Protection of Diesel Exhaust Aftertreatment Systems: A Thermodynamic and Experimental Evaluation

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Can Additives be Used to Protect Exhaust Catalysts and Traps

Ethyl

- Background
- Theory behind scavenging
- Results of preliminary testing in lean-NOx traps
- Possible applications

Diesel Exhaust Aftertreatment

- Emissions regulations are driving the implementation of exhaust aftertreatment for diesel powered vehicles
- Systems issues - hardware, fuel & lubricant
- Many current and proposed aftertreatment hardware technologies are negatively effected by sulfur and phosphorous, other deactivators?
- Is a potential solution scavenging P & S with additives before interaction with hardware??

Additives are Widely Used in Diesel Fuel

Ethyl

- **Detergents** - maintaining engine cleanliness
- **Ignition (cetane) improvers** - improve engine operation, reduce white smoke and noise, lower emissions, improve cold start and provide refinery flexibility
- **Lubricity Additives** - inhibit wear - pumps and injectors
- **Operability additives** - reduce or eliminate wax build-up and filter plugging problems in cold weather
- **Stability additives, conductivity improvers, demulsifiers, biocides**
- **Combustion Improvers** - reduce smoke and particulates
- **Light-off additives/catalysts (FBCs)** for particulate traps
- **Phosphorous and sulfur scavengers???**

Fuel Additives May Help Maintain Catalyst's Efficiency and Improve Durability

Ethyl

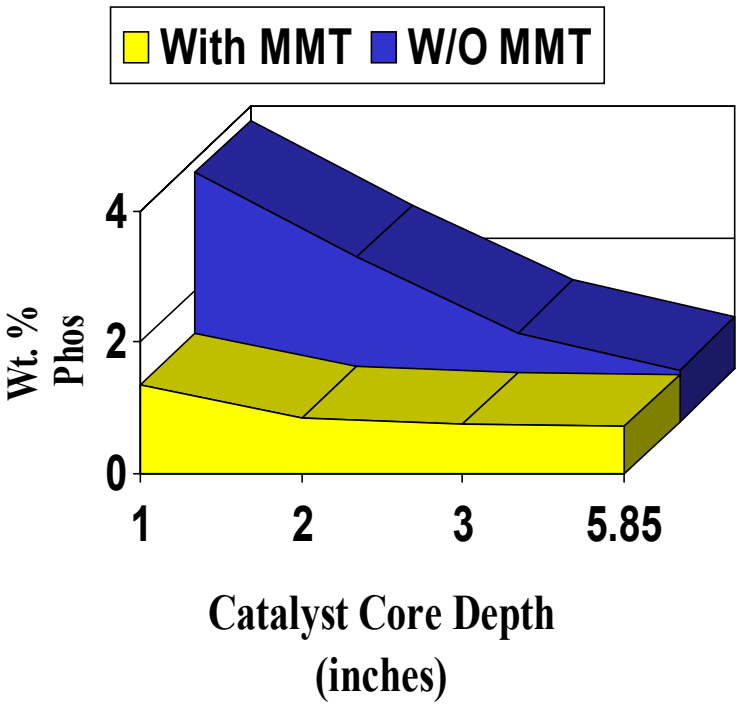
- P & S chemistry used in motor oil to prevent wear and oxidation (prevents engine sludge)
- Sulfur is naturally occurring in diesel fuel
- Manganese based fuels additive, MMT, combustion products have been shown to scavenge phosphorus and sulfur and reduce deposition on catalysts

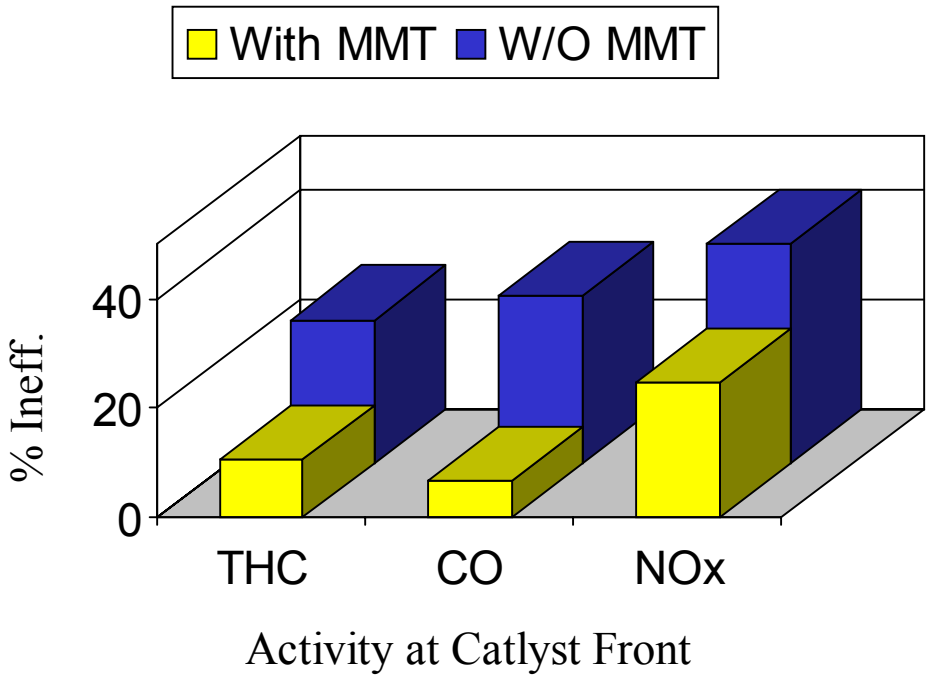
"Use of MMT significantly reduces phosphorus and zinc retention levels at catalyst inlets…" ***Major OEM SAE Paper 821193***

