TRANSMURAL CATALYSIS

High Efficiency Catalyst Systems for NOx Adsorbers and SCR

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NECESSITY IS THE MOTHER OF INVENTION

There is a compelling need for the reduction of NOx under lean exhaust conditions from diesel engines for

- 2010 on-road FTP emissions levels,
- NTE on-road compliance and
- emerging non-road emissions regulations.

Proposed technologies include NOx adsorbers or SCR catalyst systems (lean NOx catalysts do not offer sufficient reduction).

THE TRANSMURAL INNOVATION

- Delivering an externally added exhaust reduction reagent precisely
  - *where* it is required in a catalytic device,
  - *when* it is required,

  rather than mixed with the bulk of the flow, as in conventional NOx adsorbers and SCR systems.
- Precise delivery of reductant in *time* and *space* in a catalytic system, rather than just in *time* alone.

THE MOTIVATION

- Maximize the emissions reduction potential of diesel exhaust aftertreatment, specifically for NOx reduction.
- Minimize fuel and/or reductant consumption.
- Improve aftertreatment durability.
- Improve system control and eliminate reductant slip.

THE BASIS OF THE INVENTION

Trans = across or through *mural* = wall

Transmural Catalysis is a novel, generic catalytic arrangement

- A reagent (example: ammonia or fuel) is introduced either continuously or in a pulsed fashion through a porous wall into a through-flow catalytic passage, rather than along with the bulk of the flow as in a conventional catalytic device.

ADVANTAGES OF TRANSMURAL CATALYSIS

- Allows for the more efficient use of reductant as it is introduced directly to or immediately adjacent to the catalytic (and storage) sites.
- Can reduce the storage material and/or the precious metal loading requirement of catalysts.
- Provides for rapid catalyst response and a high level of thermal management (more degrees of freedom in aftertreatment control).
- Can be a more efficient arrangement for implementing NOx adsorbtion or selective catalytic reduction in diesel aftertreatment.

THE STATE OF THE ART IN NOx EMISSIONS REDUCTION

- NO_x adsorbers
  - are attractive because they use fuel as a reductant
  - suffer a fuel efficiency penalty
  - have thermal management problems
- Two leg systems are bulky
- Single leg systems require whole exhaust to be fuel-rich

