Johnson Matthey

Americas hydrogen and syngas technical training seminar

Industrial SMR Aftertreatment Solutions

Leo DeRita

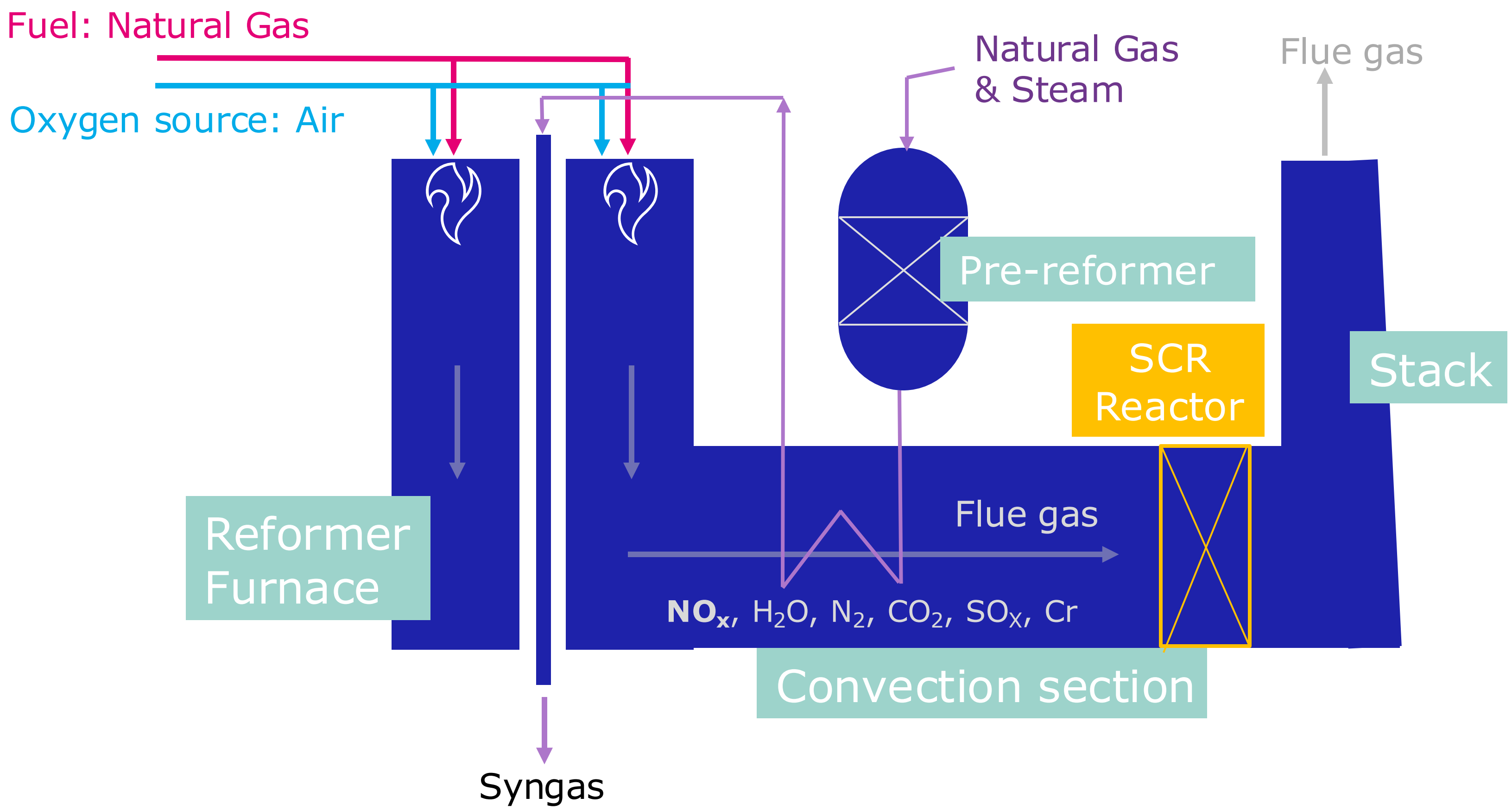
NO_x emissions from SMR processes

SMR is an endothermic process.

Heat is required for the SMR reaction to proceed.

NO_x emissions are formed during the combustion of fuel in the reformer furnace.

Where NO_x regulations apply, SMR units are typically equipped with **Selective Catalytic Reduction** (SCR) systems.



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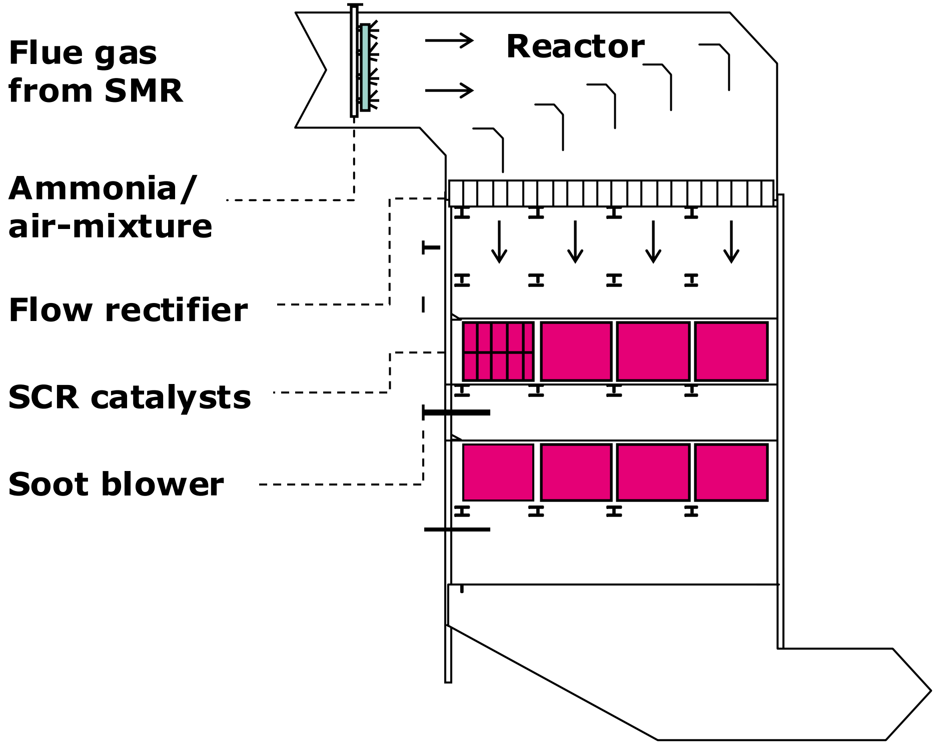
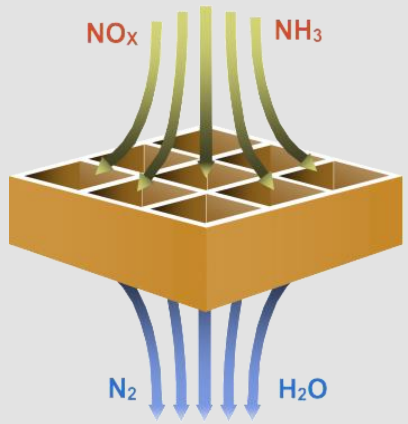
Selective Catalytic Reduction (SCR)