- Will show that catalysts aged using fuel treated with MMT display less degradation than catalysts aged using fuel without MMT and maintain higher conversion efficiency.

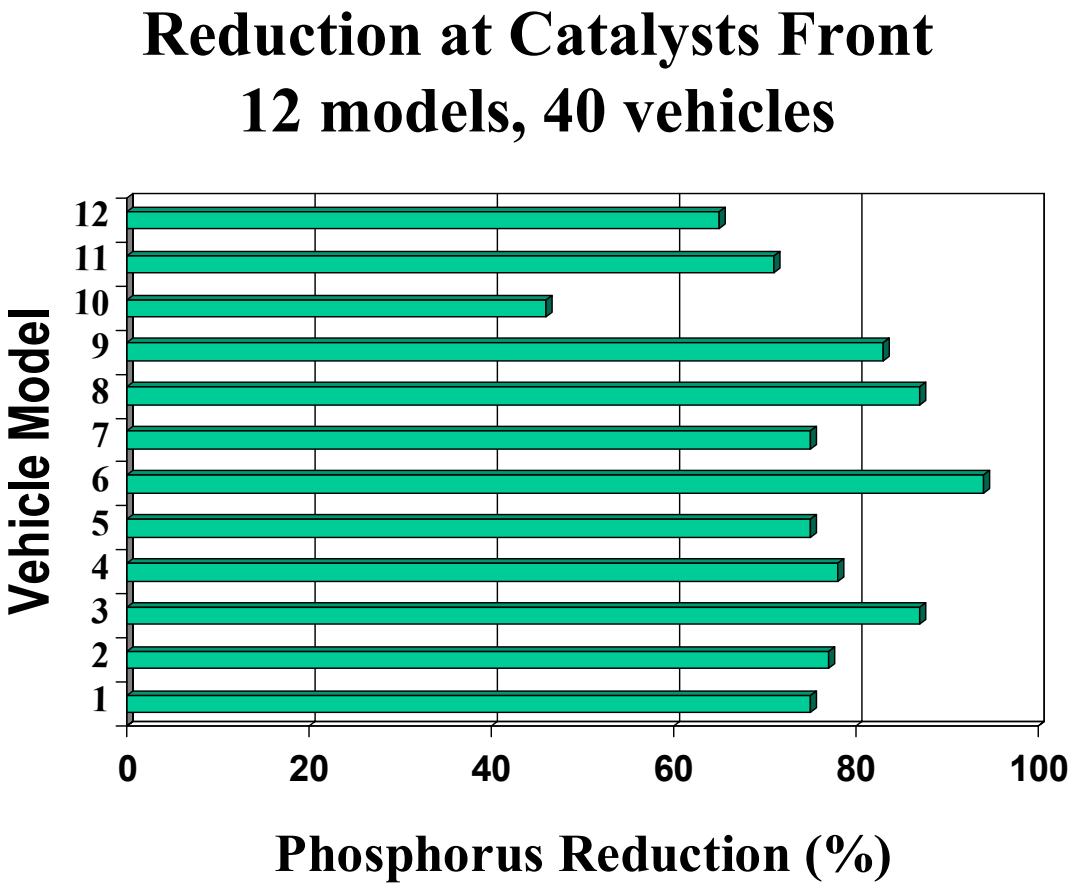
MMT Can Reduce Phosphorous Deposition

1993 Tier 0 (gasoline) vehicles, 100,000 mile





Phosphorus Deposition is Reduced with Use of MMT Treated Gasoline



Oxidation and TWC, close coupled and under-floor placement

Combustion Products of MMT from Gasoline Engine

Ethyl

Mn present primarily in divalent form

Cycle/mile	MnO's	$MnSO_4$	Mn^{++}(Phos)
FTP 4K	21	36	43
UDC 4K	24	29	47
Average	**23**	**33**	**45**
FTP 40K	26	37	36
UDC 40K	27	29	44
Average	**26**	**33**	**40**

