JM

Johnson Matthey
Inspiring science, enhancing life

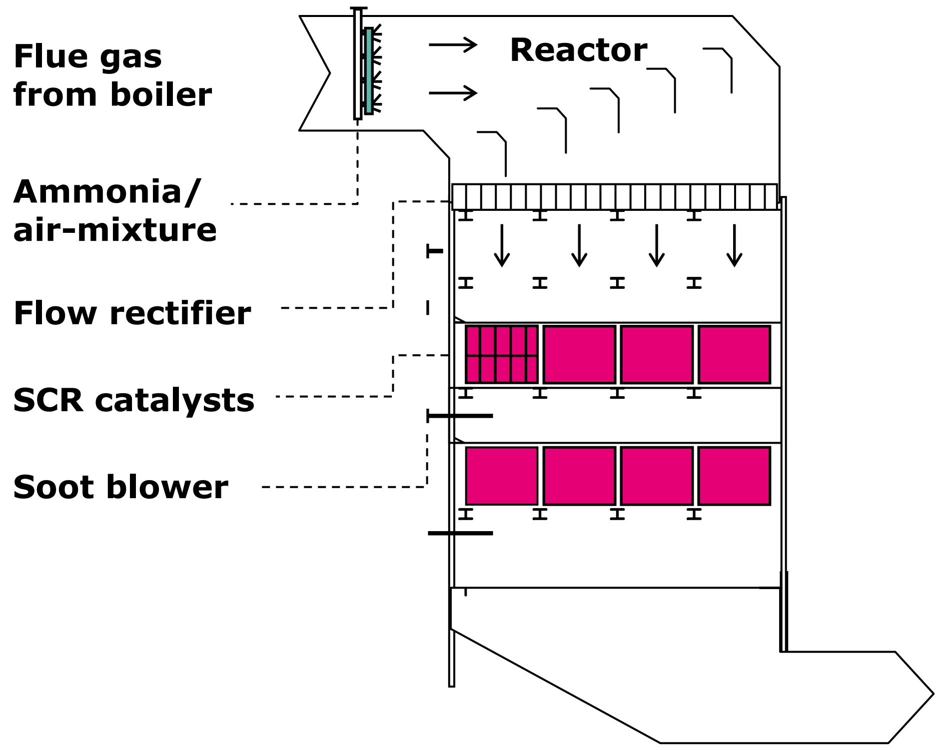
Americas hydrogen and syngas technical training seminar

Selective Catalytic Reduction (SCR)

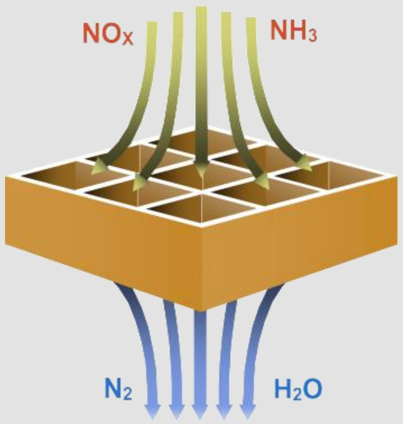
Kevin Doura

Selective Catalytic Reduction (SCR)

Inlet: NO_x, NH_3, O_2, SO_X, H_2O, N_2, CO_2



Outlet: N_2, H_2O, (SO_3) + CO_2, NO_x and NH_3 slip



NO_x is reduced by urea as follows:

- $4NO + 2(NH_2)_2CO + O_2 \rightarrow 4N_2 + 4H_2O + 2CO_2$

NO_x is reduced by ammonia across the SCR catalyst:

- $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ (standard)
- $NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$ (fast)
- $2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$ (slow)

Undesirable side reactions:

- $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ (non-selective oxidation)
- $2SO_2 + O_2 \rightarrow 2SO_3$
- $2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4$
- $NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4$

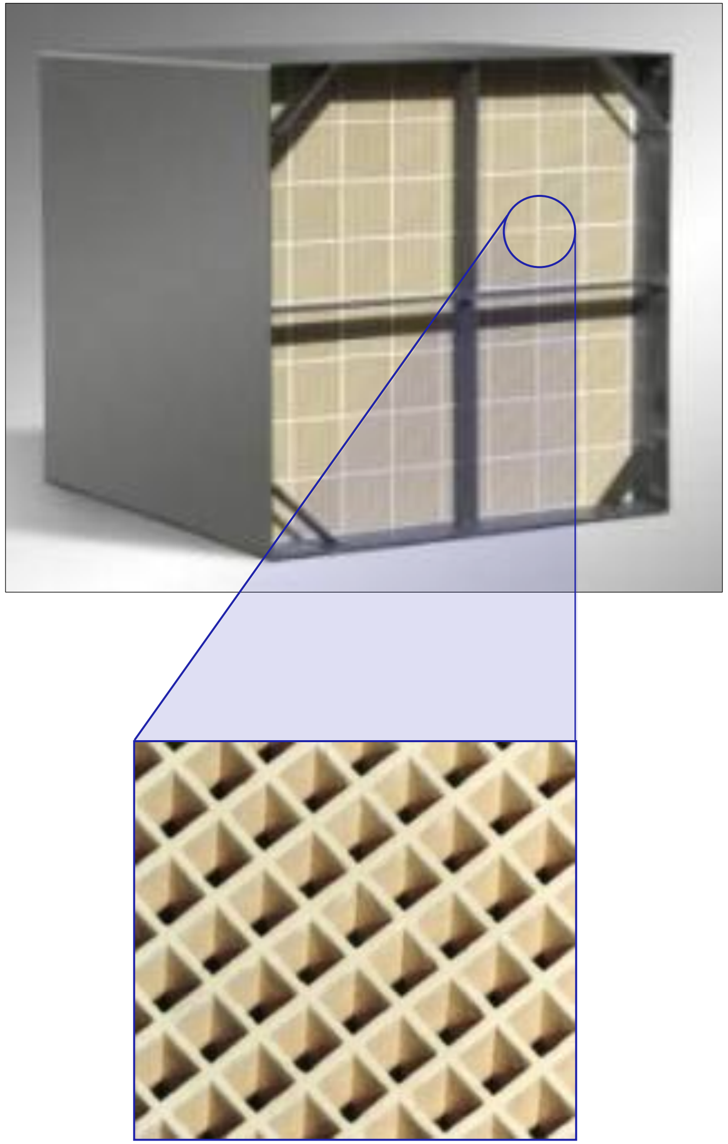
Extruded ceramic honeycomb SCR catalyst

Low to medium-dust application

High specific surface area

High activity

Variable length and number of cells (6-300 CPSI)



The data included herein were collected in a Johnson Matthey laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing. These are indicative data and do not represent a guarantee that the tested catalyst or emissions system will pass the relevant emissions legislation.

Relative SCR catalyst operating temperatures

Higher vanadium loading increases NO_x conversion at low temperature

Lower vanadium loading is better at higher temperature

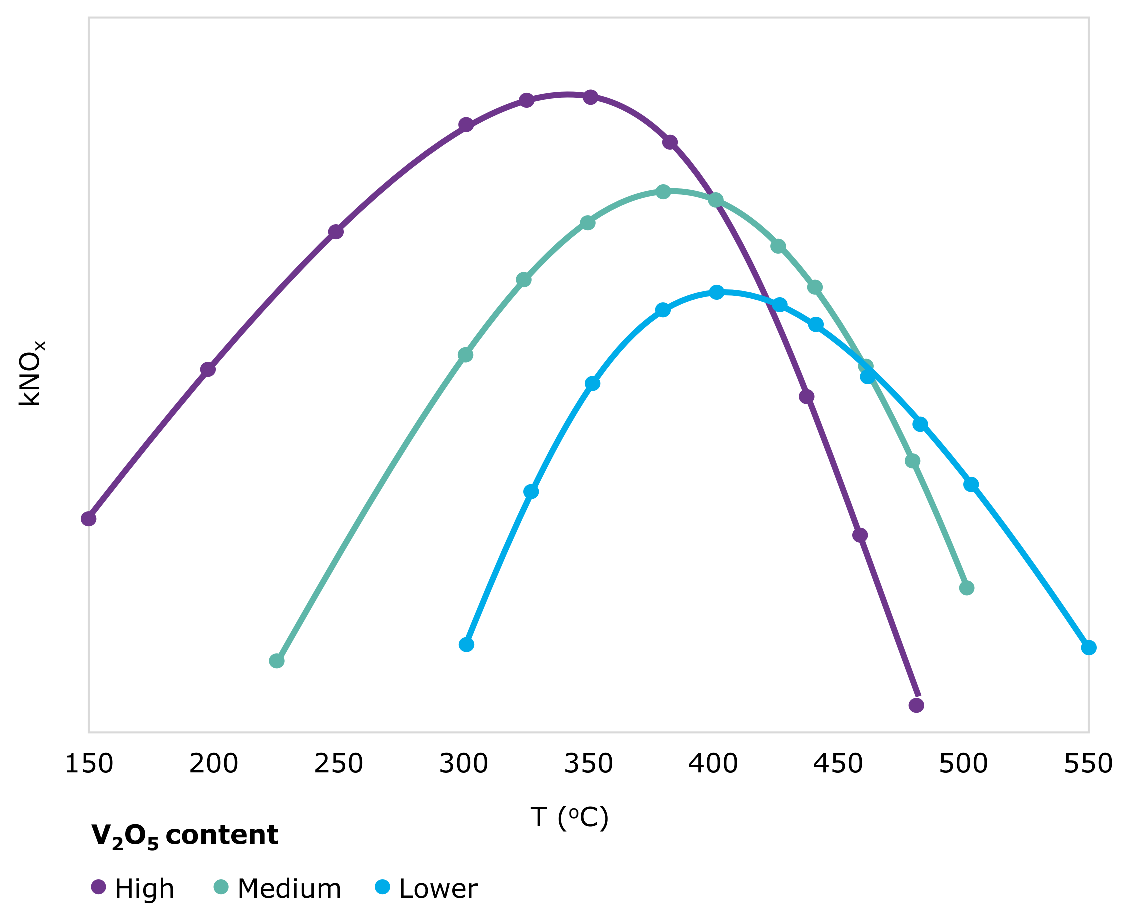
Higher V promotes the undesired reaction:

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

$$kNO_x = -\frac{\text{exhaust flow rate}}{\text{(cat volume)*(GSA)}} * \ln(1-x)$$

x = fraction NO_x conversion

GSA = geometric surface area (function of cell density)



The data included herein were collected in a Johnson Matthey laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing. These are indicative data and do not represent a guarantee that the tested catalyst or emissions system will pass the relevant emissions legislation.