Photo: APBF-DEC Project

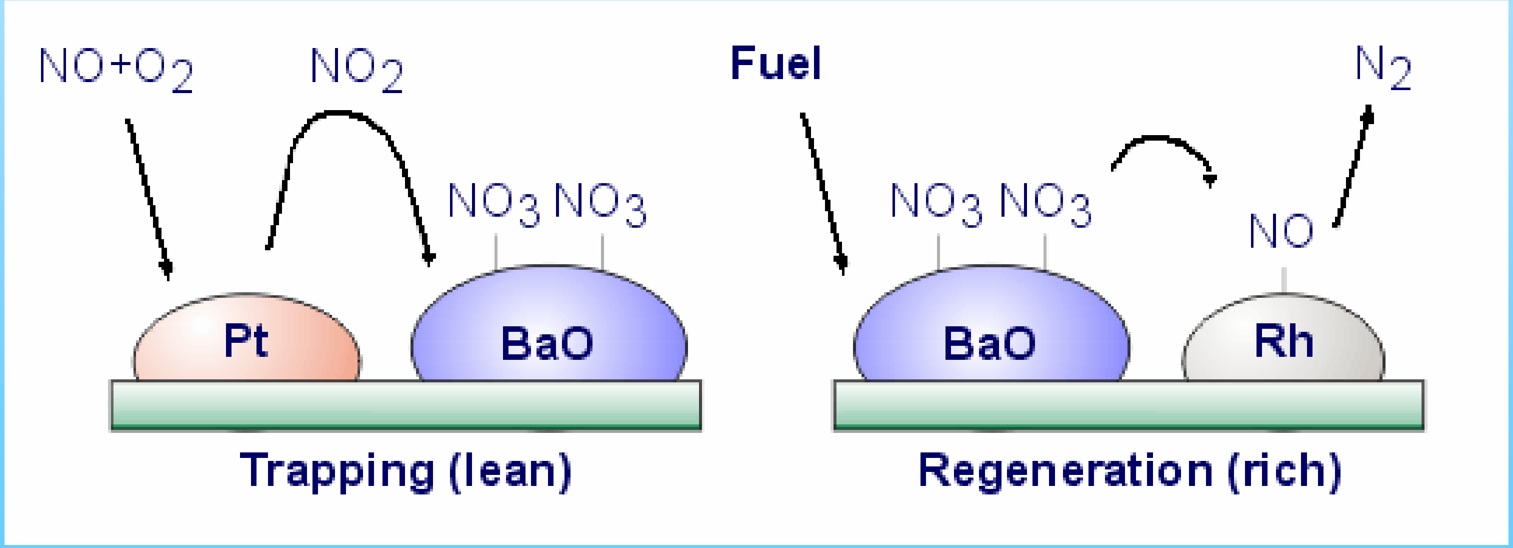
NOx ADSORBER MECHANISM – 1

- Lean exhaust operation:
  - Oxidize NO to NO_2
  - Store NO and NO_2

Occurs readily

- Rich exhaust operation:
  - Release NO
  - Reduce NO

Requires reducing atmosphere



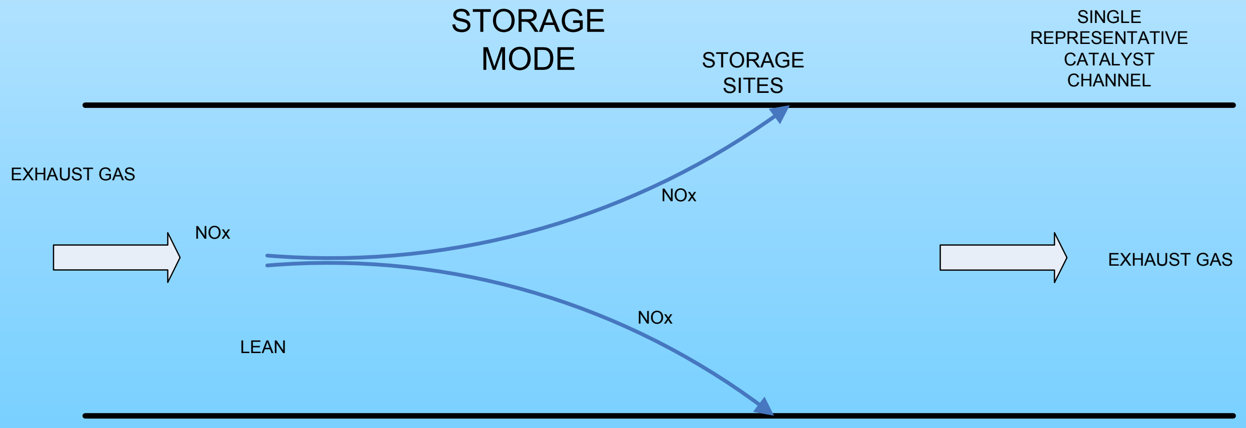
NOx ADSORBER MECHANISM – 2

- Oxidize NO to NO_2 on catalyst sites:
  - $2NO + O_2 \leftrightarrow 2NO_2$
- Adsorb and store NOx on the alkaline metal sites :
  - $BaCO_3 + 2NO_2 + 1/2O_2 \leftrightarrow Ba(NO_3)_2 + CO_2$
  - $BaCO_3 + 2NO + O_2 \leftrightarrow Ba(NO_3)_2 + CO_2$
- Release NO during rich operation (O_2 deficient – requires the addition of appreciable quantities of fuel)
  - $Ba(NO_3)_2 + 3CO \leftrightarrow BaCO_3 + 2NO + CO_2$
- Reduce NO on the catalyst sites:
  - $2NO + 2CO \leftrightarrow 2N_2 + 2CO_2$

CONVENTIONAL THROUGH-FLOW NOx ADSORBER

- Storage phase. NOx present in the exhaust stream is stored on the storage sites on the catalyst substrate under lean exhaust chemistry conditions.

CONVENTIONAL NOx ADSORBER

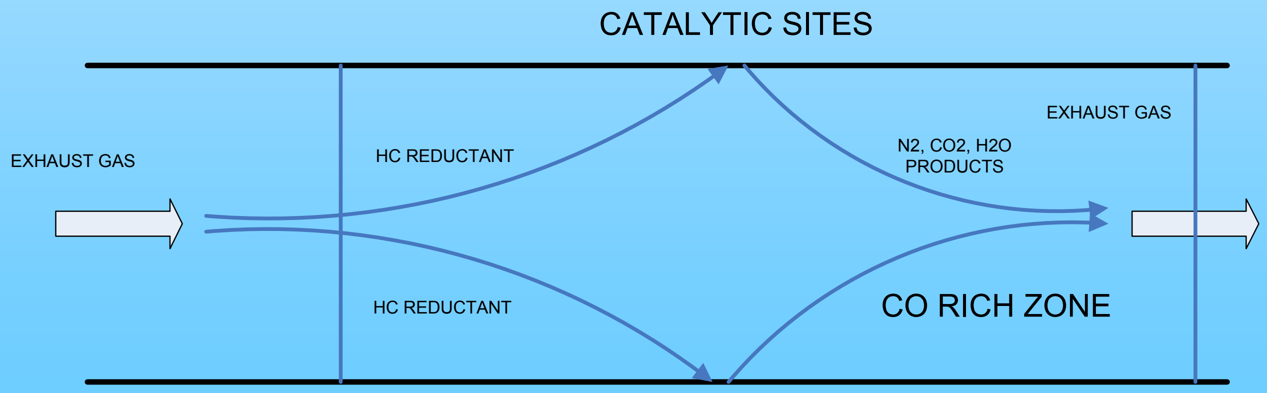


CONVENTIONAL THROUGH-FLOW NOx ADSORBER

- Regeneration phase. Reductant is injected in the exhaust flow to deplete the whole exhaust stream of oxygen before it contacts the stored NOx. Then NO is released and catalytically reduced.