Vehicle operation and mileage accumulation did not effect primary species

XAS K-edge analysis

Combustion Products from Diesel Engine Operating on Mn Treated Diesel Fuel

Ethyl

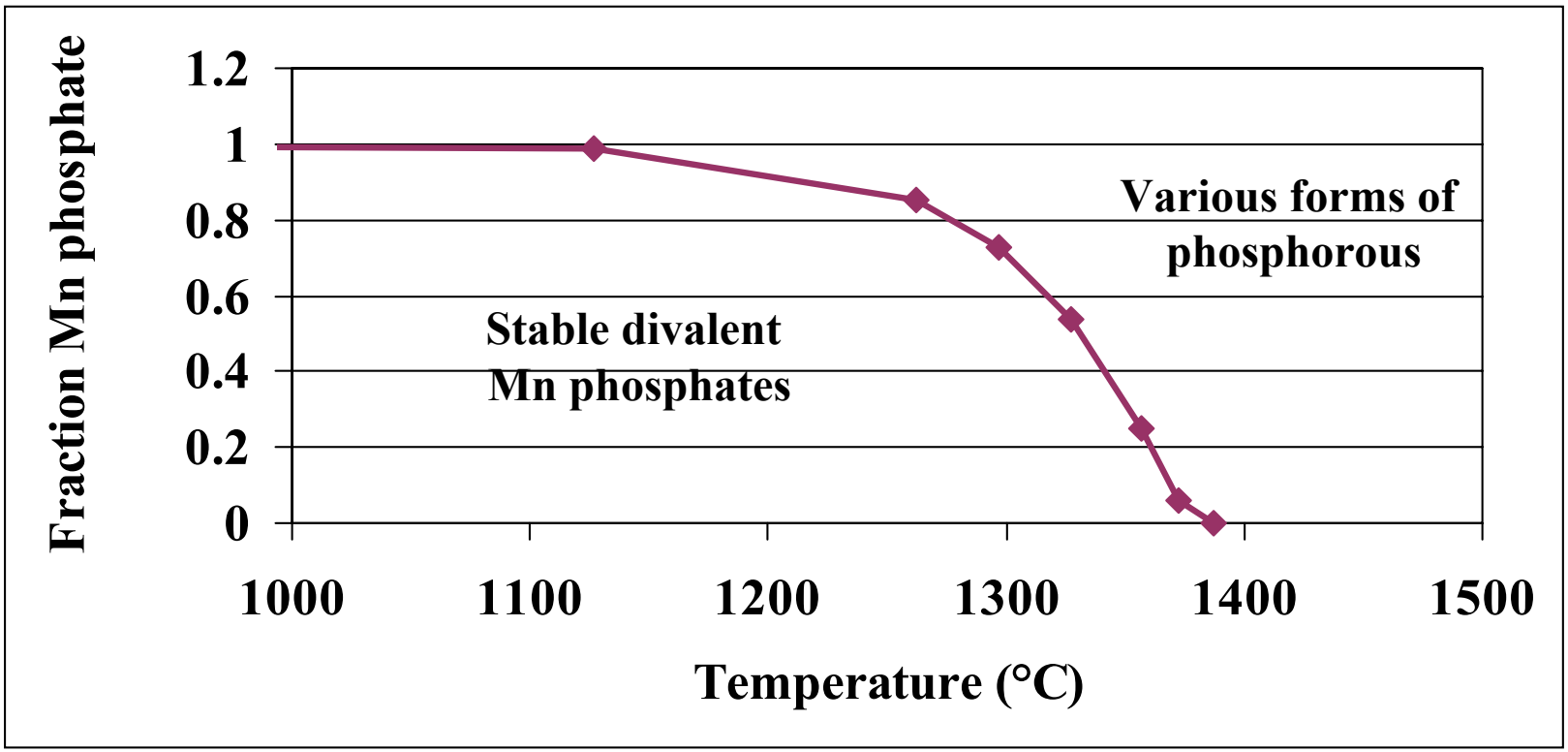
- Samples generated in HDD over transient engine dynamometer cycle
- Manganese present in divalent form as mixture of Mn phosphate, Mn sulfate and Mn oxide

