Johnson Matthey
Inspiring science, enhancing life

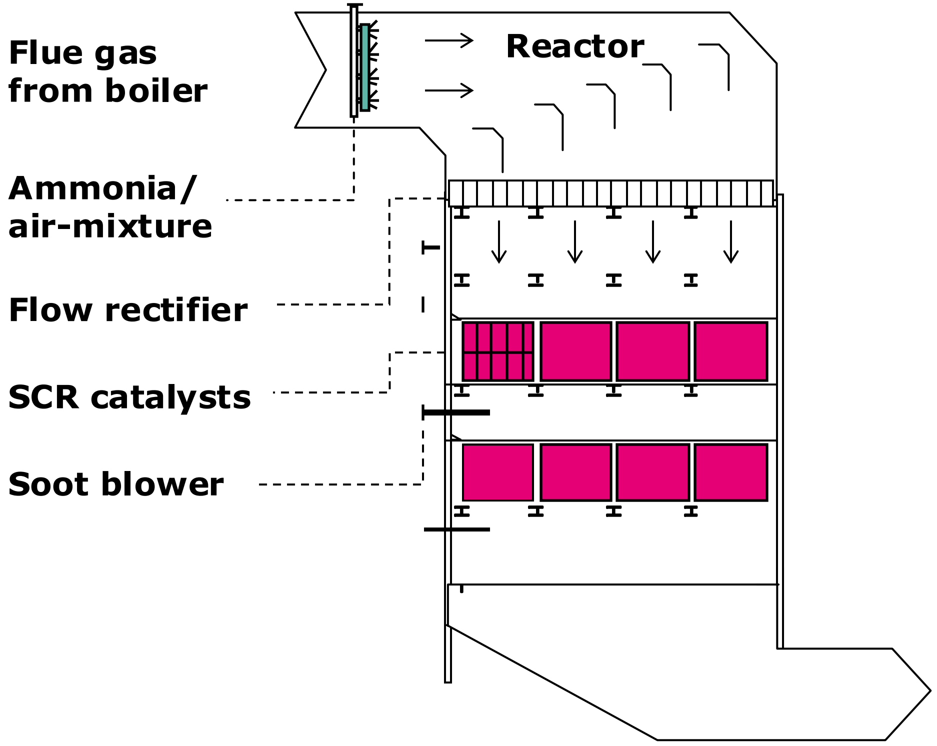
Americas hydrogen and syngas technical training seminar

Selective Catalytic Reduction (SCR)

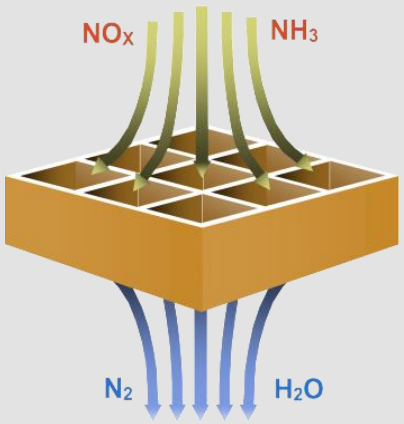
Silvia Alcove-Clave

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)
- $2SO_2 + O_2 \rightarrow 2SO_3$
- $2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4$
- $NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4$