CONVENTIONAL NOx ADSORBER

REGENERATION
MODE



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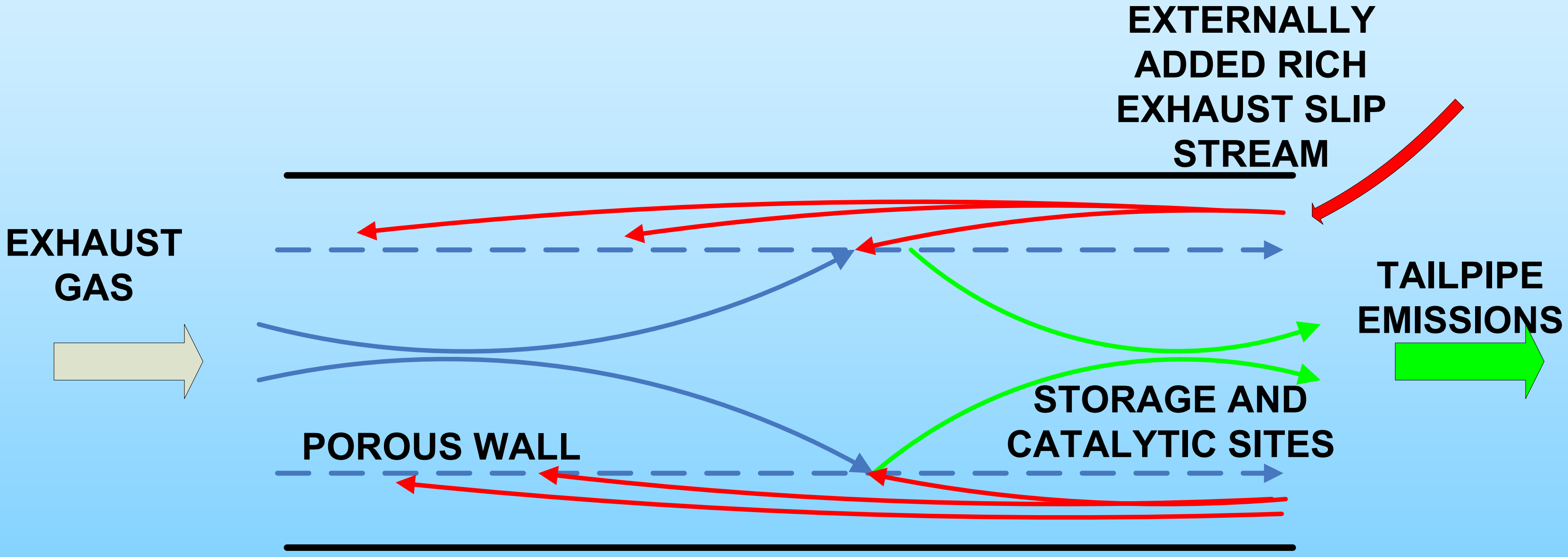
TRANSMURAL CATALYSIS FOR NOx ADSORBERS



