Hydrothermal aging modeling for SCR catalysts

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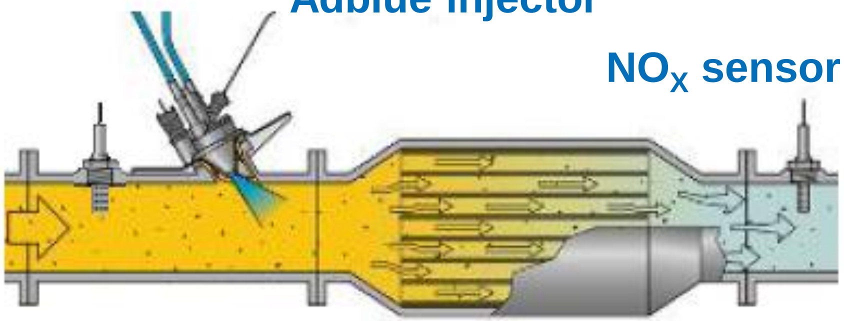
2015 CLEERS WORKSHOP

INSTITUT CARNOT
IFPEN Transports Energie

IFP Energies nouvelles

Interest of SCR modeling for control purpose

- **Urea-SCR is one of the most common technology used by car and truck manufacturers to meet the latest NO_X emission standards**
  - **requires to optimize urea injection in order to limit ammonia slip while keeping a good NO_X reduction efficiency**



- **In this context, system simulation has significant advantages to set up optimal injection strategy:**
  - ***Physical modeling*: modeling level is adapted for control laws design in order to obtain accurate and consistent results in every real life case**
  - ***Fast calculation time*: about 10 times faster than the real time for a complex exhaust line coupled with a high frequency control**

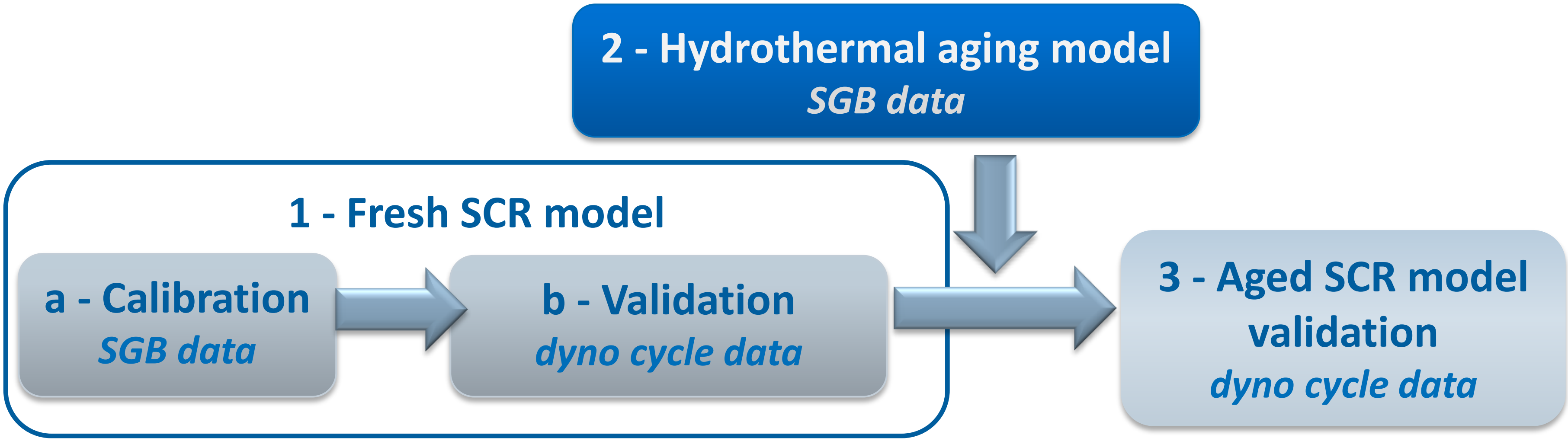
Importance of aging on SCR performances

- **During engine lifetime, performance degradation of the SCR catalyst is observed due to harsh exhaust conditions**
  - **frequent filter regeneration subjects the SCR catalyst to high temperatures**
  - **hydrothermal aging will strongly decrease DeNOx and NH_3 storage properties of the catalyst**

- **Modeling hydrothermal aging impact on the catalyst allows to adapt urea injection strategy and avoid excessive amount of ammonia slip**
  - **only way to adapt injection strategy over the complete vehicle lifetime**

➔ Is there a way to model efficiently hydrothermal aging impact on a SCR catalyst ?

Approach: from fresh to aged SCR model



- ***1 - Fresh SCR model set up and validation:***
  - **a - SCR model is calibrated on specific Synthetic Gas Bench tests**
  - **b - SCR model is integrated in a complete exhaust line simulator and validated on chassis dynamometer on test cycles**
- ***2 - Aging model set up*** **from SGB tests for various aging conditions**
- ***3 - Aging model validation*** **on dyno on test cycles using an aged SCR**

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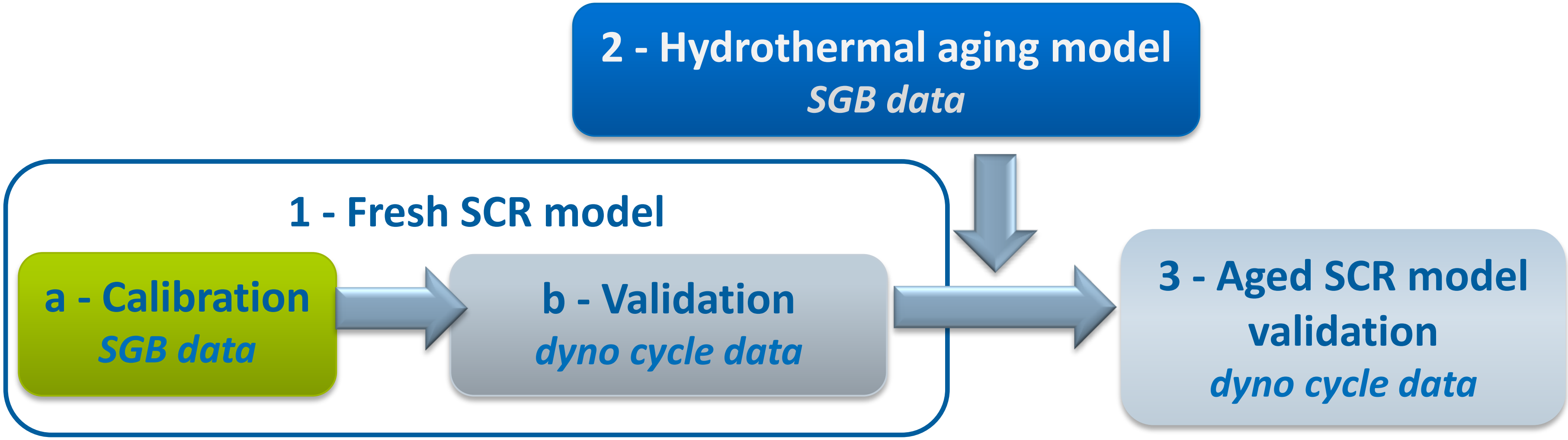