	% Mn Sulfate	% Mn Phos	% Mn Oxide
1	43	54	6
2	45	55	1

XAS K-edge analysis

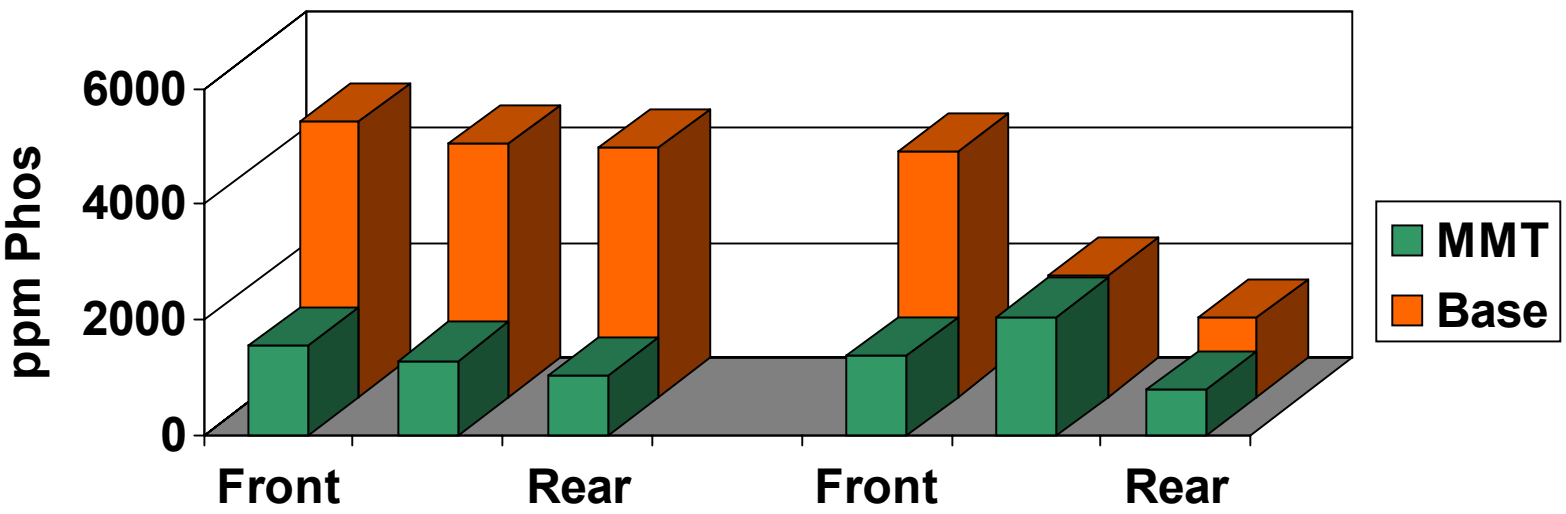
Proposed Mechanism For Phosphorus Scavenging

Manganese from combustion of MMT interacts directly with phosphorus in the combustion chamber to form divalent manganese phosphate