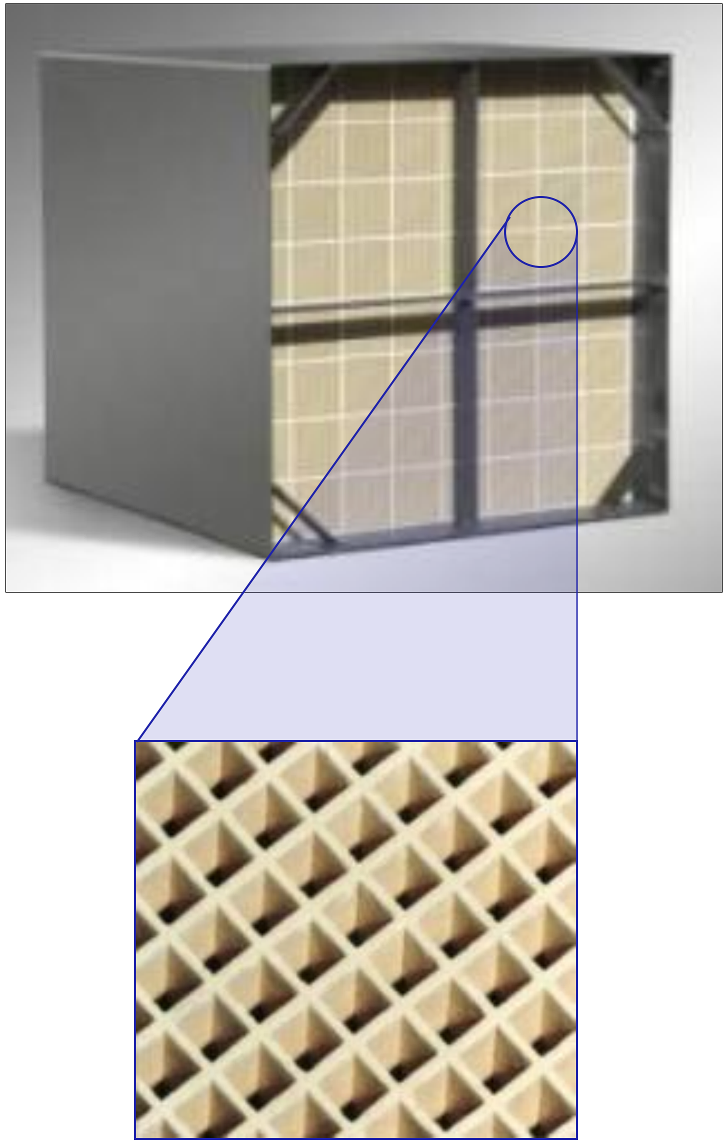
Extruded ceramic honeycomb SCR catalyst

Low to medium-dust application

High specific surface area

High activity

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



JM

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

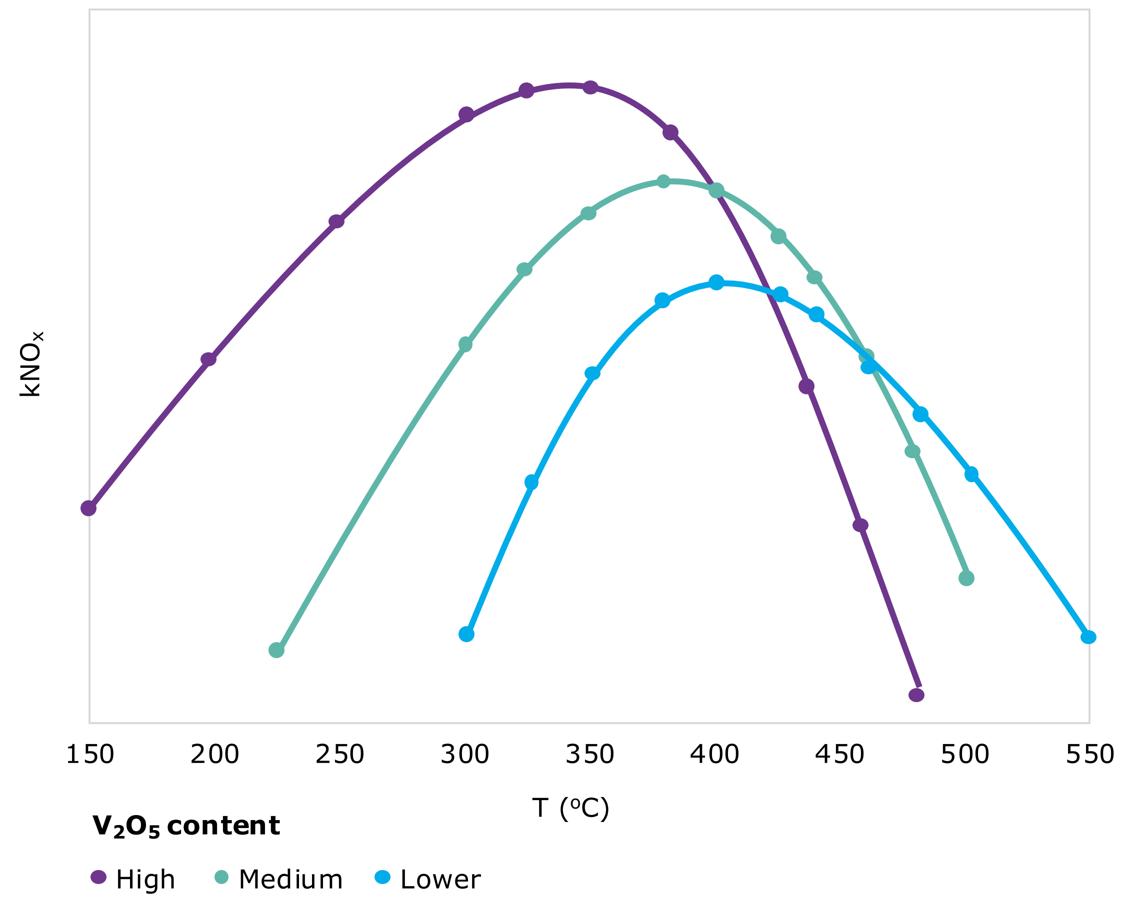
Higher V promotes the undesired reaction:

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

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

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

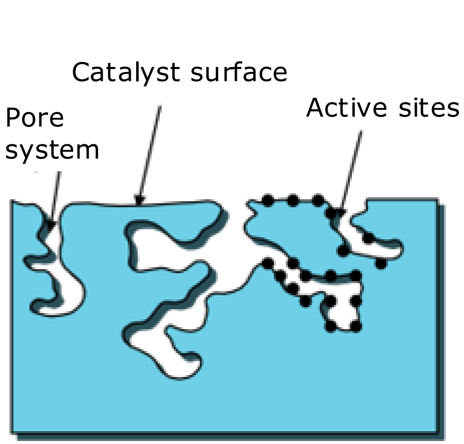
CC
Combined Cycle

SC
Simple Cycle

Deactivation mechanisms

Poisoning

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

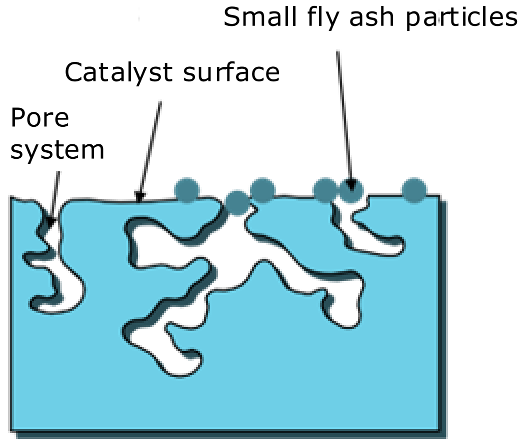


Adsorption of ammonia **inhibited**

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

Plugging

Microscopic blockage of the pore system by small fly ash particles

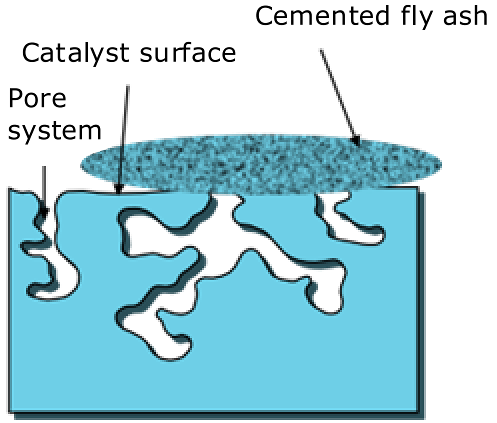


Fly ash particles are **diffusing** into the **catalyst pores**

Catalyst micro pore systems **plugged mechanically**

Masking

Macroscopic blockage of catalyst surface by cement fly ash



Reactive particles **grow on the surface**

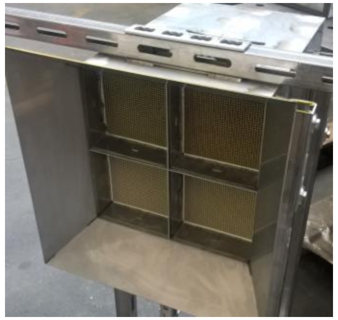
Due to **high amount** of **calcium oxide in the ash**

Steam methane reformer field experience

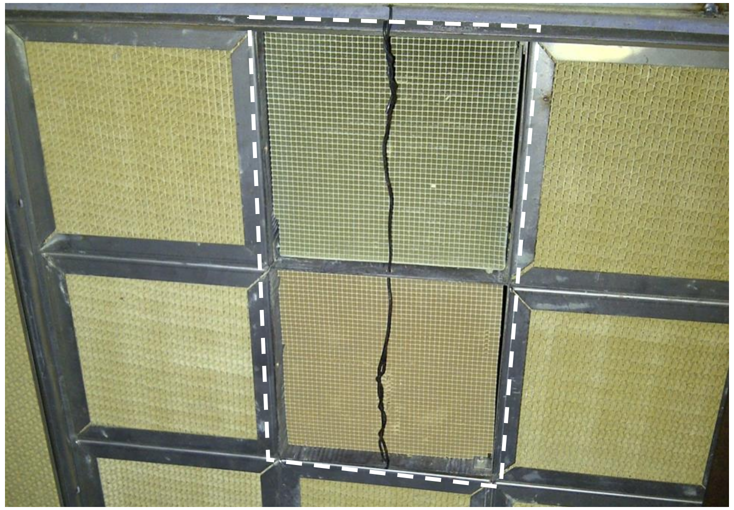
Main driver for catalyst deactivation in Steam Methane Reformer (SMR)

Masking

Poisoning - Chromium (Cr)



