NOx Adsorber Catalysts: Sorption, Regeneration, and DeSulfation

Jim Parks, Aaron Watson, Greg Campbell, Bill Epling, Larry Campbell
EmeraChem (Formerly Goal Line Environmental Technologies), Knoxville, TN

2nd DOE CLEERS Workshop: NOx Adsorbers
Ford Scientific Research Laboratory, Dearborn, MI
October 16-7, 2001

Technical Contact:
Jim Parks
EmeraChem
11141 Outlet Drive
Knoxville, TN 37932
www.emerachem.com

SCONOx™ Catalyst Chemistry

SCONOx™ Operation is Cyclic

(1) Sorption Period: Oxidation/Capture Occurs

- $2\ NO + O_2 + Pt + K_2CO_3 \text{ ----> } KNO_2 + KNO_3 + Pt + CO_2$
  - $2NO_2 + K_2CO_3 \text{ --> } KNO_2 + KNO_3 + CO_2$
  - $2NO_2 + 1/2\ O_2 + K_2CO_3 \text{ --> } 2KNO_3 + CO_2$
  - $3NO_2 + K_2CO_3 \text{ --> } 2KNO_3 + CO_2 + NO$

(2) Regeneration Period: Reduction/Reactivation

Reduction with Hydrogen [Efficient at Temperatures As Low As 150˚C]:

- $KNO_2 + KNO_3 + Pt + 4\ H_2 + CO_2 \text{ ----> } 2\ KOH + N_2 + CO_2 + Pt + 3\ H_2O \text{ ----> } K_2CO_3 + N_2 + 4\ H_2O + Pt$

Reduction with Hydrocarbons [Efficiency Dependent on Light-Off]:

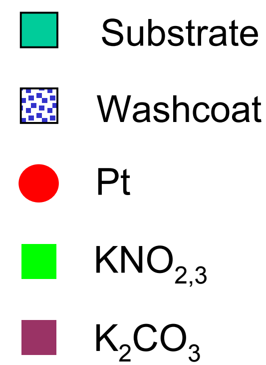
- $KNO_2 + KNO_3 + Pt + HC \text{ ----> } 2\ KOH + N_2 + CO_2 + Pt + H_2O \text{ ----> } K_2CO_3 + N_2 + 2\ H_2O + Pt$

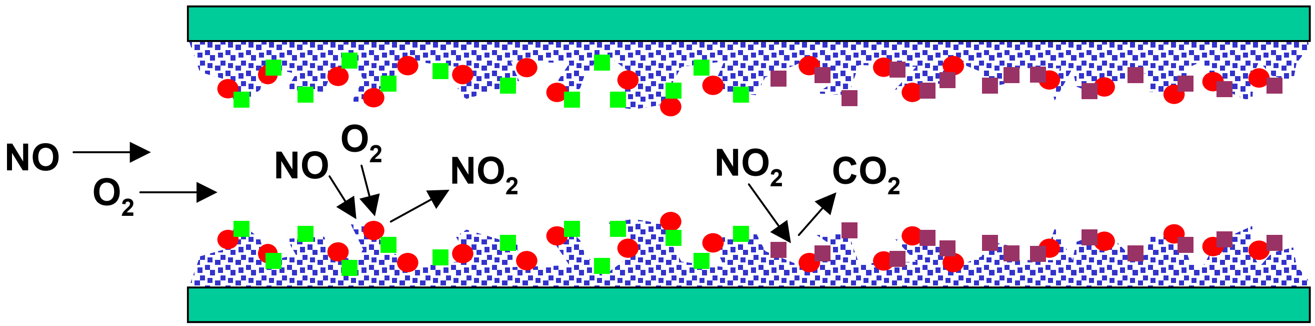
EmeraChem

Chemistry in Catalyst Cell

•Sorption (Oxidizing Atmosphere)

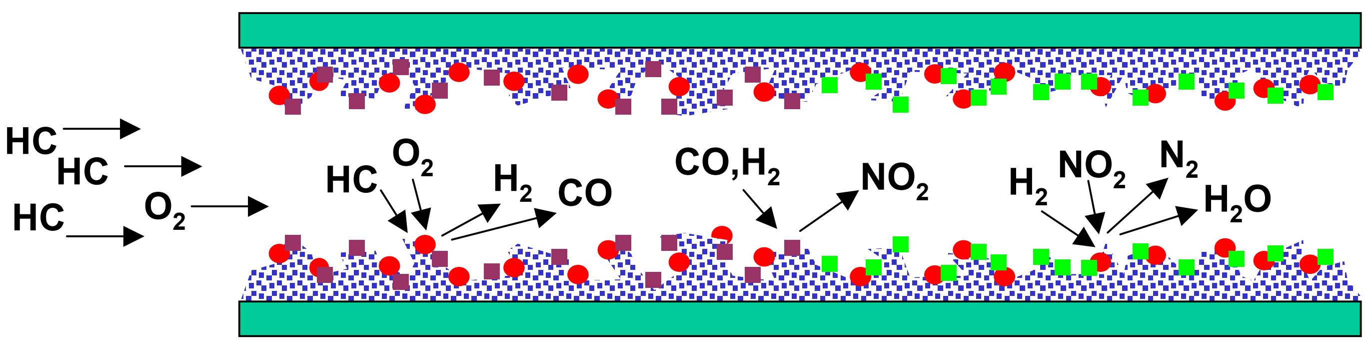
$2\ NO + O_2 + Pt + K_2CO_3$ ----> $KNO_2 + KNO_3 + Pt + CO_2$





•Regeneration (Reducing Atmosphere)