Phosphorus Deposition on Oxidation Catalyst - Mn Treated Fuel

Diesel Oxidation Catalyst



First Brick Second Brick

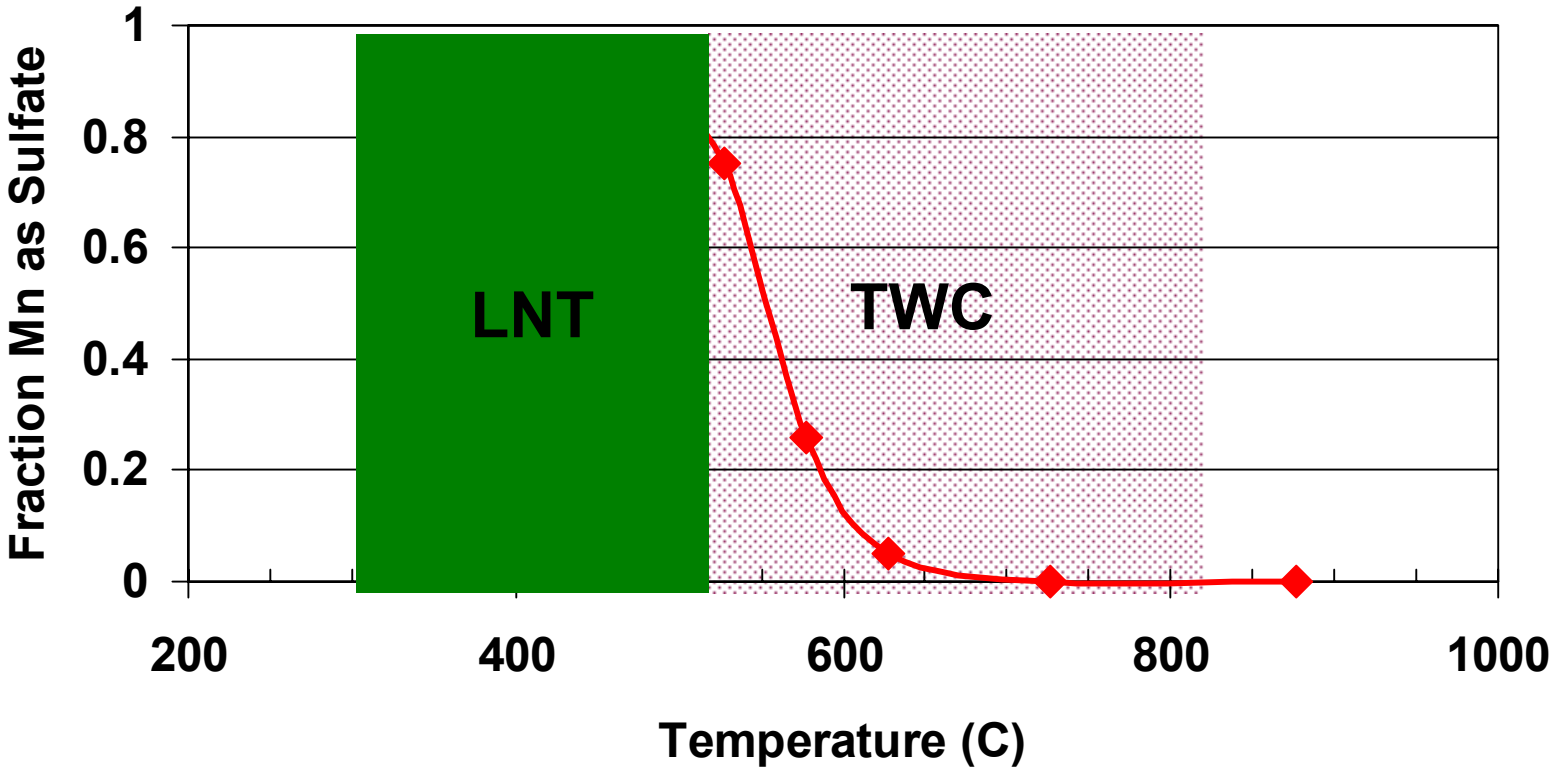
50,000 miles, durability cycle

Sulfur Scavenging with LNTs

Proposed Mechanism For Sulfur Scavenging

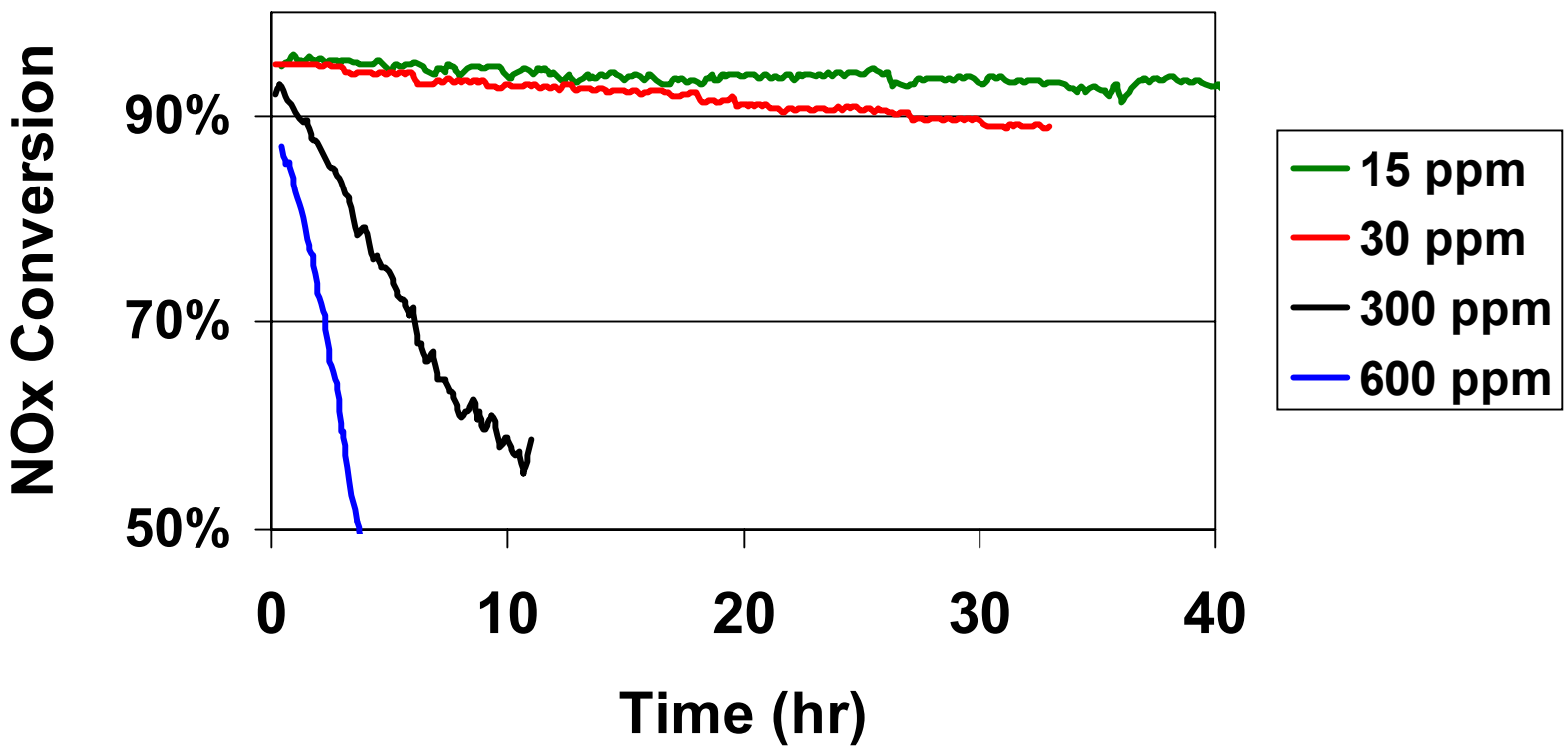
Ethyl