Fresh - JM



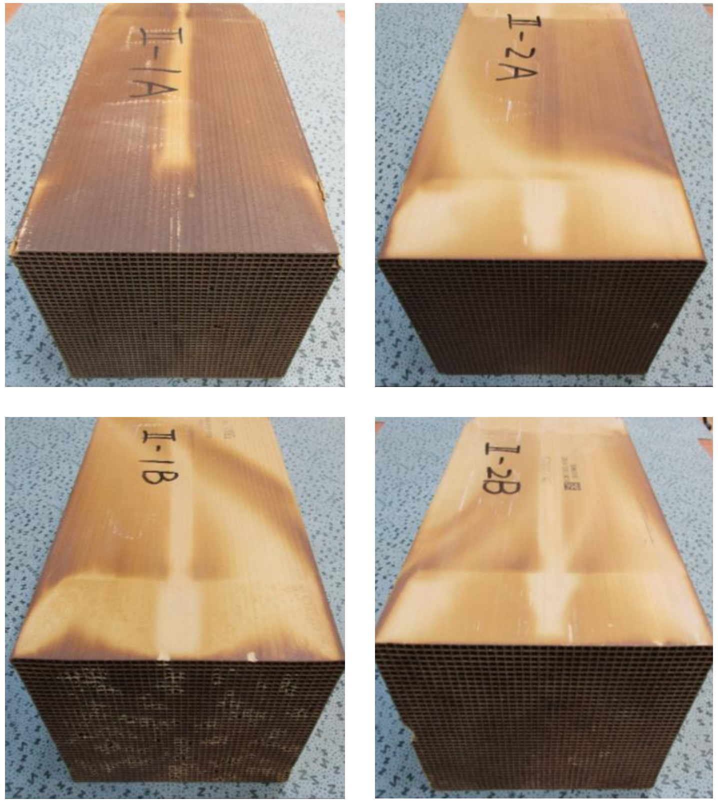
40K hrs SMR - JM

Visual Inspection of the parts

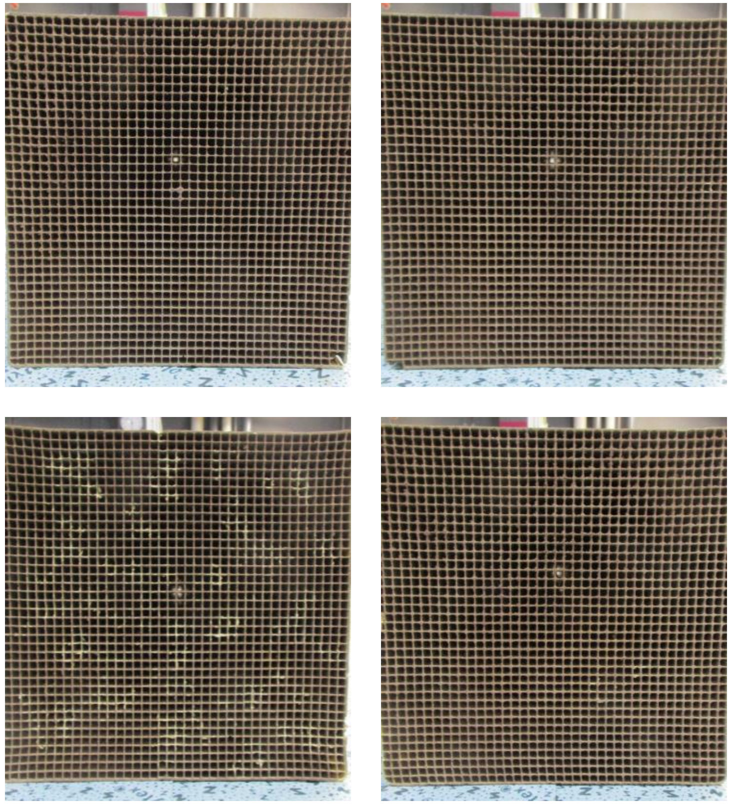
No blockage of the catalyst channels by ash or other flue impurities observed on JM catalysts

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.

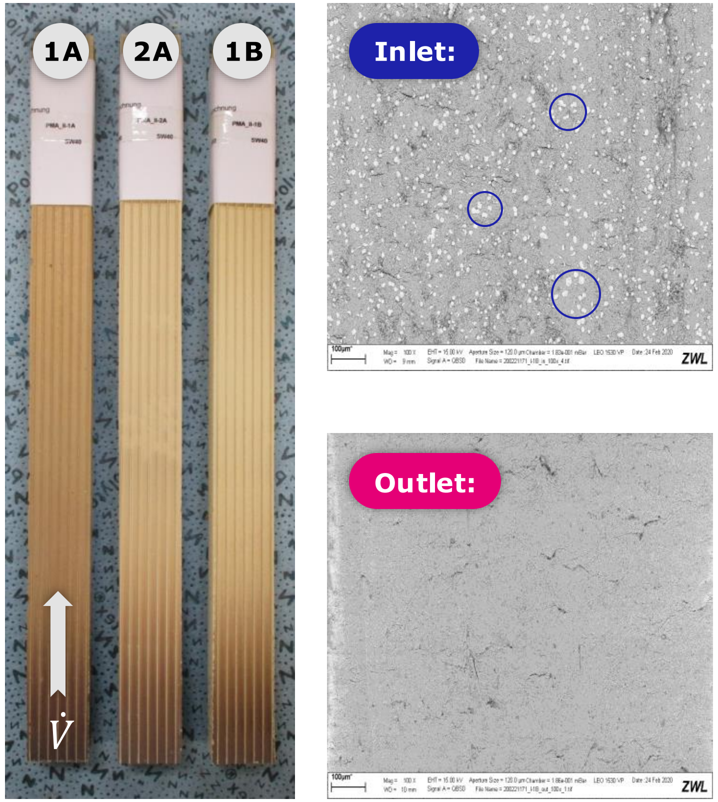
Visual discoloration of field returns due to poisons and ash