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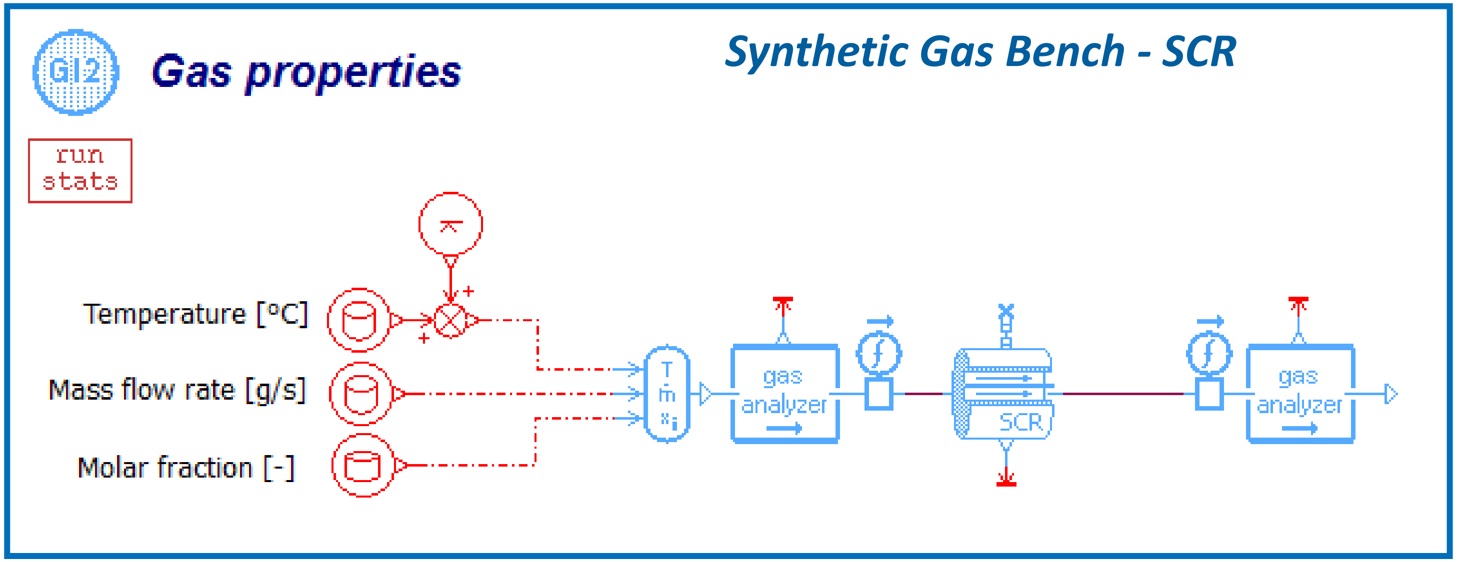
Fresh SCR model presentation – Reactor scale

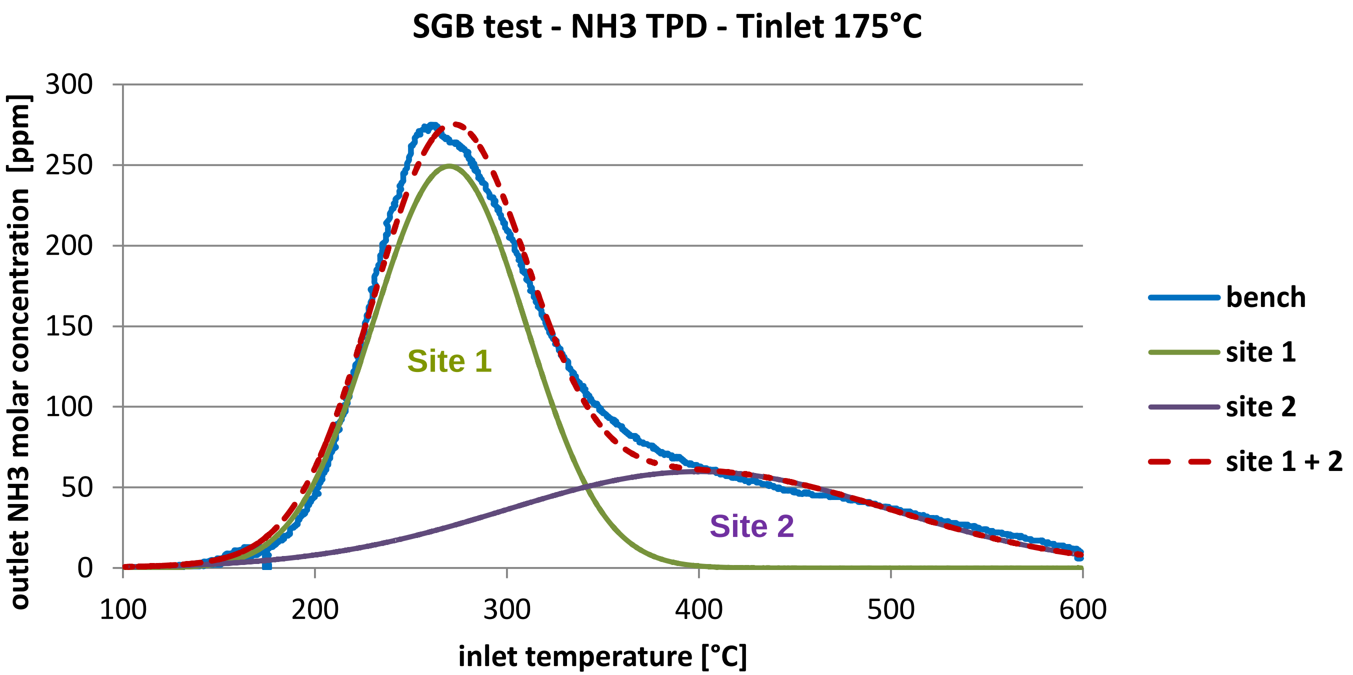
- **LMS Imagine.Lab Amesim model of SGB SCR using IFP-Exhaust library**



- **reactions considered: NH_3 adsorption/desorption, DeNOx reactions (standard, fast & NO_2 SCR) and NH_3 oxidation**
- **isolated sample: no thermal exchanges considered**
- **SCR sample geometry: length = 3 inches, diameter = 2 inches, 350 cpsi**

SCR modeling set up for NH_3 storage on SGB test

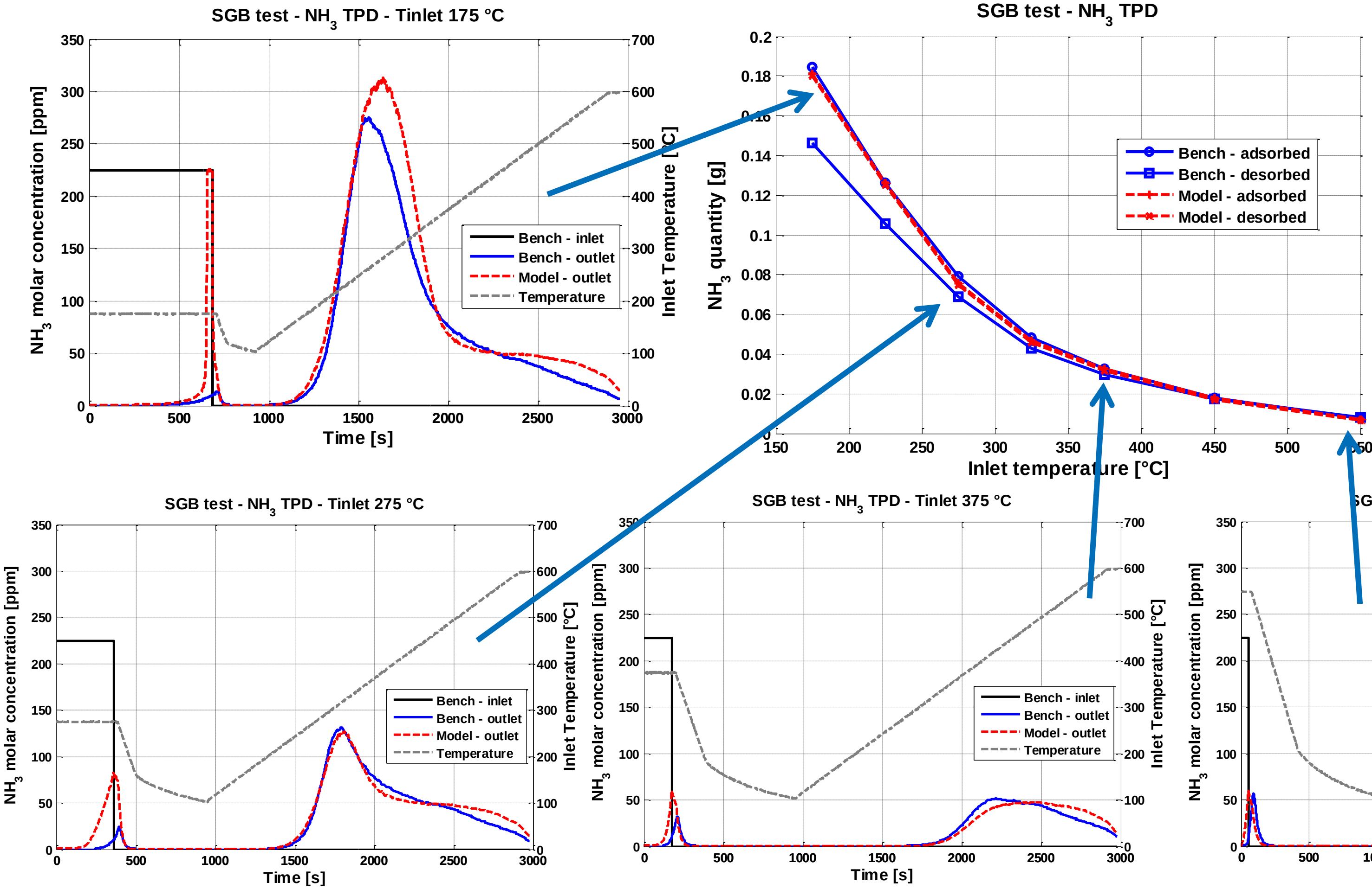
- **From NH_3 TPD observation, two adsorption sites can be considered**