Manganese from combustion of MMT interacts with sulfur species in the exhaust as the exhaust temperatures drop to form Mn sulfate Mn sulfate is stable below 500°C question.



Sulfur Impact on NOx Trap

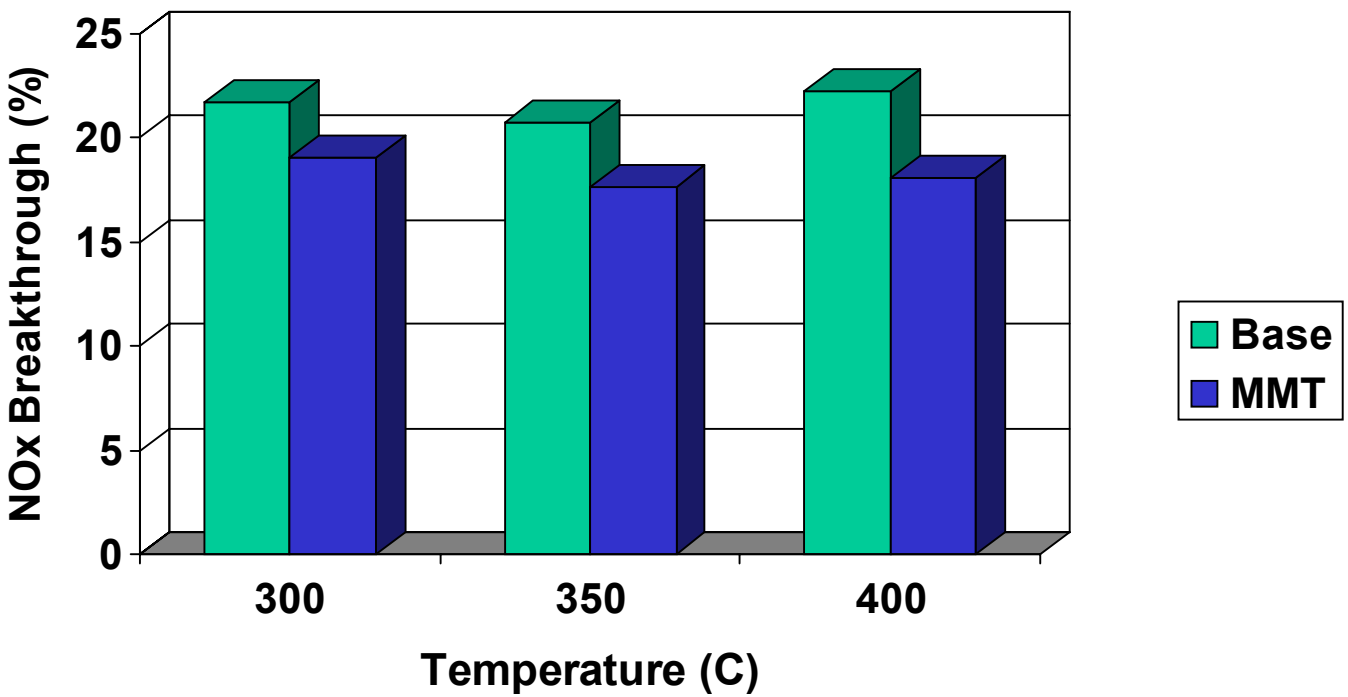
Increased sulfur increases rate
at which NOx conversion declines