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

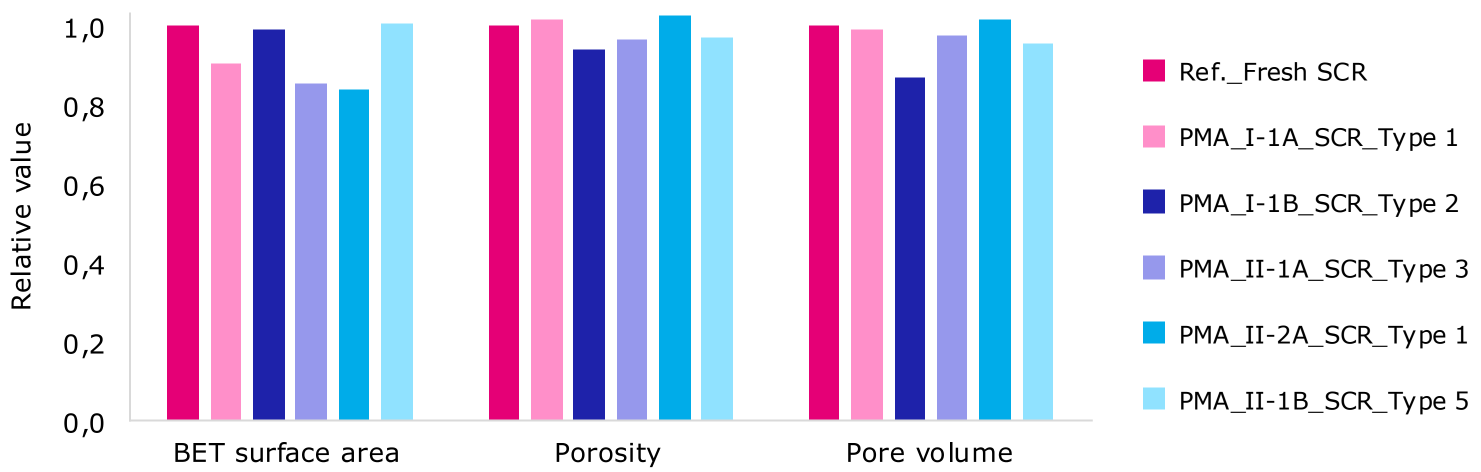


Deposition of **particulate ash** on inner walls of inlet side found



No particulate ash deposition at outlet side of the catalysts observed

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 chemical analysis

EDX: surface chemical anlaysis

Where are deposits/ poisons located

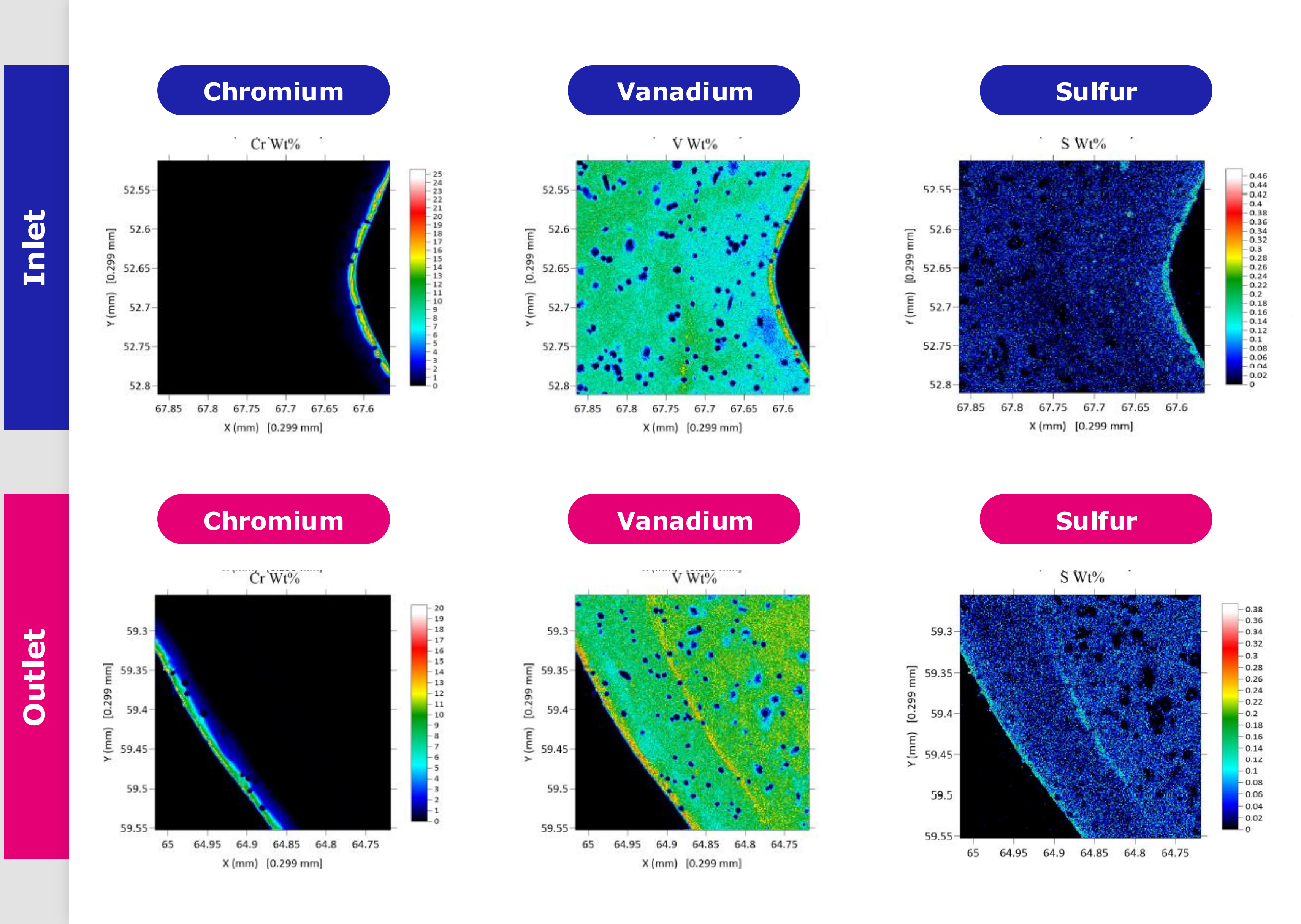
Several mechanisms may overlap

⇒ Cr the primary driver

JM

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



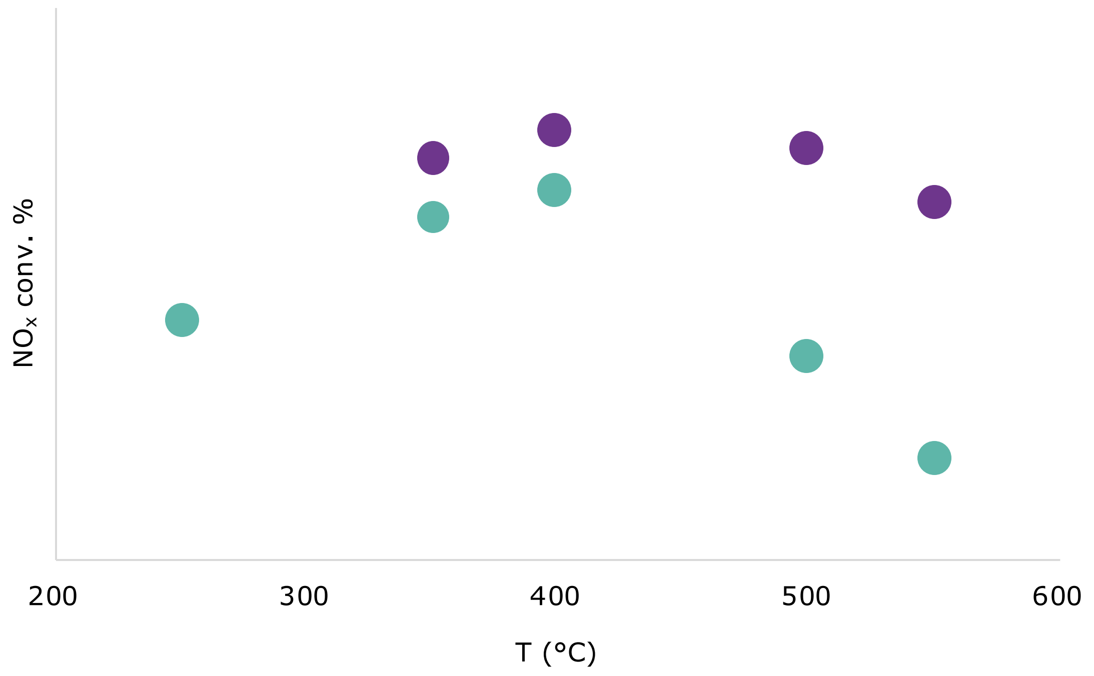
JM

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.

