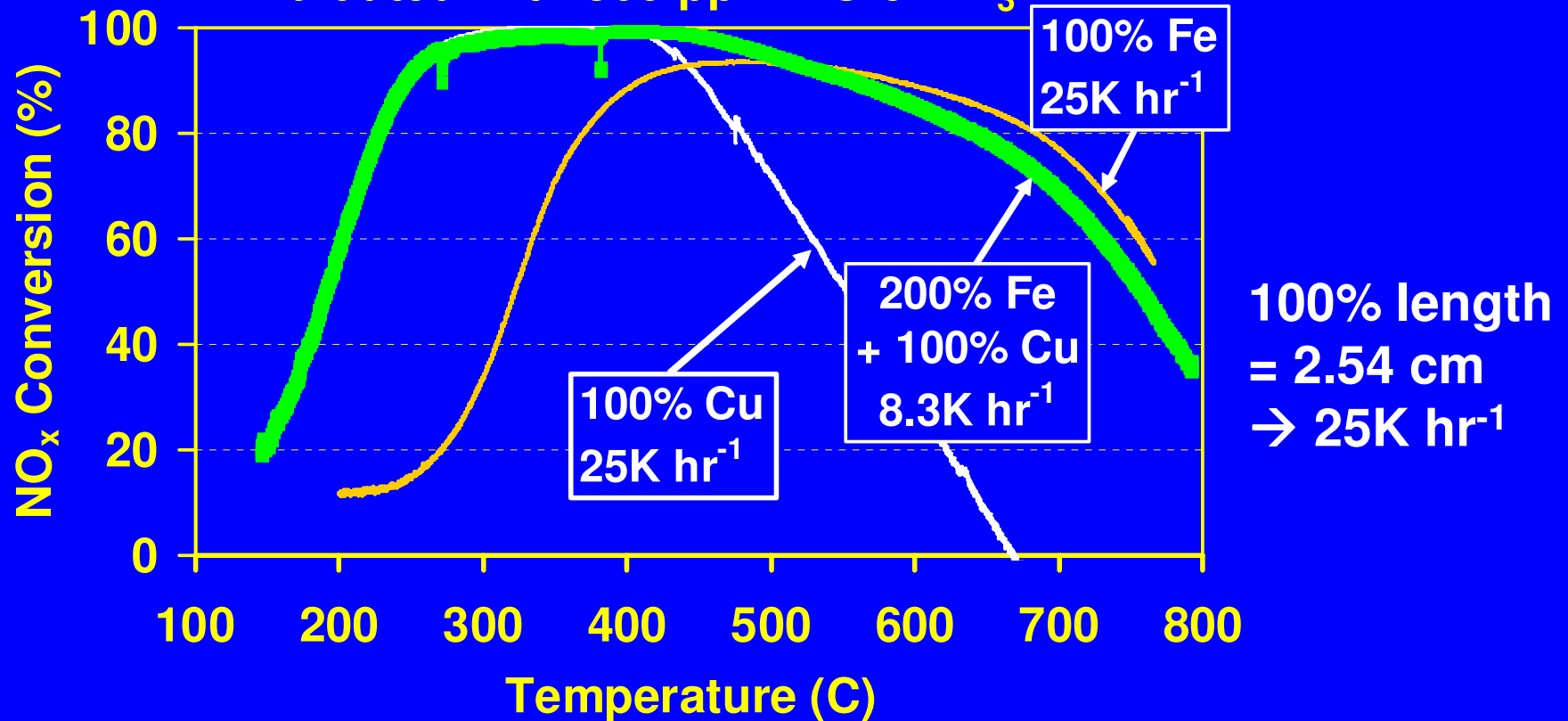
Aged (50% to 300% Fe SCR) + (50% or 100% Cu SCR)
Evaluated with 500 ppm NO and NH₃ at Different Temperatures



Optimized System = 200% Fe SCR + 100% Cu SCR catalyst
→ Resulting space velocity = 8.3K hr⁻¹