Commercial LNT. Aging conducted in a laboratory system

NOx Breakthrough After Operating LNT 46 Hours on 30 ppm Sulfur Fuel

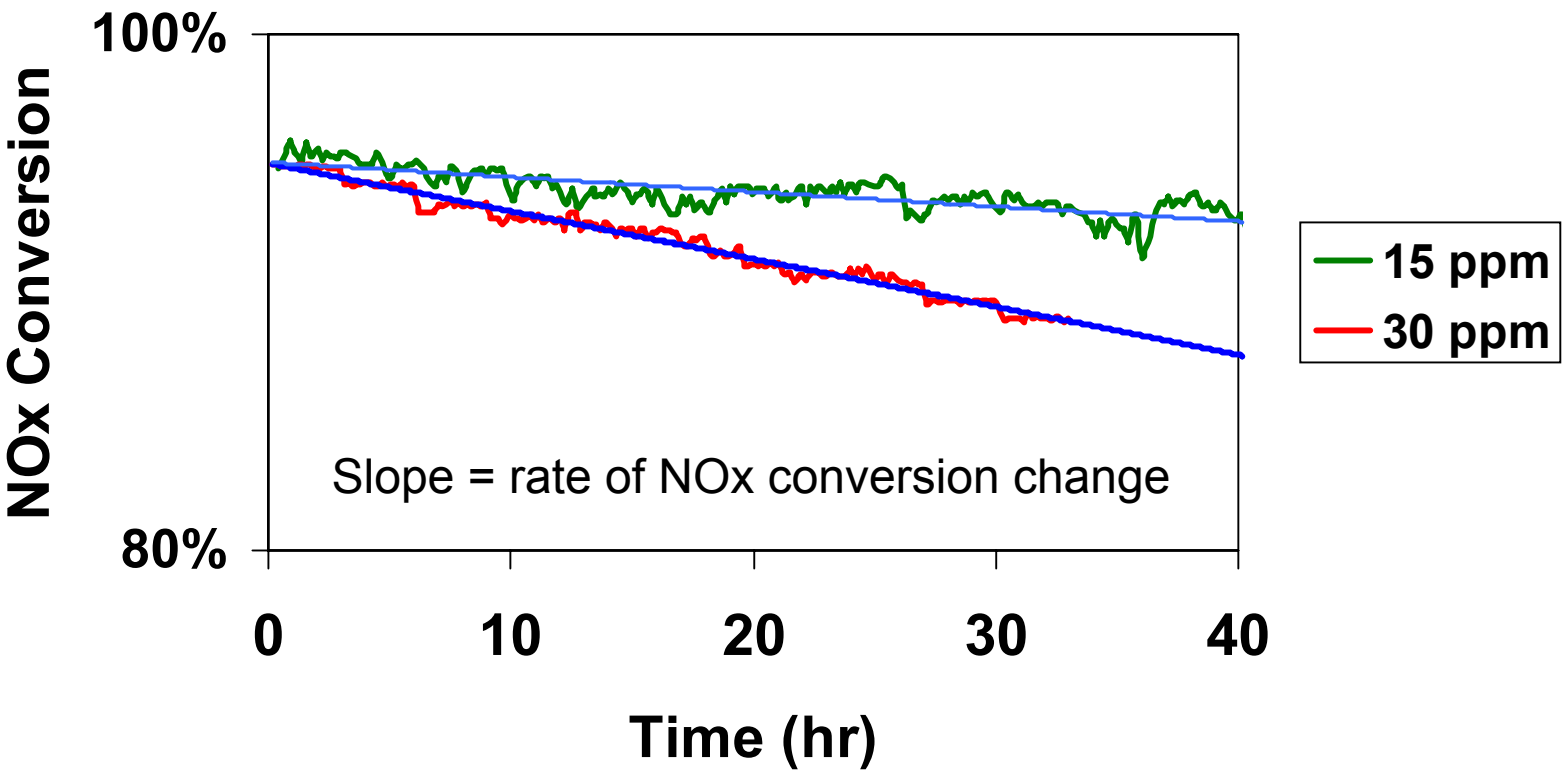
NOx breakthrough about 15-20% greater with base fuel