EXTERNALLY ADDED RICH EXHAUST SLIP STREAM

EXHAUST GAS

TAILPIPE EMISSIONS

STORAGE AND CATALYTIC SITES

POROUS WALL

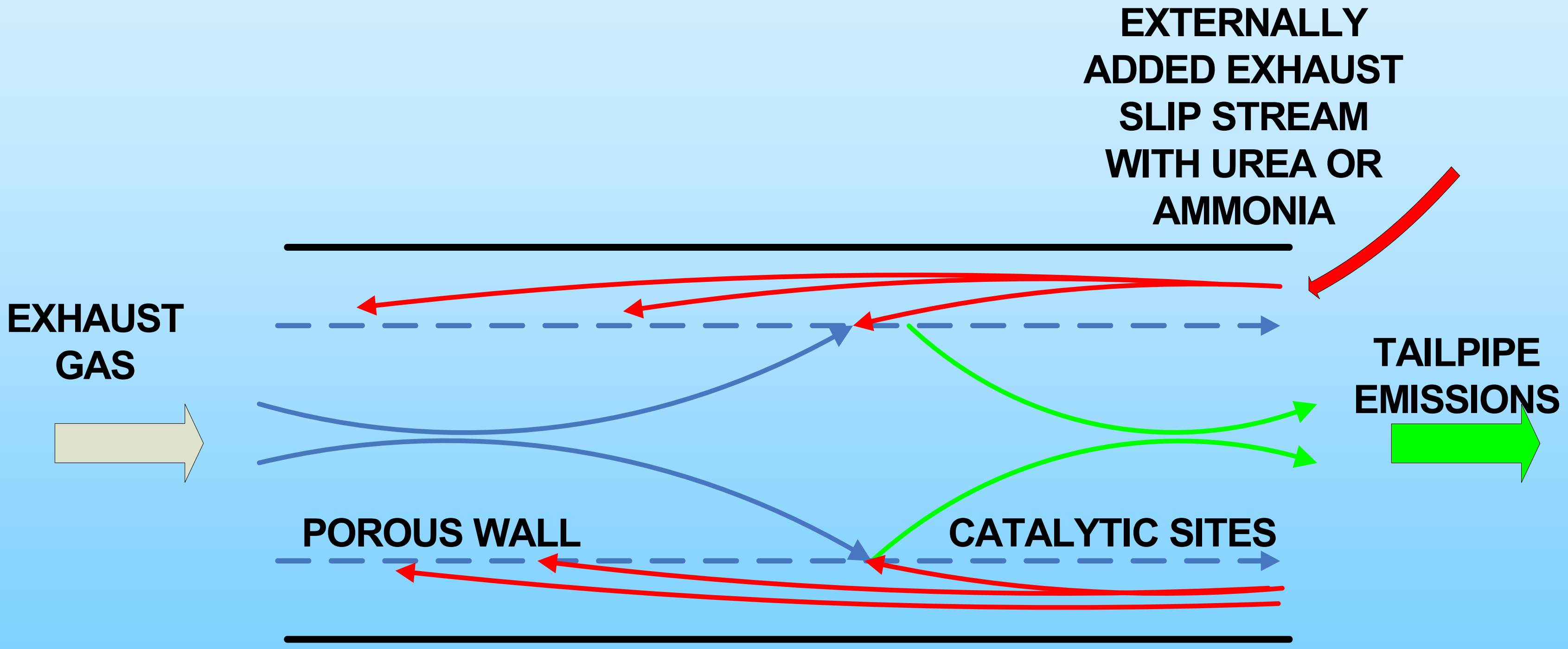
Transmural Catalysis
Advantages – for NOx adsorbers

- Revives the advantages of NOx adsorbers – puts them back on an equal footing with SCR (fuel penalty of as little as 1% possible).
- Allows a significant reduction in fuel usage for reductant.
- Does not require whole exhaust stream to be made rich or oxygen deficient – just a thin boundary layer.
- Diffusion and transport of molecules to the rich boundary layer is assured – this principle is proven by existing gas-wall interactions in catalytic converters.
- Reducing flow can vary in flowrate and fuel 'richness' – from very lean to rich sooting limit.

THE STATE OF THE ART IN NOx EMISSIONS REDUCTION

- Selective catalytic reduction (SCR)
  - is the favored solution for 2010 HDD
  - requires ammonia or urea on board
  - can suffer from reductant slip (unregulated but harmful)
  - may be difficult to manage for NOx reduction requirements of over 80%
  - must be used in conjunction with engine-out NOx reduction technologies

TRANSMURAL CATALYSIS FOR SCR

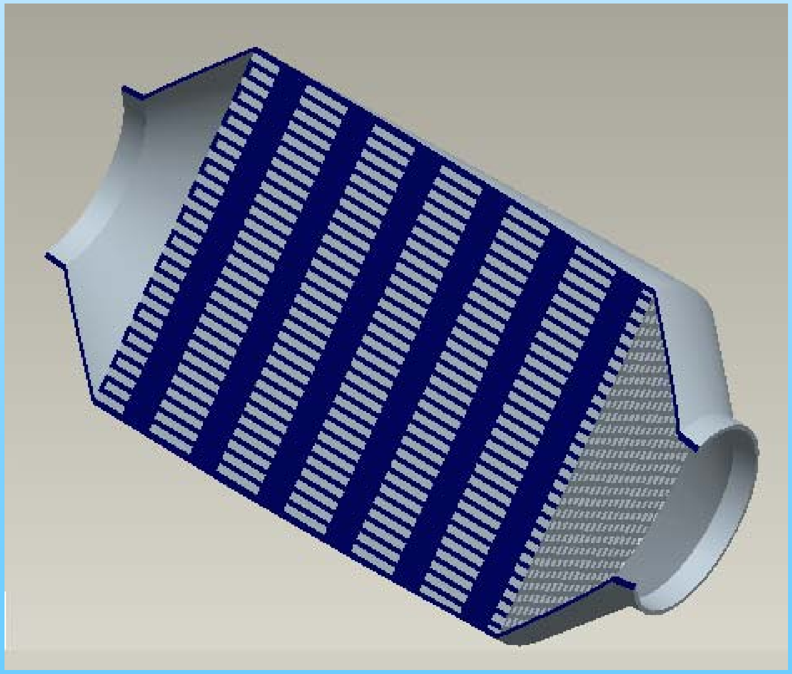


DISADVANTAGES OF CURRENT NOx REDUCTION SYSTEMS

- NO_x adsorbers
  - Dual modes of operation (lean exhaust storage/accumulation and rich exhaust reduction) with single adsorber inconsistent with on-road diesel engine operation.
  - Fuel efficiency penalty associated with regeneration due to the requirement that the whole exhaust flow be made fuel rich, or oxygen deficient.
- Selective catalytic reduction (SCR)
  - Requires significant urea storage capacity (catalyst acts as a ‘sponge’) due to the fact that it is difficult to track changes in incoming NOx concentration.
  - This leads to the requirement that the device only be operated at a less than optimal conversion rate (at an average of say 80% conversion) to prevent ammonia slip.
  - Offers an integrated or averaged NOx conversion capability rather than a real-time load-following, transient high efficiency conversion capability.