- **NH_3 adsorption reaction for each adsorption site:**
  - $NH_3 + Si \leftrightarrow NH_3{-}S_i$
  - $r_{ad} = k_{ad} \times [NH_3] \times (1 - \theta_{NH3})$ - $k_{de} \times e^{-\frac{Ede \times (1 - alpha \times \theta_{NH3})}{R \times T_s}} \times \theta_{NH3}$

SCR model calibration for NH_3 storage on SGB test

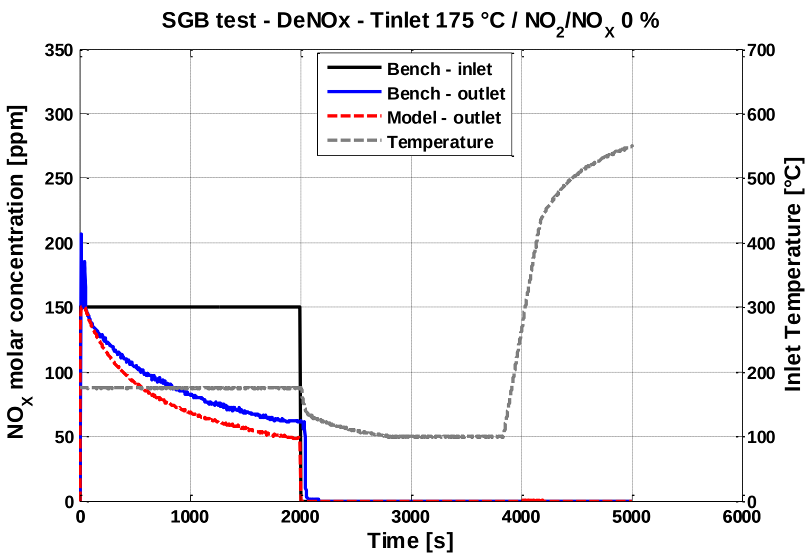
- **NH_3 storage calibration is done on NH_3 TPD tests with various inlet temperature**

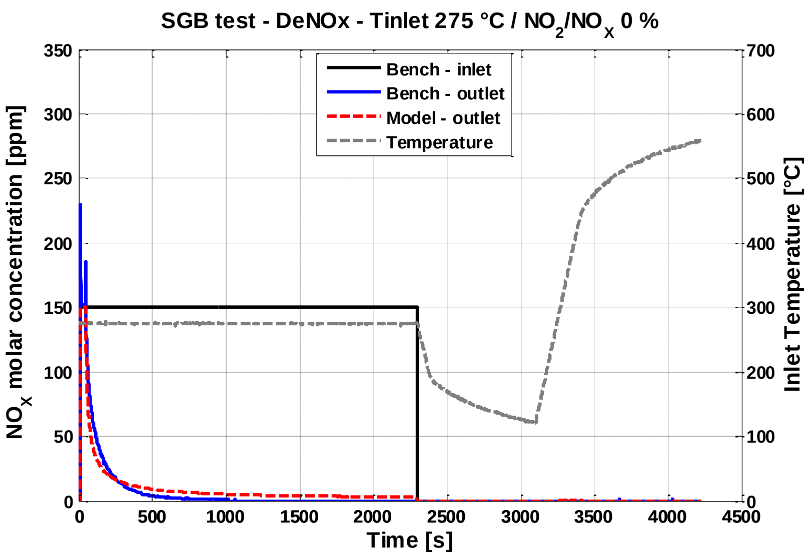


Good results consistency for the overall test data

SCR model calibration for DeNOx reaction on SGB test

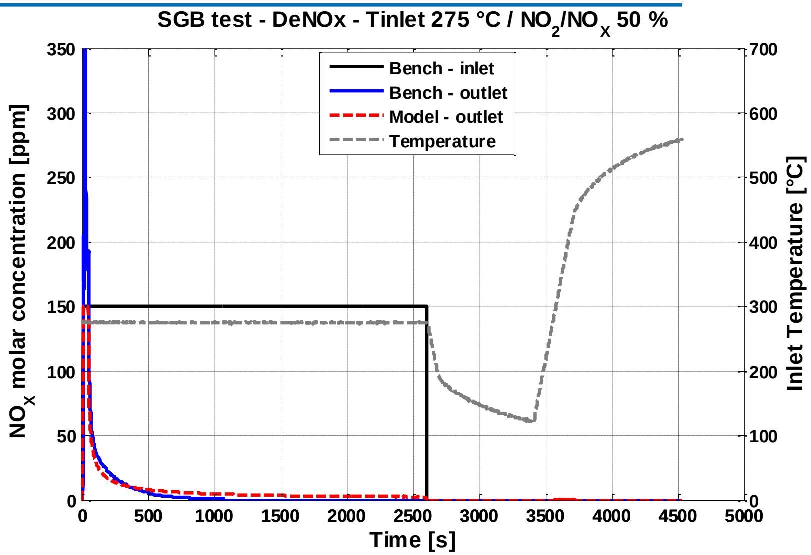
- **Standard SCR reaction calibration:**
  - $4\ NH_3\text{-}S_i + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O + 4\ S_i$
  - $r_{std} = k_{std} \times e^{-\frac{E_{std}}{R \times T_s}} \times [NO] \times \theta_{NH3}$
  - Calibration is done on DeNOx SGB test with an upstream NO_2/NOx ratio of 0 %



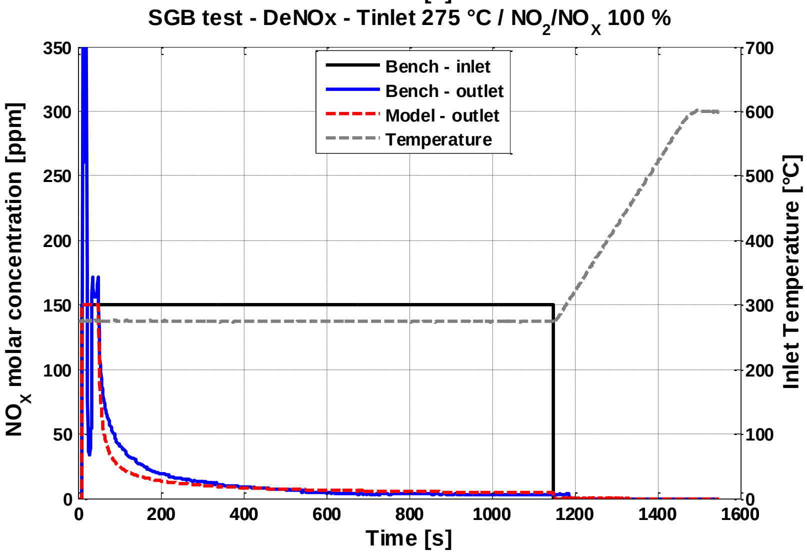


SCR model calibration for DeNOx reaction on SGB test

- **Fast SCR reaction calibration:**
  - $2\ NH_3\text{-}S_i + NO + NO_2 \rightarrow 2\ N_2 + 3\ H_2O + 2\ S_i$
  - $r_{fast} = k_{fast} \times e^{-\frac{E_{fast}}{R \times T_s}} \times [NO] \times [NO_2] \times \theta_{NH3}$
  - calibration is done on DeNOx SGB test with an upstream NO_2/NO_x ratio of 50 %