Maximizing Temperature Window

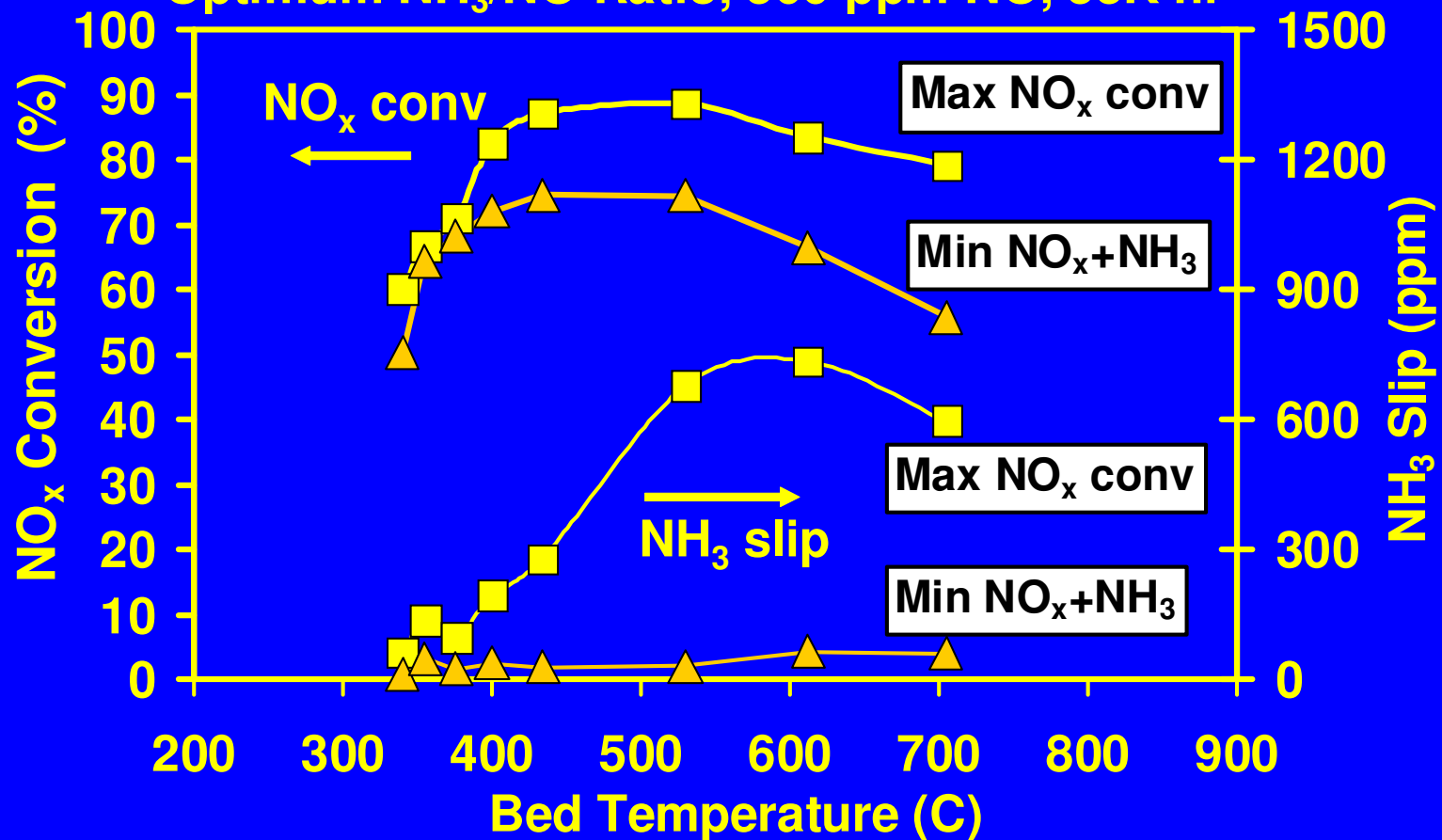
200% Fe SCR + 100% Cu SCR Catalyst
Evaluated with 500 ppm NO & NH₃



- Good performance at low & high temperatures
- Low catalyst costs due to absence of PGM
- Backpressure and/or packaging could be issues, particularly on small vehicles

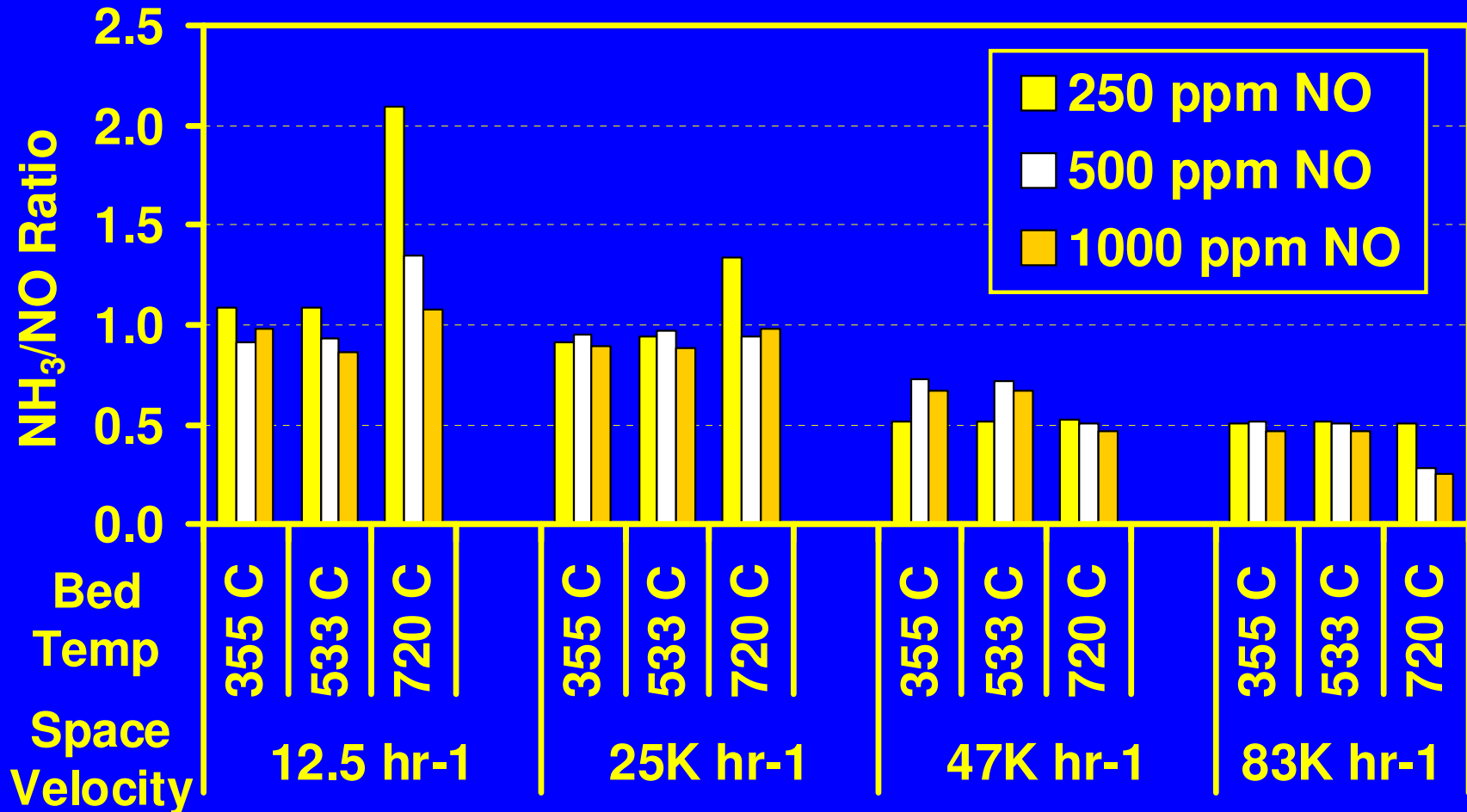
NH₃/NO Ratio

Fe SCR Catalyst aged 34 hrs 800°C Lean
Optimum NH₃/NO Ratio, 500 ppm NO, 55K hr⁻¹