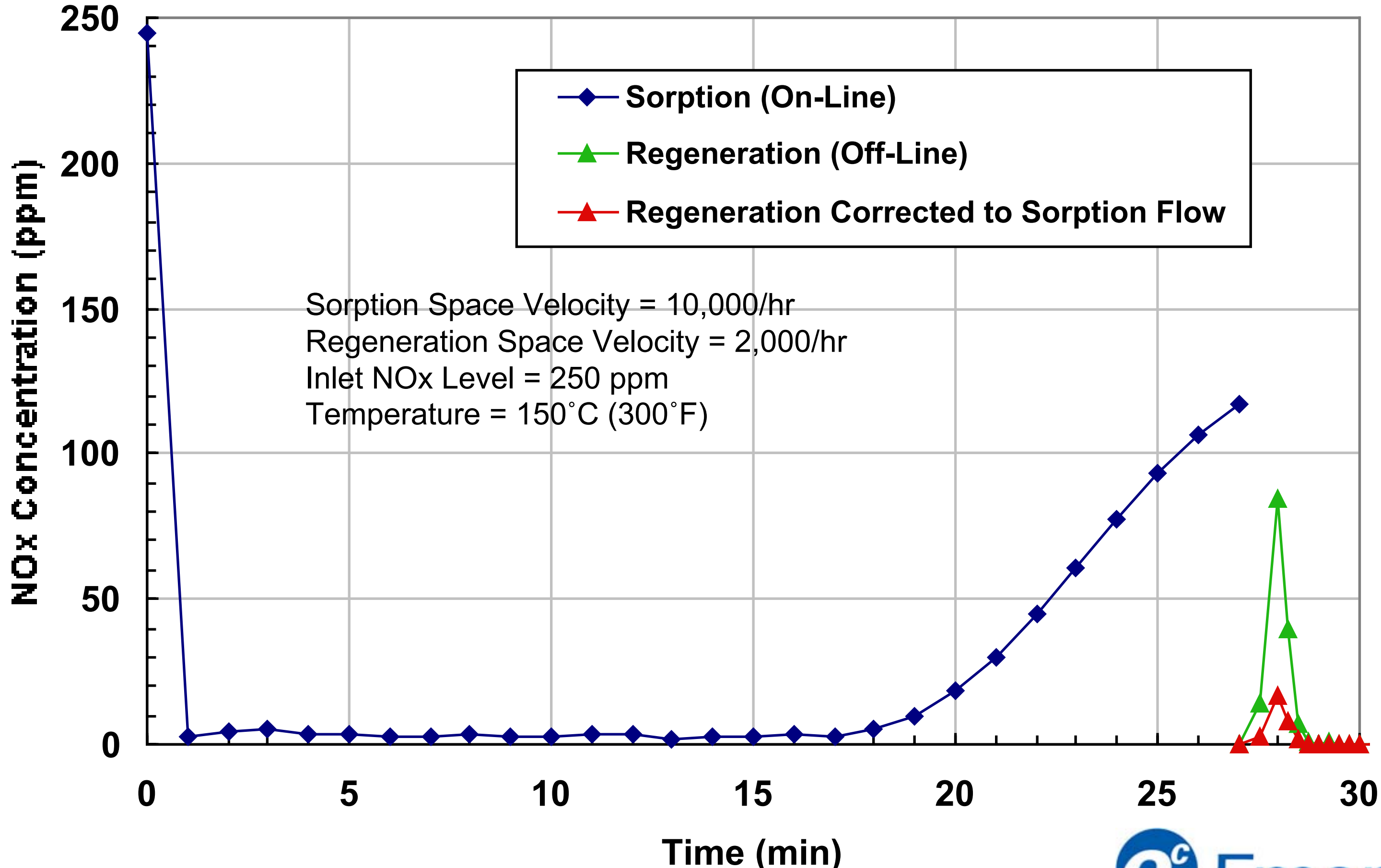
$KNO_2 + KNO_3 + Pt + CH_4$----> $2\ KOH + N_2 + CO_2 + Pt + H_2O$ ----> $K_2CO_3 + N_2 + 2\ H_2O + Pt$



EmeraChem

Bench Reactor Data: Sorption/Regeneration Cycle

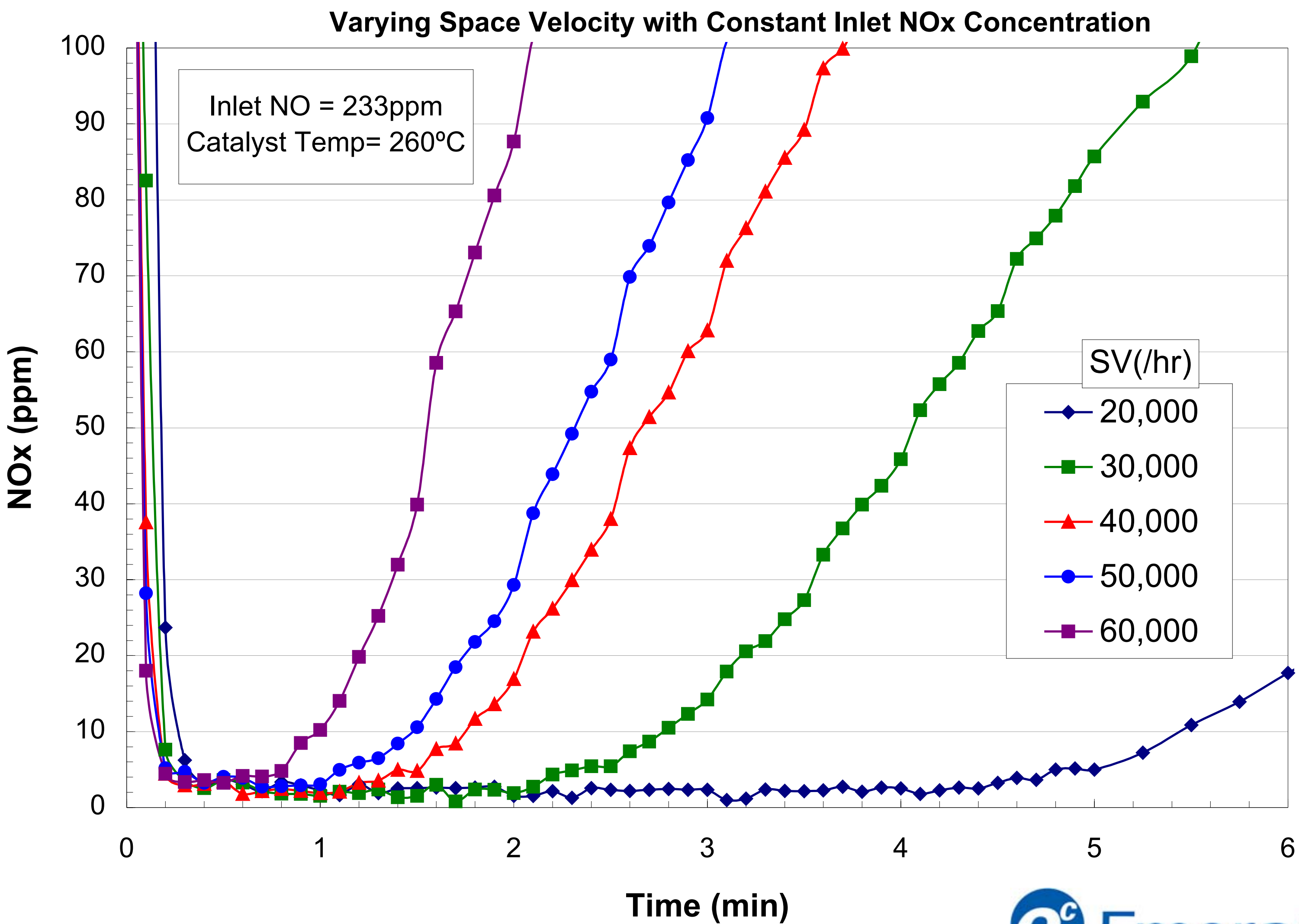
- Simulated Exhaust Flowed Over Catalyst in Bench Scale Reactor
- Sorption Plot Shows Catalyst Site Saturation Beginning at 19 minutes
- Small "Puff" of NOx is Emitted in Regeneration
- NOx Conversion is a Function of Sorption Cycle Period