Typical conditions:

SMR vs other SCR applications

Impact on design:

- T, O_2 and H_2O concentrations
- NO_x concentration
- Conversion targets
- NH_3 Slip
- Operating period
- Future T window – higher >500°C (932°F)

Application	SMR	Gas turbines	Carbon black
Temp. window (°C)	275-450	CC: 300-400 SC: 470-550	300-360
NO_x conc. (ppm,@ref. O_2)	**30-60**	~10-80	200-400
Act O_2 (%)	**1.2**-5.6	12-16	2.6-5
Ref. O_2 (%)*	3	15	7
H_2O conc. (%)	16.5-27.8	10	~40
NO_x conv. target (%)	70-95	80-99	80-94
NH_3 slip (ppm)	1-10	2-10	<5
Guarantee period (oph)	26,000-**44,000**	8,000/16,000	24,000
Pressure drop limit (mbar)	2.5-10	2	10

* Depends on local requirements/legislation

SMR
Steam Methane Reforming

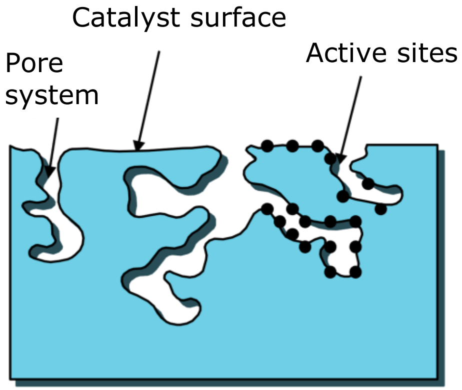
CC
Combined Cycle

SC
Simple Cycle

Deactivation mechanisms

Poisoning

Deactivation of the active sites by chemical attack (e.g. alkalis, phosphorus)

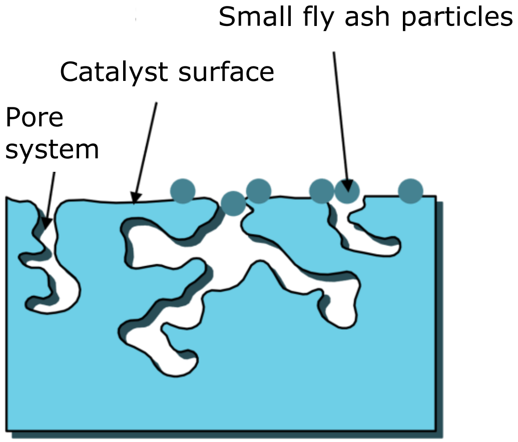


Adsorption of ammonia **inhibited**

$DeNO_x$-reactions **aren't possible any more**

Plugging

Microscopic blockage of the pore system by small fly ash particles

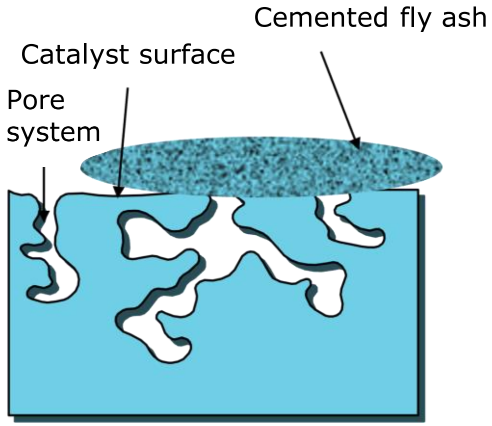


Fly ash particles are **diffusing** into the **catalyst pores**

Catalyst micro pore systems **plugged mechanically**

Masking

Macroscopic blockage of catalyst surface by cement fly ash



Reactive particles **grow on the surface**

Due to **high amount** of **calcium oxide in the ash**

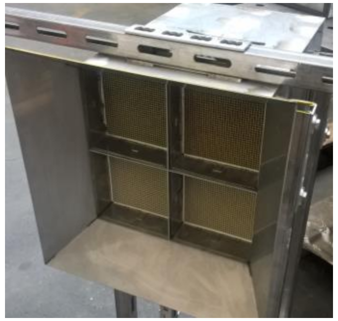
The data included herein were collected in a Johnson Matthey laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing. These are indicative data and do not represent a guarantee that the tested catalyst or emissions system will pass the relevant emissions legislation.

Steam methane reformer field experience

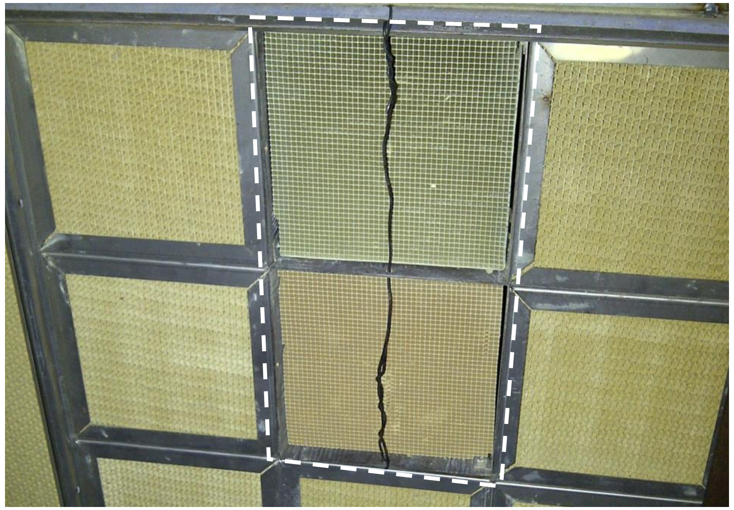
Main driver for catalyst deactivation in Steam Methane Reformer (SMR)

Poisoning - Chromium (Cr)

Masking



Fresh - JM



40K hrs SMR - JM

Analytical methods:

Activity testing (fresh vs. aged)

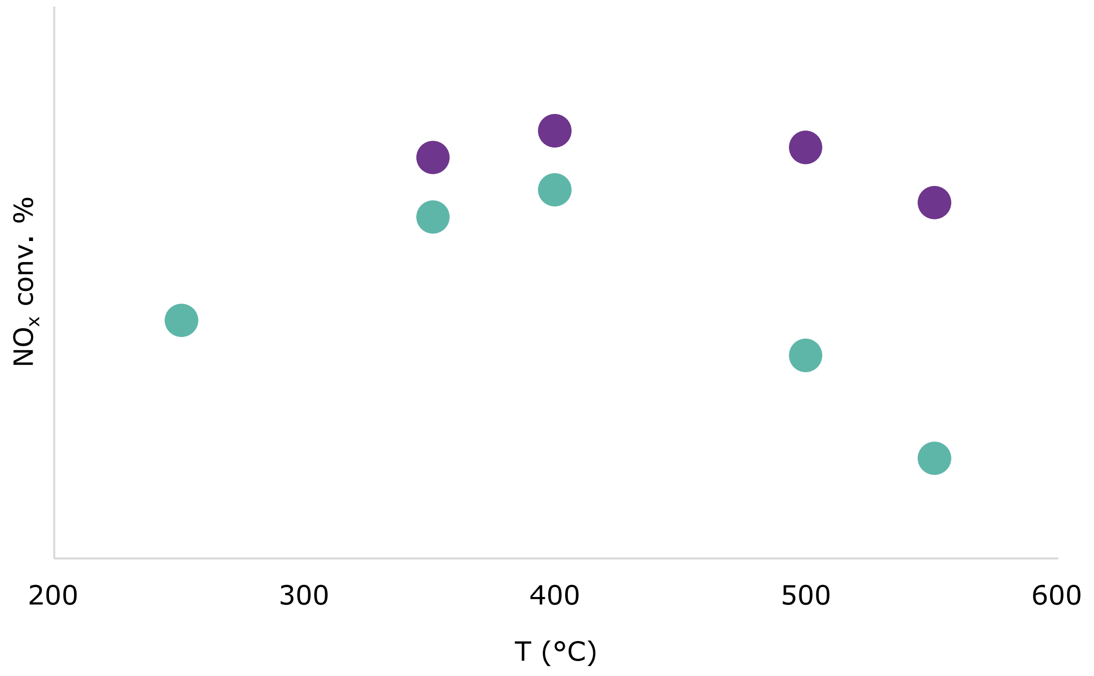
Chemical analysis – surface vs. bulk composition

Physical parameters – surface area, pore volume

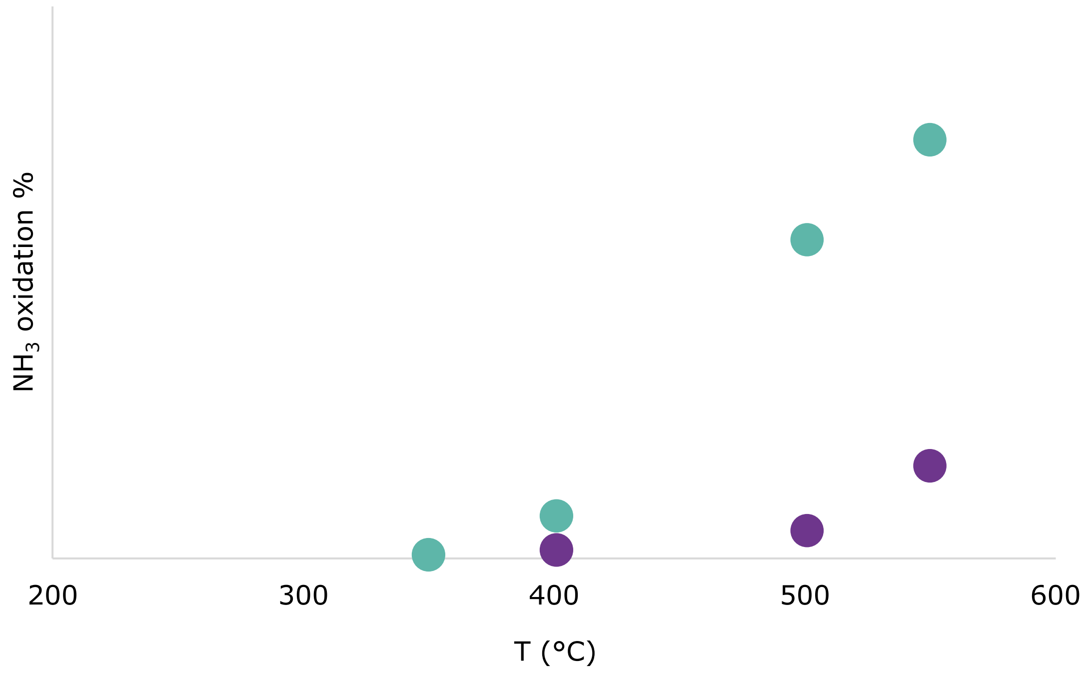
Catalytic activity negatively influenced by Cr deposition