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 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)
- $4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O$ (non-selective oxidation)
- $2SO_2 + O_2 \rightarrow 2SO_3$
- $2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4$

SINOx extruded ceramic honeycomb SCR catalyst

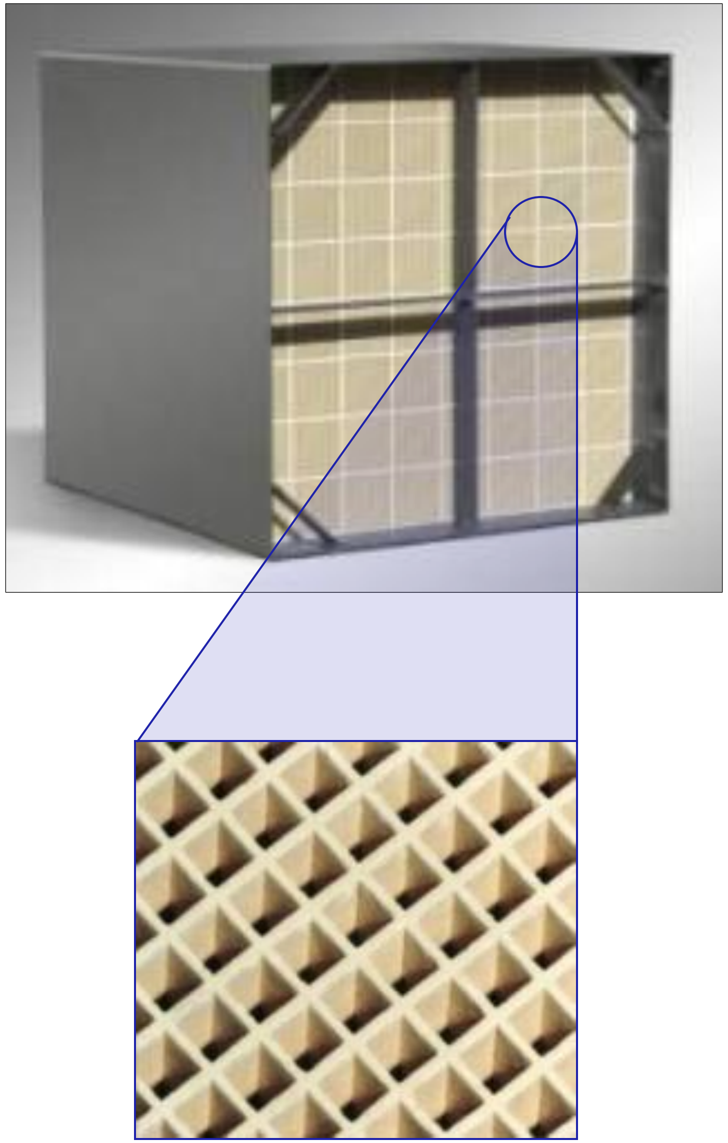
Made entirely of active materials

Low to medium-dust application

High specific surface area

High activity

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



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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:

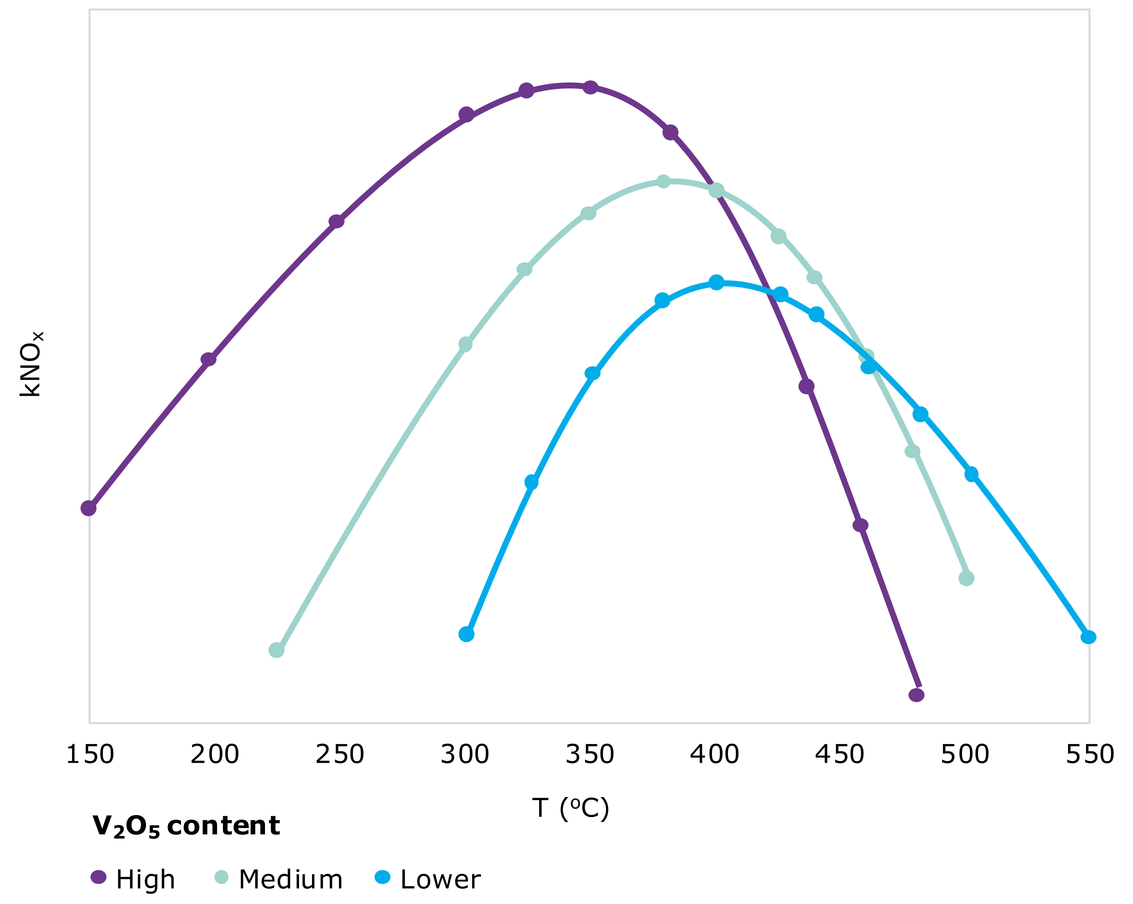
$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O$$

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

x = fraction NO_x conversion

GSA = geometric surface area (function of cell density)