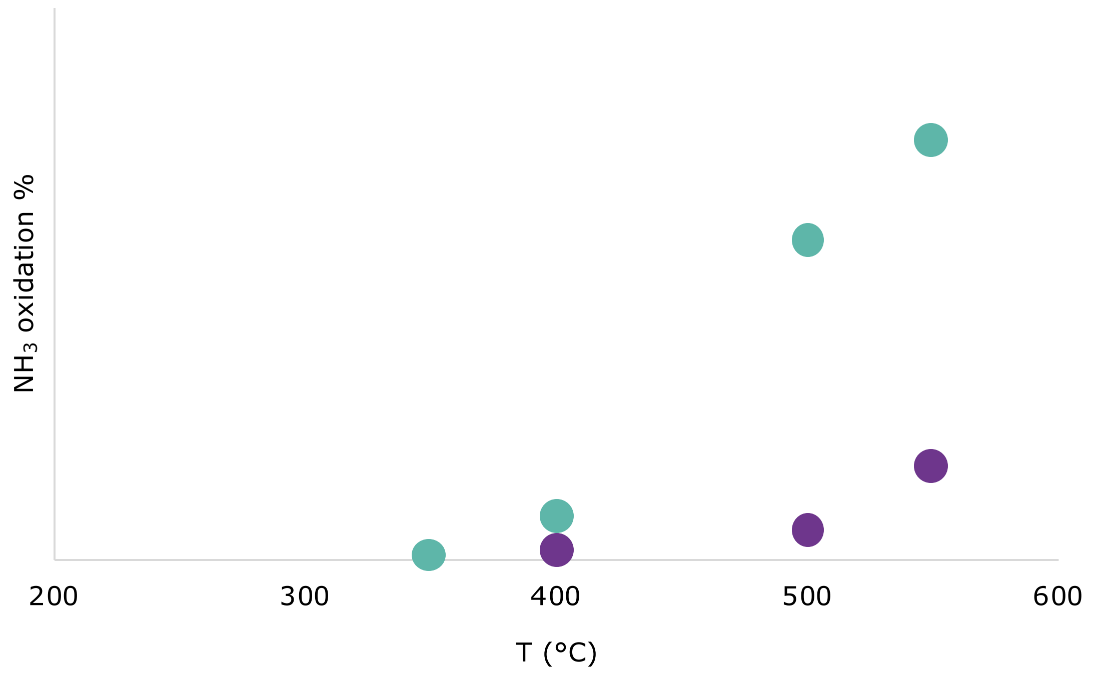
Catalytic activity negatively influenced by Cr deposition

- Fresh ref.
- SMR field aged

Impact of Cr – NO_x conversion



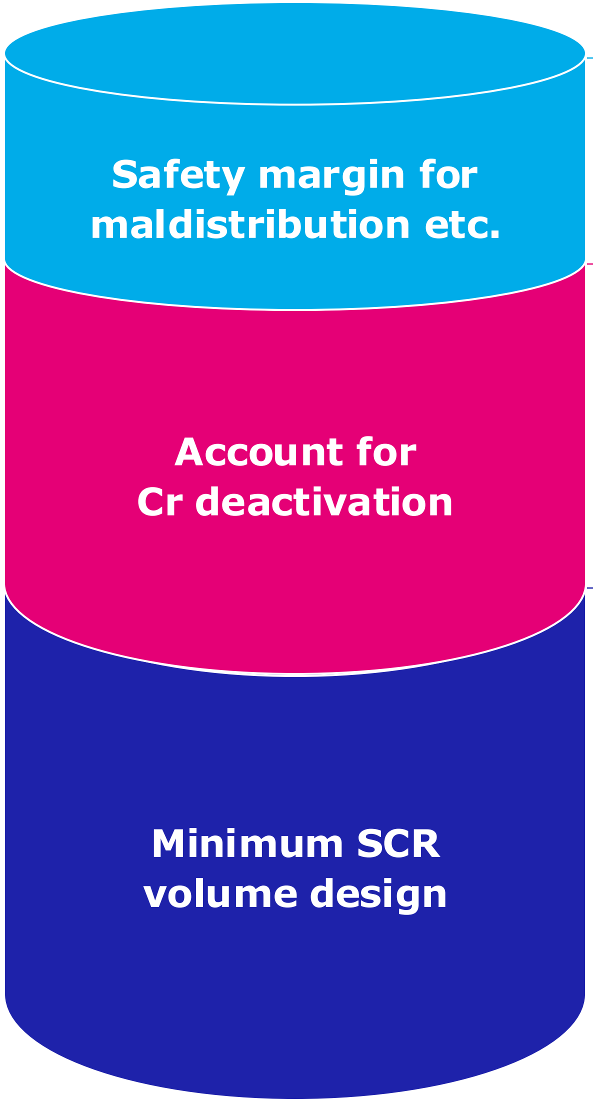
Impact of Cr – NH_3 oxidation



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.

SCR catalyst design considerations for SMR applications



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

- 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

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.