- Fresh ref.
- SMR field aged

Impact of Cr – NO_x conversion



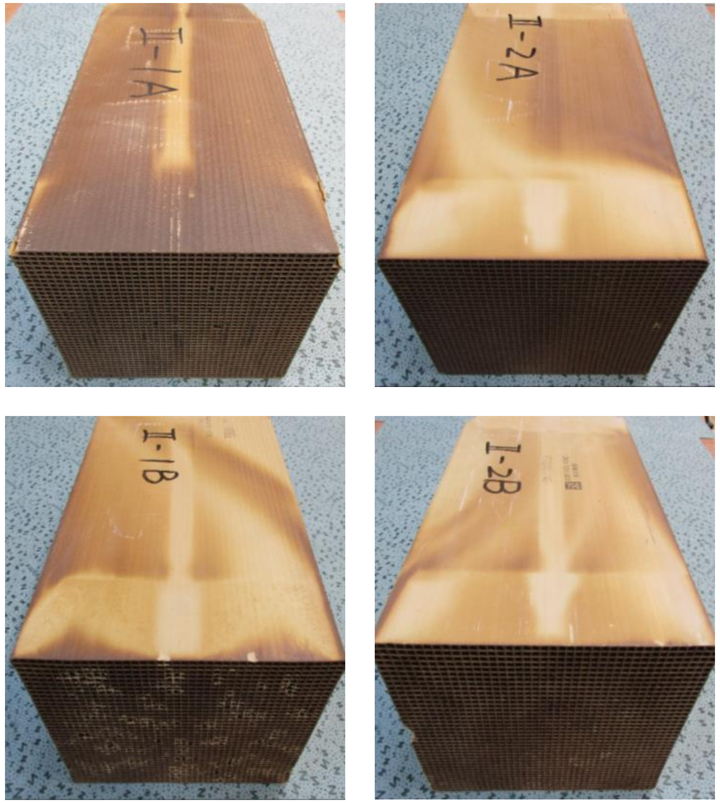
Impact of Cr – NH_3 oxidation



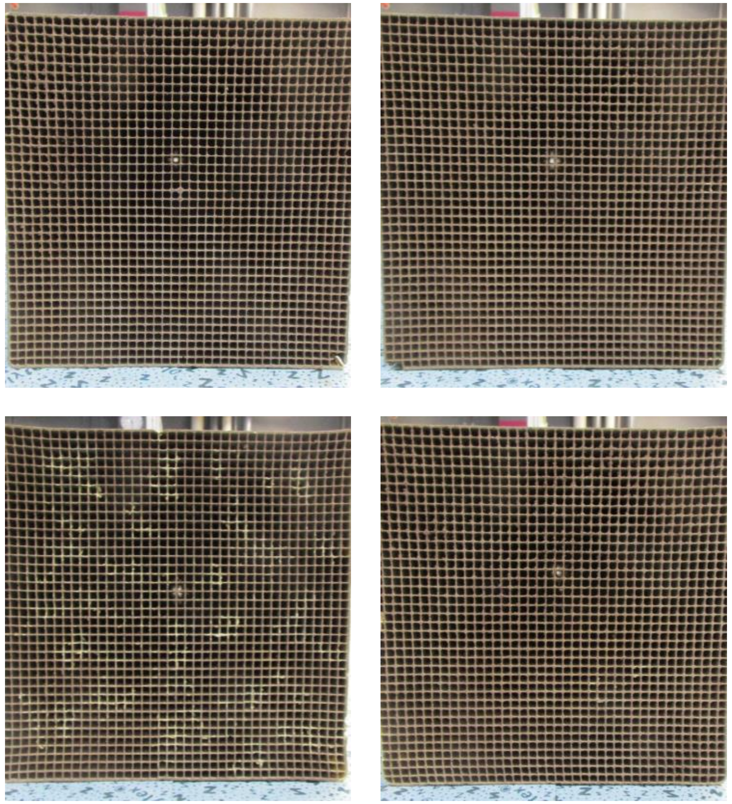
Chromium (Cr) – the higher the T, the higher the impact

The data included herein were collected in a Johnson Matthey laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing.
These are indicative data and do not represent a guarantee that the tested catalyst or emissions system will pass the relevant emissions legislation.

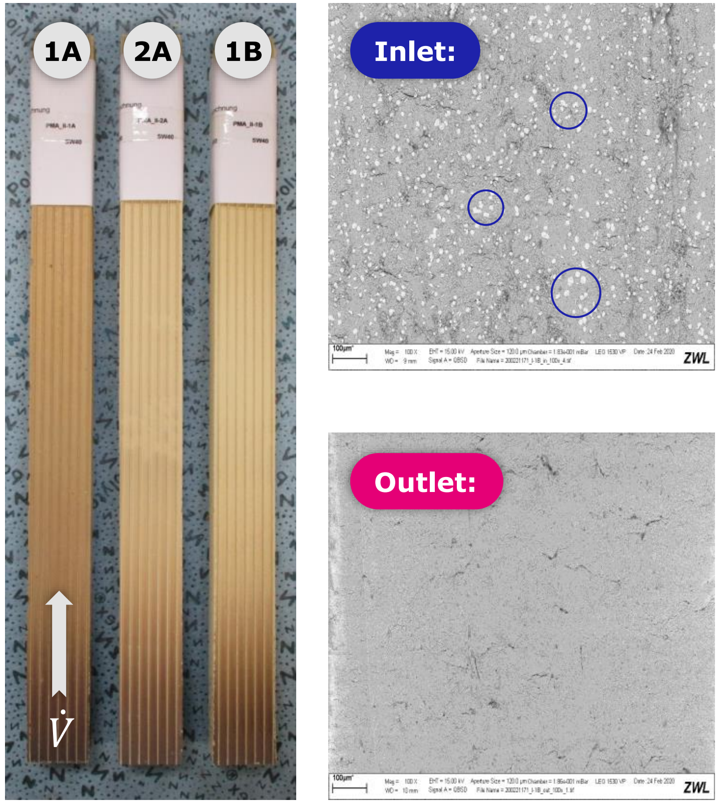
Visual discoloration of field returns due to poisons and ash



Discolouring on the shell, face side and inner channels (inlet side) was shown



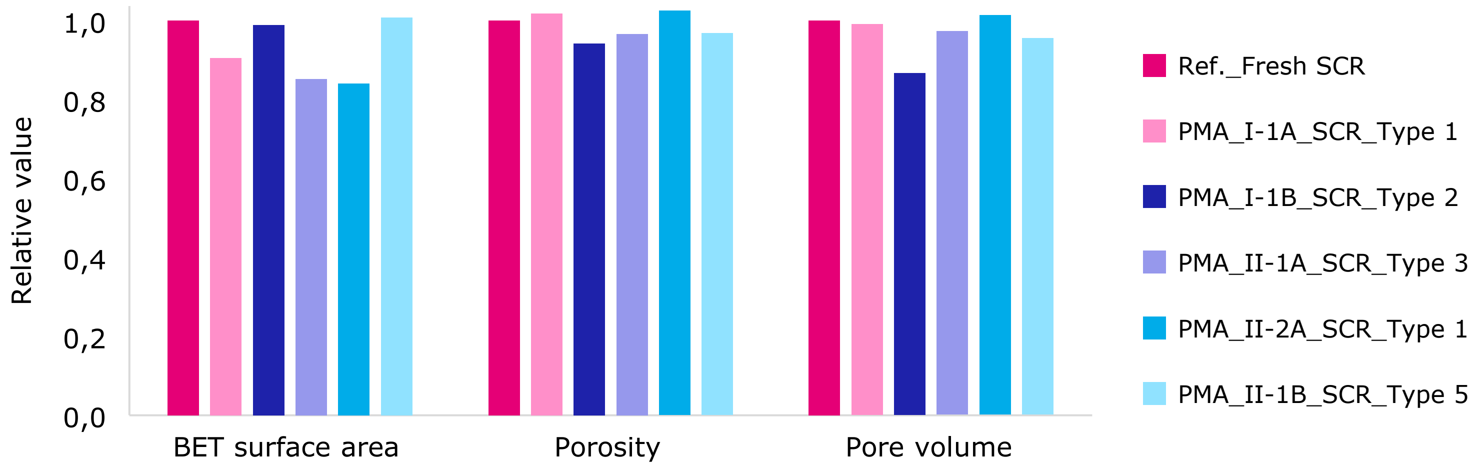
Deposition of **particulate ash** on inner walls of inlet side found



No particulate ash deposition at outlet side of the catalysts observed

The data included herein were collected in a Johnson Matthey laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing. These are indicative data and do not represent a guarantee that the tested catalyst or emissions system will pass the relevant emissions legislation.