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

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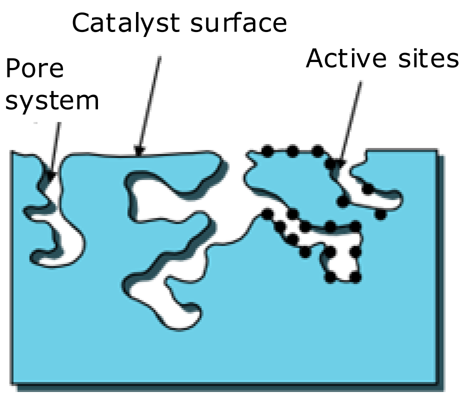
Deactivation mechanisms

Poisoning

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

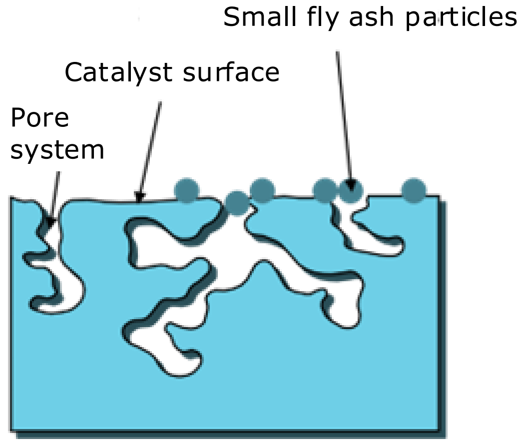


Adsorption of ammonia **inhibited**

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

Plugging

Microscopic blockage of the pore system by small fly ash particles

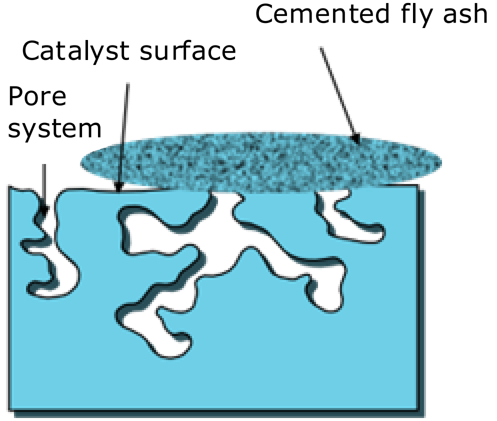


Fly ash particles are **diffusing** into the **catalyst pores**

Catalyst micro pore systems **plugged mechanically**

Masking

Macroscopic blockage of catalyst surface by cement fly ash



Reactive particles **grow on the surface**

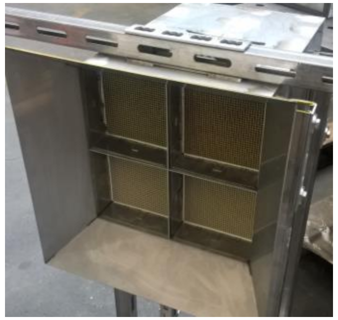
Due to **high amount** of **calcium oxide in the ash**

Steam methane reformer field experience

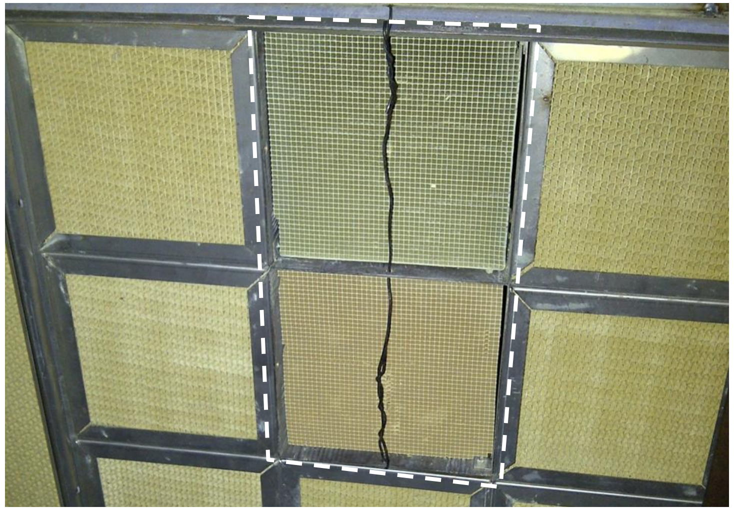
Main driver for catalyst deactivation in Steam Methane Reformer (SMR)

Masking

Poisoning



Fresh - JM



40K hrs SMR - JM

Analytical methods:

- **Chemical analysis** – surface vs. bulk composition
- **Physical parameters** – surface area, pore volume
- **Activity testing** (fresh vs. aged)