EmeraChem

NOx Sorption: Varying Space Velocity

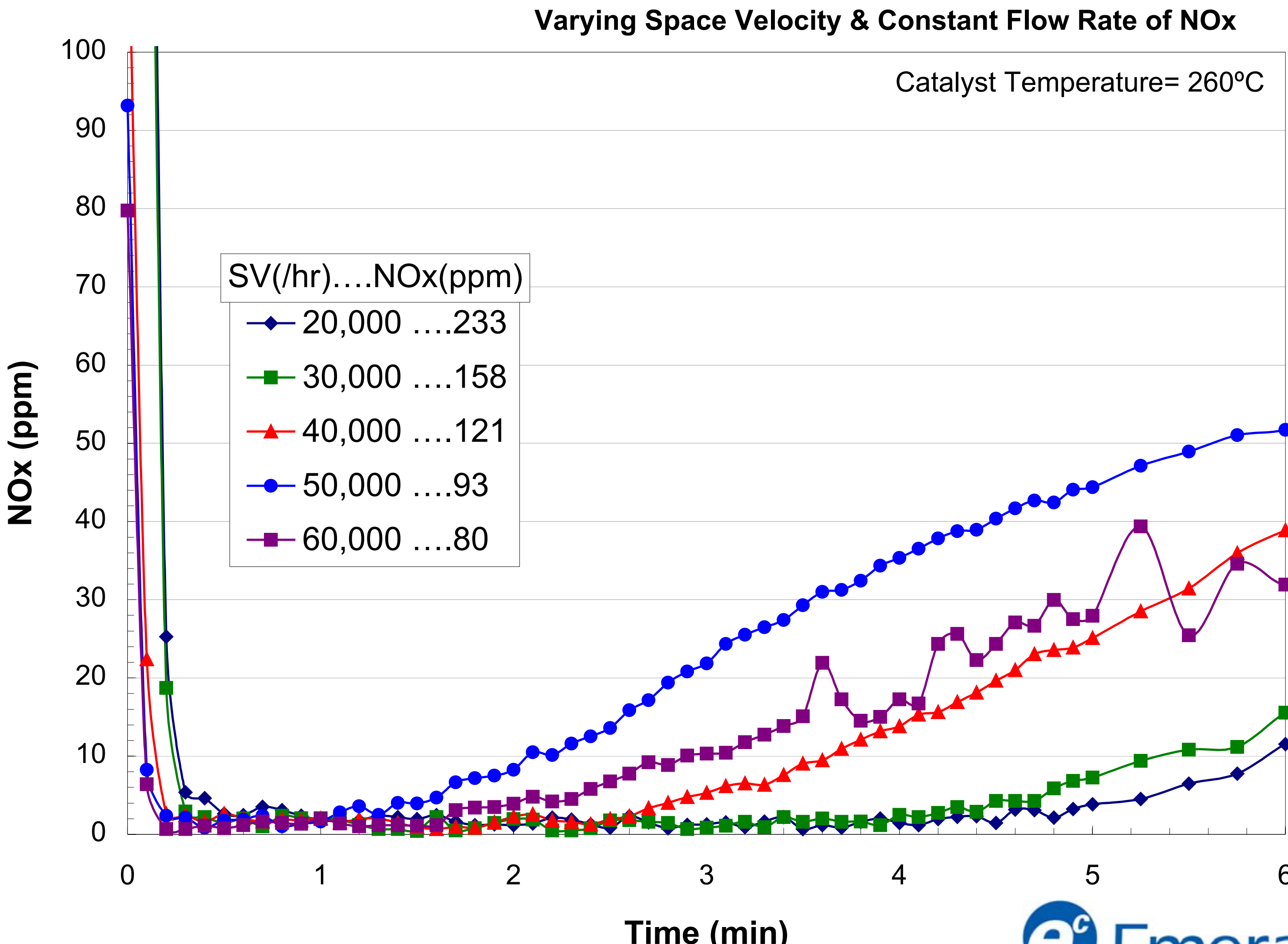
- Constant Inlet NOx Concentration; Varying Inlet NOx Mass Flow
- Conversion Efficiency High for SV of 60k/hr When Capacity Sufficient



EmeraChem

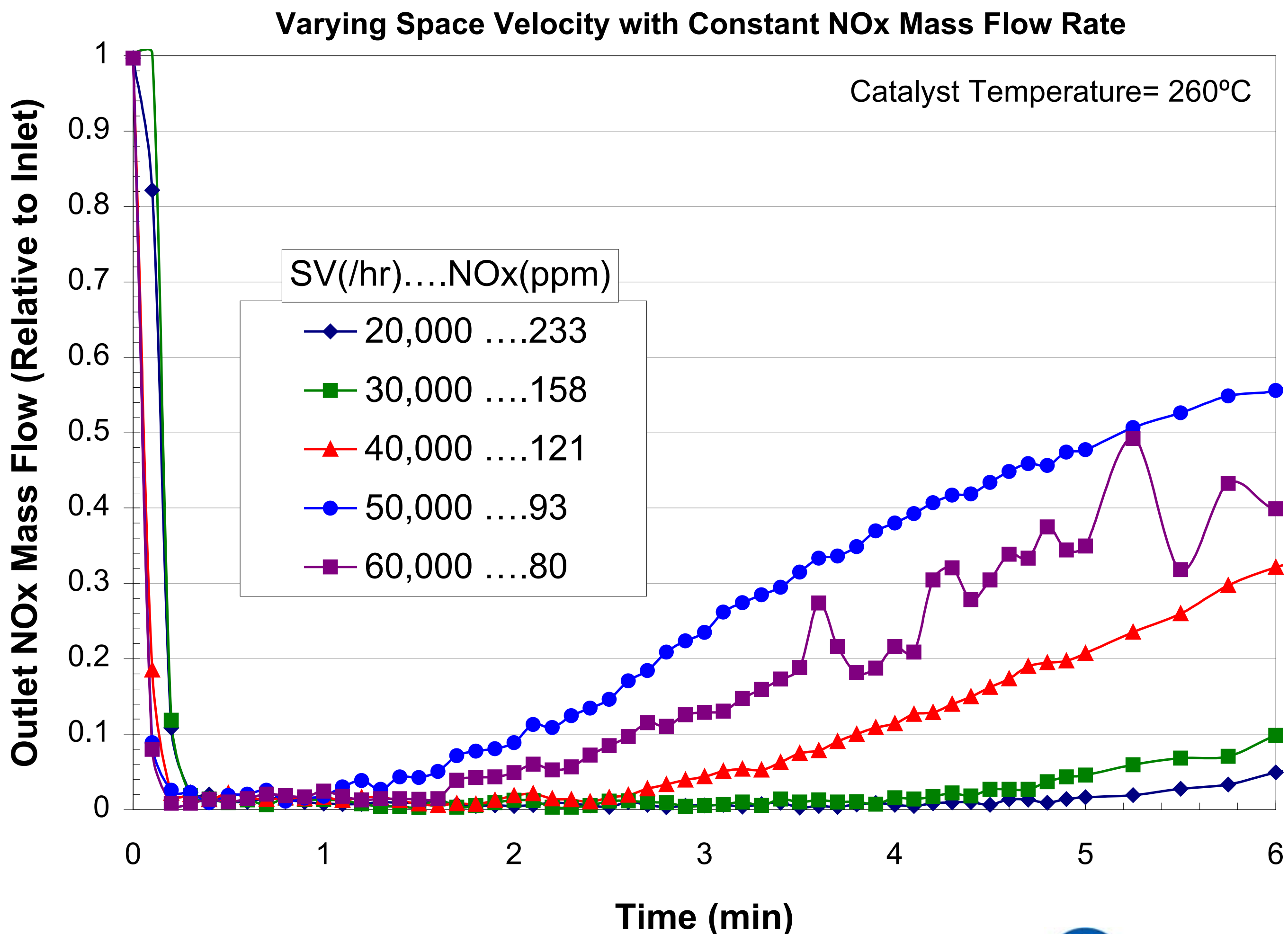
Varying Space Velocity with Constant Mass Flow