Combination of physical-chemical techniques used to identify deactivation mechanisms



Compound as wt% oxide	CrO_3	Fe_2O_3	SO_3	K_2O
XRF [Bulk]	0.1-2	~0.2	~0.2	<0.15
EDX [Surface]	3.8-45	0.1-1.3	0.3-2	nd

No signs of thermal aging or pore plugging

BET, PR distribution provides insight into thermal aging and/ or pore pluggage

XRF: bulk chemcial analysis

EDX: surface chemical anlaysis

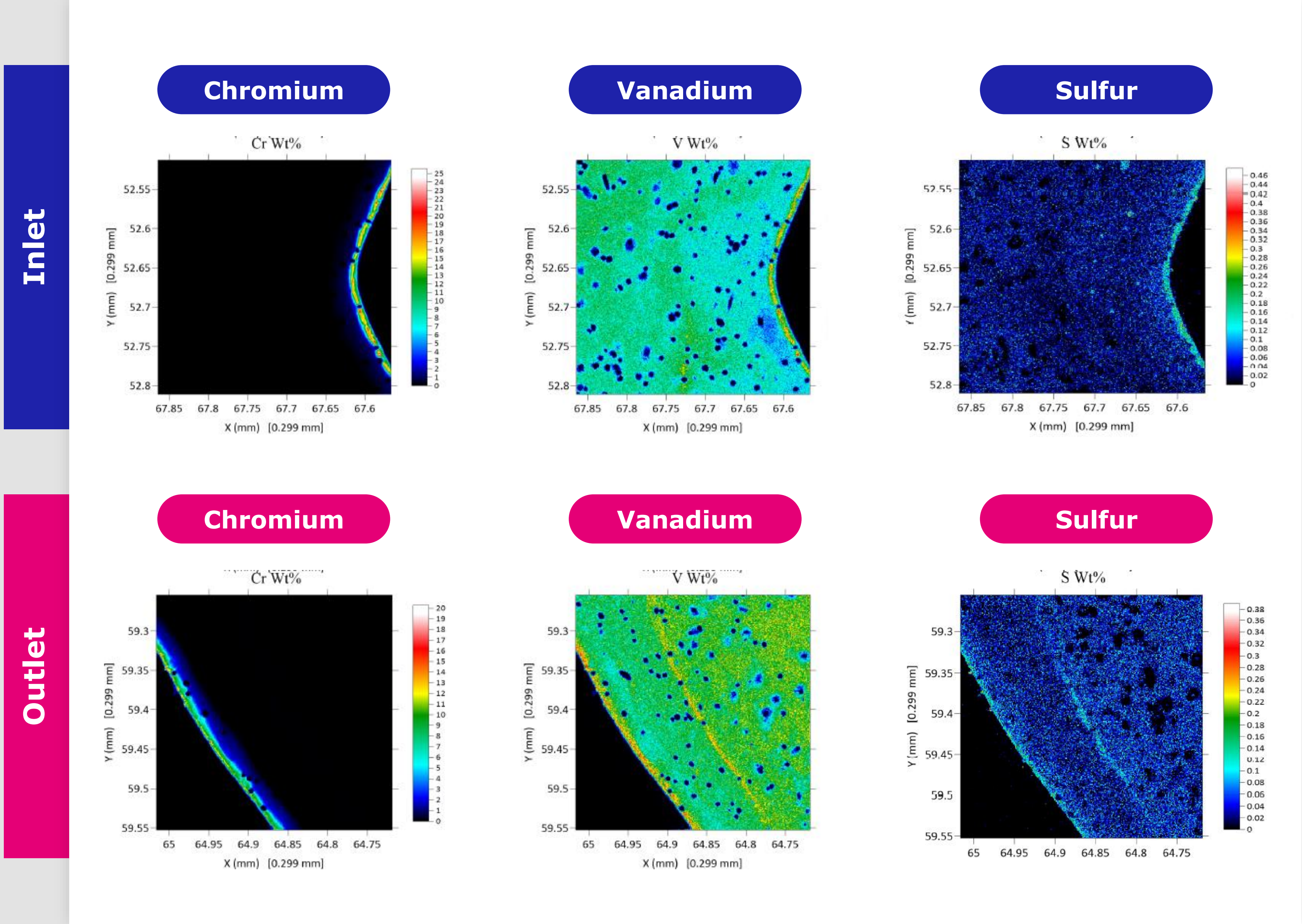
Where are deposits/ poisons located

Several mechanisms may overlap

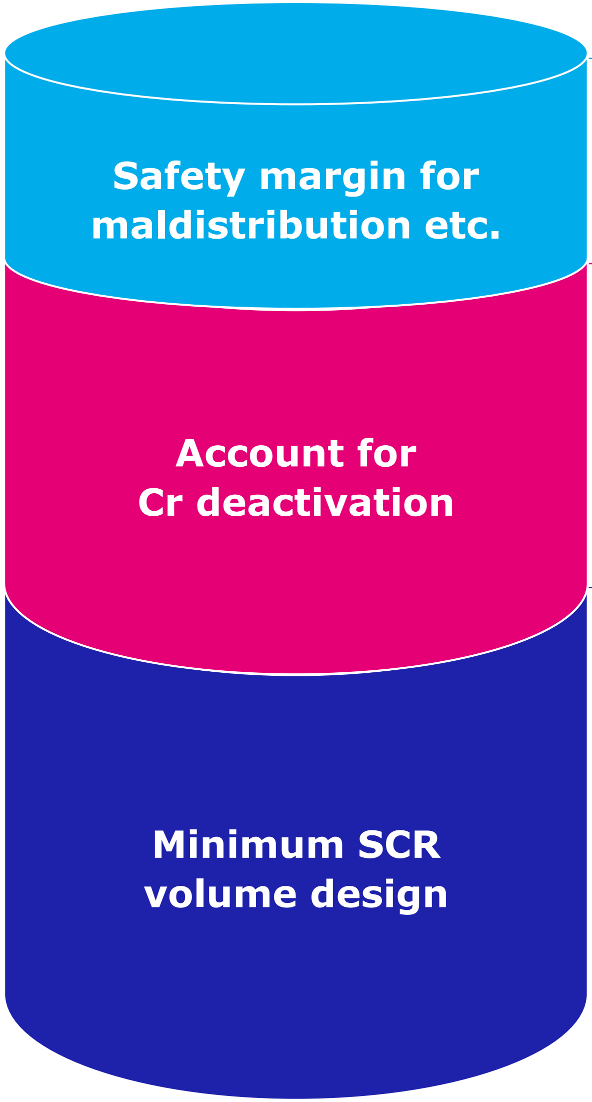
⇒ Cr the primary driver

The data included herein were collected in a Johnson Matthey laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing. These are indicative data and do not represent a guarantee that the tested catalyst or emissions system will pass the relevant emissions legislation.

Elemental mapping by EPMA reveals Cr concentrates at surface



SCR catalyst design considerations for SMR applications



- Flow maldistribution (flow rate, NH_3/NO_x)
- Catalyst errosion

- Fuel type (e.g. diesel, process off gas, biomass, NG etc.)
- Catalyst poisons
- Deactivation mechanisms

- Application type (high dust, low dust)
- NO_x reduction requirement
- NH_3 Slip requirements
- Max SO_2-to-SO_3 conversion
- Warranty time
- Pressure drop limitation
- Space limitations (reactor layout)
- Flue gas data: flow, temperature, NO_x, O_2, H_2O, SO_2