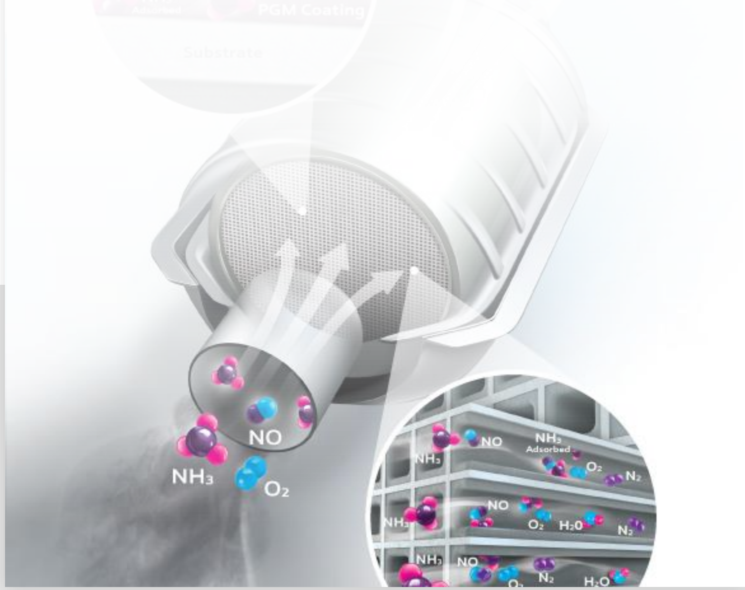
Future outlook

Ammonia slip catalyst

Increase of NH_3 slip

Overdosing at high temperature

Improved plant performance



High temperature SCR catalyst

Increased system efficiency

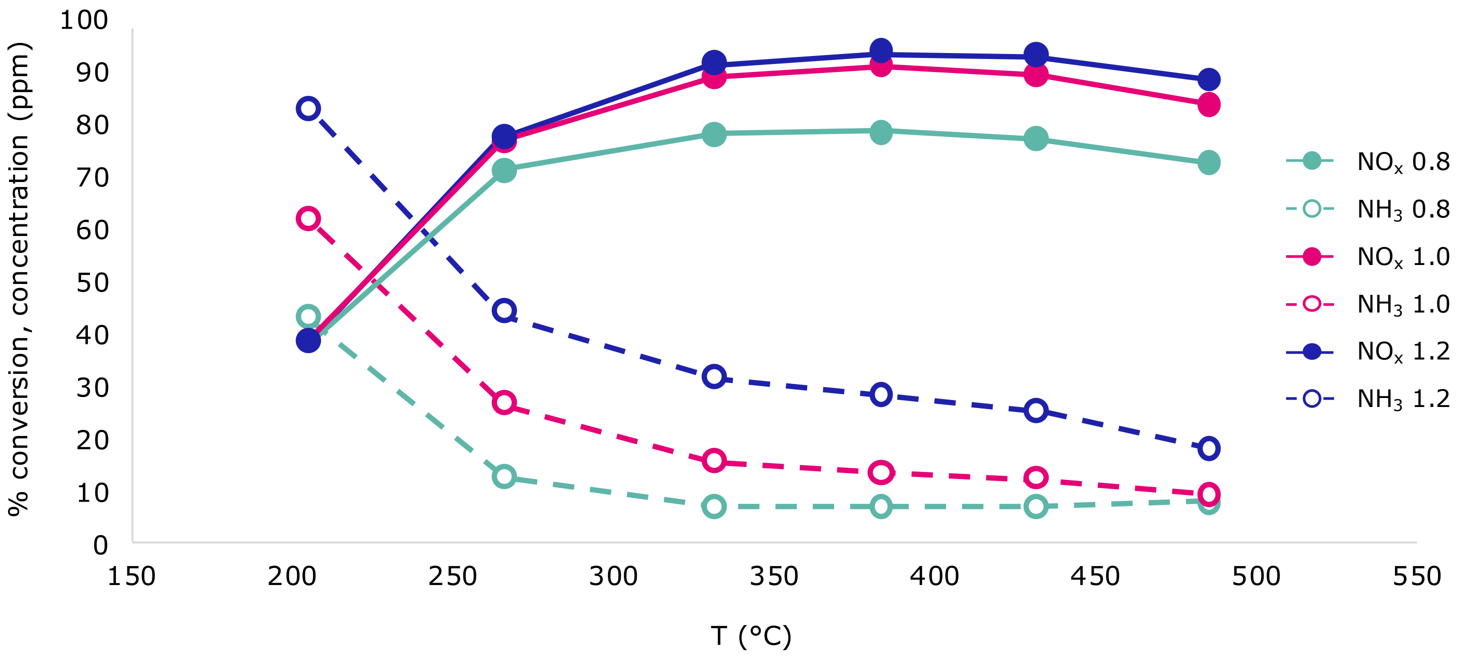
Higher application temperatures

Reduced CO_2 footprint

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.

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

Challenge: high NO_x conversion at low NH_3 slip



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

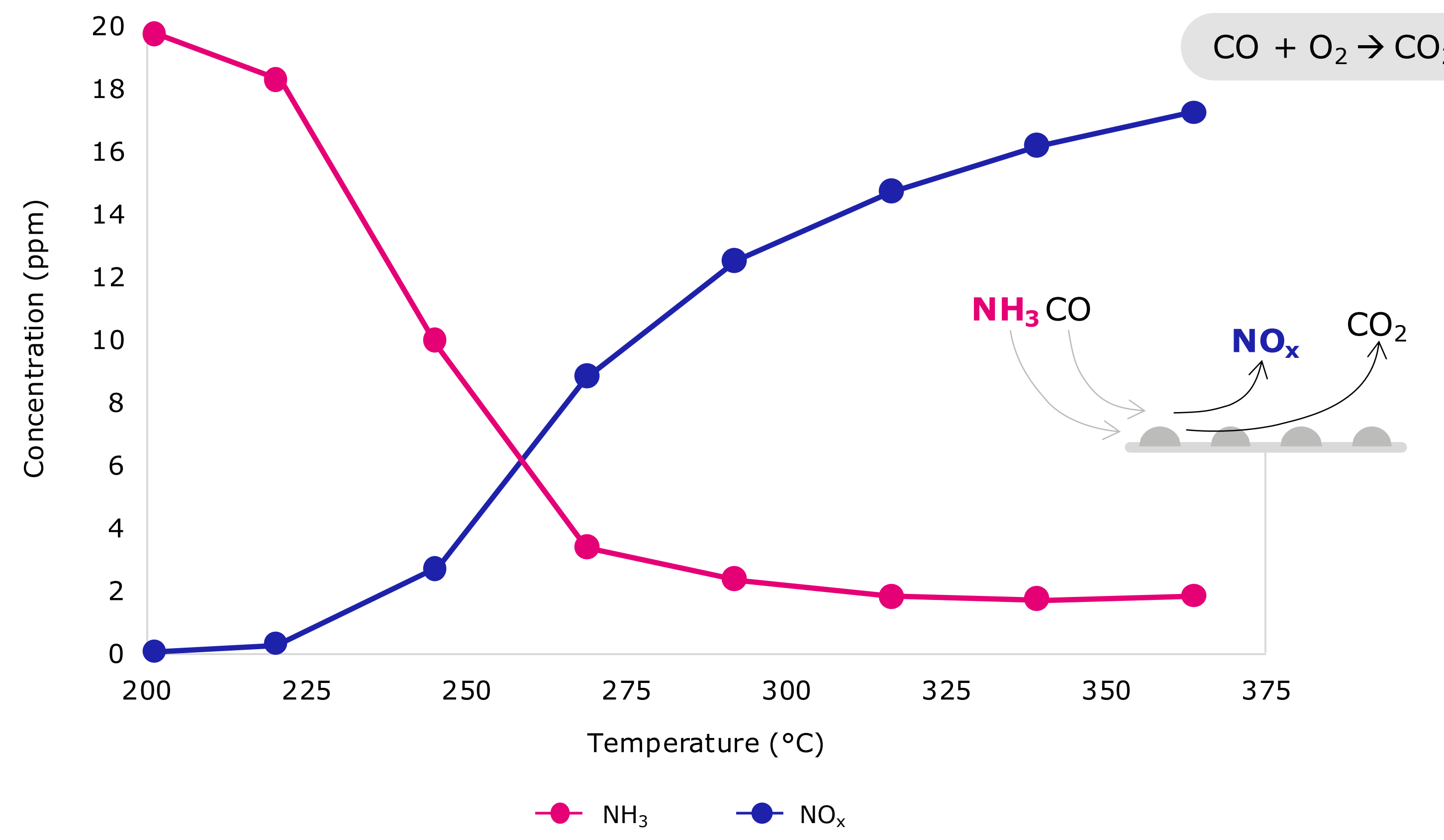
The data included herein were collected in a Johnson Matthey laboratory which has not been certified by the relevant authorities/agencies to perform emissions testing. These are indicative data and do not represent a guarantee that the tested catalyst or emissions system will pass the relevant emissions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