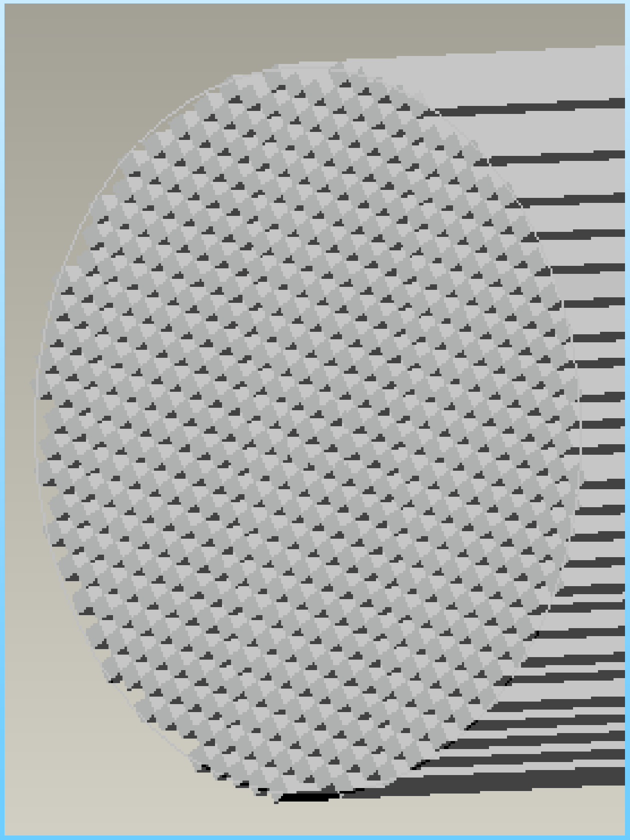
Potential Configurations

- Monolith with porous walls similar to a DPF
  - arrangements to simplify reductant introduction
- Large porous wall interface (eg. double helical)