- Constant Inlet NOx Mass Flow; Varying Inlet NOx Concentration
- Sorption Profiles More Similar, But Variation Occurs



Data Normalized to Inlet NOx Mass Flow

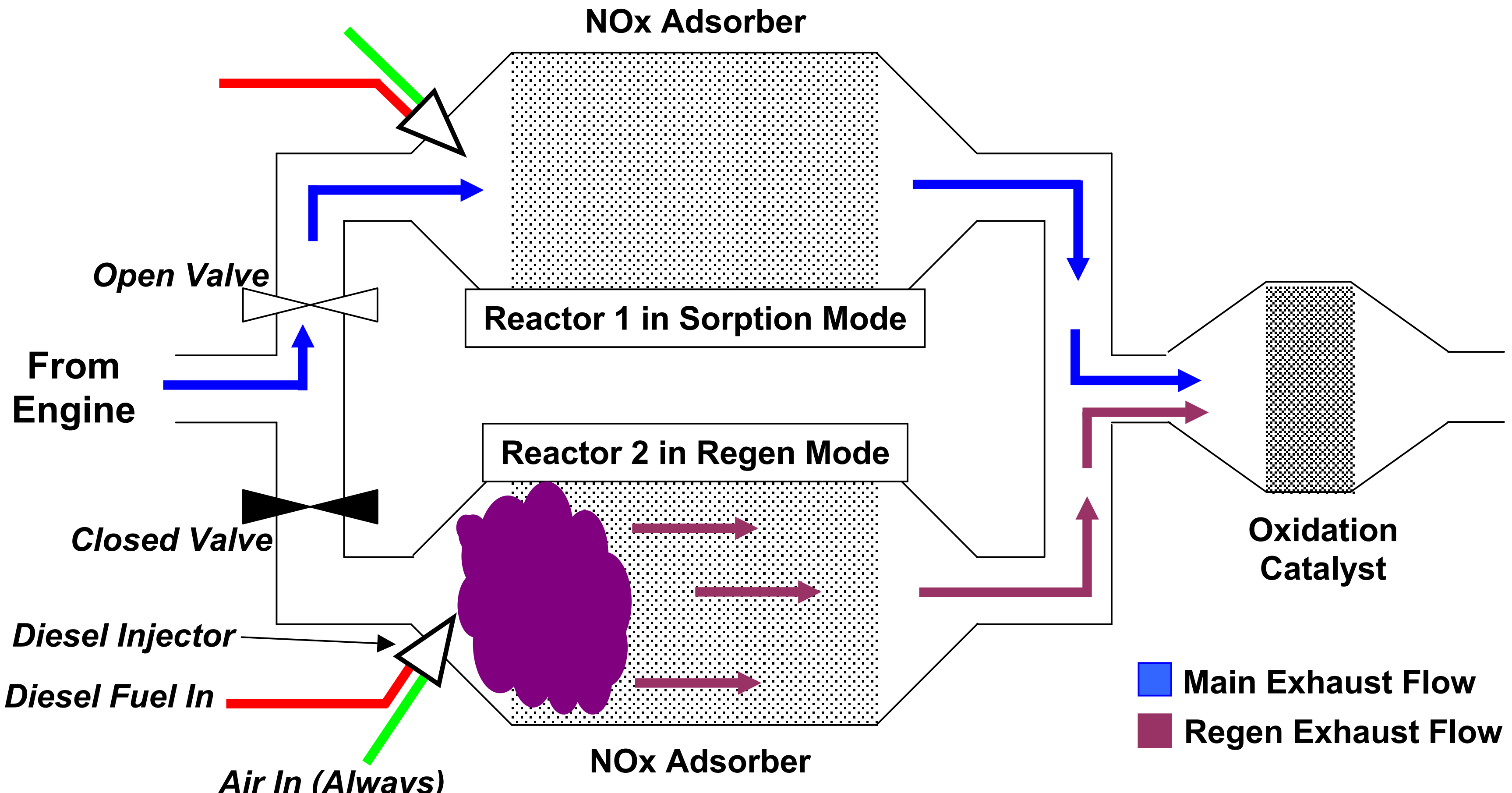
- Same Data with Varying Space Velocity
- Variation in NOx Sorption Profile Still Evident
- Does NO->NO2 Conversion and Pore Diffusion, etc. Cause Variation?