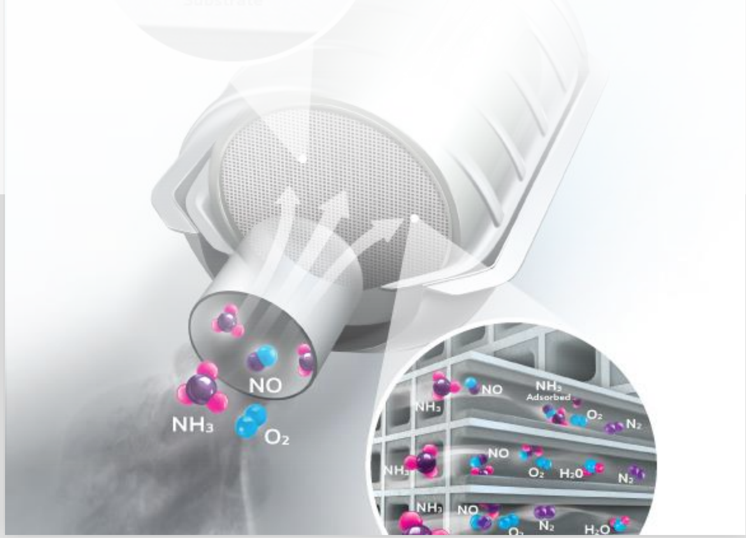
Future outlook

Ammonia slip catalyst

Increase of NH_3 slip

Overdosing at high temperature due to NH_3 oxidation

Requires **alternative solutions**



High temperature SCR catalyst

Increased system efficiency

Higher application temperatures

Reduced CO_2 footprint

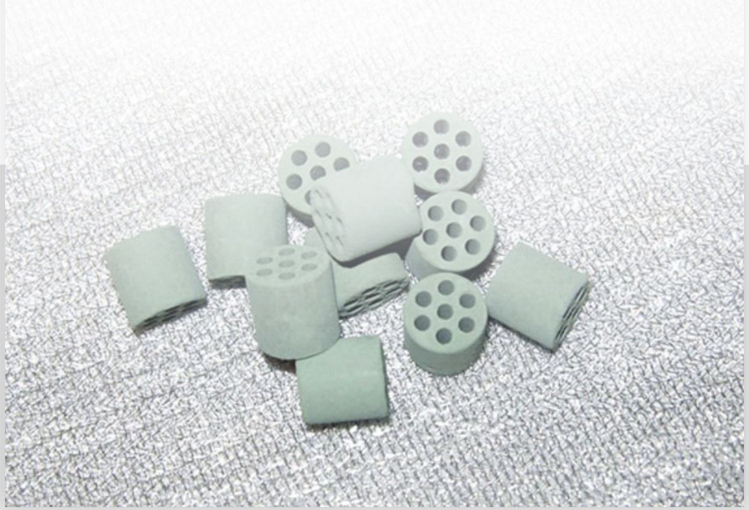
Cracking and N_2O catalyst

NH_3 as a **feed gas**

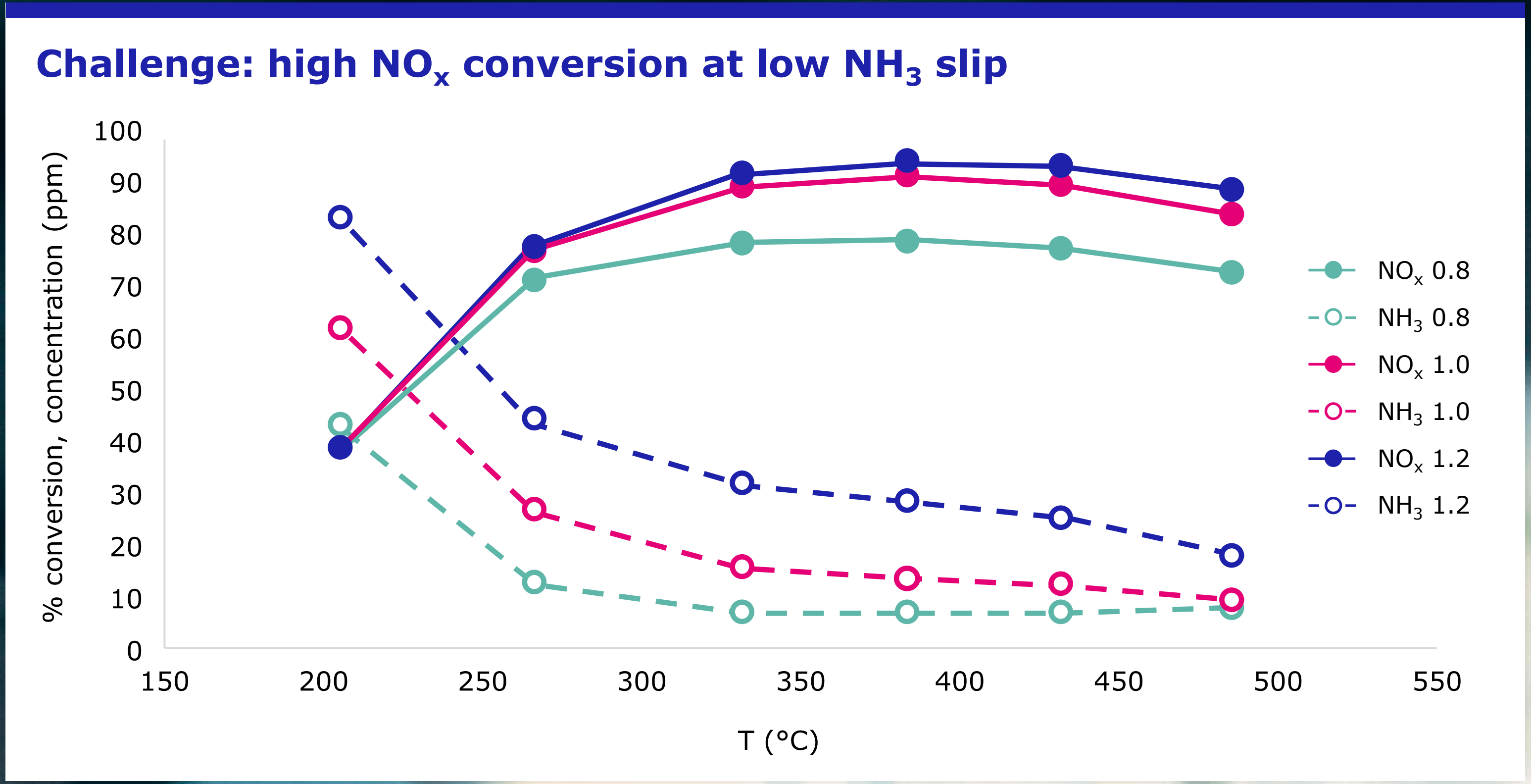
Ammonia **cracking**

N_2O abetment **possible**

We can provide a **solution!**



Ammonia Slip Catalyst (ASC) can boost NO_x conversion, reduce NH_3 slip, compensate for non-uniform NH_3 distribution, and oxidize CO/VOCs



Non-uniform NH_3 distribution can result in localized ANRs

ANR <1 results in incomplete NO_x conversion

ANR >1 results in NH_3 slip

Non-uniform NH_3 distribution can be a result of:

Control system

Gas flow characteristics

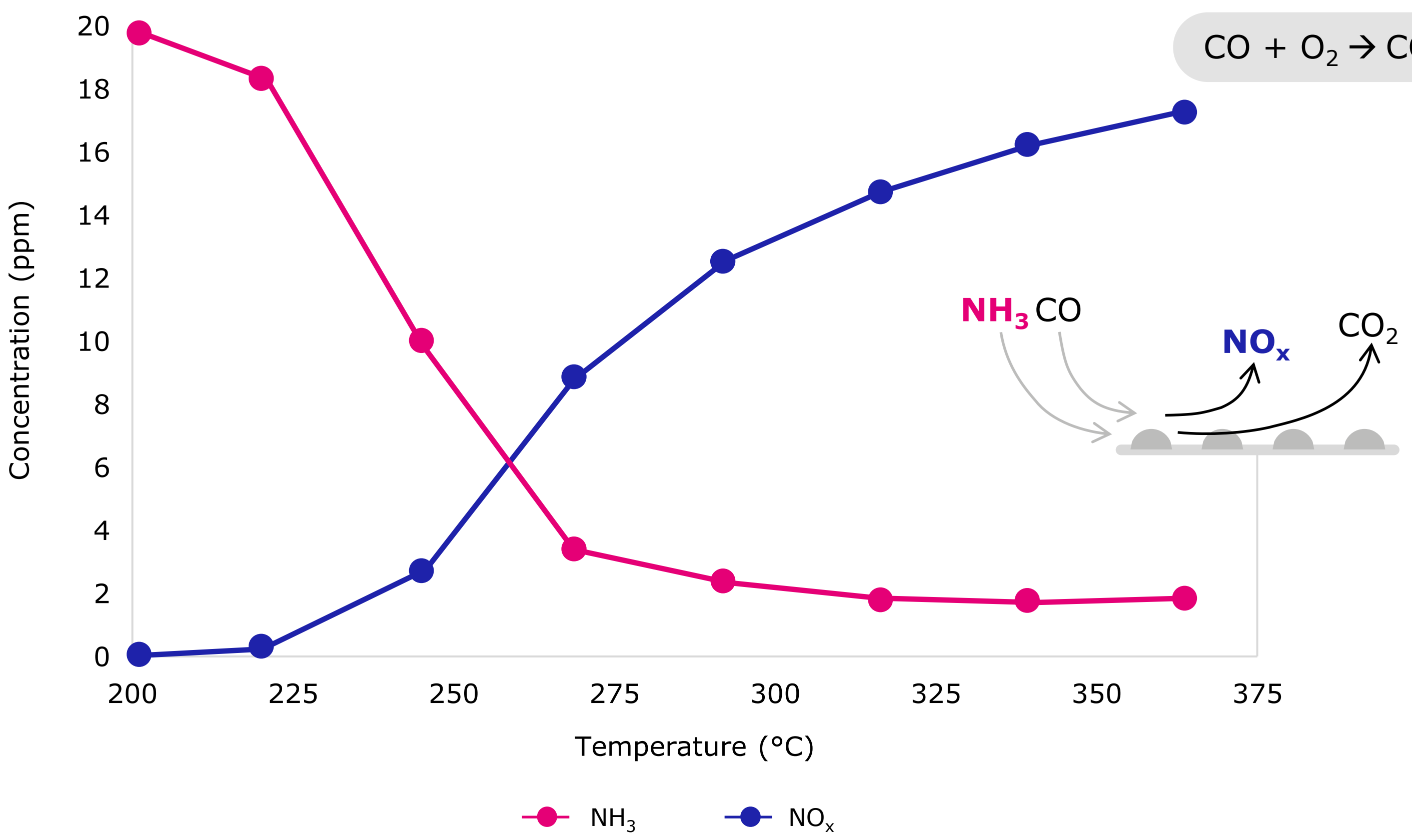
Fluctuating load

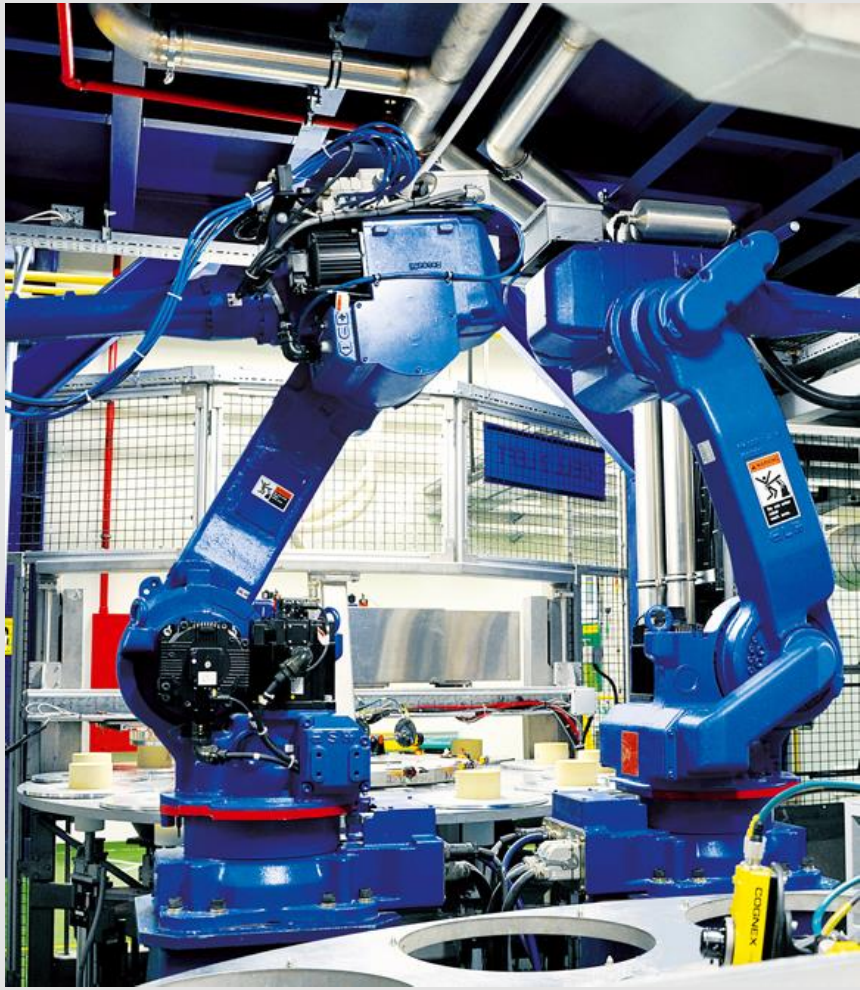
Previous generation ASC exhibit excellent activity (High NH_3/CO conversion) but poor selectivity (NO_x production)