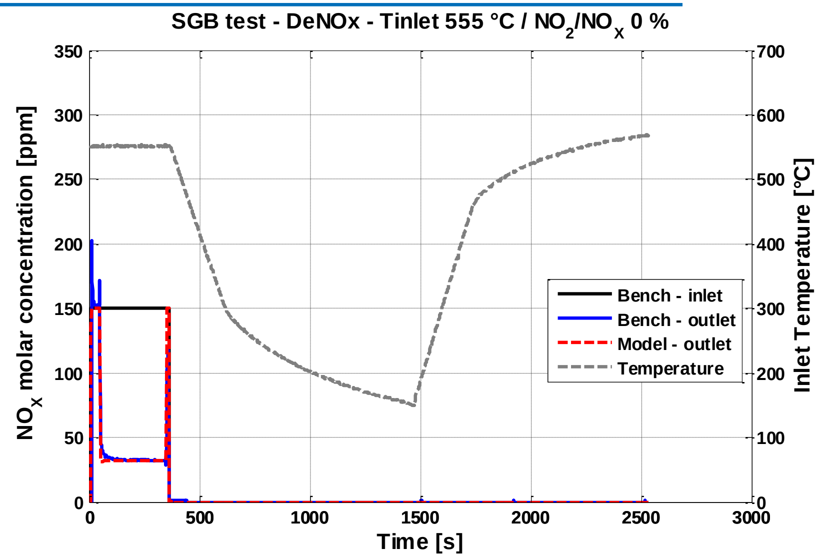


- **NO_2 SCR reaction calibration:**
  - $4\ NH_3\text{-}S_i + 3\ NO_2 \rightarrow 5{,}5\ N_2 + 6\ H_2O + 4\ S_i$
  - $r_{NO2} = k_{NO2} \times e^{-\frac{E_{NO2}}{R \times T_s}} \times [NO_2] \times \theta_{NH3}$
  - calibration is done on DeNOx SGB test with an upstream NO_2/NO_x ratio of 100 %

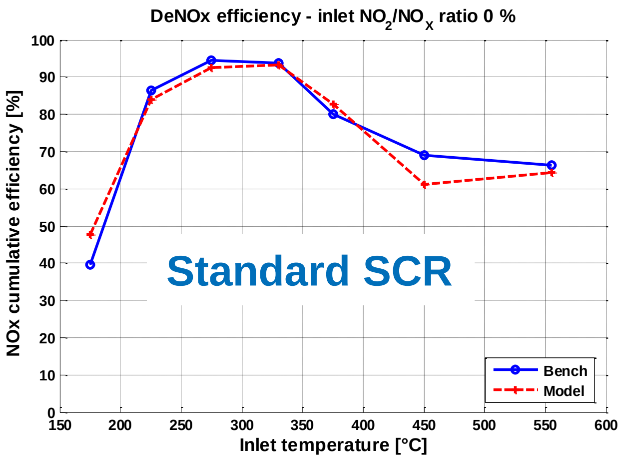


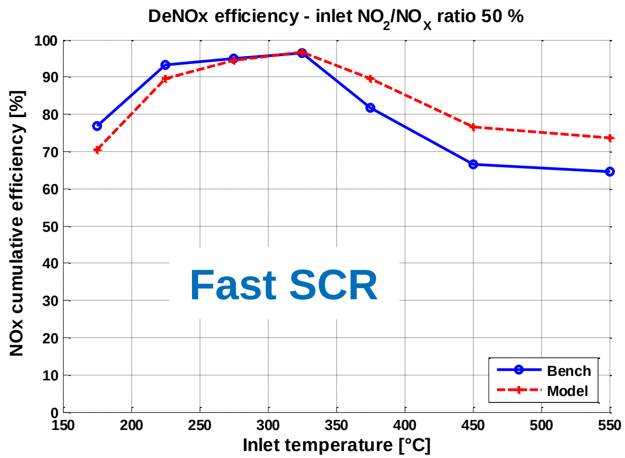
SCR model calibration for DeNOx reaction on SGB test

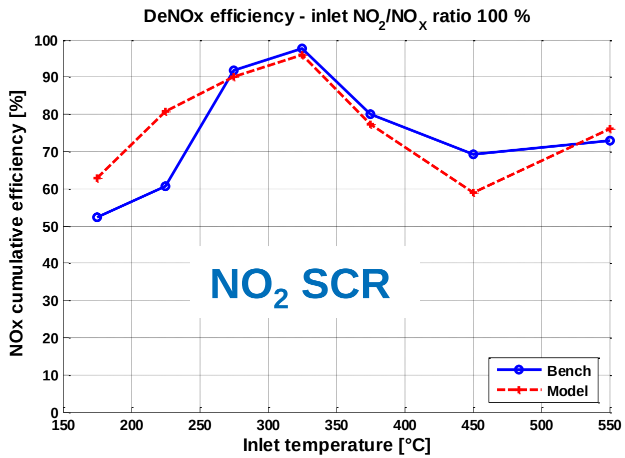
- **Ammonia oxidation reaction calibration:**
  - $4\ NH_3\text{-}S_i + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O + 4\ S_i$
  - $r_{NH3ox} = k_{NH3ox} \times e^{-\frac{E_{NH3ox}}{R \times T_S}} \times [O_2] \times \theta_{NH3}$
  - calibration is done on DeNOx SGB test with an high upstream temperature



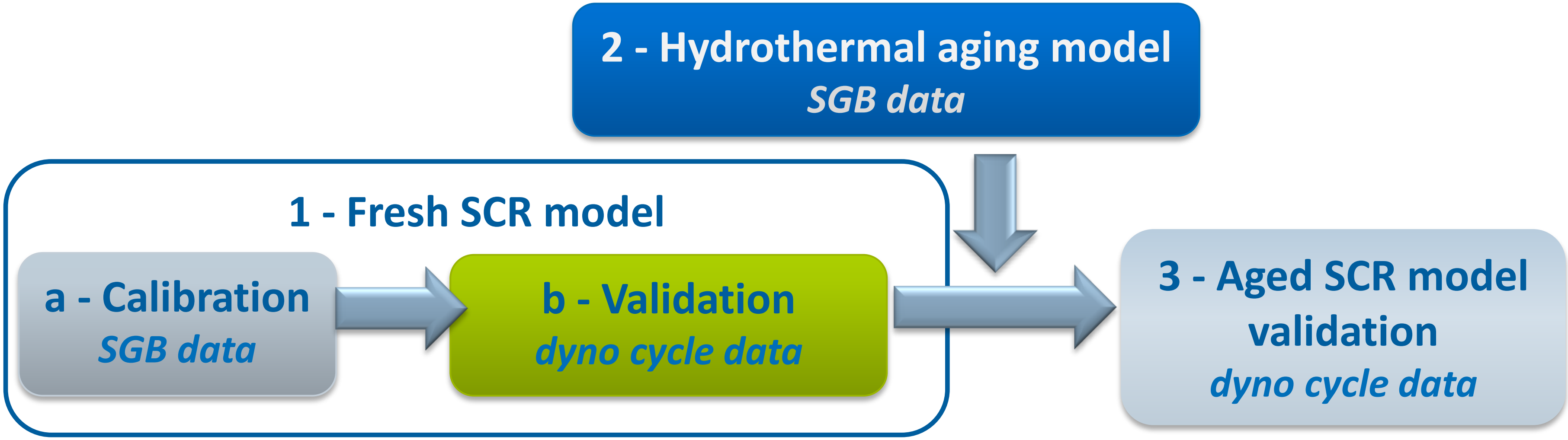
This calibration allows to obtain consistent results on the overall test data