EmeraChem

Regeneration in Diesel Applications

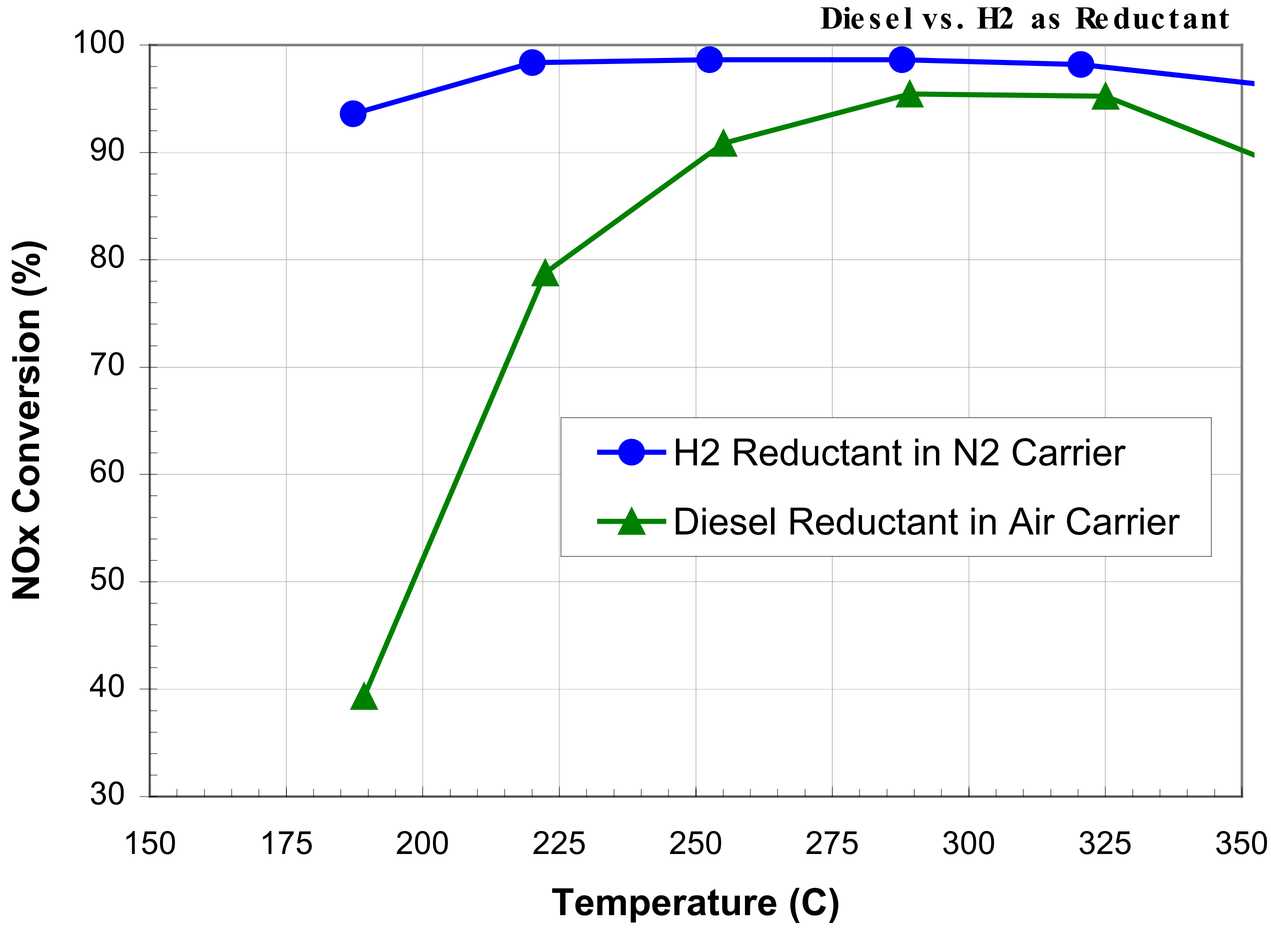
- **Net-Reducing Atmosphere Required for Regeneraton**
  - •Diesel Fuel Reductant Delivered with Air-Assisted Injector
  - •Valve on Exhaust Decreases Exhaust Flow Through Catalyst During Regen
    - •Lower Space Velocity Aids Flow Distribution and Reforming
    - •Lower Flow Requires Less Fuel to Combust Lower O2 Mass Flow



EmeraChem

Low Temp Performance: Reductant Efficiency

- NOx Sorption Efficiency a Function of Regeneration Efficiency
- Diesel More Effective when Combusted/Reformed to Lighter Reductants



EmeraChem

Control of Sulfur

- **Sulfur Masks Catalyst and Degrades NOx Performance**
  - **Sulfates are Thermodynamically Preferred Over Nitrates or Carbonates on Catalyst**

- **Control of Sulfur is Critical to Success of NOx Adsorber:**

  - **Fuel/Lub Sulfur Reduction**

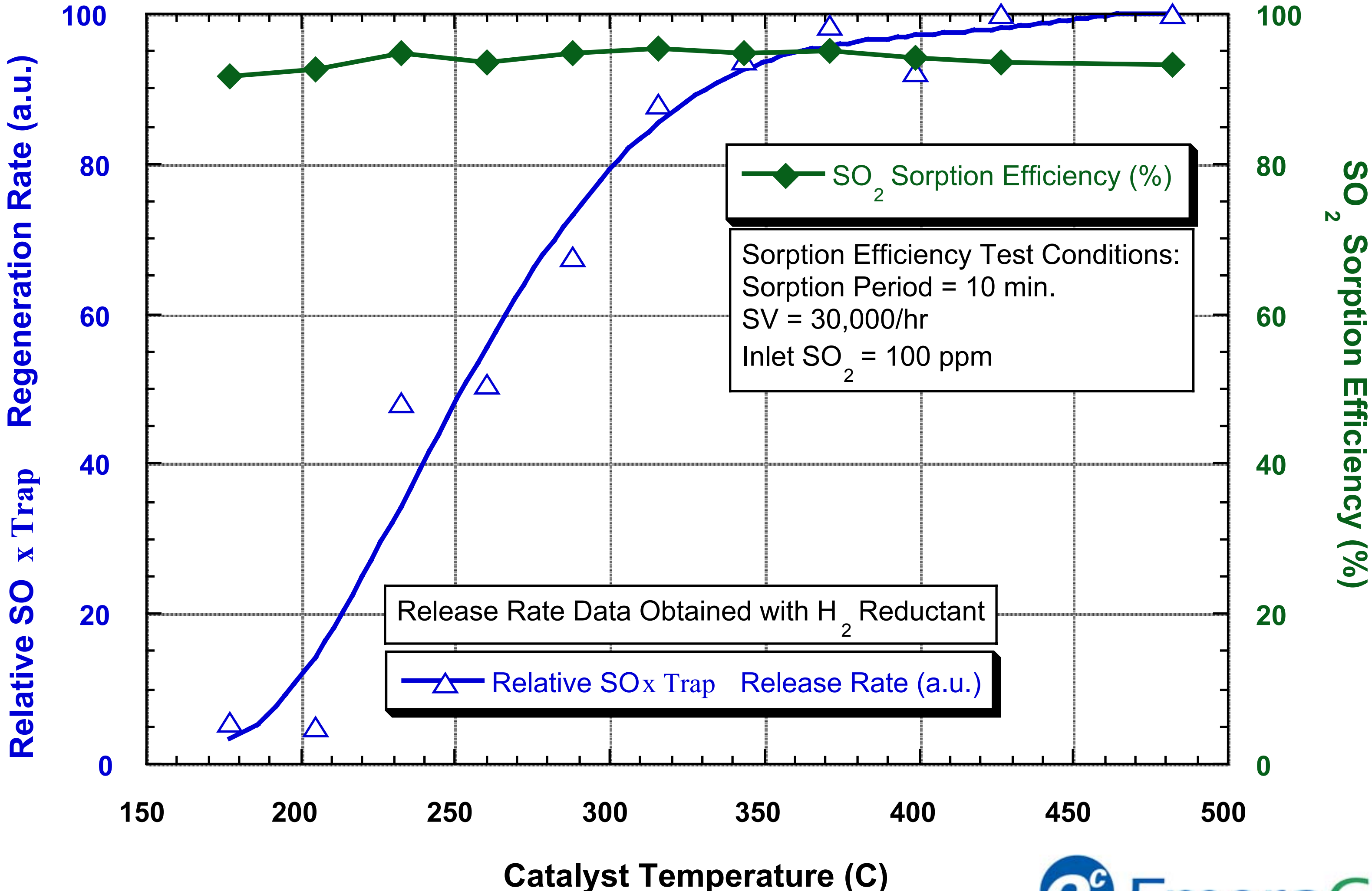
  - **Sulfur "Traps"** Can Protect Downstream NOx Adsorber
    - (1) Regenerable Traps Can Be Cleaned from Sulfur On-Line
      - SCOSOx™ Releases Sulfur as SO_2
    - (2) High Capacity Sulfur Traps Can Be Serviced