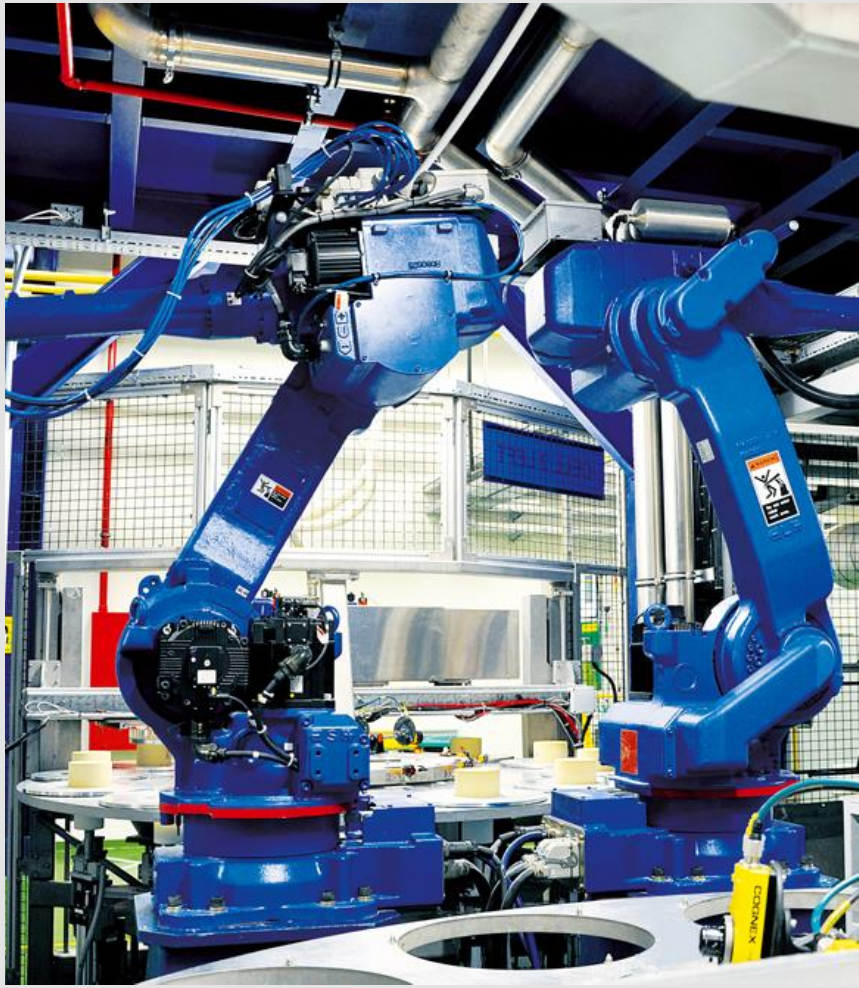
Previous generation ASC exhibit excellent activity (High NH_3/CO conversion) but poor selectivity (NO_x production)

Non-selective ammonia slip catalyst

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

$CO + O_2 \rightarrow CO_2$



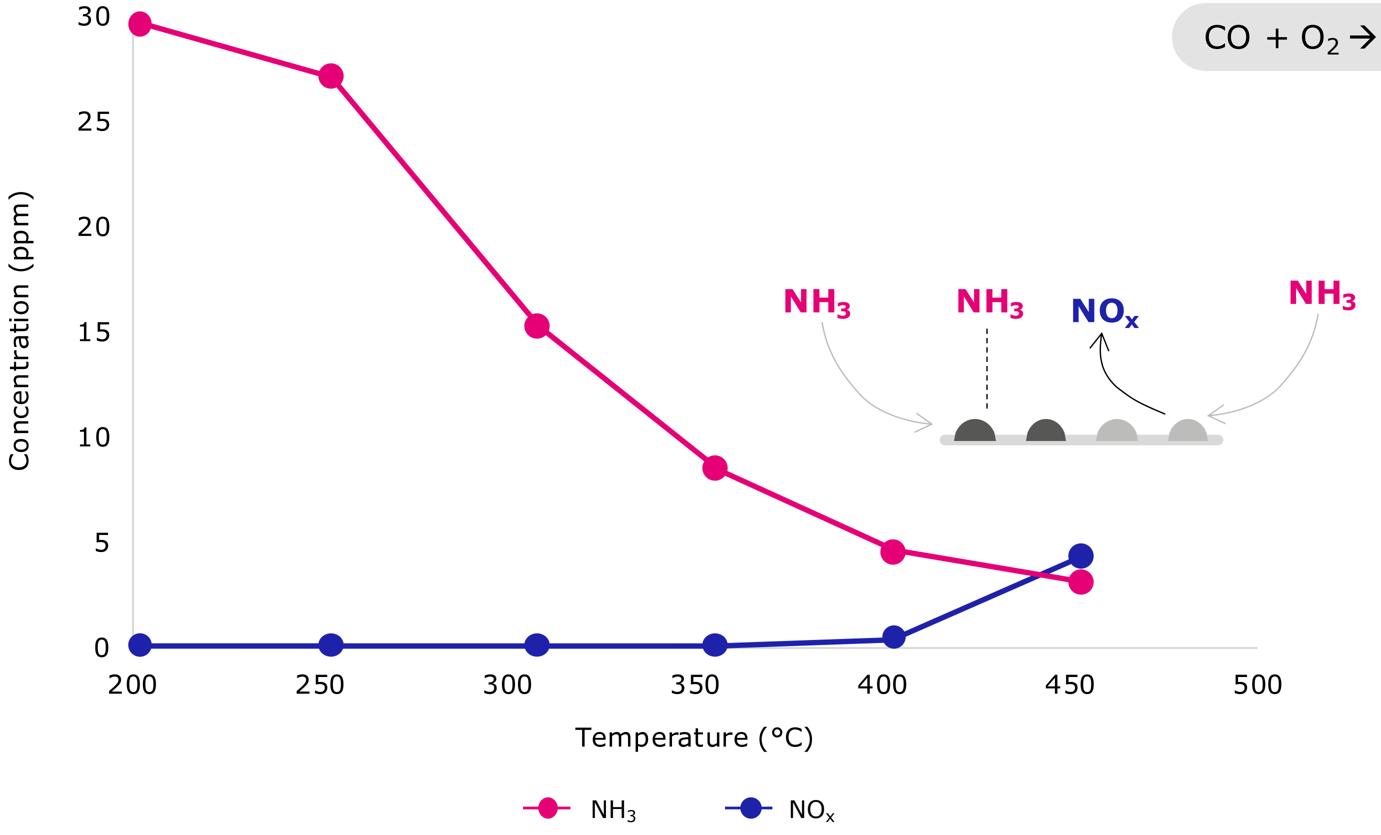


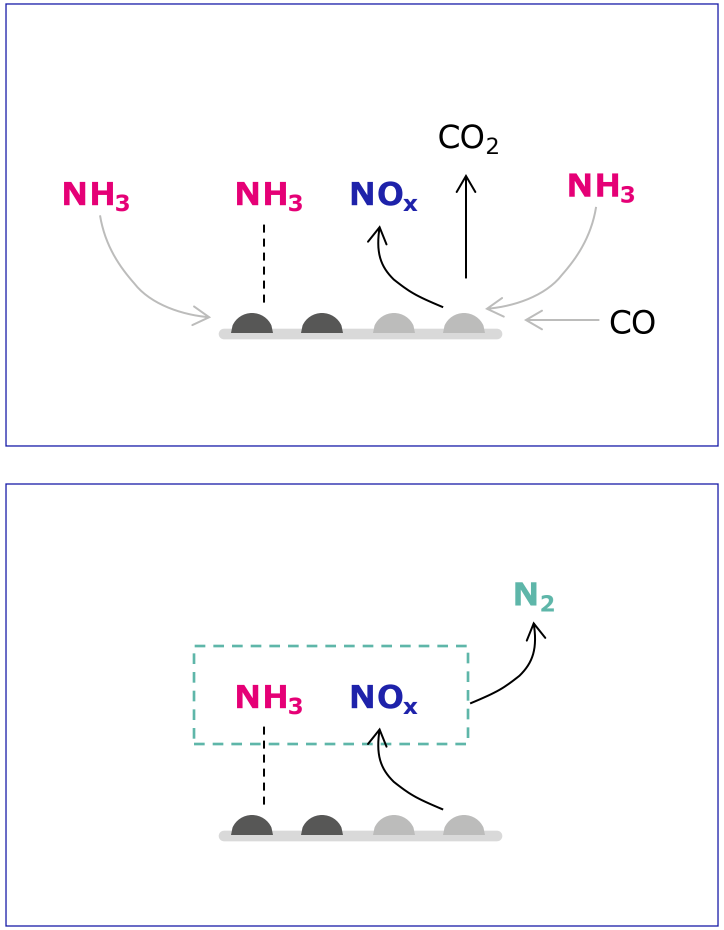
Advanced ASC performs both oxidation function and SCR function (selective to N_2) simultaneously

Selective ammonia slip catalyst

$NH_3 + O_2 \rightarrow N_2 + H_2O$

$CO + O_2 \rightarrow CO_2$





JM

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.