- > At high space velocities, NH₃/NO ratio producing maximum NO_x conversion resulted in high levels of NH₃ slip
- > Ratio producing minimum NO_x+NH₃ decreased NO_x conversion

**Fe SCR 34 hrs 800°C Lean or 750°C Stoich
NH₃/NO Ratio for minimum NO_x+NH₃ vs SV & T**

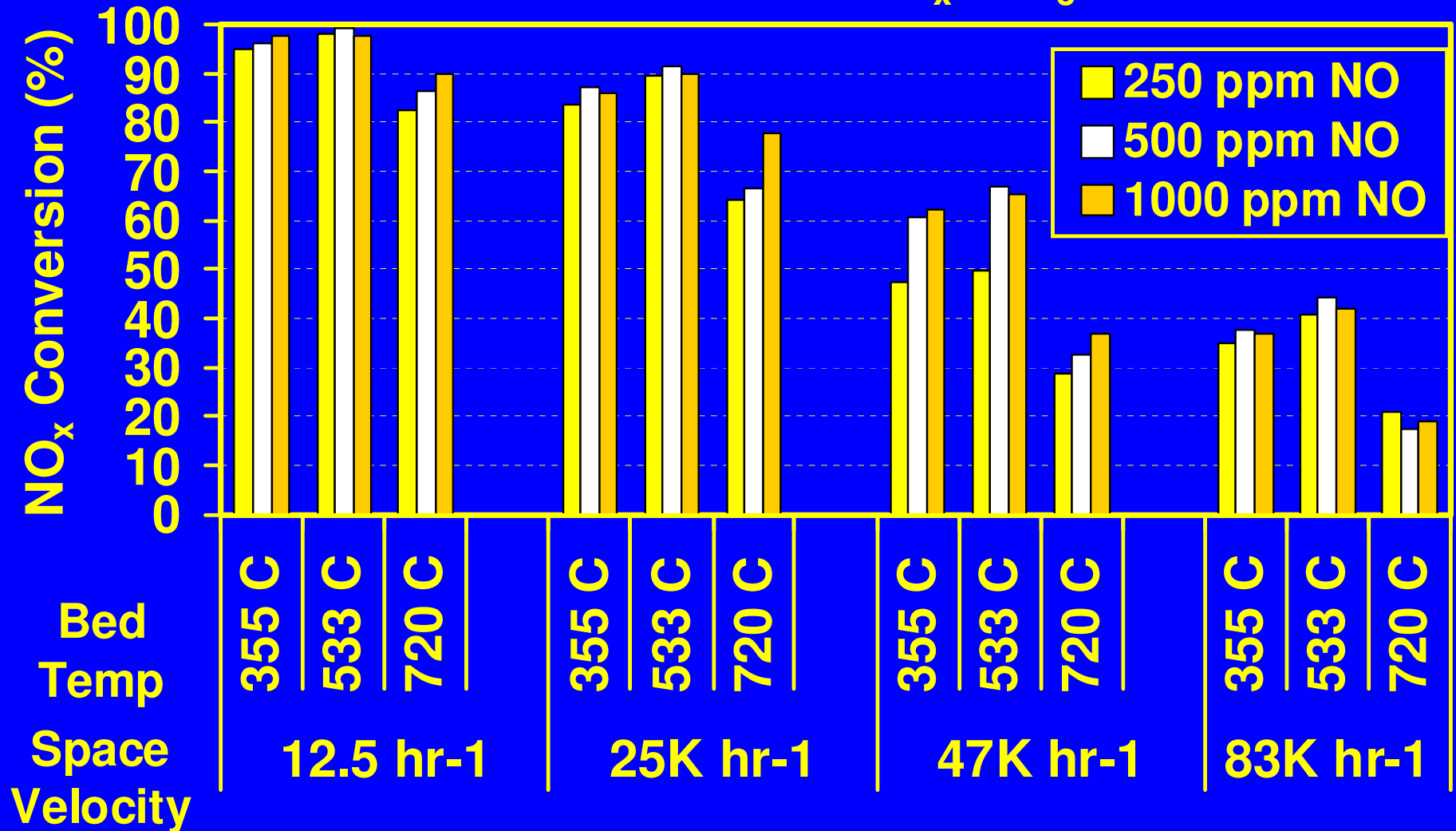


At 12.5K & 25K hr⁻¹, optimum NH₃/NO ratios for minimum NO_x+NH₃ near 1.0 (or above), allowing high NO_x conversions.

At higher SV, optimum ratios << 1.0, limits conversions.

> Kinetic limitations and the need to limit NH₃ slip

**Fe SCR 34 hrs 800°C Lean (or 750°C Stoich)
Conversion for minimum NO_x+NH₃ vs SV & T**



Largest SCR volume provided high NO_x conversions and low NH₃ slip at all T and NO concentrations.

Comparison of LNT & SCR Costs Tier 2 Bin 5 Emissions (1:1 volume/ESV)

Exhaust Sys Cost (\$)