  - **DeSulfation** of NOx Adsorbers Removes Sulfur from Catalyst and Recovers NOx Performance

EmeraChem

Regenerable S Trap Temperature Performance

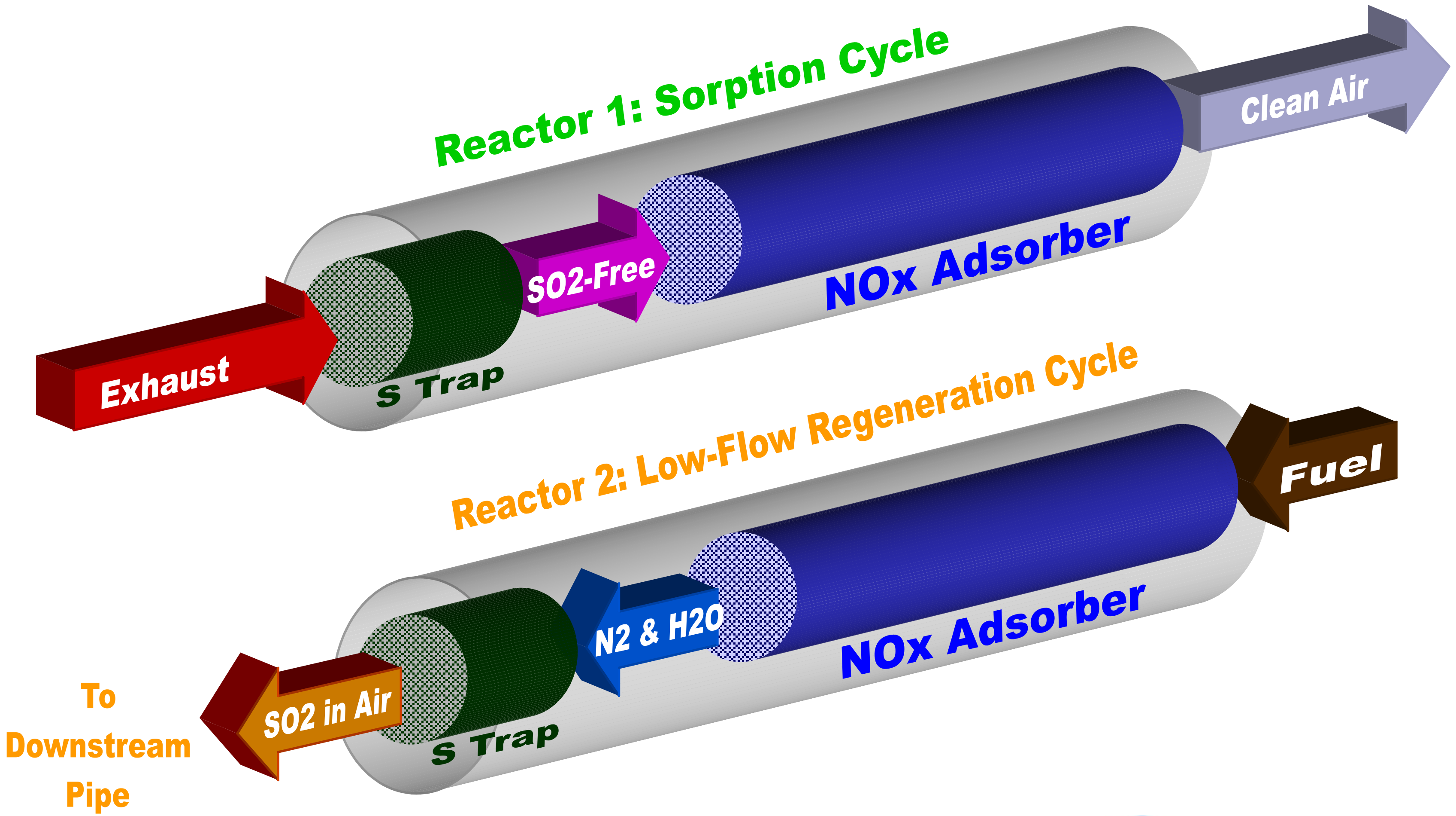
- Bench Flow Reactor Data Shown
- SO2 Sorbed Efficiently Over Wide Temperature Range
- SO2 Release is Best at Temperatures > 250 C



EmeraChem

Catalyst Geometry for Regenerable S Trap

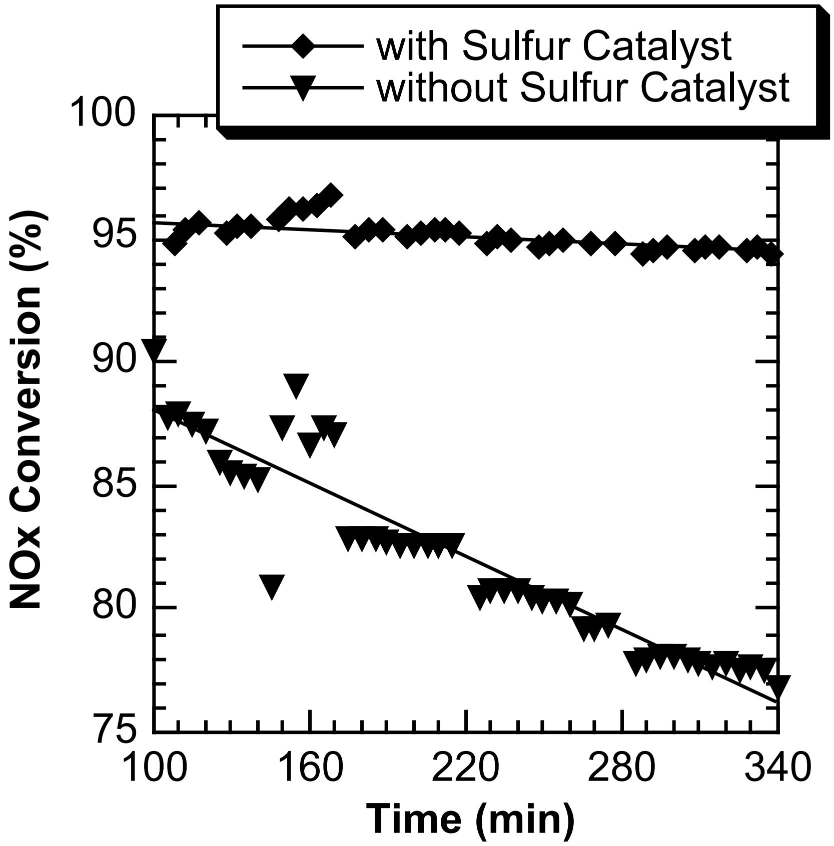
- Dual-Chamber Design Enables Efficient Regeneration Control
- Reverse Flow During Regeneration Prevents S Contact w/ NOx Adsorber
- Released SO2 Dumped in Exhaust Downstream



EmeraChem

Regenerable Sulfur Trap (Engine Test)