Approach: from fresh to aged SCR model



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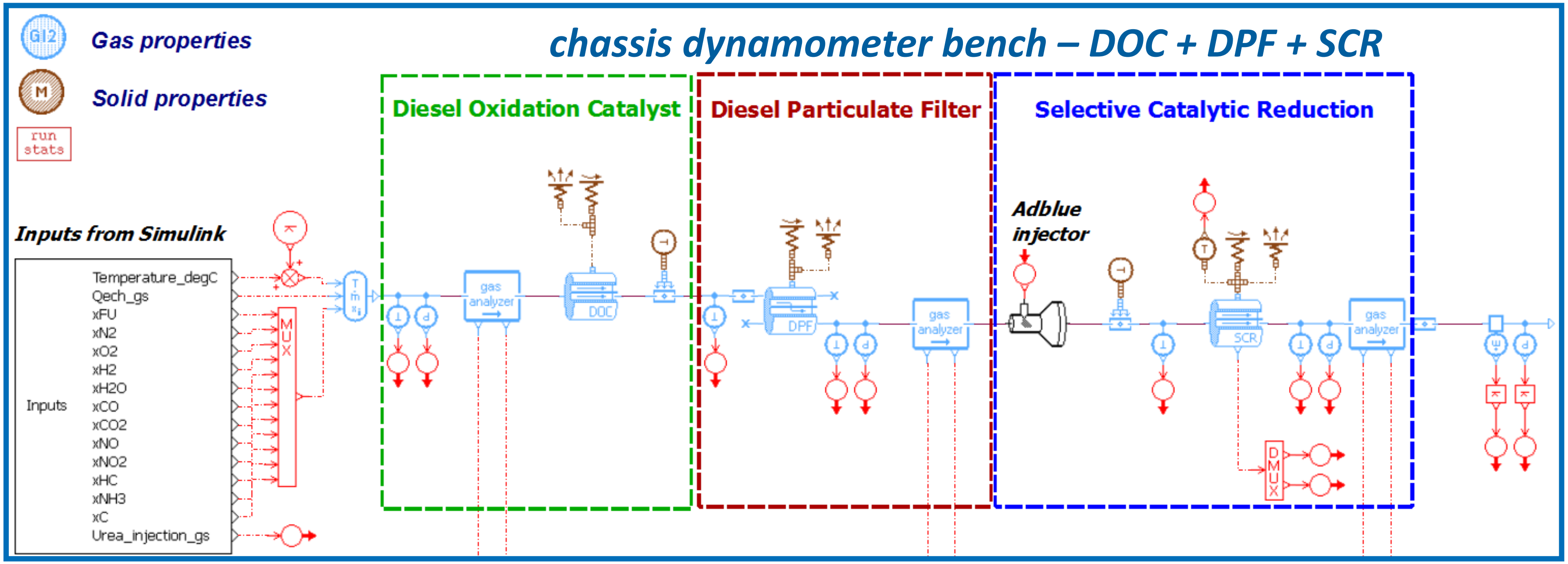
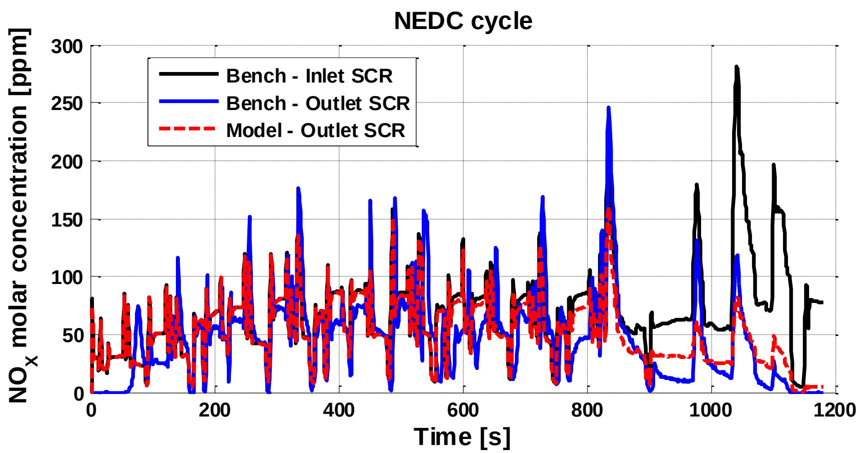
Exhaust line model presentation

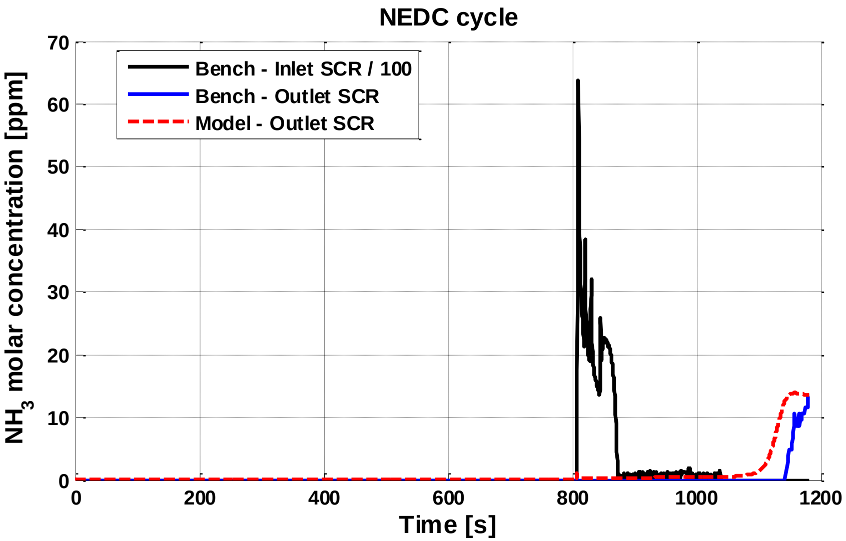
- **LMS Amesim model of a complete exhaust line composed of a DOC, a DPF and a SCR using IFP-Exhaust library coupled with a Simulink control platform**

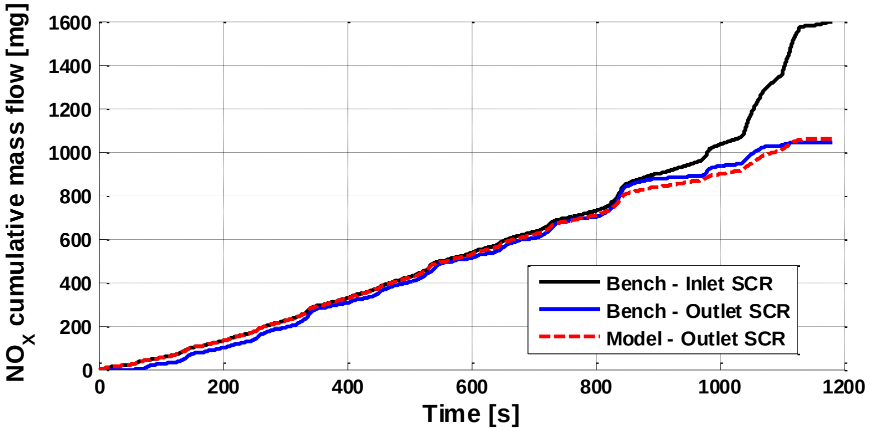


- **Upgrade from SGB models:**
  - **convective and radiative heat transfer modeled**
  - **light adjustment of catalysts calibration**

Fresh SCR cycle simulation results on NEDC cycle

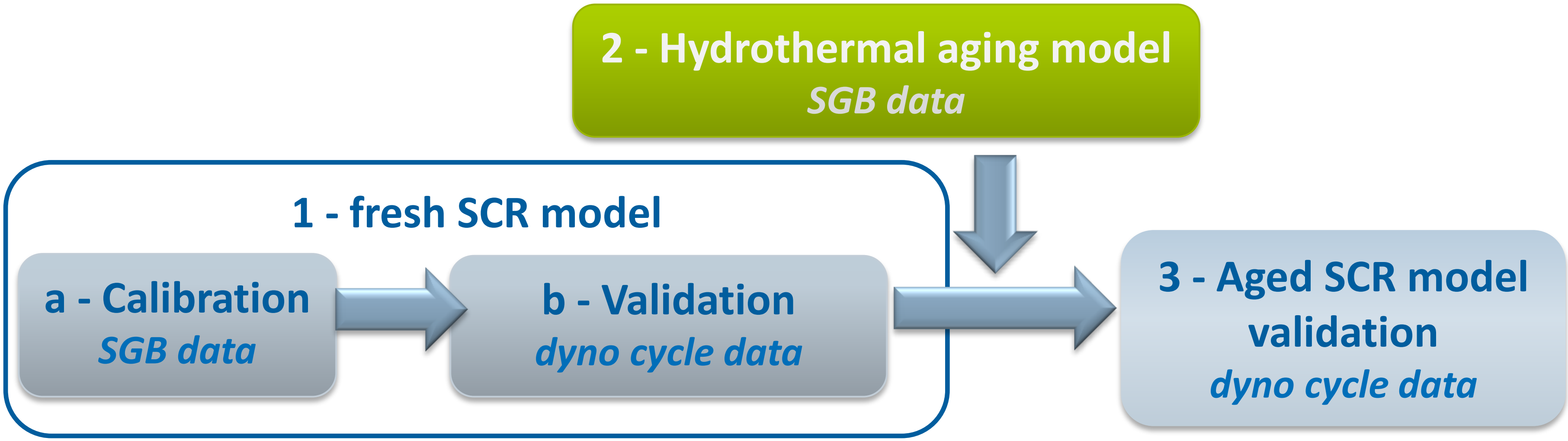






- NO_X reduction is well represented by the model
- Almost no NH_3 slip on this cycle with a fresh SCR