SCR costs include TWC, SCR catalyst, cans, sensors, urea injection system

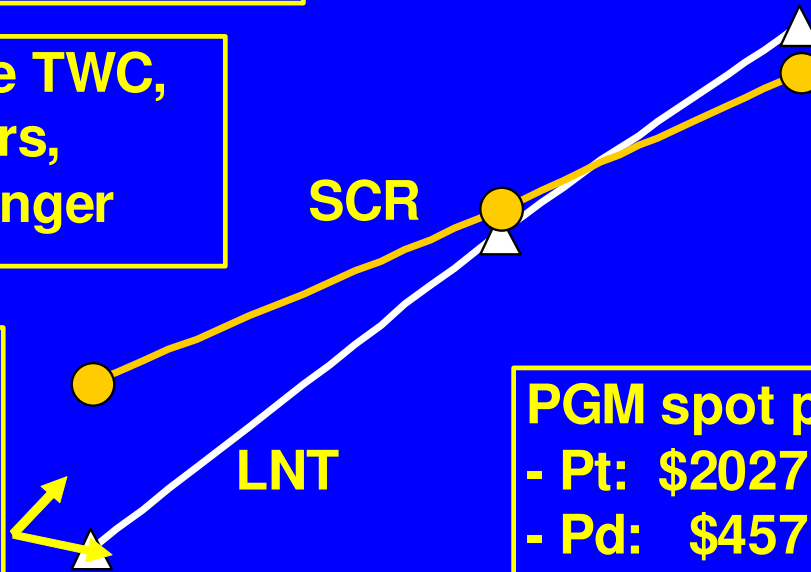
LNT costs include TWC, LNT, cans, sensors, active heat exchanger

Tier 2 Bin 5
1:1 ratio of LNT
or SCR Volume
to ESV

PGM spot prices 4-22-08
- Pt: \$2027 per oz
- Pd: \$457 per oz
- Rh: \$9080 per oz

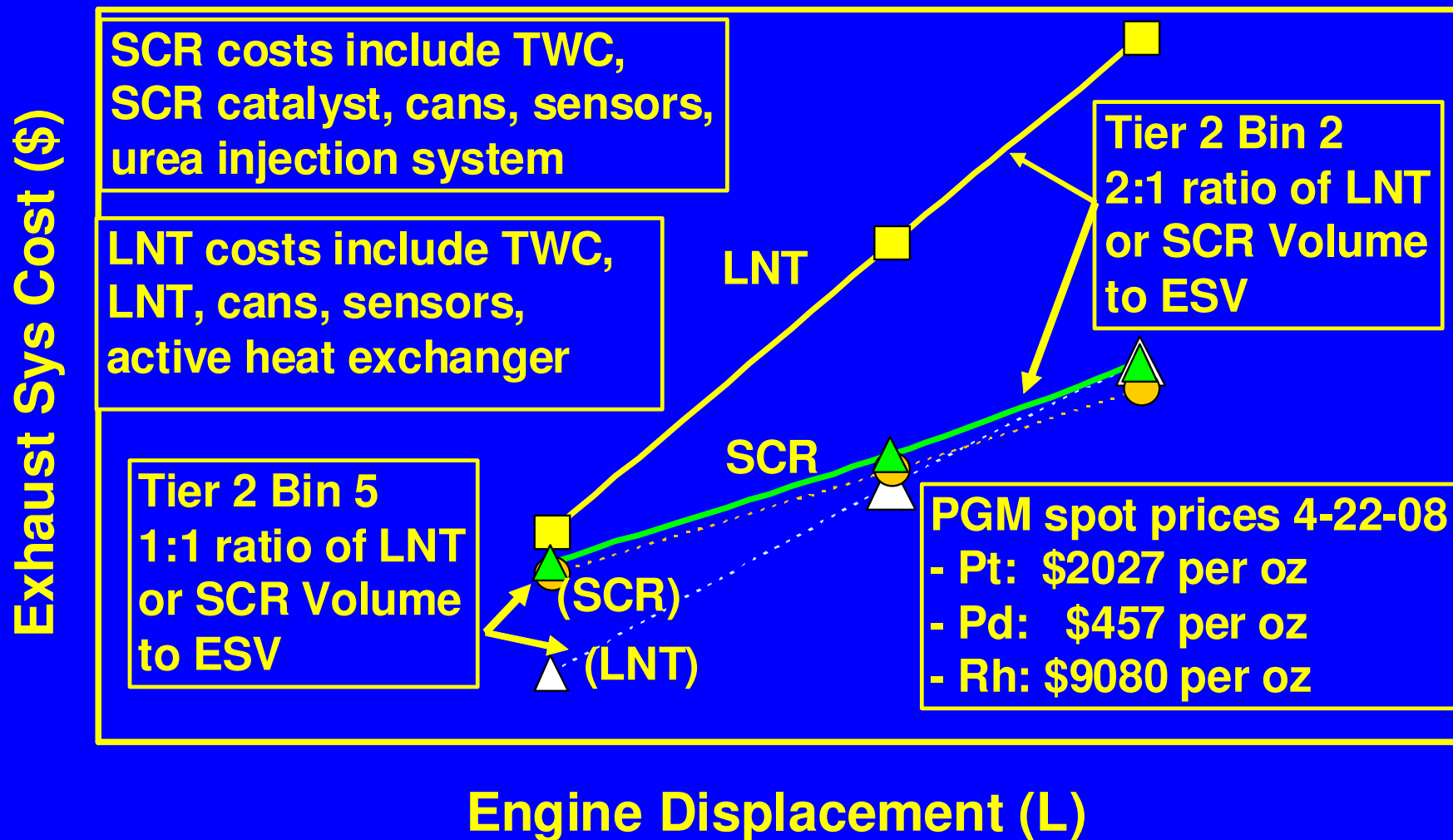
Engine Displacement (L)

For Tier 2 Bin 5 standards (1:1 volume/ESV), LNT is favorable in cost for small engines due to high cost of urea injection system.



Comparison of LNT & SCR Costs

Tier 2 Bin 2 Emissions (2:1 volume/ESV)



With Tier 2 Bin 2 standards (2:1 volume/ESV), SCR is favorable in cost even for small engines due to high cost of PGM in LNT.