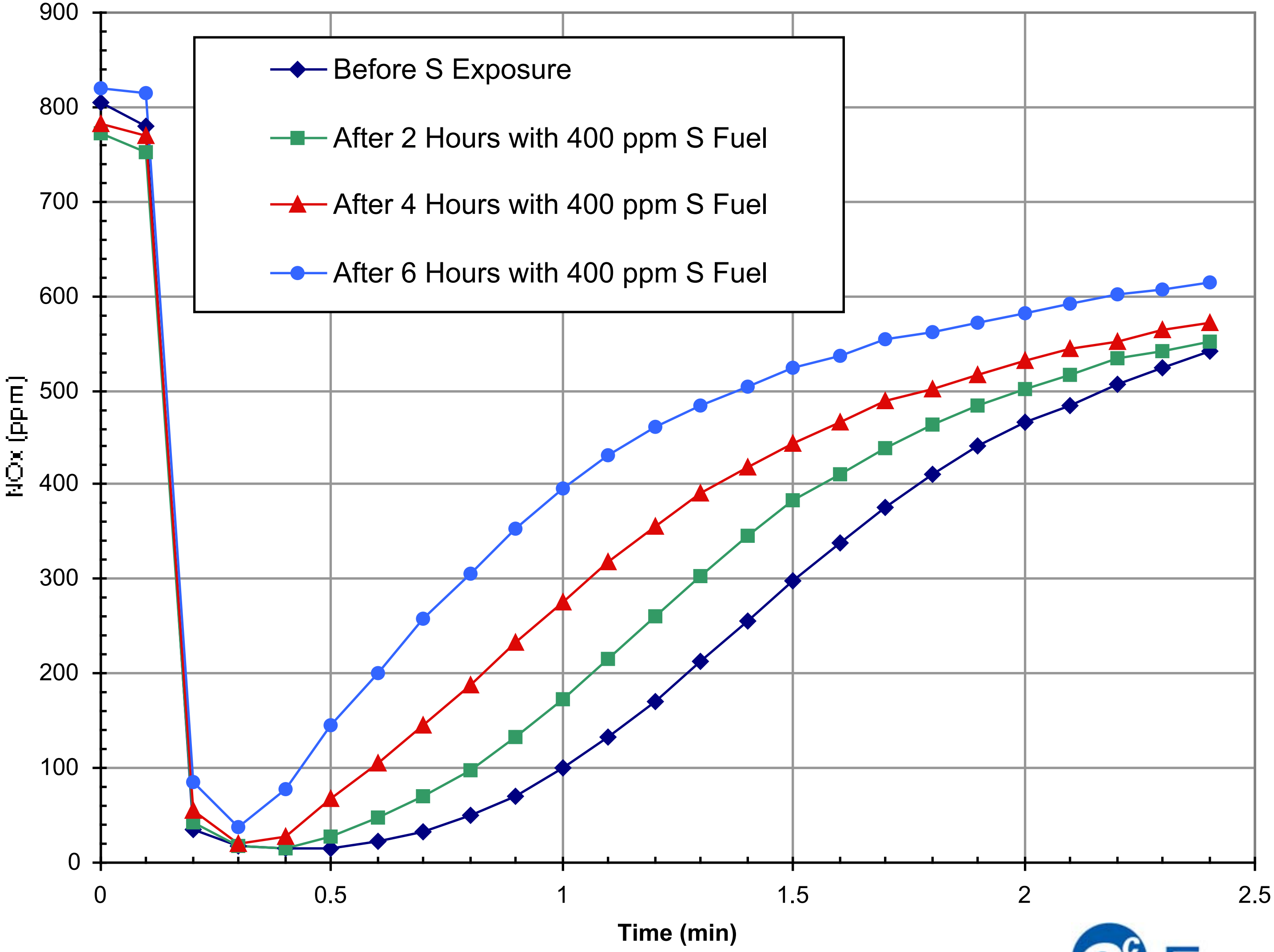
- Regenerable Sulfur Trap Used Upstream of NOx Adsorber Catalyst
- Released SO2 Dumped Downstream of NOx Adsorber



EmeraChem

Sulfur Fills Sites and Decreases NOx Capacity

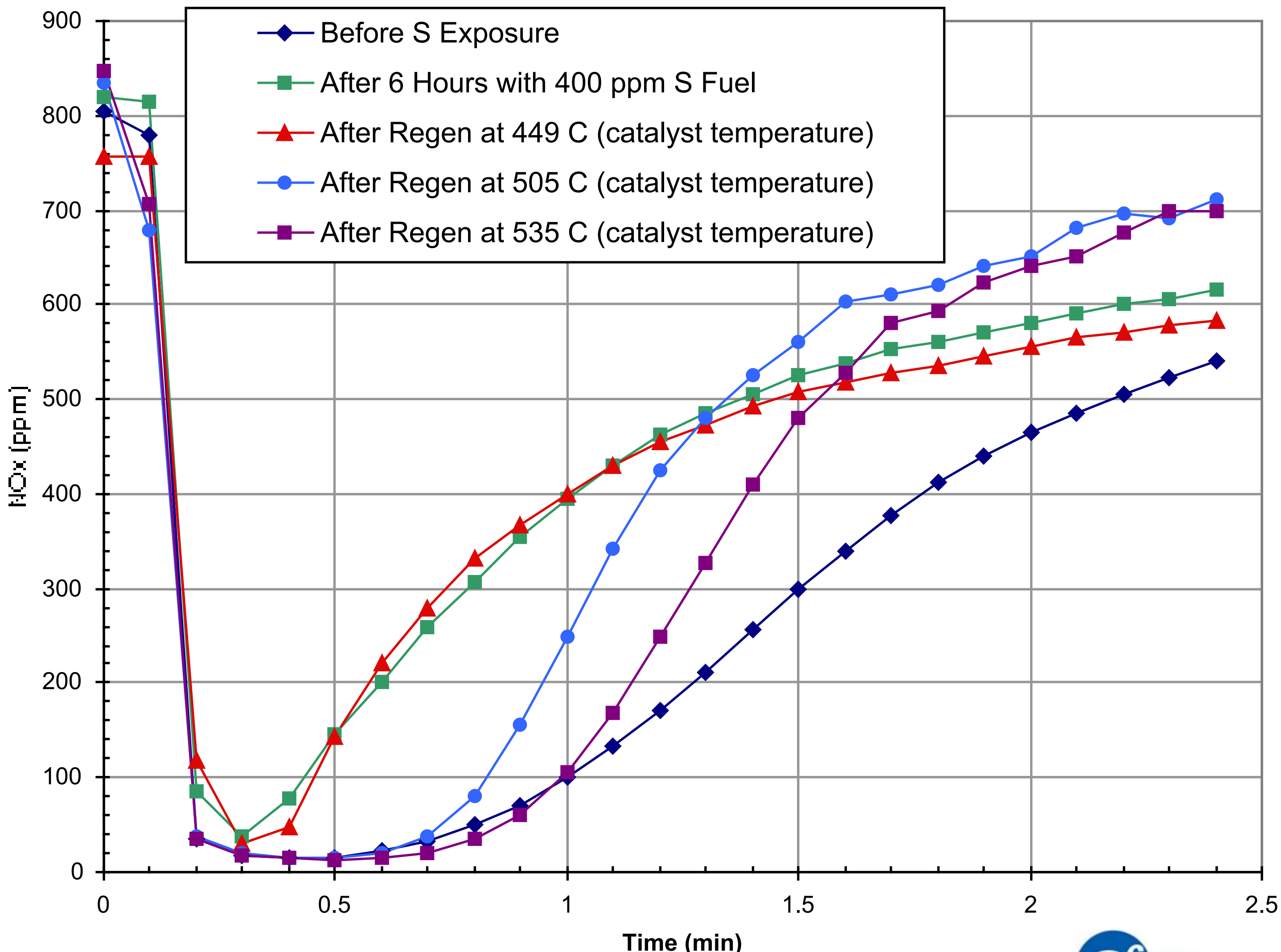
- Data Obtained at 310˚C Exhaust Temperature
- Exposure to Sulfur Decreases Catalyst NOx Performance