Approach: from fresh to aged SCR model



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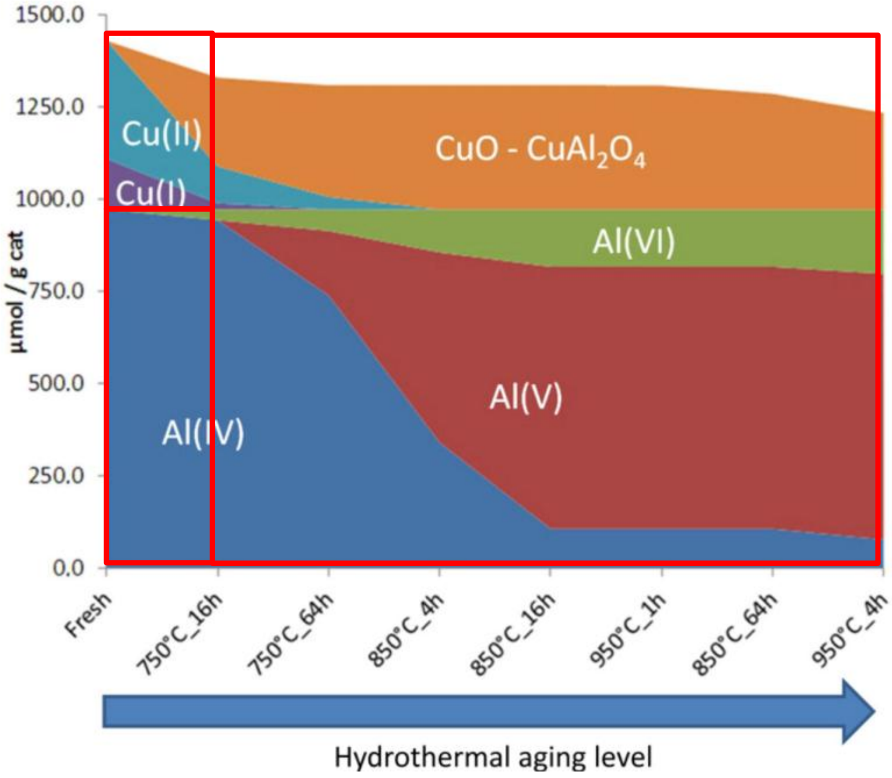
Hydrothermal aging effects on SCR catalyst : Cu-Zeolite



- **Catalyst changes with aging:**
  - **at low aging, copper migrates from exchanged positions to form copper oxide aggregates in the zeolite porosity**
  - **during this phase, copper in exchanged positions protects the zeolite structure against dealumination**
  - **with increasing aging, copper is completely removed from exchanged positions and dealumination occurs.**

Ref.

« Hydrothermal aging effects on Cu-zeolite NH_3-SCR catalyst »

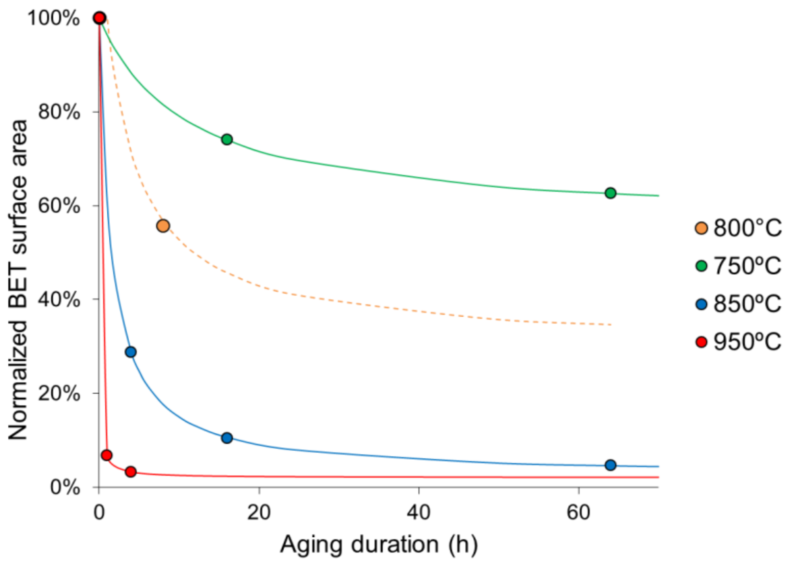
M. Valdez Lancinha Pereira, A. Nicolle, D. Berthout, IFPEN

doi:10.1016/j.cattod.2015.03.027

Hydrothermal aging effects on SCR catalyst : Cu-Zeolite

- **Aging model description:**
  - loss of copper and aluminum ions contributes to a loss of catalytic sites: *modeled by a coefficient on active surface and on NH_3 capacities*

$$S_{active}aged = Coeff_{Cu} \times Sact_{ive}\ fresh$$
$$\Omega_{NH3site1}aged = Coeff_{site1} \times \Omega_{NH3site1}\ fresh$$
$$\Omega_{NH3site2}aged = Coeff_{site2} \times \Omega_{NH3site2}fresh$$

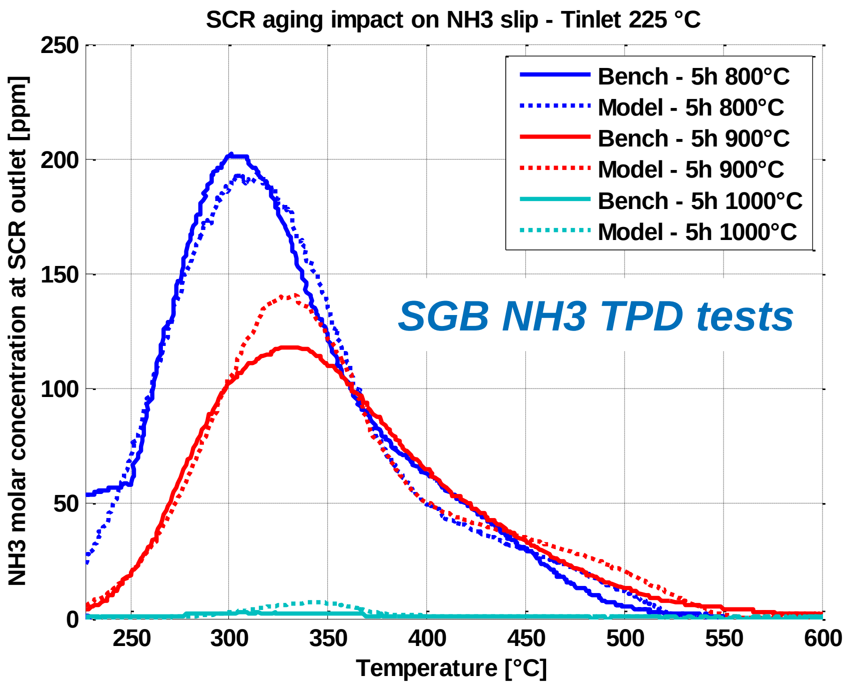


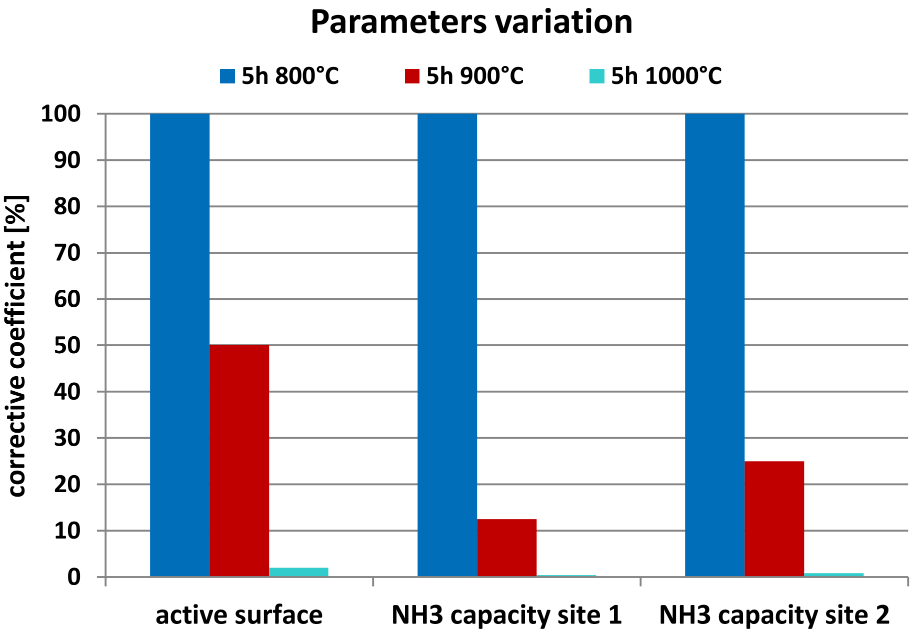
  - CuO aggregates promote NH_3 oxidation: *modeled by a coefficient on NH_3 oxidation activation energy*

$$r_{NH3ox} = k_{NH3ox} \times e^{-\frac{Coeff_{CuO} \times E_{NH3ox}}{R \times T_s}} \times [O_2] \times \theta_{NH3}$$