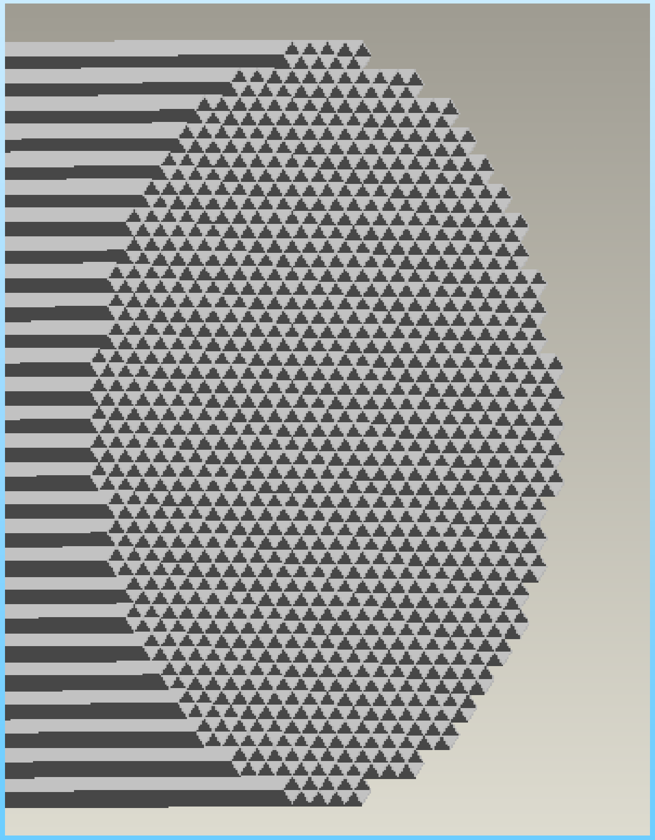


Substrate Configuration

Upstream end



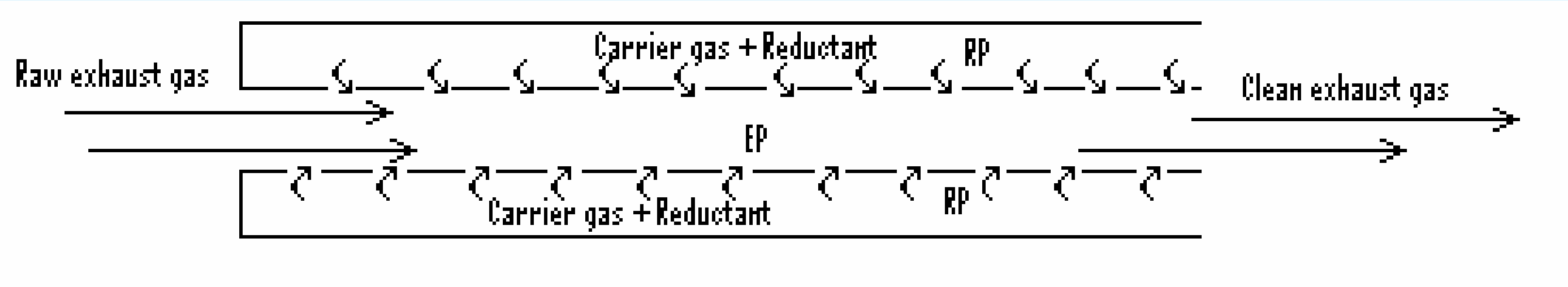
Downstream end



Substrate Design

- Wall flow design with alternate blocked passages is optimal for interfacial area but not for reductant introduction.
- For manufacturing practicality, alternating rows of exhaust flow & reductant may be desirable (reductant can be added through alternating rows in multiple configurations).
- Possible configurations also include porous metal version of the emerging corrugated stainless metal helical wound catalysts.
- Potential configurations are very open.

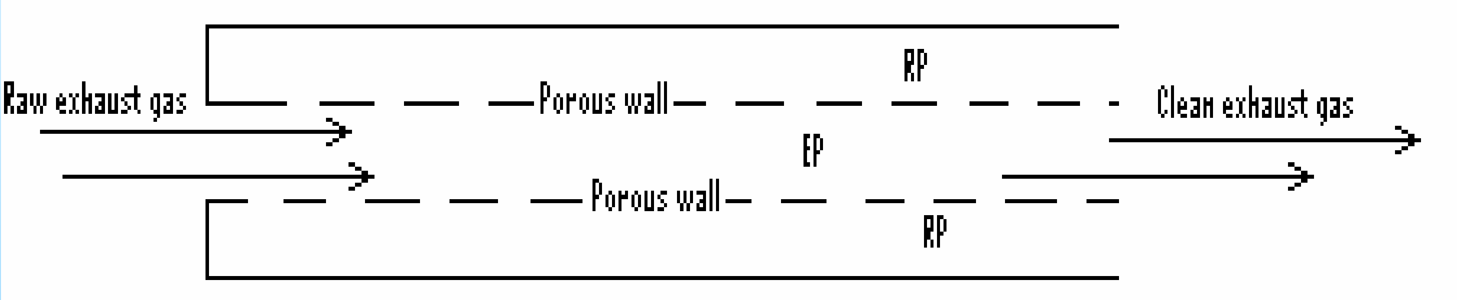
Transmural Catalysis
Continuous Operation



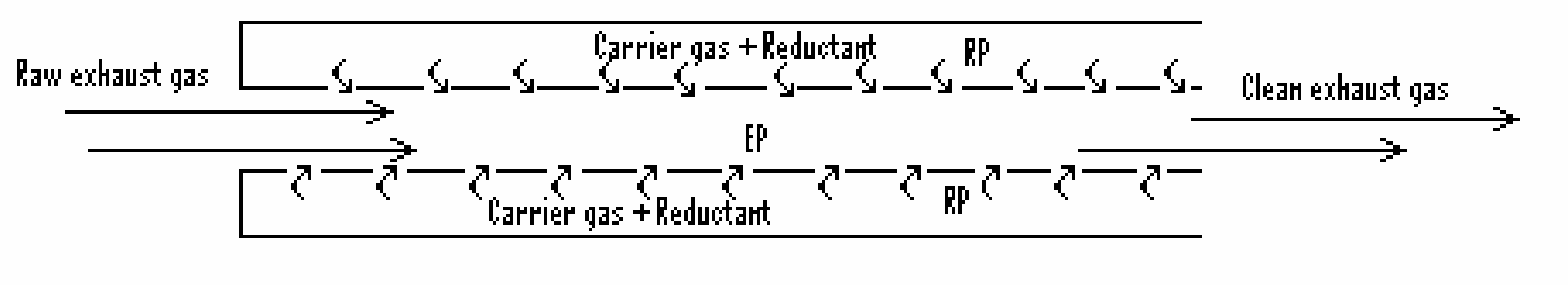
- Reductant is continuously supplied through the porous wall into the exhaust channels.
- This results in continuously rich conditions in a thin layer in the vicinity of the reductant sites.
- Continuous operation of Transmural Catalysis requires only reductant sites and does not require storage sites.