Non-selective ammonia slip catalyst

$NH_3 + O_2 \rightarrow$ **NO_x** $+ H_2O$

$CO + O_2 \rightarrow CO_2$





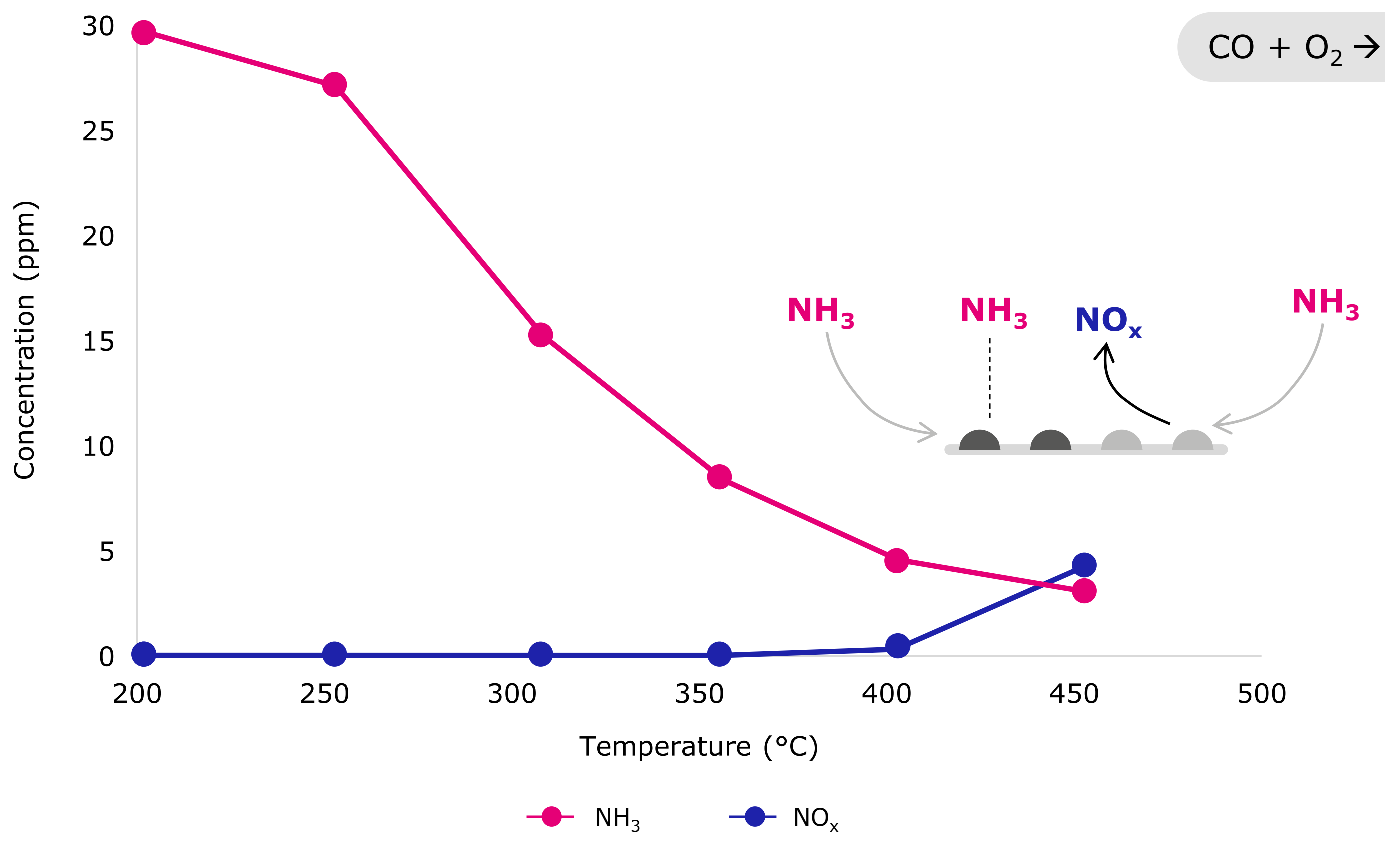
The data included herein were collected in a Johnson Matthey laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing. These are indicative data and do not represent a guarantee that the tested catalyst or emissions system will pass the relevant emissions legislation.

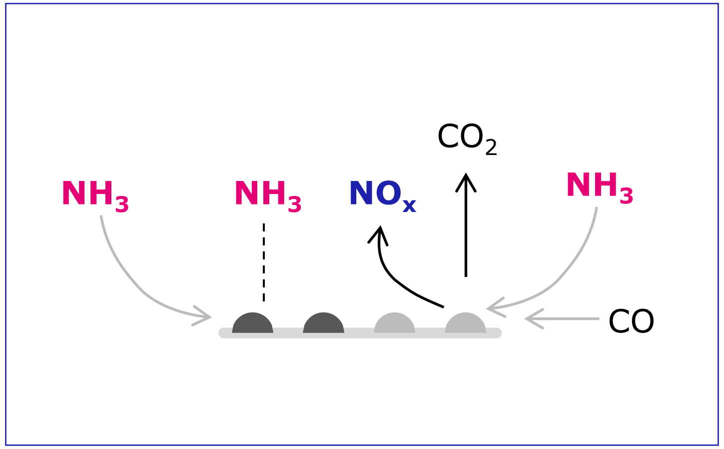
Advanced ASC performs both oxidation function and SCR function (selective to N_2) simultaneously

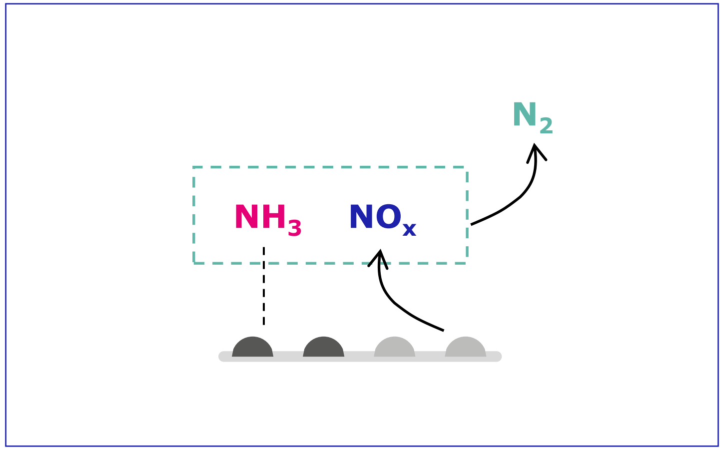
Selective ammonia slip catalyst

$NH_3 + O_2 \rightarrow N_2 + H_2O$

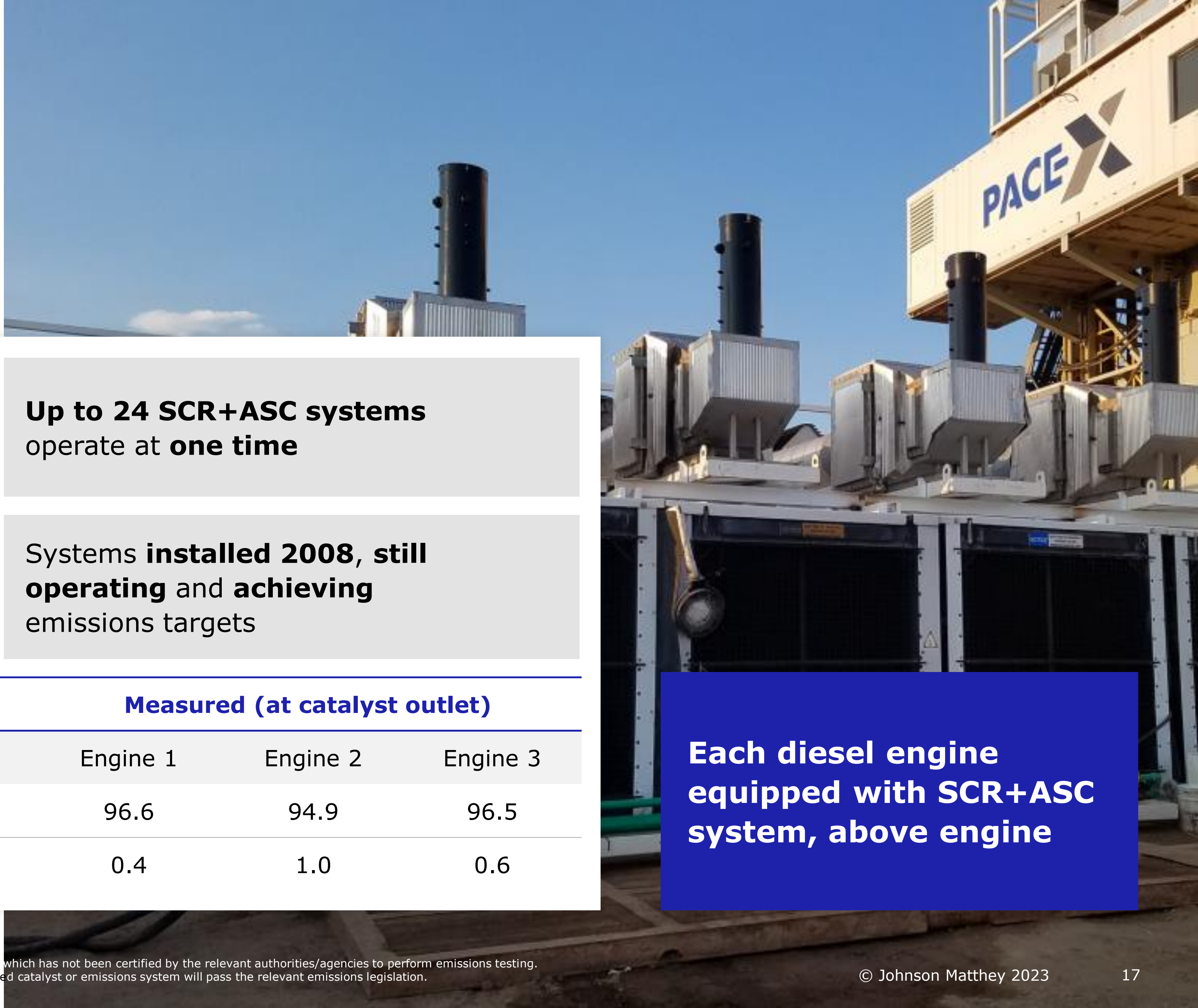
$CO + O_2 \rightarrow CO_2$







Field installation: SCR+ASC system in Wyoming Pinedale Anticline



Project demonstrated that SCR+ASC could significantly reduce NO_x at low NH_3 slip

State of Wyoming implemented emissions limits

- NO_x: 90% conversion
- NH_3 slip ≤10 ppm

Up to 24 SCR+ASC systems operate at **one time**

Systems **installed 2008, still operating** and **achieving** emissions targets

Species	Permit	Measured (at catalyst outlet)		
		Engine 1	Engine 2	Engine 3
% NO_x conversion	90% conversion	96.6	94.9	96.5
ppm NH_3 slip	≤ 10 ppm slip	0.4	1.0	0.6

Each diesel engine equipped with SCR+ASC system, above engine

The data included herein were collected in a Johnson Matthey laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing. These are indicative data and do not represent a guarantee that the tested catalyst or emissions system will pass the relevant emissions legislation.