  - no other changes in the calibration of the kinetic constants (k_j, Ea_j) determined on the fresh sample

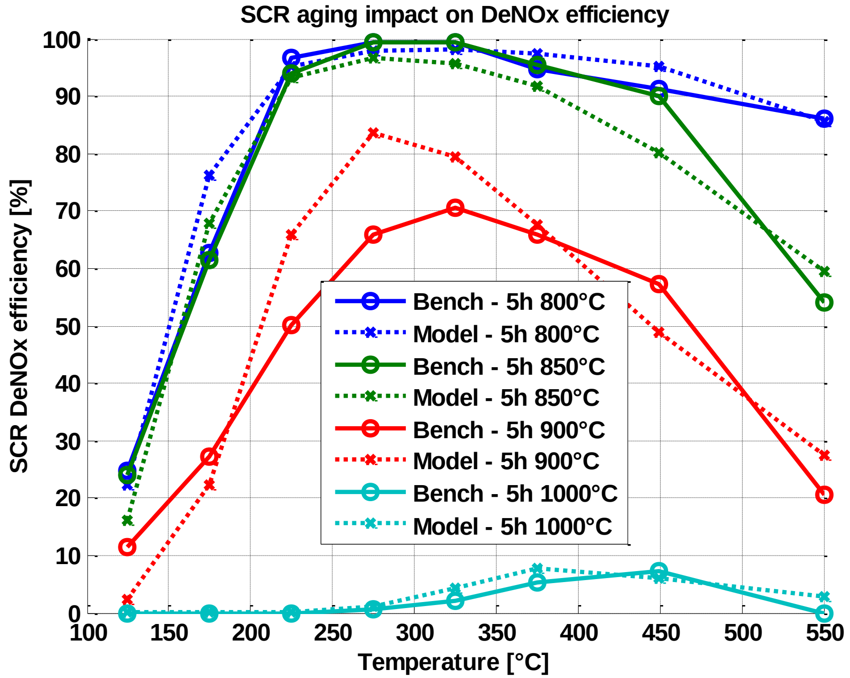
Aging impact set up for NH_3 storage - Reactor scale

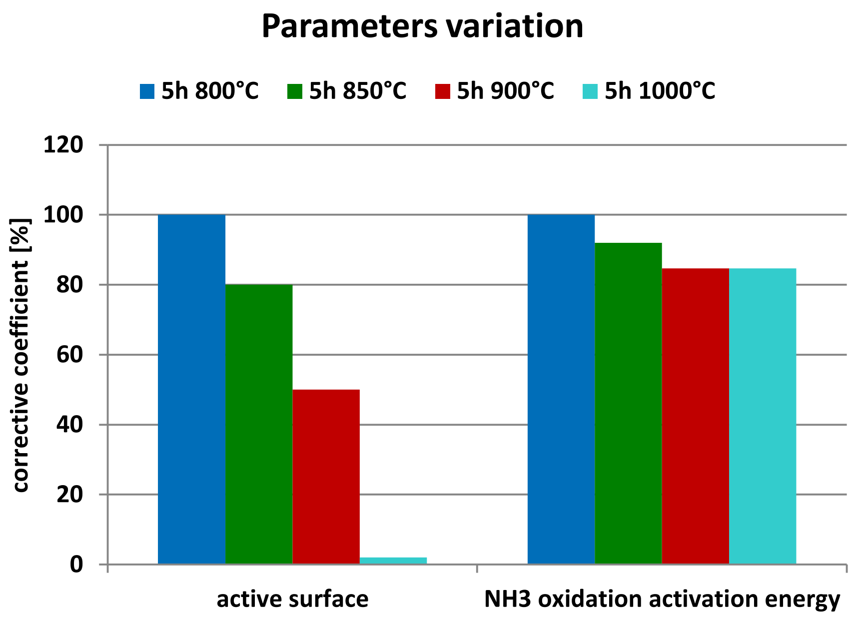




- **NH_3 storage capacity reduction with aging is observed on SGB NH3 TPD tests**
  - **hydrothermal impact on NH_3 capacity is higher on "low temperatures" NH_3 storage sites**
- **Desorption reaction rate reduction due to active surface reduction with hydrothermal aging temperature is well modeled**

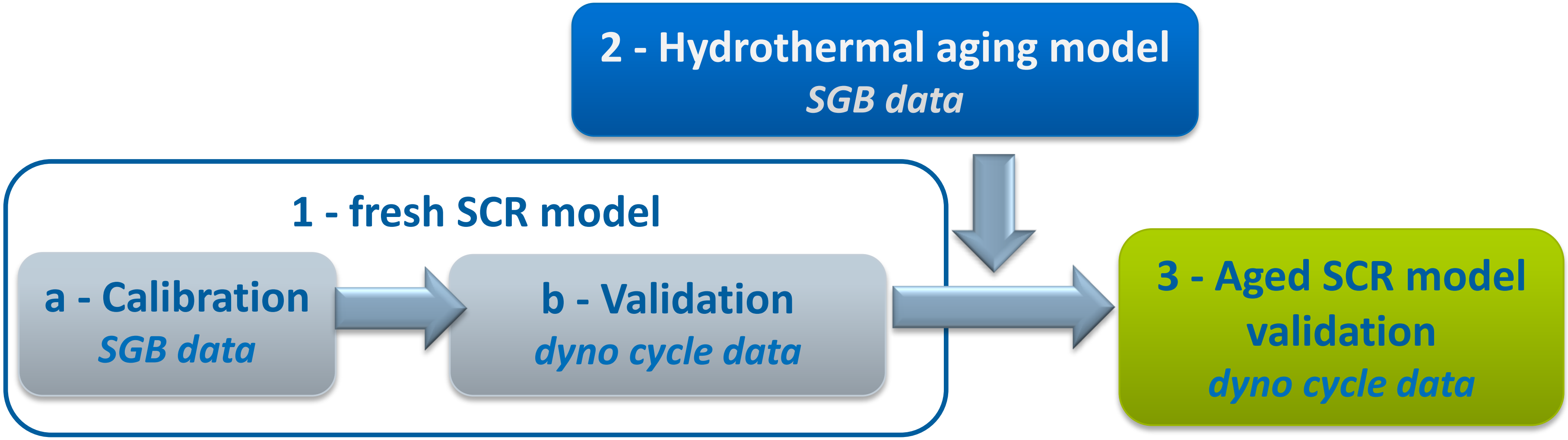
Aging impact set up for DeNOx reaction - Reactor scale





- At low hydrothermal aging temperature, main aging impact is a loss of catalyst efficiency at high temperature due on NH_3 oxidation
  - impact of CuO aggregates
- DeNOx reactions rates reduction is well represented by the reduction of the active surface in the model