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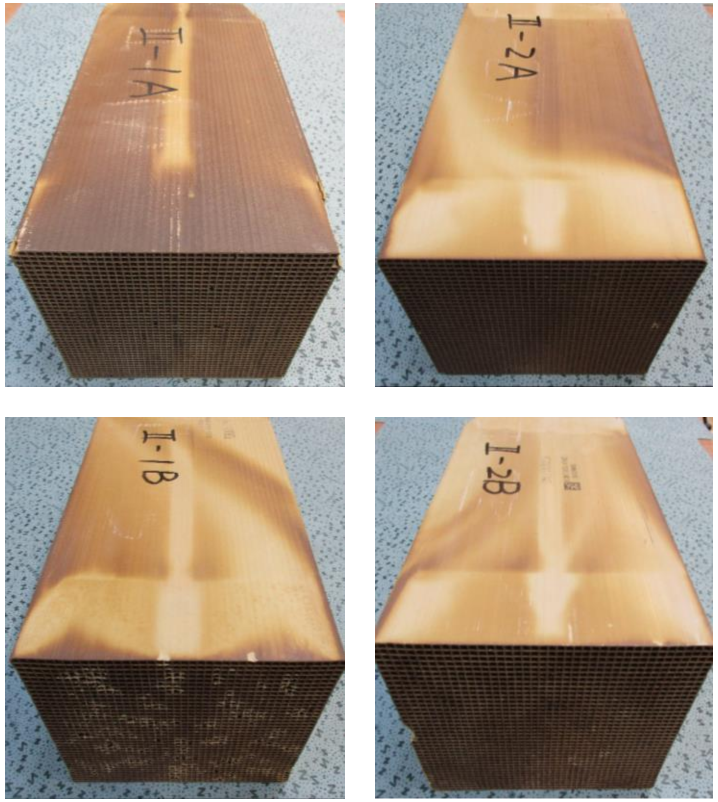
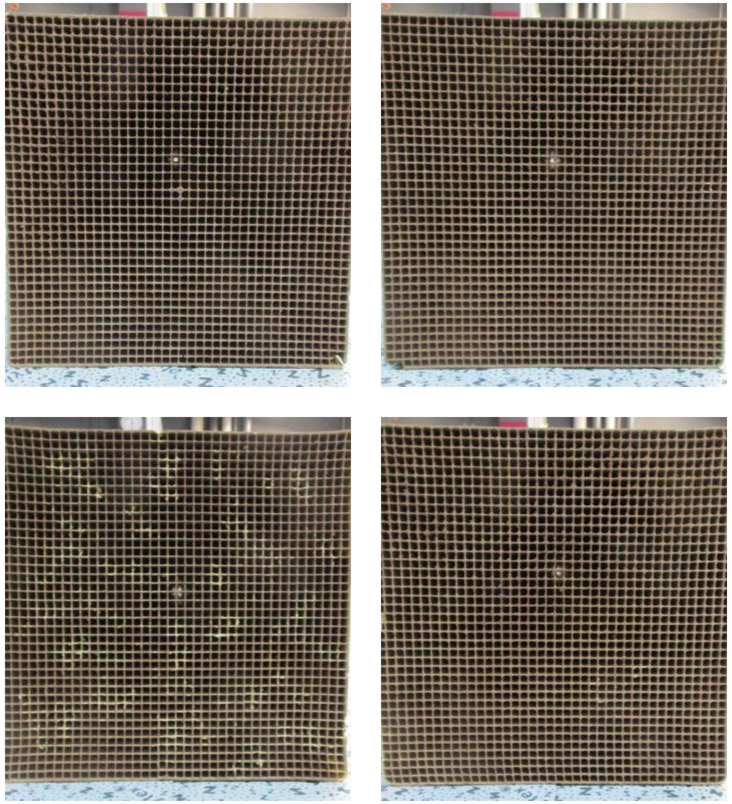
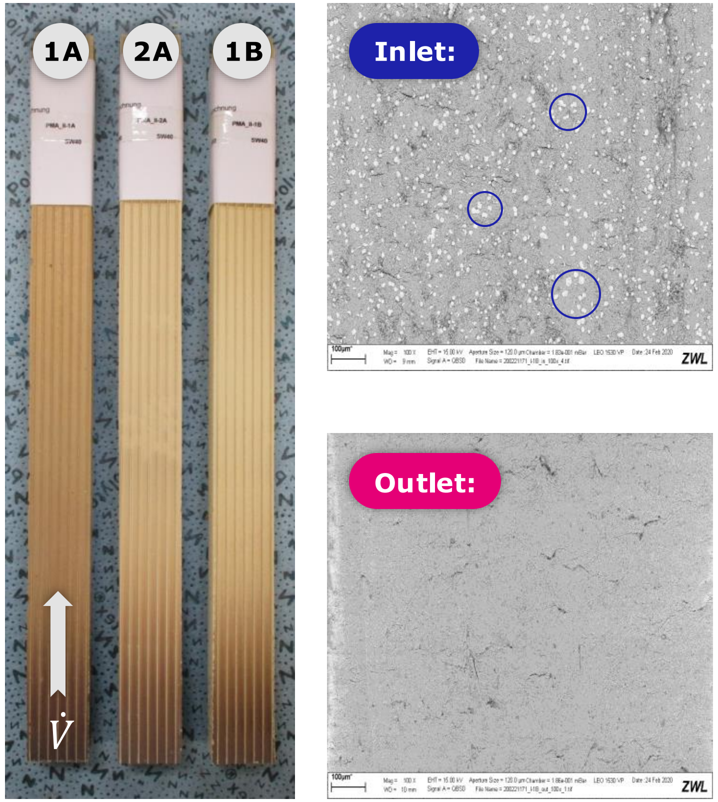
Visual discoloration of field returns due to poisons and ash



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

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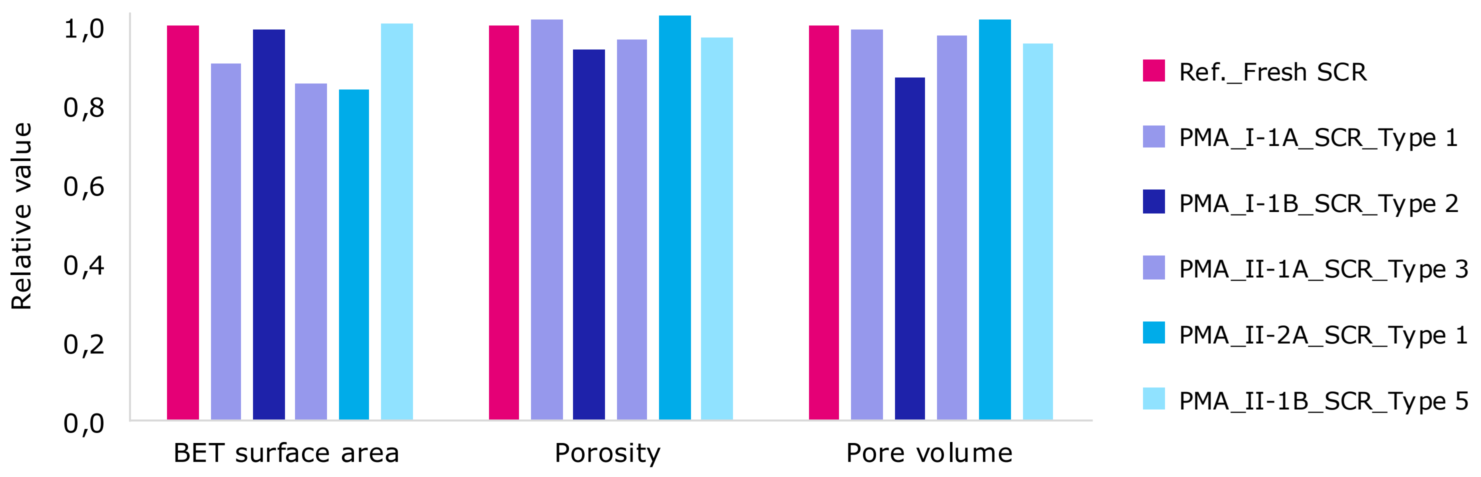
Combination of physical-chemical techniques used to identify deactivation mechanisms