EmeraChem

NOx Capacity Recovered During DeSulfation

- **Degree of NOx Capacity Recovery Dependent on Temperature**
- **Profile of NOx Sorption Differs After deSulfation**



EmeraChem

Analysis of NOx Capacity Recovery

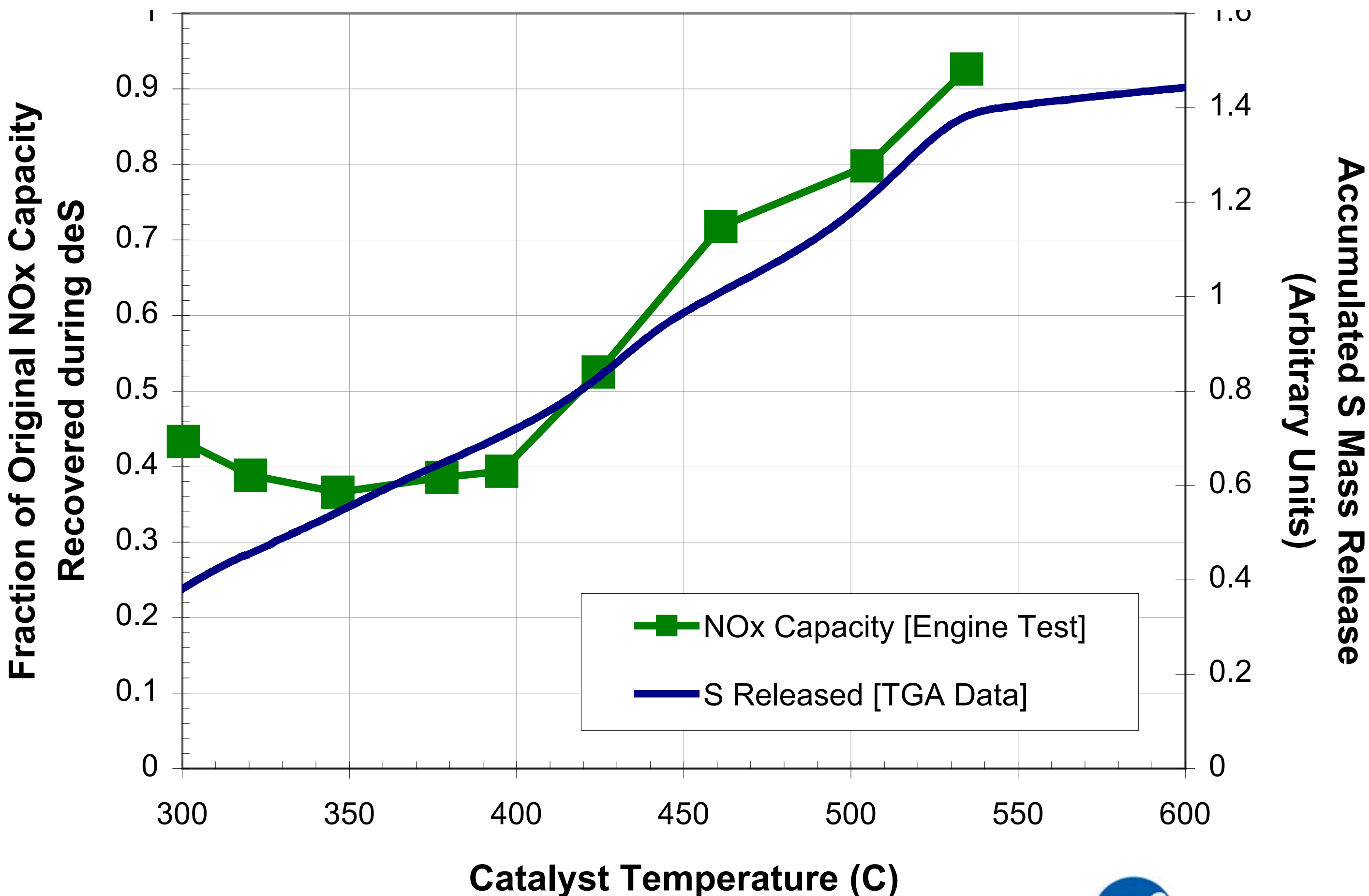
- **NOx Sorption Profile Difference Before Sulfur and After DeSulfation Results in Different NOx Capacity Recovery**
  - **NOx Capacity for Full 2.5 min. of Sorption Cycle was not Completely Recovered**
  - **NOx Capacity During 1.0 min. Sorption Cycle was Completely Recovered**

	Analysis of Full 2.5 min. Cycle		**Analysis From 0.2 to 1.2 min.**	
Run	**NOx Conversion**	**NOx Capacity (vol:vol)**	**NOx Conversion**	**NOx Capacity (vol:vol)**
Before S Exposure	65.15%	0.456	92.62%	0.259
After S Exposure	45.53%	0.319	69.34%	0.194
After Regen at 449 C	42.90%	0.278	66.04%	0.171
After Regen at 505 C	50.51%	0.364	84.85%	0.245
After Regen at 535 C	56.61%	0.412	92.13%	0.268

EmeraChem

deSulfation: S Release Recovers NOx Capacity

- Data from deSulfation Experiment on TGA and Engine Test Platform with NOx Adsorber Catalyst Shows that deSulfation (TGA Data) Corresponds with NOx Capacity Recovery (Engine Data)
- deSulfation Occurs in Temperature Range of 400 to 550ºC



EmeraChem

Non-Steady-State Processes of NOx Adsorber

Sorption

- >99% NOx Removal Prior to NOx Saturation
- NOx Storage Sites Continually Being Filled During Sorption Process

Regeneration

- Diesel Fuel Demonstrated as Reductant Source
- Combustion, Reforming, Site-Reduction, and NOx Reduction All Occur on Catalyst During Regeneration
- Fast Kinetics of Regen Process Facilitate Rapid Regen Process in Diesel Application

DeSulfation

- Sulfur Masks Catalyst Ability to Remove NOx
- DeSulfation Renews Catalyst's Ability to Remove NOx
- DeSulfation Process is Current Main Area of Focus
    - Thermal Dependence
    - Kinetics
    - Repeatability

EmeraChem