Approach: from fresh to aged SCR model



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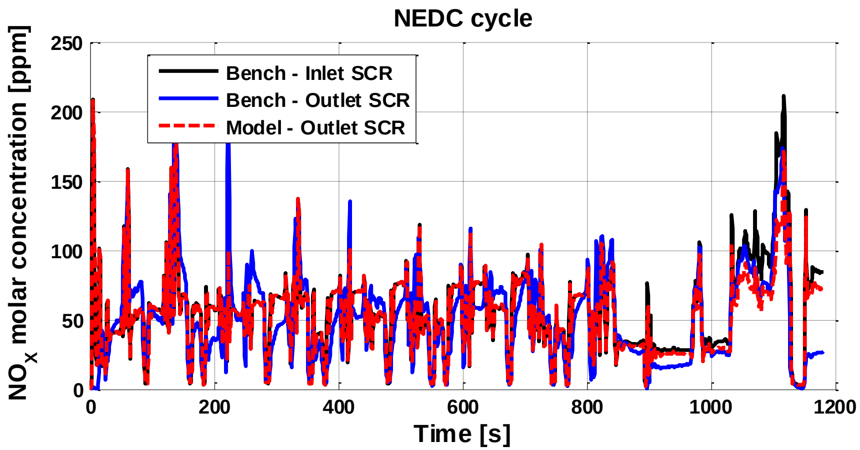
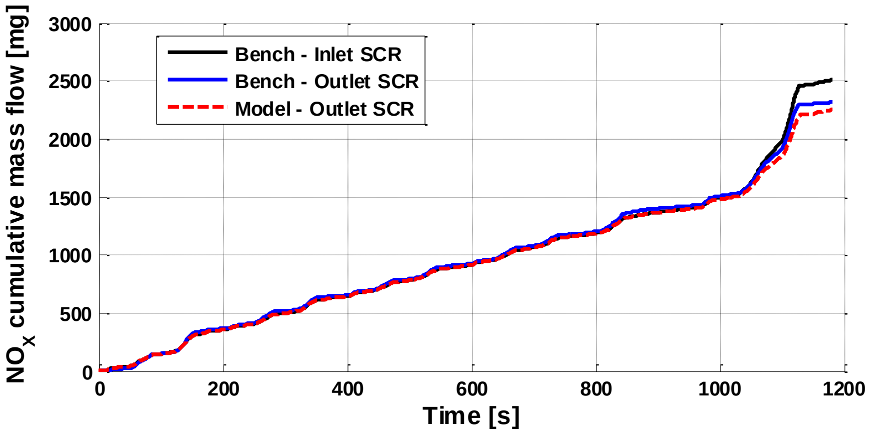
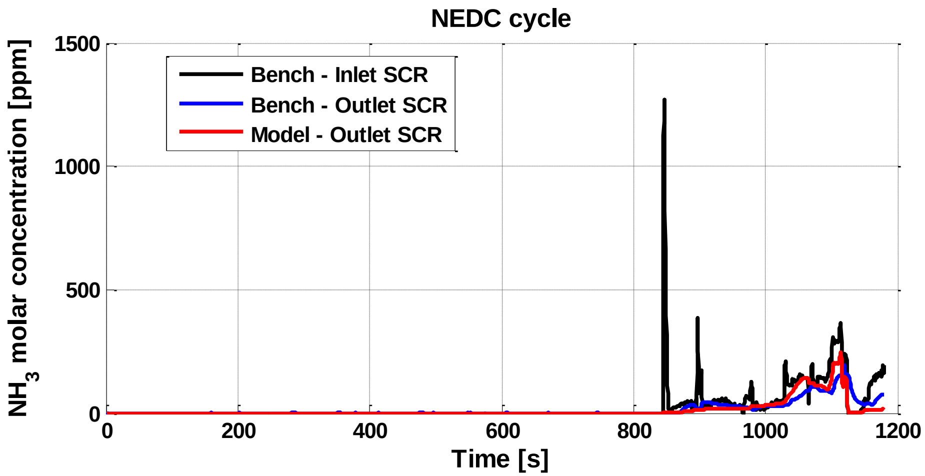
5h 1000°C aged SCR cycle simulation results - NOx

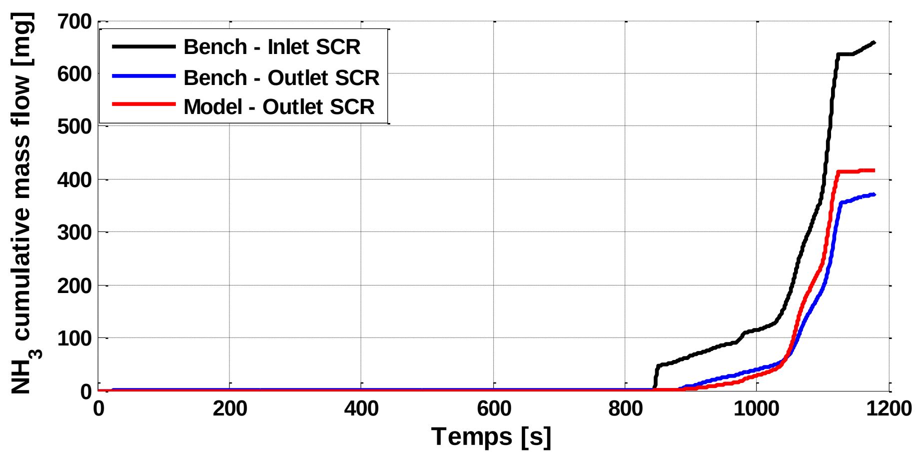




- NEDC cycle is realized with an aged SCR
  - hydrothermal aging of 5h at 1 000°C
- Coefficients from previous aging model are used:
  - Active surface: 2 %
  - NH_3 capacity of site 1: 0,5 %
  - NH_3 capacity of site 2: 1 %
  - NH_3 oxidation activation energy: 85 %
- Impact on DeNOx efficiency is well modeled

5h 1000°C aged SCR cycle simulation results - NH_3





- **Impact on NH_3 slip is well modeled : right timing and level of release**
- **While NH_3 slip for the fresh SCR was almost inexistent, more than half of NH_3 injected quantity is released in the atmosphere for the aged SCR**

➔ ***Injection strategy can be optimized***

Summary

- **Simple hydrothermal aging model with reduced parameterization:**
  - **one coefficient for active surface reduction**
  - **two coefficients for NH_3 storage capacities, close to active surface coefficient**
  - **one coefficient for NH_3 oxidation activation energy**
- **Need only SGB data**
- **Consistency in results on NO_X and NH_3**

- **Efficient methodology to model SCR aging impact from a fresh SCR calibration**

➔ ***This hydrothermal aging model will be integrated in IFP-Exhaust library for the next LMS Amesim release***

Innovating for energy

For further questions, please contact:

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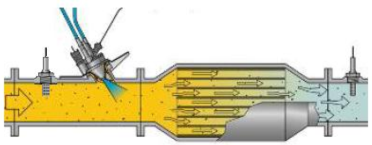
Back up: IFP-Exhaust Library

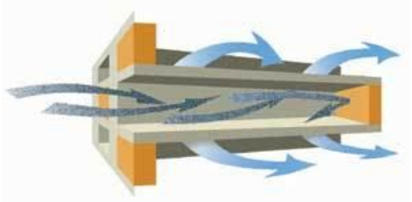
Library dedicated to the after-treatment devices modeling

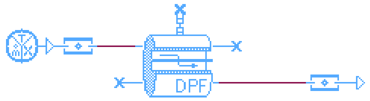
MiL, SiL and HiL capabilities

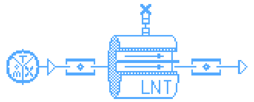


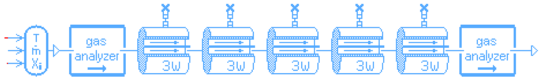
Catalysts and Filters
(DOC, DPF,LNT,SCR, SCR-F & 3WC)

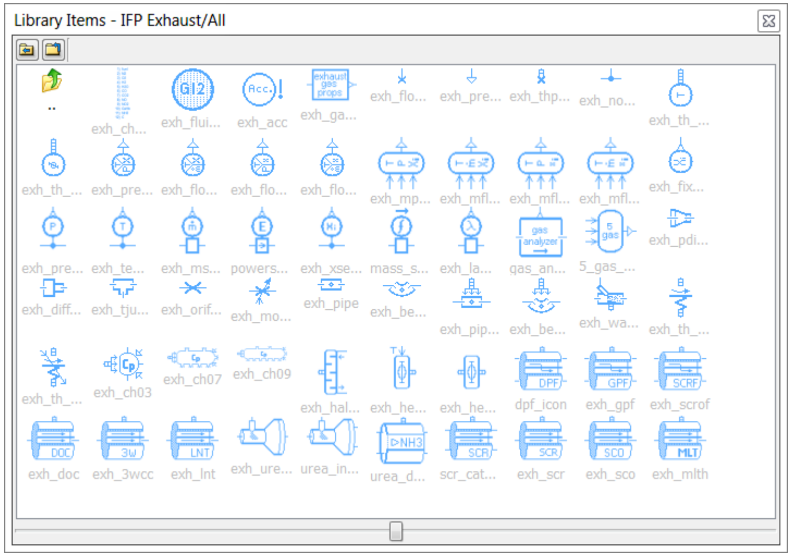
Pneumatic flow
(pipes, orifices, volumes.)











Heat transfer
(free and forced convection)

Sensors and Sources
(temperature, pressure, species)