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

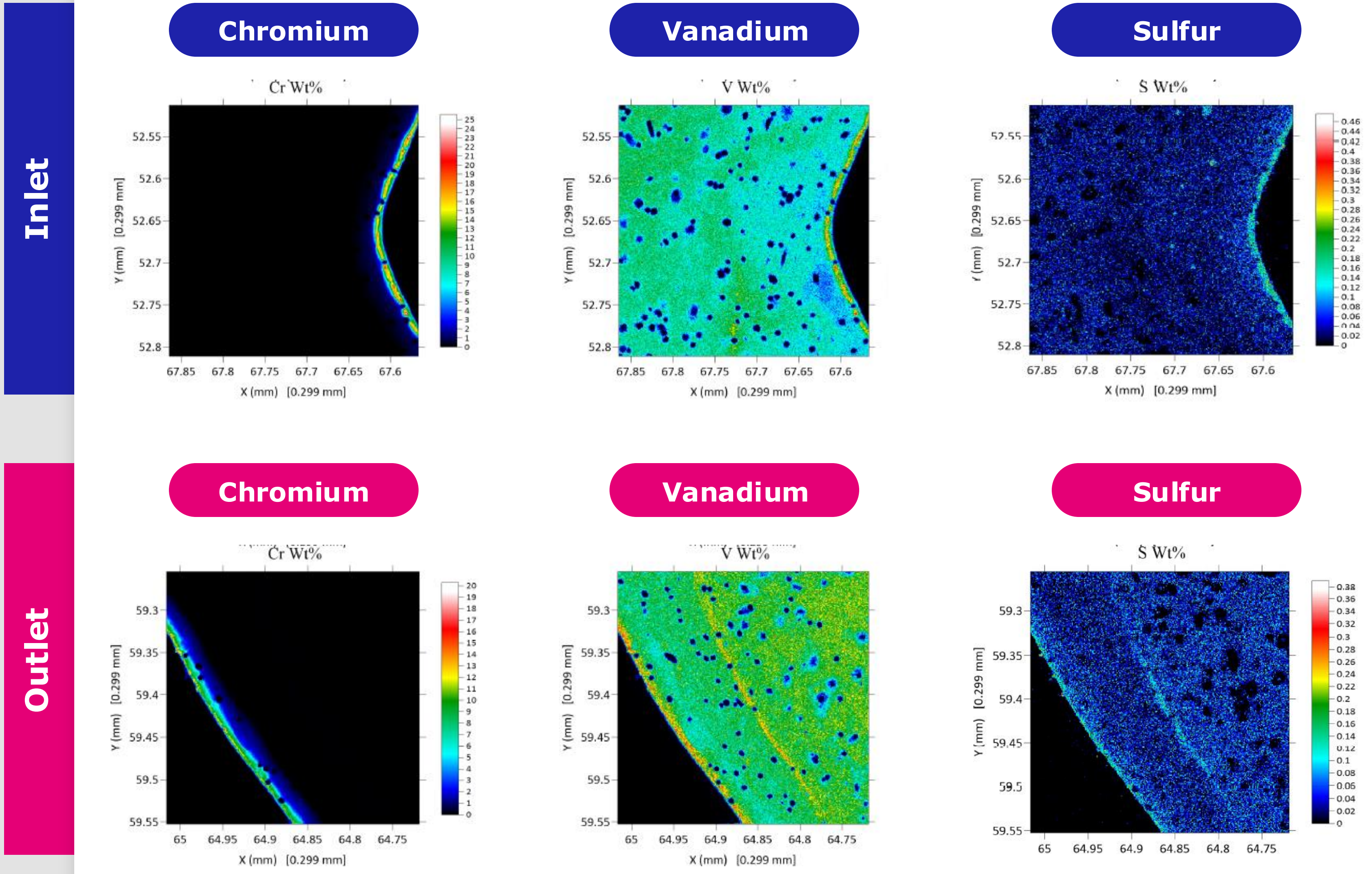
EDX: surface chemical anlaysis

Where are deposits/ poisons located

Several mechanisms may overlap

⇒ Cr the primary driver

Elemental mapping by EPMA reveals Cr concentrates at surface



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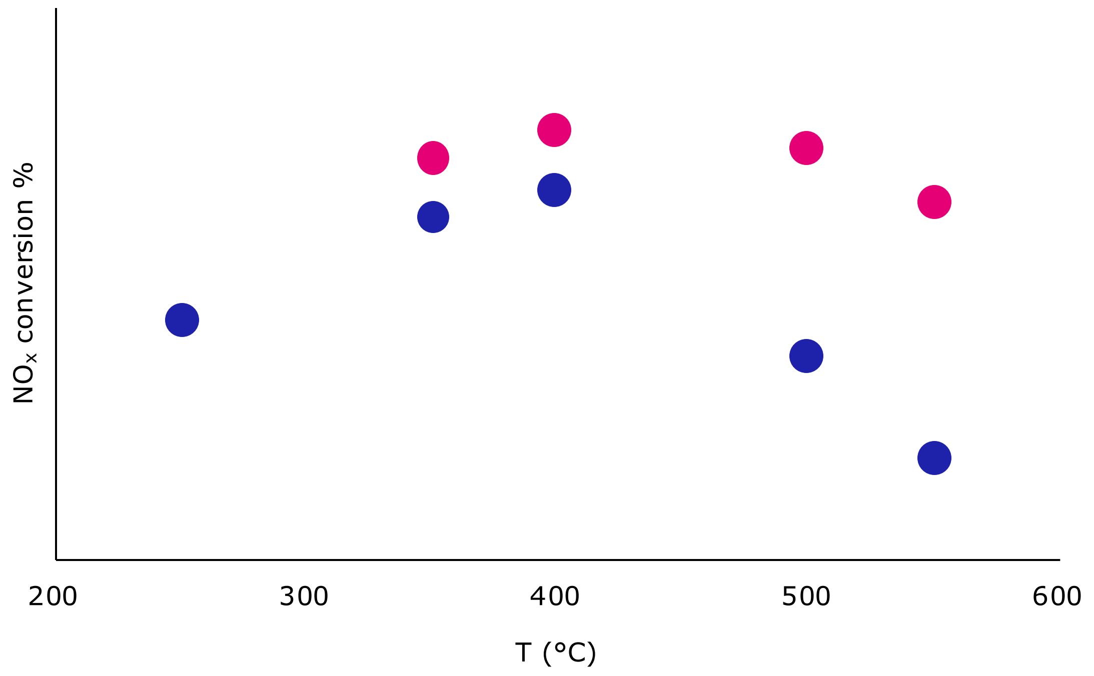
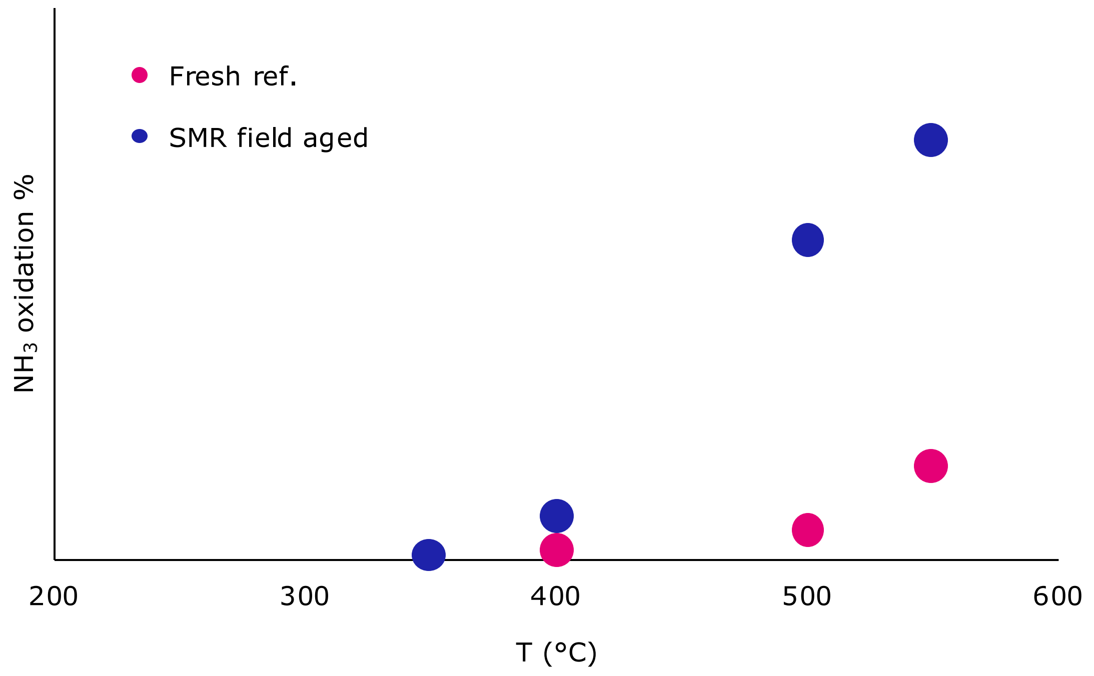
Catalytic activity negatively influenced by Cr deposition