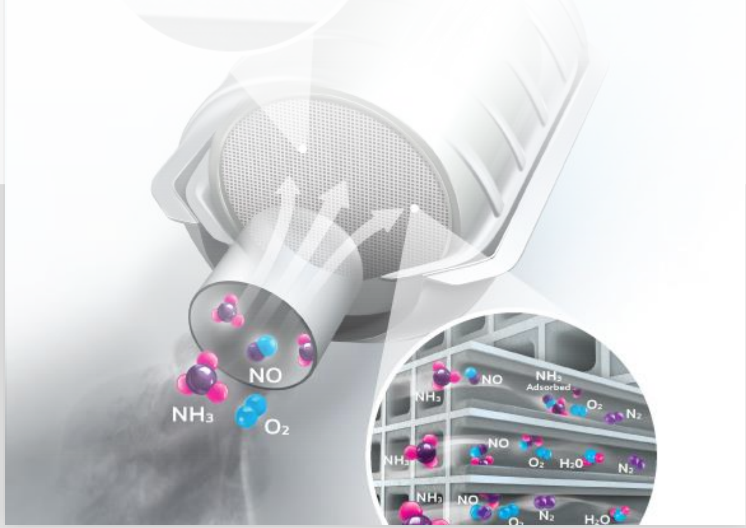
Future outlook

Ammonia slip catalyst

Increase of NH_3 slip

Overdosing at high temperature due to NH_3 oxidation

Requires **alternative solutions**



High temperature SCR catalyst

Increased system efficiency

Higher application temperatures

Reduced CO_2 footprint

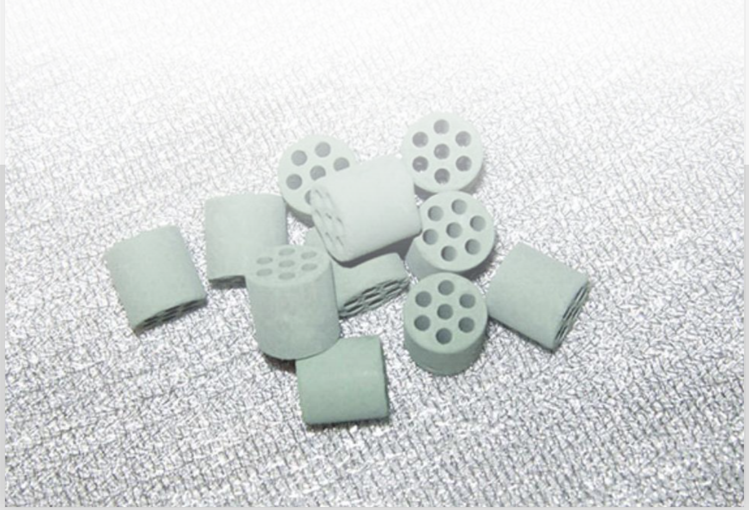
Cracking and N_2O catalyst

NH_3 as a **feed gas**

Ammonia **cracking**

N_2O abetment **possible**

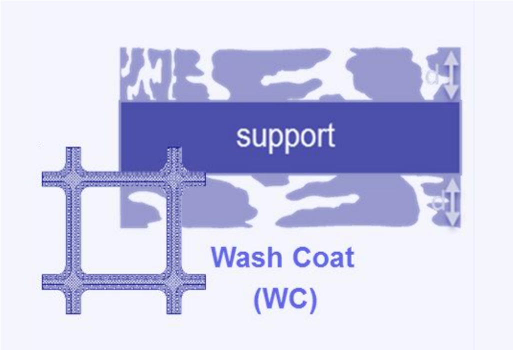
We can provide a **solution!**



The data included herein were collected in a Johnson Matthey laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing. These are indicative data and do not represent a guarantee that the tested catalyst or emissions system will pass the relevant emissions legislation.

Next generation high temperature SCR catalyst (SCN7000):

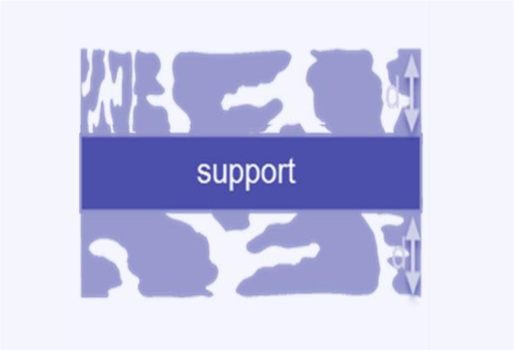
developed for operation between 842°F-1202°F (450°C-650°C)



Increase active mass/ WC loading

→

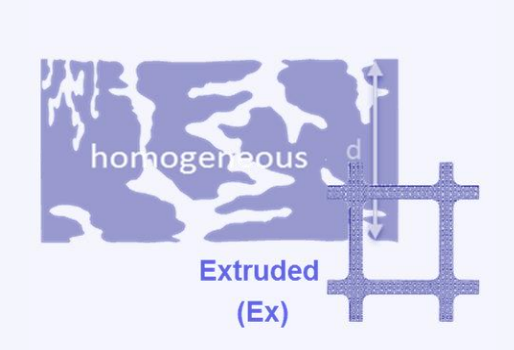
Increase pressure drop



Increase active mass

→

Reduce pressure drop



Advantages of Ex-HT-SCR (SCN7000):

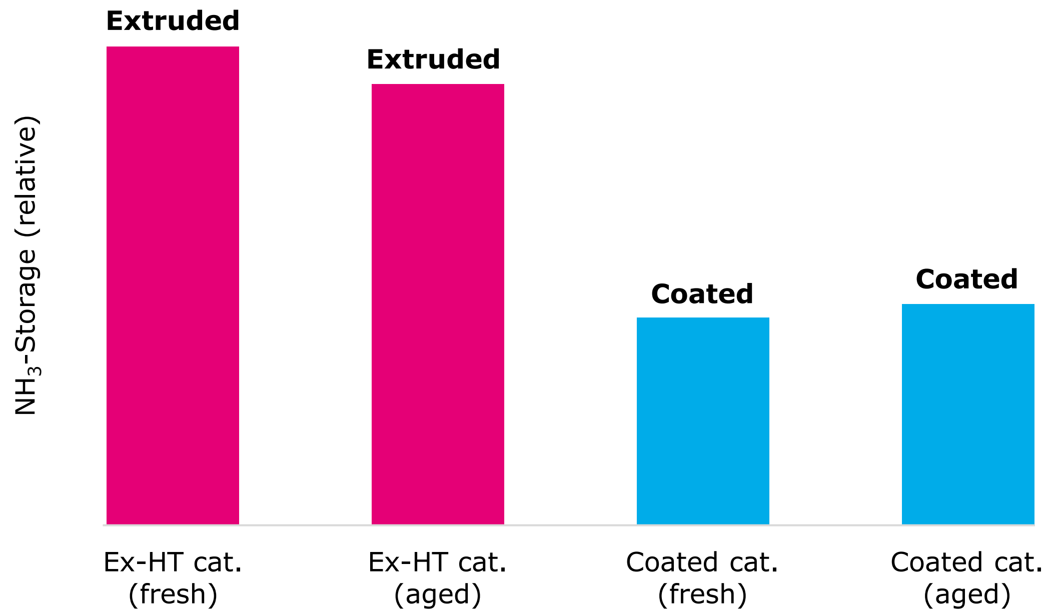
- High activity/stability
- High active mass of extruded products
- High geometrical surface area from high CPSI

Superior NO_x reduction activity
High resistance to poison
High NH_3-storage capability
Low catalyst volume
Low pressure drop
Low thermal mass and weight

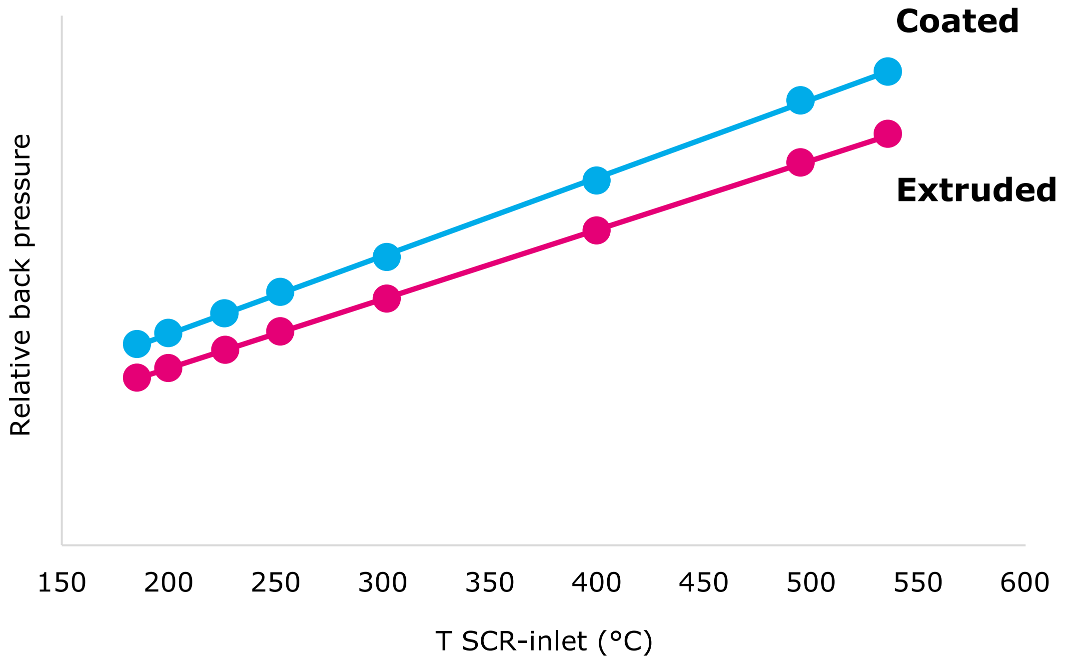
The data included herein were collected in a Johnson Matthey laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing. These are indicative data and do not represent a guarantee that the tested catalyst or emissions system will pass the relevant emissions legislation.