Transmural Catalysis
Pulsed Operation

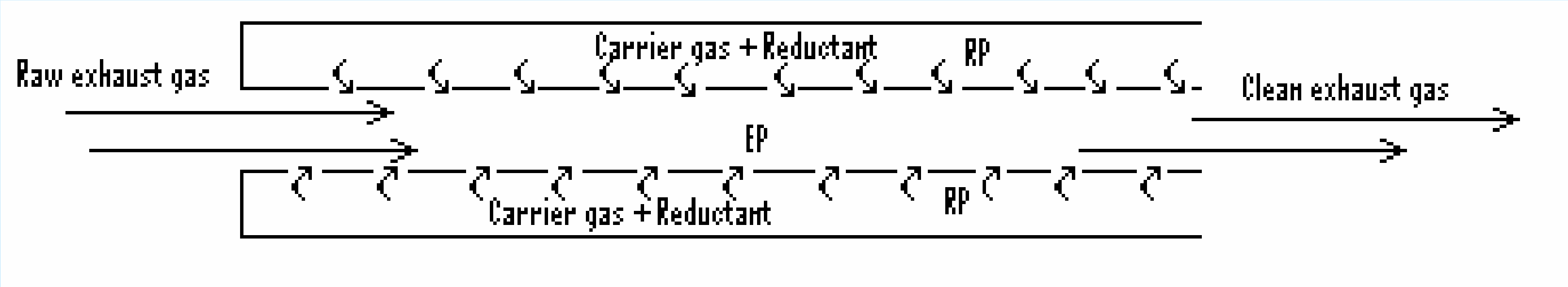
- Storing phase. No transmural flow. NOx is stored on the storage sites (as in a conventional adsorber).



- Regenerating phase. Reductant is supplied periodically through the porous wall (with varying 'richness', and flowrates of reducing flow). NO is released and reduced. Reductant may also be used to reduce NO before it reacts with oxygen.



Transmural Catalysis
- SCR



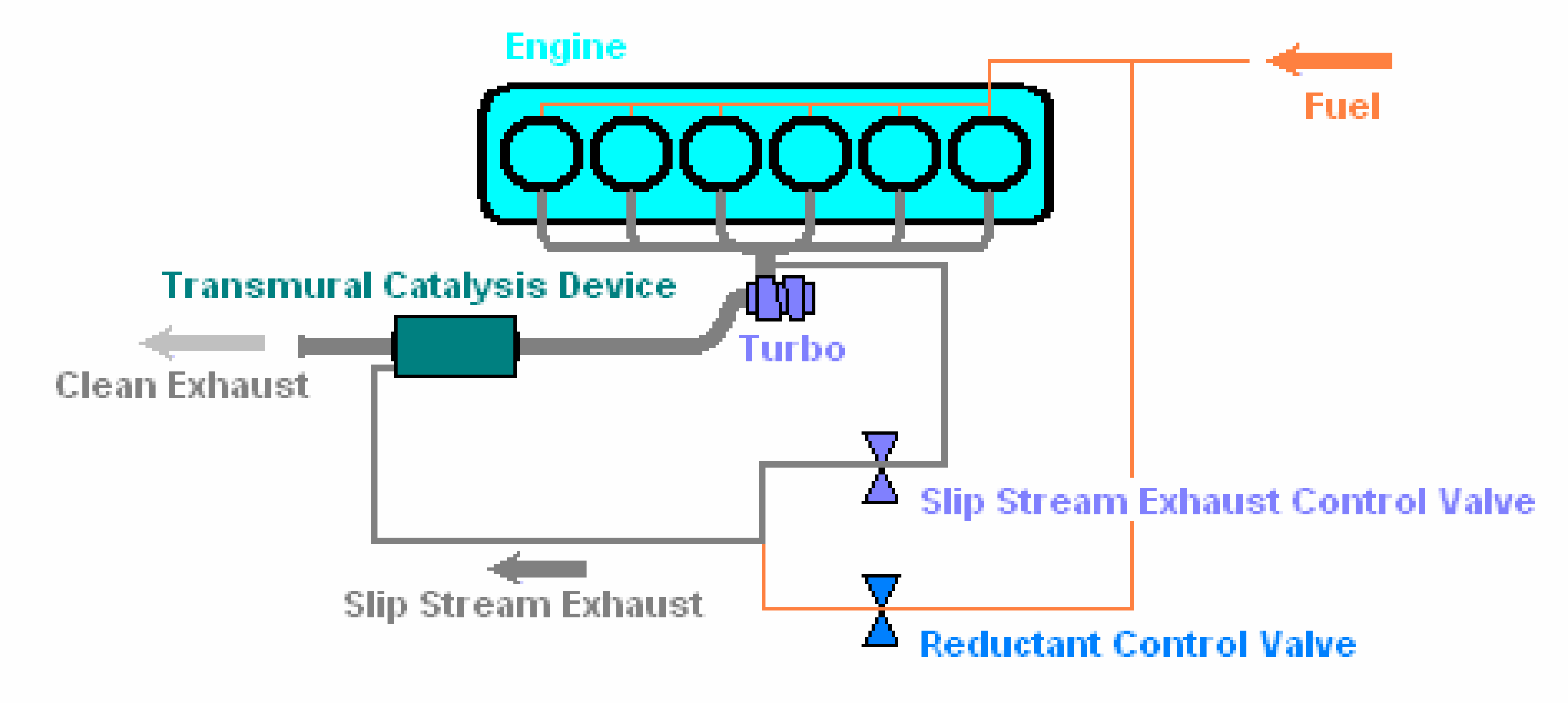
- Urea is supplied continuously through the porous wall into the exhaust channels (in proportion to exhaust NOx rate).
- Continuous operation of Transmural Catalysis requires only active catalytic sites and does not require any significant number of storage sites.
- Improves the ‘response’ of the SCR device to changes in engine-out NOx – the substrate does not need to be an urea ‘sponge’ – reduces urea slip.