Impact of Cr – NO_x conversion



Impact of Cr – NH_3 oxidation



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

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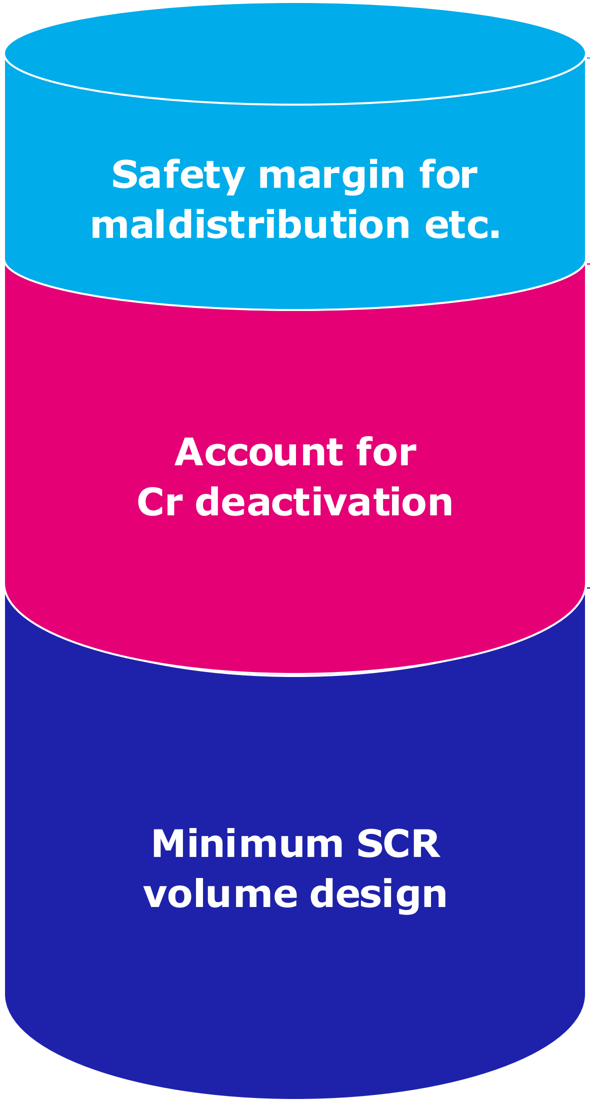
SCR catalyst design considerations for SMR applications



- 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

JM

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Innovative solutions to enhance NO_x performance

High temperature SCR catalyst

Increased system efficiency

Higher application temperatures

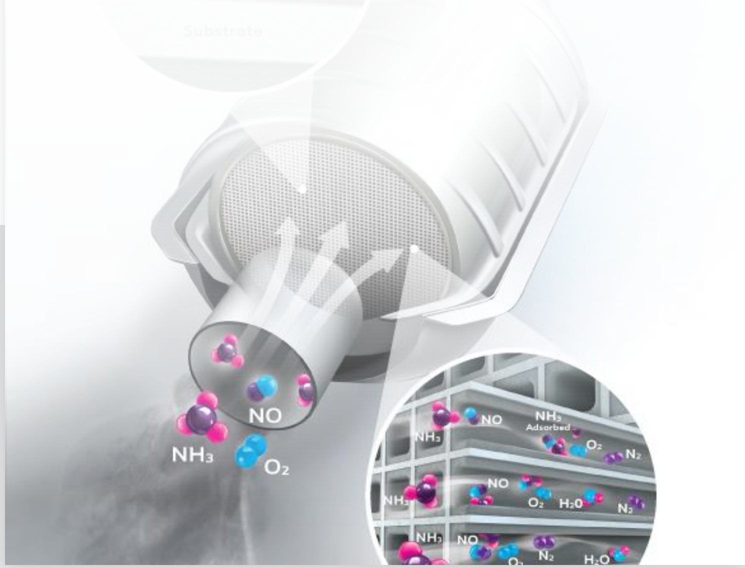
Reduced CO_2 footprint

Ammonia slip catalyst

Low NH_3 slip, high NO_x conversion

Allows for **higher ANR** (overdosing)

Helps with flow maldistribution



Chromium-getter

Protects downstream catalysts

Improves plant performance

Reduces early shutdowns

We can provide a **solution!**

JM

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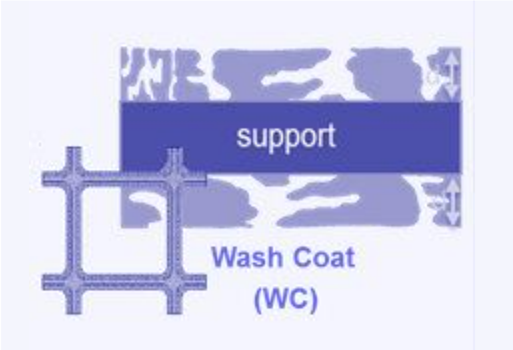
SCR High Temperature catalyst (SINOx-HT):

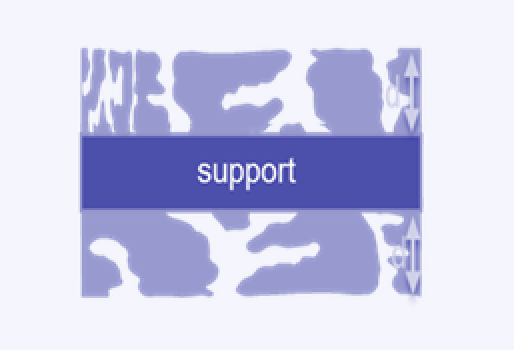
Developed for operation between 450°C-650°C (842°F-1202°F)



Increase
active mass/
WC loading

→

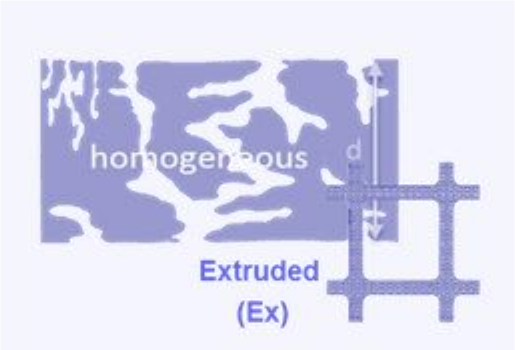
Increase
pressure
drop



Increase
active mass

→

Reduce
pressure
drop



Advantages of SINOx-HT:

- 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

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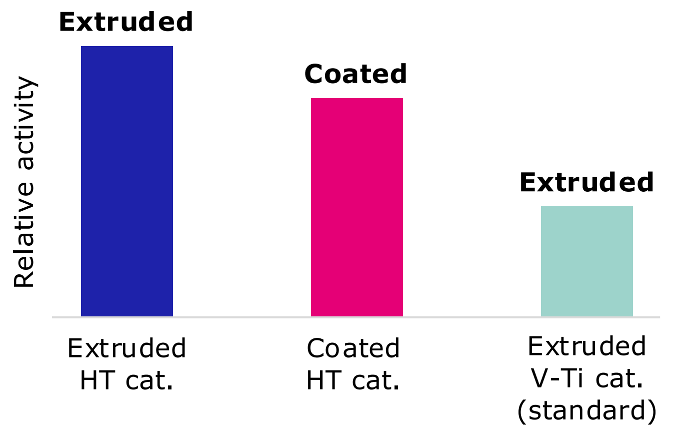
Advanced high temperature SCR catalyst (SCN7000) significantly outperforms standard V-Ti catalyst and washcoated catalysts

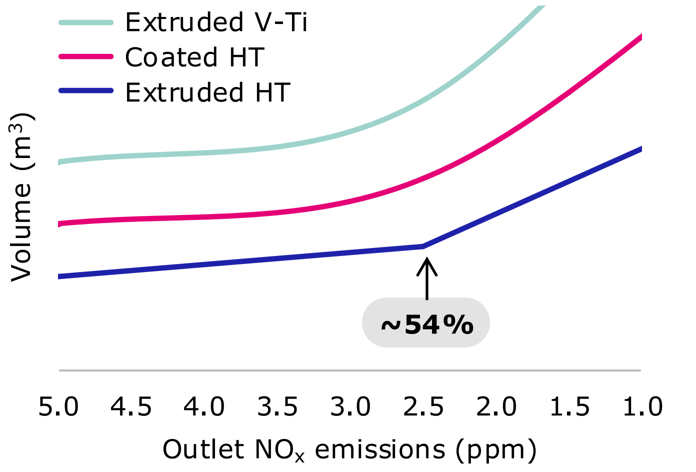
SCR activity

T=550°C (1022°F); NH_3/NO_x=1



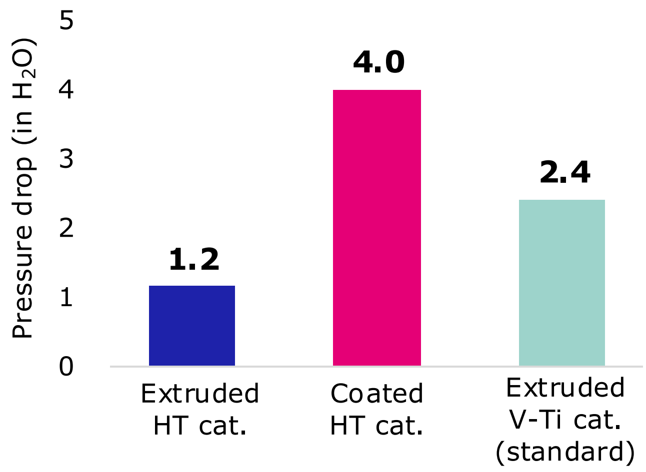
Catalyst volume

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

JM

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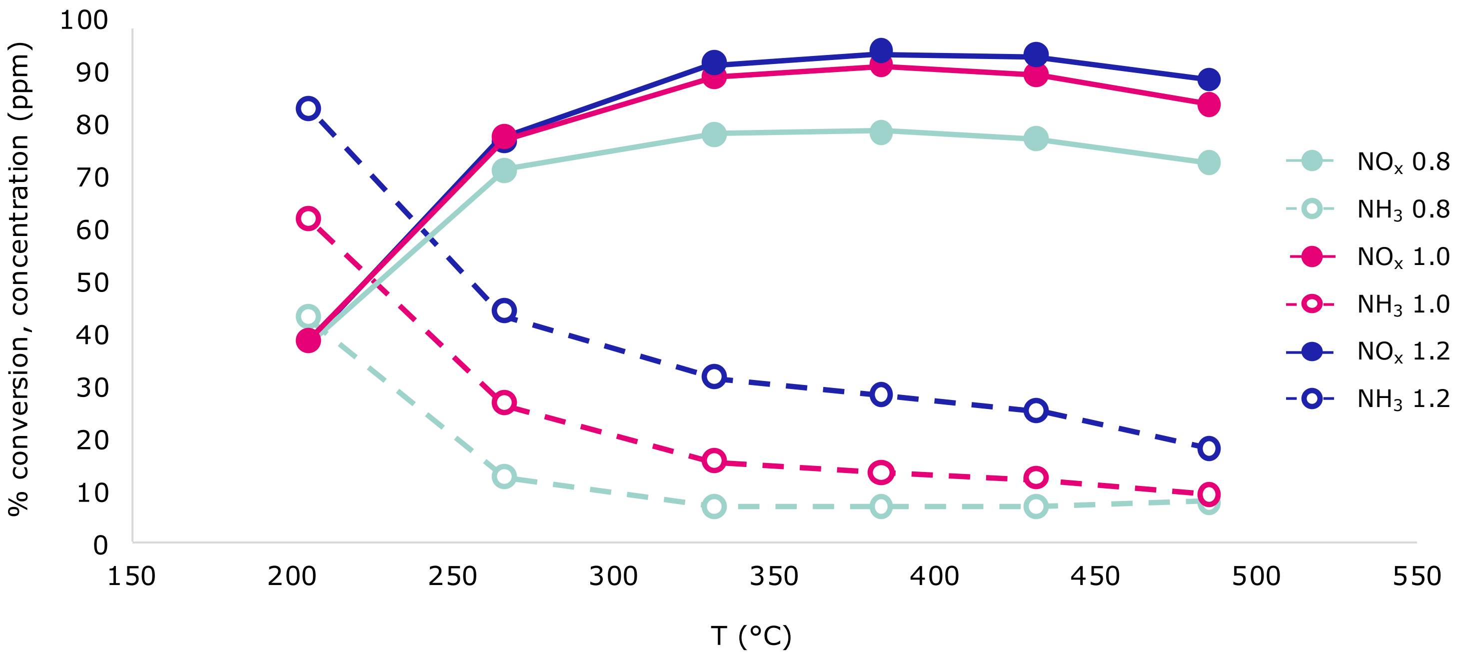
Ammonia Slip Catalyst (ASC) can boost NO_x conversion, reduce NH_3 slip, compensate for non-uniform NH_3 distribution, and oxidize CO/VOCs