High NH_3-storage capacity and low pressure drop key to advancement

NH_3-storage capacity



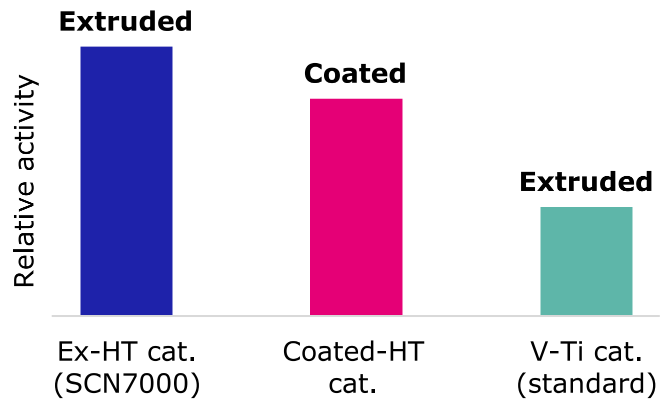
Pressure drop



Advanced high temperature SCR catalyst (SCN7000) significantly outperforms standard V-Ti catalyst and washcoated catalysts

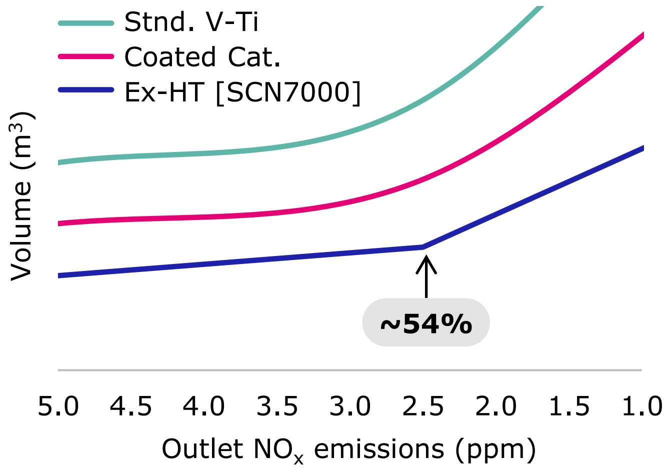
SCR activity

T=550°C (1022°F); NH_3/NO_x=1



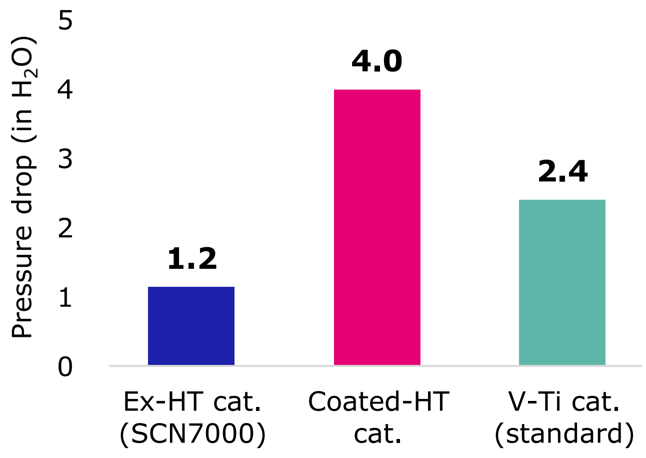
Catalyst volume

T=550°C (1022°F); NH_3/NO_x=1



Pressure drop

T=550°C (1022°F); NH_3/NO_x=1



Superior SCR activity, reduced catalyst volume, and lower pressure drop aligned to tightened emission regulations of next generation power systems

Field demonstration of high temperature SCR catalyst for thousands of hours to understand failure modes

Alternate application to SMR

Initial deactivation during start

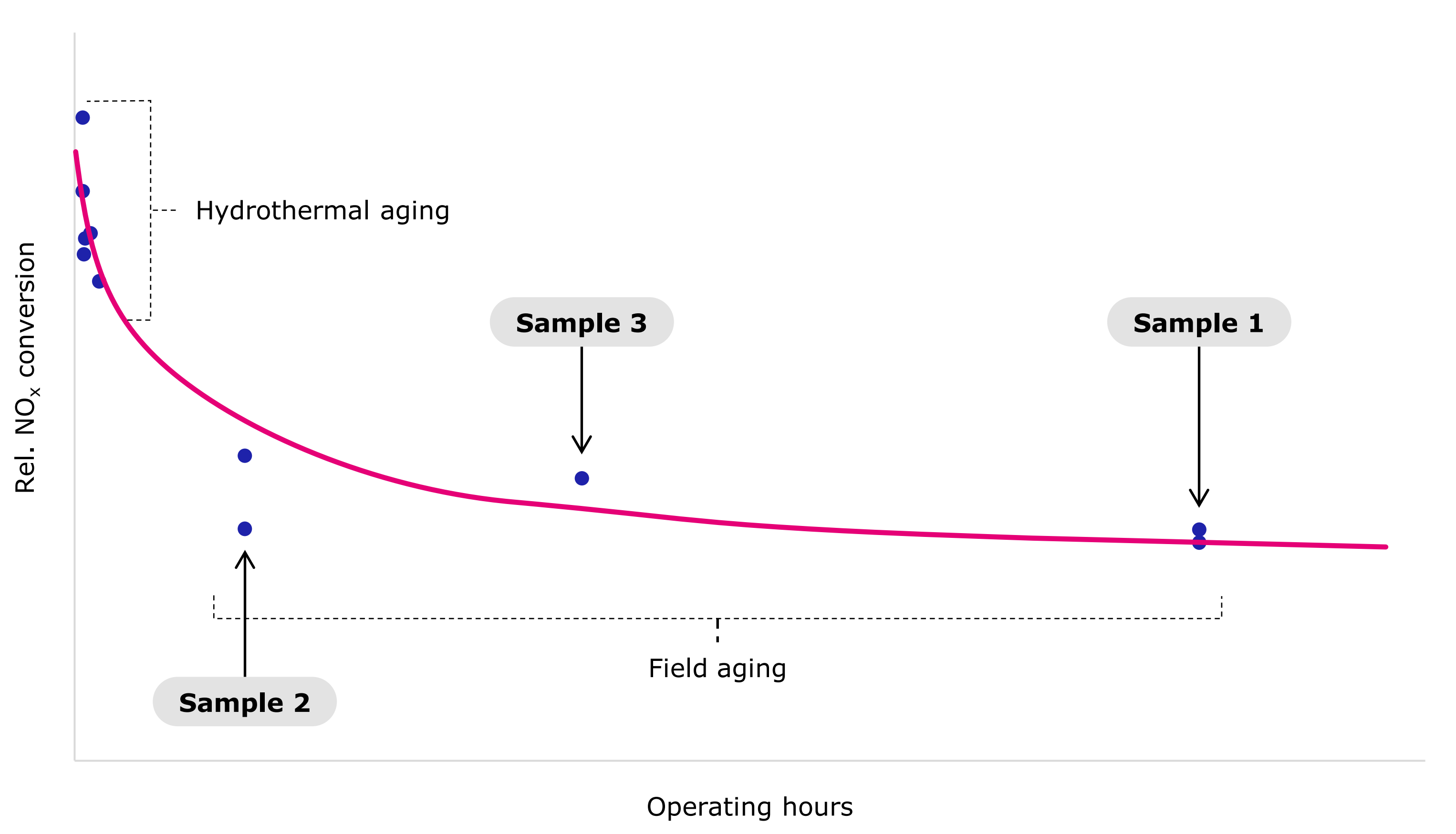
Gradual steady-state over time

No increase in NH_3 oxidation

Laboratory testing provides limited insights

- Cannot mimick flue gas deposits
- **Field testing critical**

SCR performance example



The data included herein were collected in a Johnson Matthey laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing. These are indicative data and do not represent a guarantee that the tested catalyst or emissions system will pass the relevant emissions legislation.

Summary

Selective catalytic reduction (SCR) catalysts used to reduce NO_x emissions

- Formulation defined based on SCR design temperature
- Next generation SCR technology for high temperatures (842°F-1202°F) commercially available

Chromium (Cr) deposition is primary failure mode for steam methane reformer (SMR) applications

- Cr deposits primarily on the catalyst surface
- Results in increased ammonia (NH_3) oxidation
- Careful design considerations required to meet lifetime requirements

Ammonia slip catalyst (ASC) allows continuous operation at higher NH_3/NO_x ratios (ANRs)

- Results in higher NO_x conversion while maintaining low NH_3 slip
- Improve plant performance by reducing back-end deposits (saves O&M costs for removal)
- Active for CO and/or VOC oxidation
- Can help compensate for non-ideal NH_3 distribution

The data included herein were collected in a Johnson Matthey laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing. These are indicative data and do not represent a guarantee that the tested catalyst or emissions system will pass the relevant emissions legislation.


JM
Johnson Matthey
Inspiring science, enhancing life