Conclusions

SCR with urea is attractive alternative to LNT for lean NO_x control on stratified-charge direct-injection gasoline (GDI) engines,

- Wider temperature window
- Lower catalyst costs
- More robust to NO level
- No rich purges

State-of-the-art Fe/zeolite & Cu/zeolite SCR formulations have sufficient durability for underfloor applications on GDI engines

Sulfur poisoning resulted in modest decrease in NO_x conversion

Cu SCR desulfated under lean conditions in 5 minutes at 600°C

Fe SCR desulfated under lean conditions in 5 minutes at 750°C

Zoned combination of Fe SCR + Cu SCR (2:1 ratio) with space velocity of 8.3K hr⁻¹ provided high NO_x conversion over broad range of temperature

Large SCR volume + optimized NH₃/NO ratios resulted in high NO_x conversions and low NH₃ slip over broad range of T and NO levels

NO_x Control at Low Temperatures

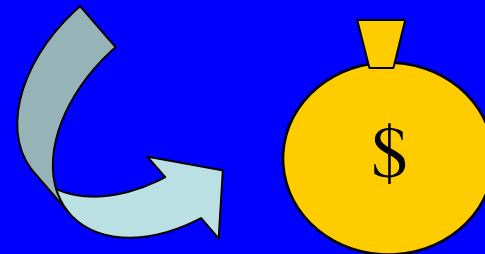
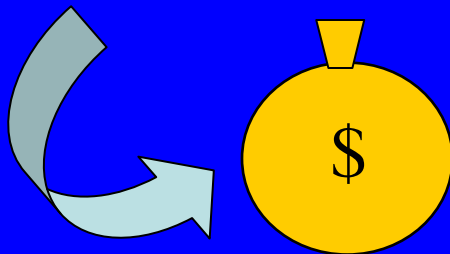
Diesel engines and turbo-charged lean-burn gasoline engines
> Low exhaust temperatures at low & medium loads
> Often below optimum range for LNTs (300-350°C)

LNT

Pt ↑ Increase NO oxidation
Rh ↑ Increase NO_x reduction
→ Purgability at low T
(SAE 2007-01-1055)

SCR

Low catalyst costs (no PGM)
Urea injection system (\$\$)



in-situ LNT+SCR



Cu SCR uses NH_3 generated by LNT during rich purges to

- > Decrease NO_x release from LNT during purge by promoting reaction between NH_3 & released NO_x**
- > Adsorbs NH_3 and uses it to decrease NO_x slip from LNT during next lean period**

Cost-effective method to improve conversion at low T

- > Gain low temperature benefit of SCR without urea injection system**

Could allow Rh reduction in high-loaded zone of LNT

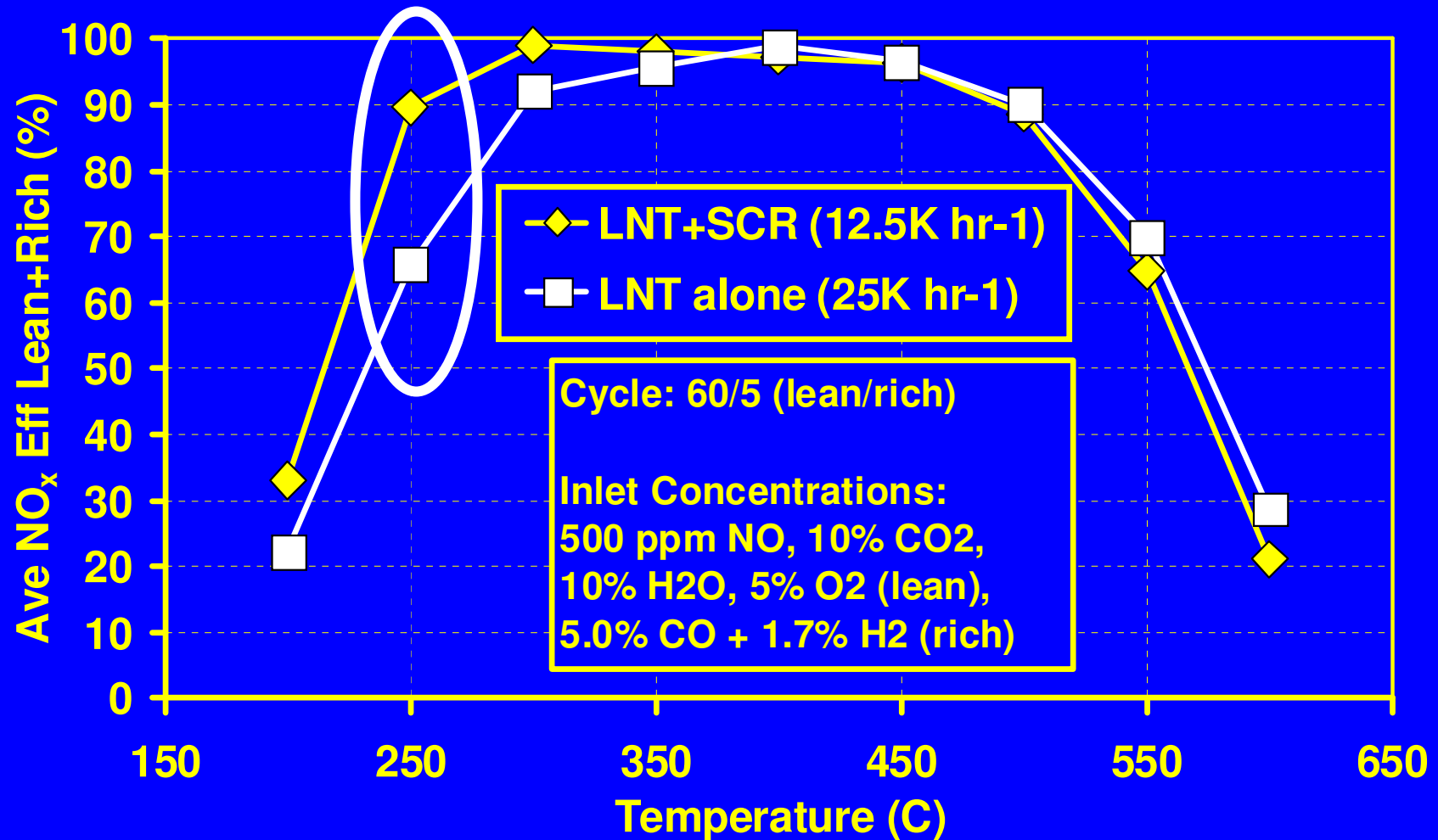
SCR catalyst is effective for reducing H_2S during desulfations