Transmural Catalysis Advantages – for SCR

- Allows a significant reduction in urea usage for reductant.
- Does not require the catalyst substrate to be an urea ‘sponge’.
- Allows for much better metering of the urea reductant, and therefore promises much better overall NOx reduction rates.

Exhaust Aftertreatment Layout

(positive pressure gradient available for small exhaust slip stream)



Simulation of Transmural System

- Transport of NO from bulk to catalytic surface
- Oxidation of NO to NO_2
- Diffusion of NO and NO_2 from the surface to the fronts
- Storage of NO and NO_2 on alkaline metal sites
- Release NOx in the form of NO
- Diffusion of NO to surface
- Reduction of NO to N_2 and CO_2

Storage Phase

- Transport of NO from bulk to catalytic surface

$$\frac{\delta C^B}{\delta t} = -v\frac{\delta C^B}{\delta z} + D_b\frac{\delta^2 C^B}{\delta z^2} - a_v k(C^B - C^S)$$

- v=gas velocity, C=concentration in the bulk and at the surface, D_b=diffusion coeff., a_v=catalytic surface, k=mass convection constant
- NO balance equation at the surface

$$a_v k(C^B - C^S) + a_v r_{ox} - a_P D_P \frac{C^S - C^P}{R - \xi_p} = 0$$

- r_{ox}=oxidation coeff., D_p=diffusion coeff., a_p=specific storage phase surface
- NO balance equation at the storage front

$$-2r_{sp} + D_P\frac{C^S - C^P}{R - \xi_p} = 0$$

- r_{sp}=storage coeff.
- Front position change

$$\frac{\delta \xi_p}{\delta t} = -\frac{D_P}{2c_p\Theta_c\xi_p}\left(\frac{C_{NO}^S - C_{NO}^P}{r - \xi_p}\right)$$

- Θ=carbon mole fraction in solid phase

Regeneration Phase

- NO balance equation at the surface

$$a_v k(C^B - C^S) - a_v r_{red} - a_P^{\max} r_{reg} = 0$$

- r_{red}=reduction coeff., r_{reg}=regenerating coeff., D_p=diffusion coeff., a_p=specific storage surface
- NO balance equation at the storage front

$$-2r_{reg} + D_P \frac{C^S - C^P}{R - \xi_p} = 0$$

- r_{reg}=regenerating coeff.
- CO balance equation at the surface

$$a_v k(C^B - C^S) + a_v r_{red} - 2a_P^{\max} r_{reg} = 0$$

- r_{red}=reduction coeff., r_{reg}=regenerating coeff., D_p=diffusion coeff., a_p=specific storage surface
- CO balance equation at the storage front

$$-3r_{reg} + D_P^{reg} \frac{C^S - C^P}{R - \xi_p} = 0$$

- r_{reg}=regenerating coeff.

Tuttlies, U.; Schmeiser, V.; Eigenberger, G.; A new simulation model for NOx storage dynamics

Transmural Catalysis

A novel catalyst concept formulated for:

- A variety of transportation & industrial processes, with clear benefits in diesel engine NOx reduction
- Specifically diesel and lean burn or GDI engines
- Minimizing reductant usage in regeneration
- Reducing the storage and precious metal loading requirement for NOx adsorbers
- Continuous or pulsed operation
- Also suitable for SCR or nSCR systems
- Reduces the ammonia storage requirement for SCR
- Managing active surface area temperature (for example over the NTE zone and during high power operation)
- Builds upon well-understood concepts.

SYSTEM DESIGN PLANS

- Continue NOx adsorber modeling to verify catalyst efficiency and function & to optimize substrate geometry, device size & frequency of pulsation.
- Identify wall porosity for even reductant distribution.
- Extend modeling to SCR catalyst system.
- Demonstrate NOx reduction using a benchtop system with only one channel devoted to exhaust flow.
- Develop full scale development unit for HDD for both NOx adsorbers and SCR.
- Investigate engine control vs. transmural catalysis tradeoffs to optimize overall engine fuel economy while assuring emissions compliance.

TRANSMURAL CATALYSIS

- Patent pending (application US 2006/0107654 A1, May 2006).
- Developed by Nigel Clark, West Virginia University, and Chris Atkinson, Atkinson LLC.
- Patent assigned to West Virginia University.
- Technology has been licensed to Pandora Energy Technologies LLC, a limited liability company established to further the development of the technology.

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