Catalyst aged with base fuel followed by regeneration and then MMT fuel aging. Base fuel did not contain additive. MMT fuel contained MMT at 18 mg Mn/liter

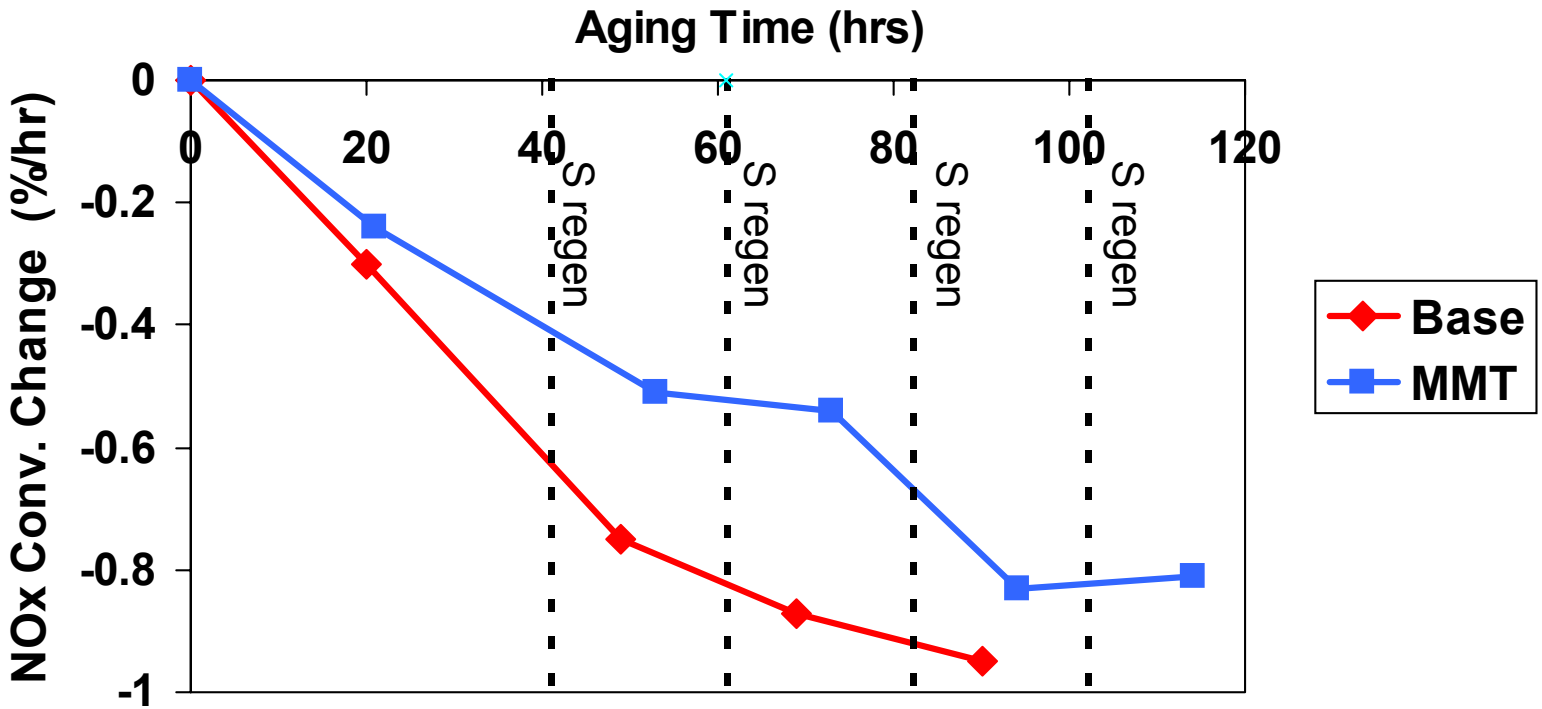
Rate of NOx Conversion Change

Rate of NOx Conversion Change Increases with Sulfur



Commercial LNT. Aging conducted in a laboratory system

Rate of NOx Conversion Change Consecutive S Regeneration



Commercial NOx trap aged with base (30 ppm S) fuel.
Base fuel treated @ 18 mg Mn/liter for MMT case.

Summary and Plans

- Fuel additives are commonly used to solve fuel and hardware problems and provide refining flexibility. Additive scavenging of catalyst deactivators could improve catalyst durability and efficiency.
- P and S scavenging has been demonstrated under diesel exhaust conditions
  - Observed reduced degradation from P deposition
  - Reduce S contamination of aftertreatment system
  - May be possibly to extend the time between catalyst desulfurizations.
- Aftertreatment equipped diesel engine demonstrations are underway