Cu SCR does not improve NO_x conversion at high T

- > LNT volume determined by requirements under high flow and high temperature conditions**

LNT+SCR in-situ

LNT+SCR, Aged 4.5 hrs 700°C w/ Wobbles (deSO_x)
Evaluated on 60/5 Test

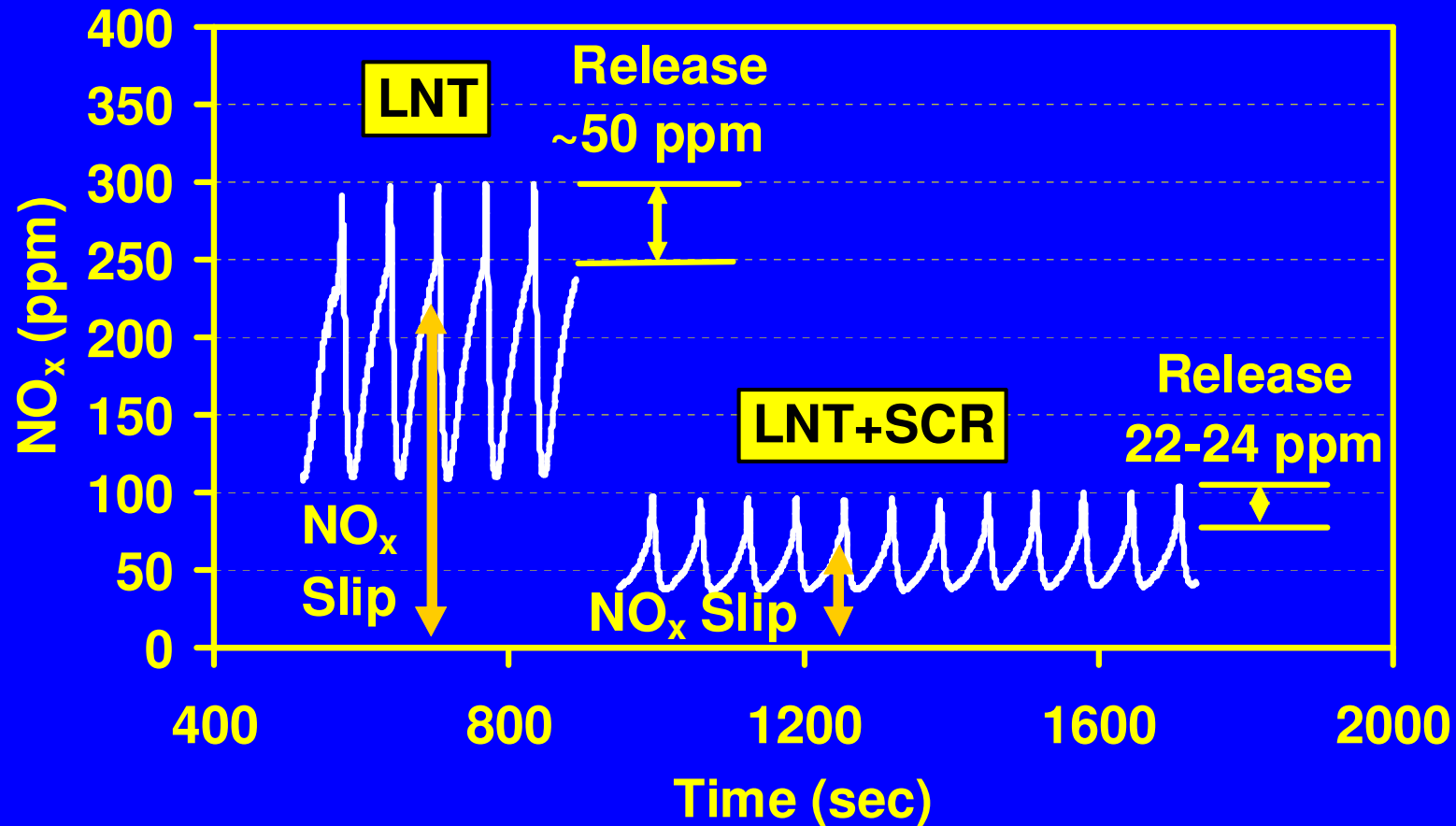


Cu SCR improves NO_x conversion at 250-300°C.