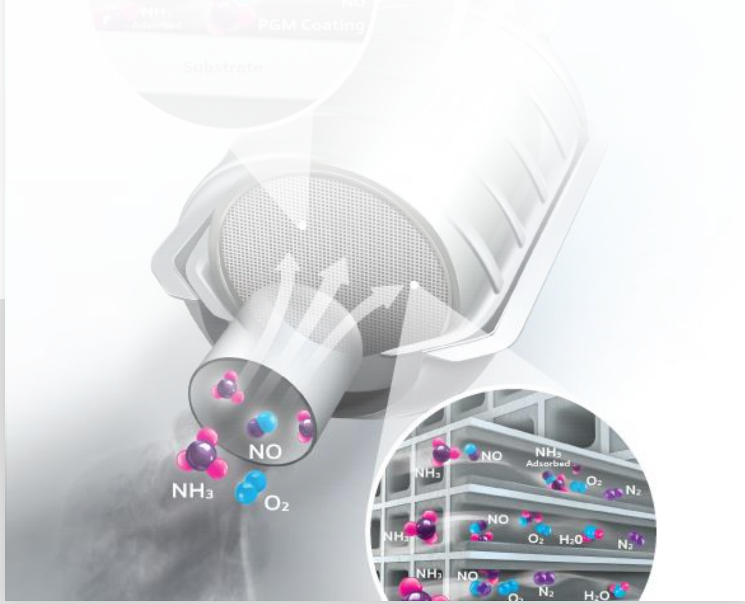
Future outlook

Ammonia slip catalyst

Increase of NH_3 slip

Overdosing at high temperature

Improved plant performance



High temperature SCR catalyst

Increased system efficiency

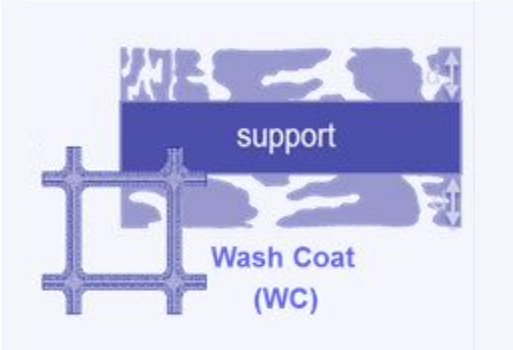
Higher application temperatures

Reduced CO_2 footprint

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):

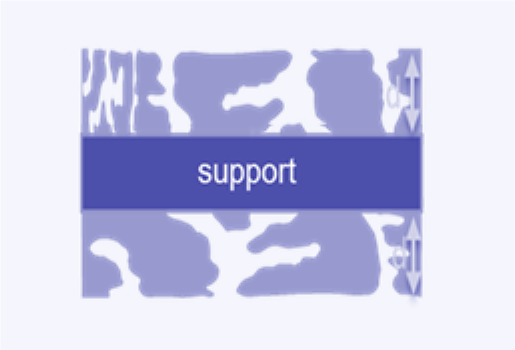
developed for operation between 842°F-1202°F (450°C-650°C)



Increase
active mass/
WC loading

→

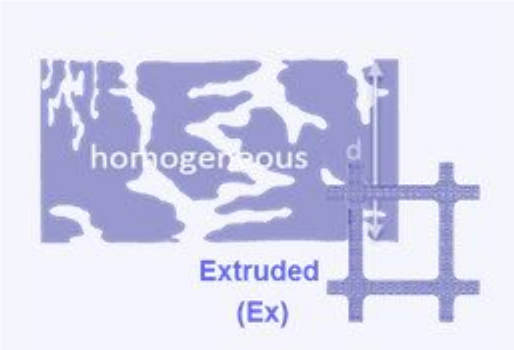
Increase
pressure
drop



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

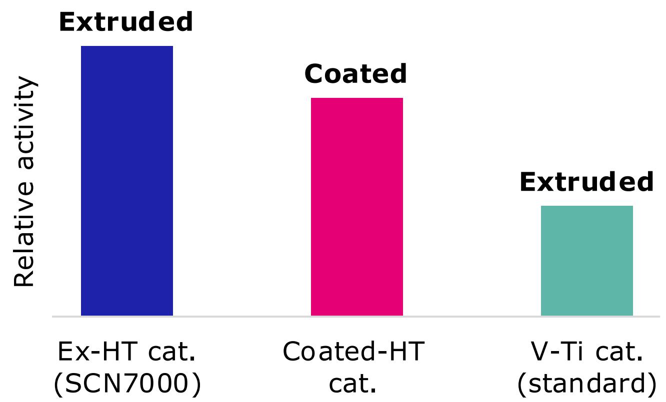
JM

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

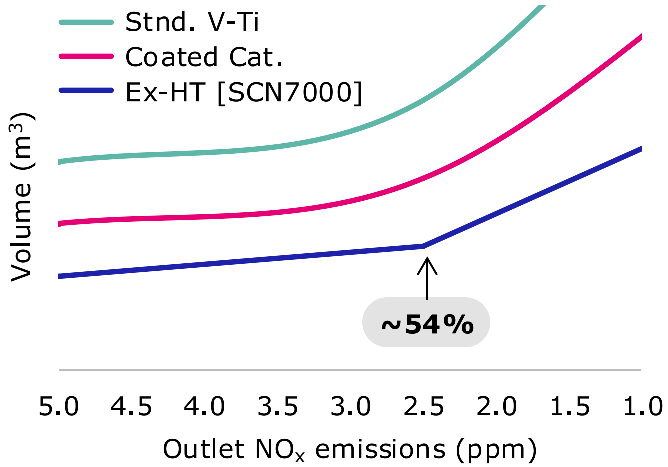
SCR activity

T=550°C (1022°F); NH_3/NO_x=1



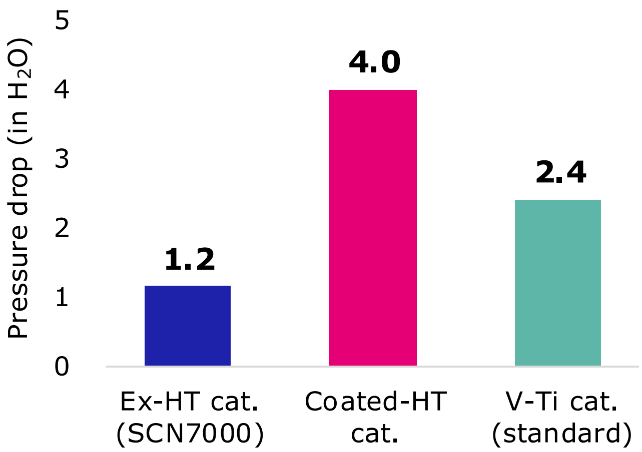
Catalyst volume

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

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.


JM
Johnson Matthey
Inspiring science, enhancing life