LNT+SCR in-situ

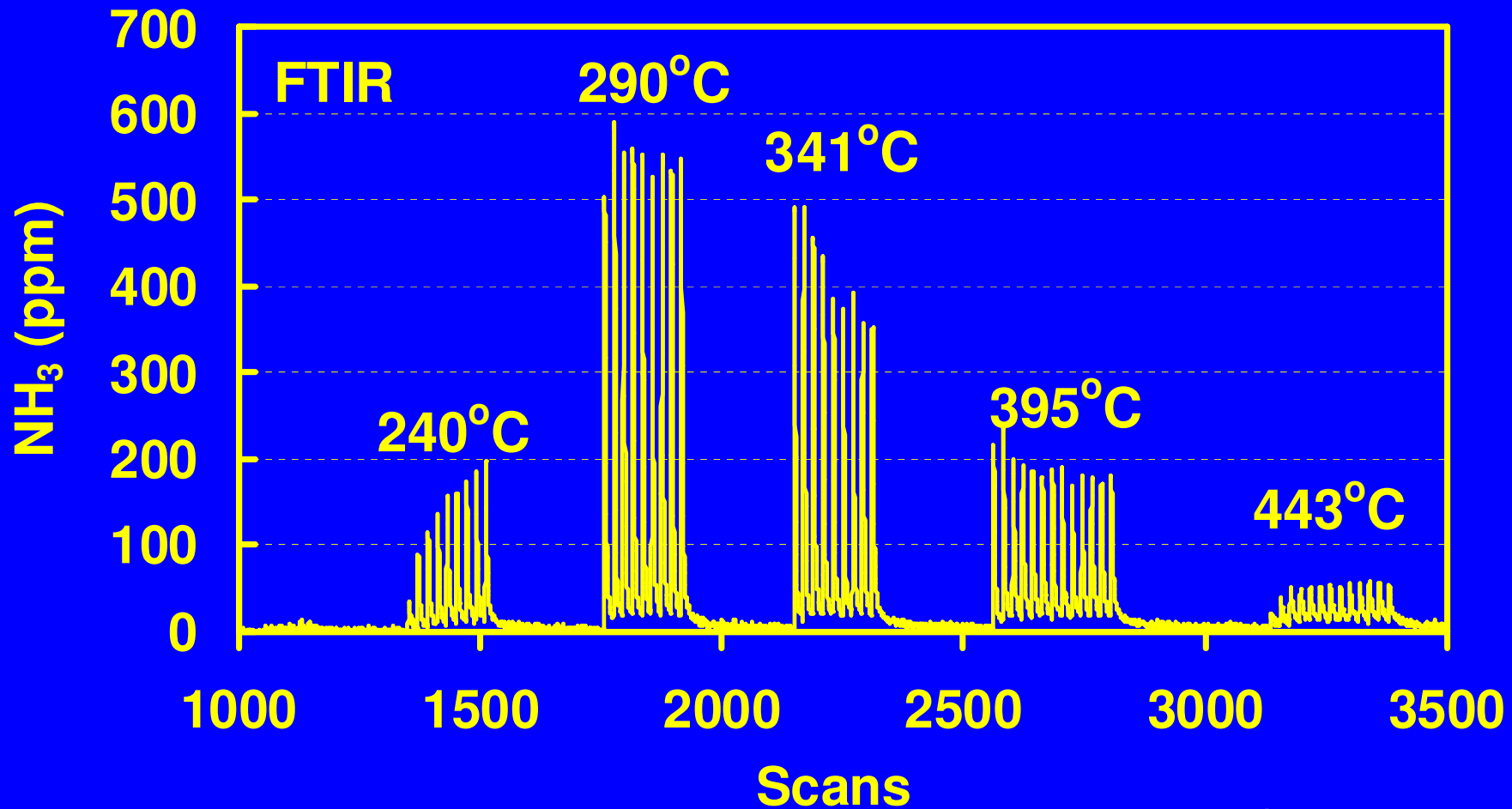
LNT + Cu/Zelite SCR at 250°C

Aged 700°C 4.5 hrs with A/F wobbles (deSOx)



The NO_x release during purges and the NO_x slip during lean operation both decrease with SCR installed behind LNT.

NH₃ vs Inlet Temperature, 60/5, 30K hr⁻¹ LNT from MB E-320, 120K miles equiv.

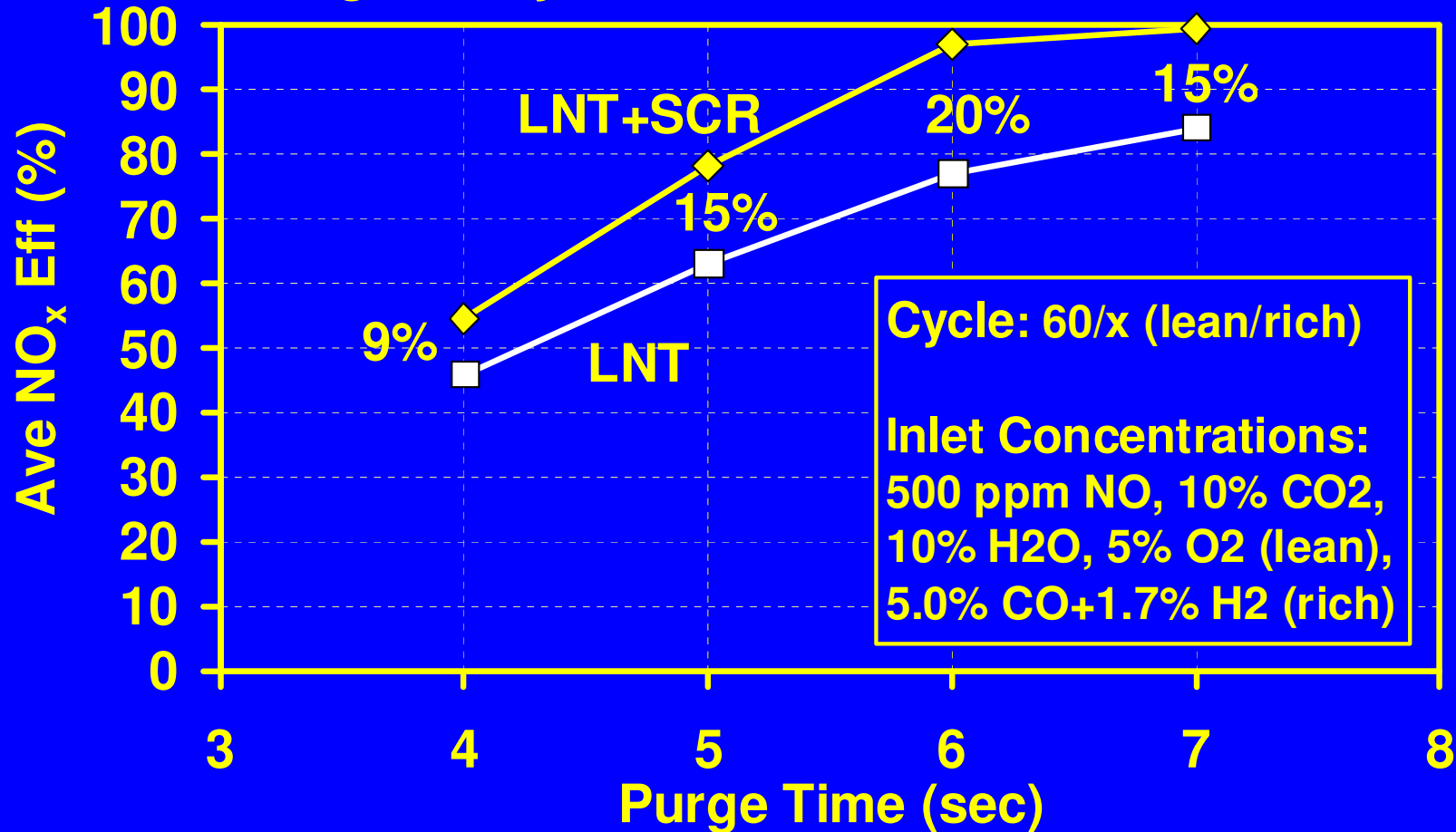


Under these conditions, the NH₃ slip from the LNT maximized at around 300°C.

Courtesy of
Lifeng Xu, FMC

LNT+SCR in-situ

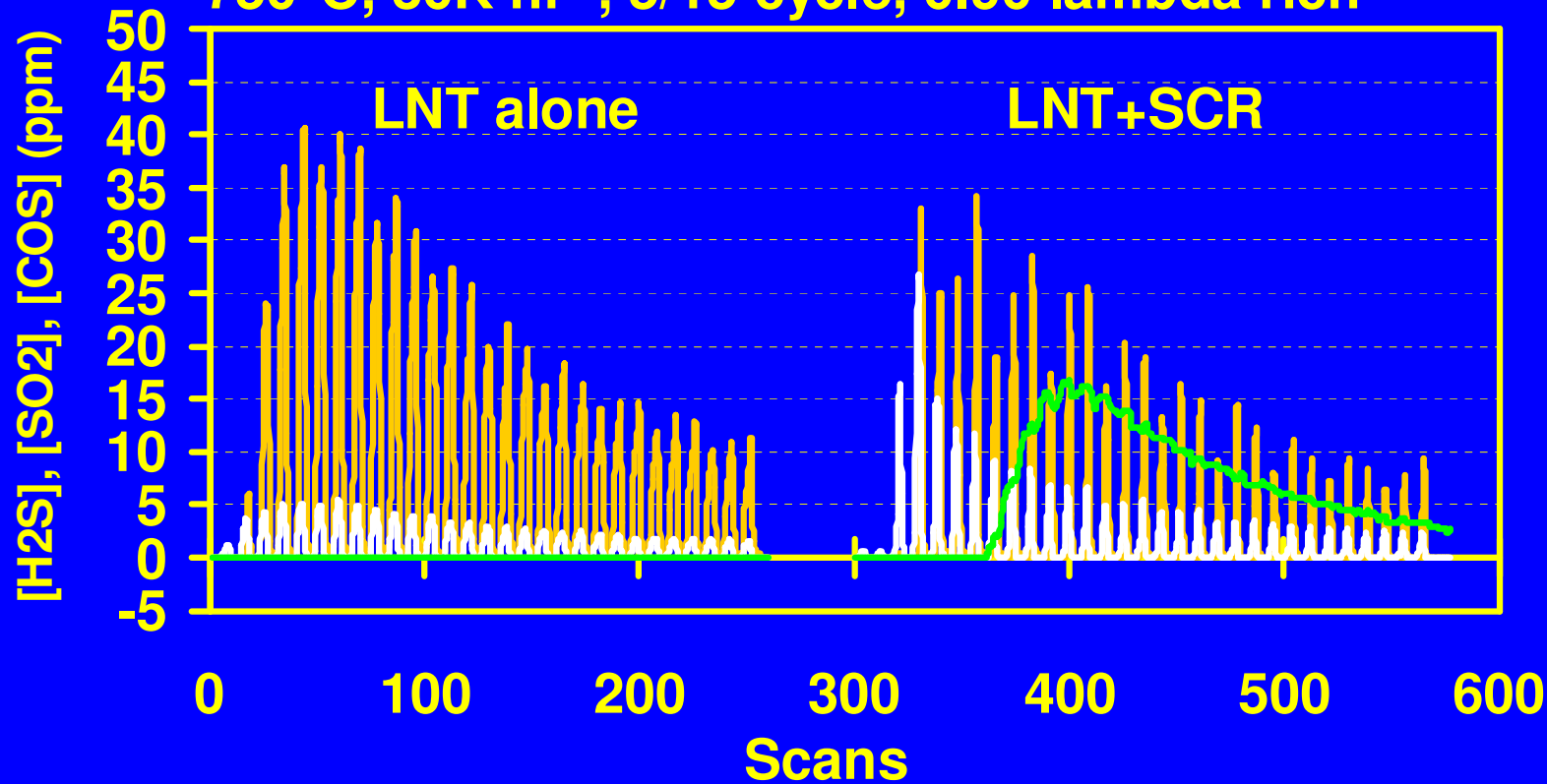
LNT+SCR, Aged 13.5 hrs at 700°C Wobbles
Purge Study at 250°C with 5%CO+1.7% H₂



Benefit of SCR increases as purge time increases
- LNT generates more NH₃

Effect of SCR Catalyst on H₂S Emissions

LNT & SCR from MB E-320, 50K mi Equiv
750°C, 30K hr⁻¹, 5/15 cycle, 0.90 lambda rich



— H₂S(ppm) — COS(ppm) — SO₂(ppm)

SCR oxidizes H₂S from LNT
into SO₂ (and COS).

Courtesy of
Lifeng Xu, FMC

Conclusions

Adding Cu SCR catalyst behind LNT is a cost-effective method for improving low temperature NO_x performance

The SCR catalyst reduces the purge NO_x release as well as the NO_x slip during lean operation

Addition of Cu SCR catalyst may allow some reduction in Rh level in high loaded zone of LNT

Benefit of SCR increases with increasing purge time
- Increased NH₃ production from LNT

SCR helps decrease H₂S emissions during desulfations

Cu SCR catalyst provides no benefit at high temperatures
- Required LNT volume determined at high flows & T

Need rich breakthrough from LNT to generate NH₃ for SCR
- HC and CO slip could be issues