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

JM

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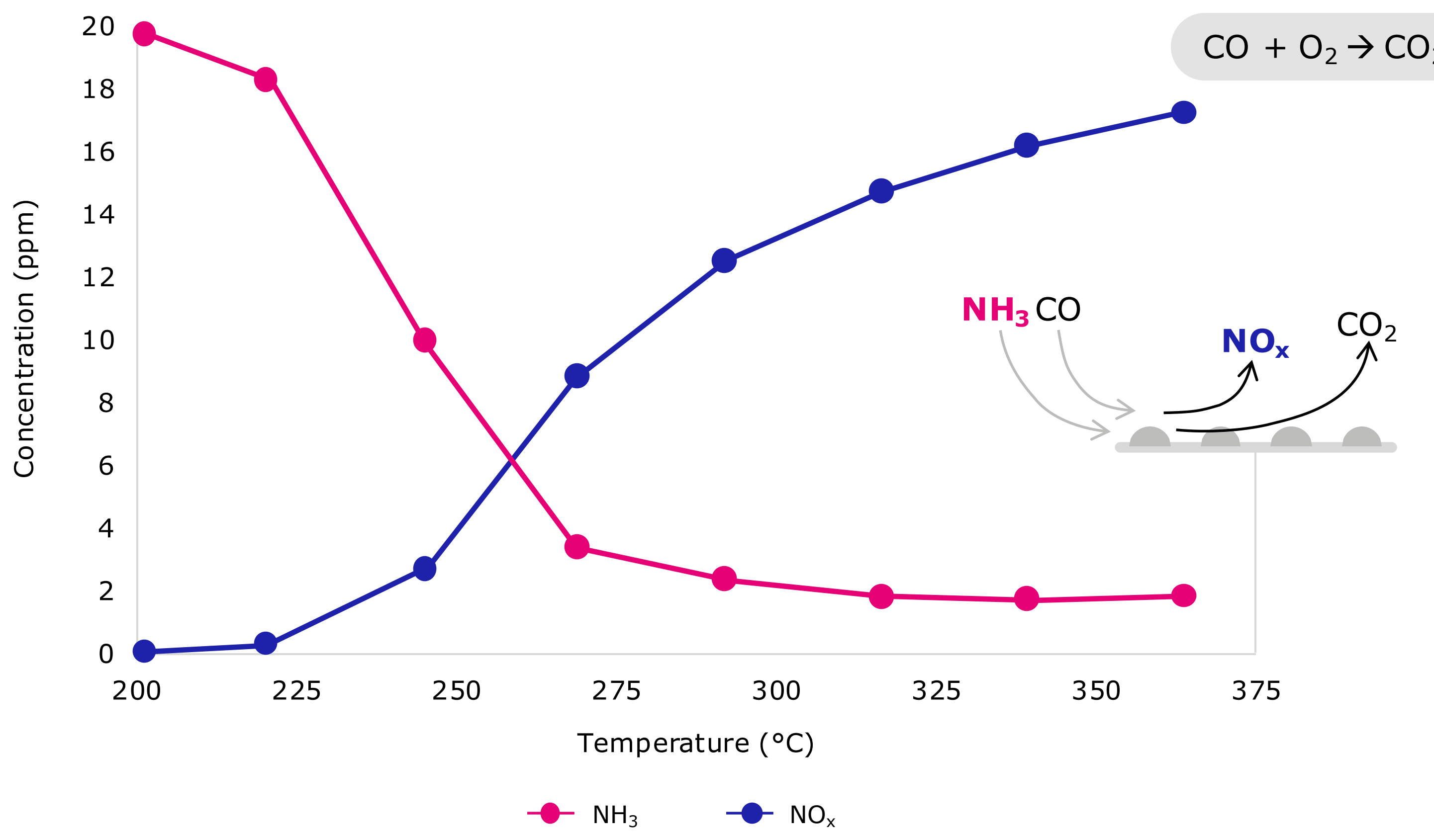
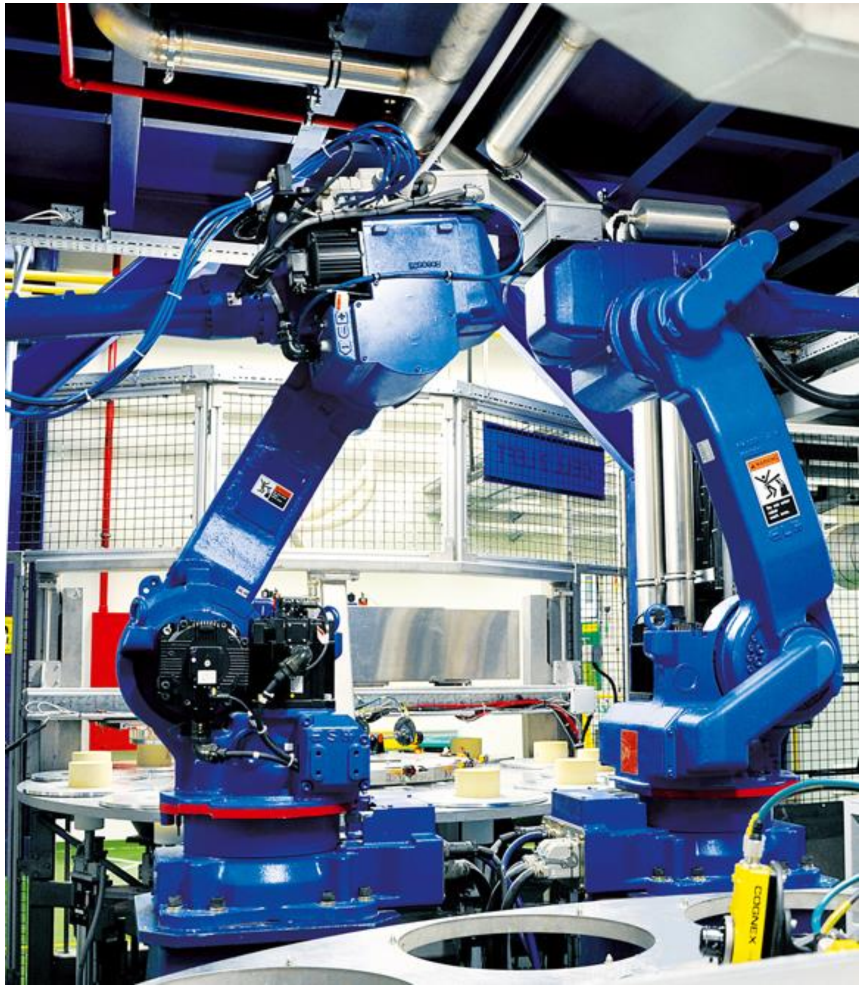
Previous generation ASC exhibit excellent activity (High NH_3/CO conversion) but poor selectivity (NO_x production)

Non-selective ammonia slip catalyst

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

$CO + O_2 \rightarrow CO_2$





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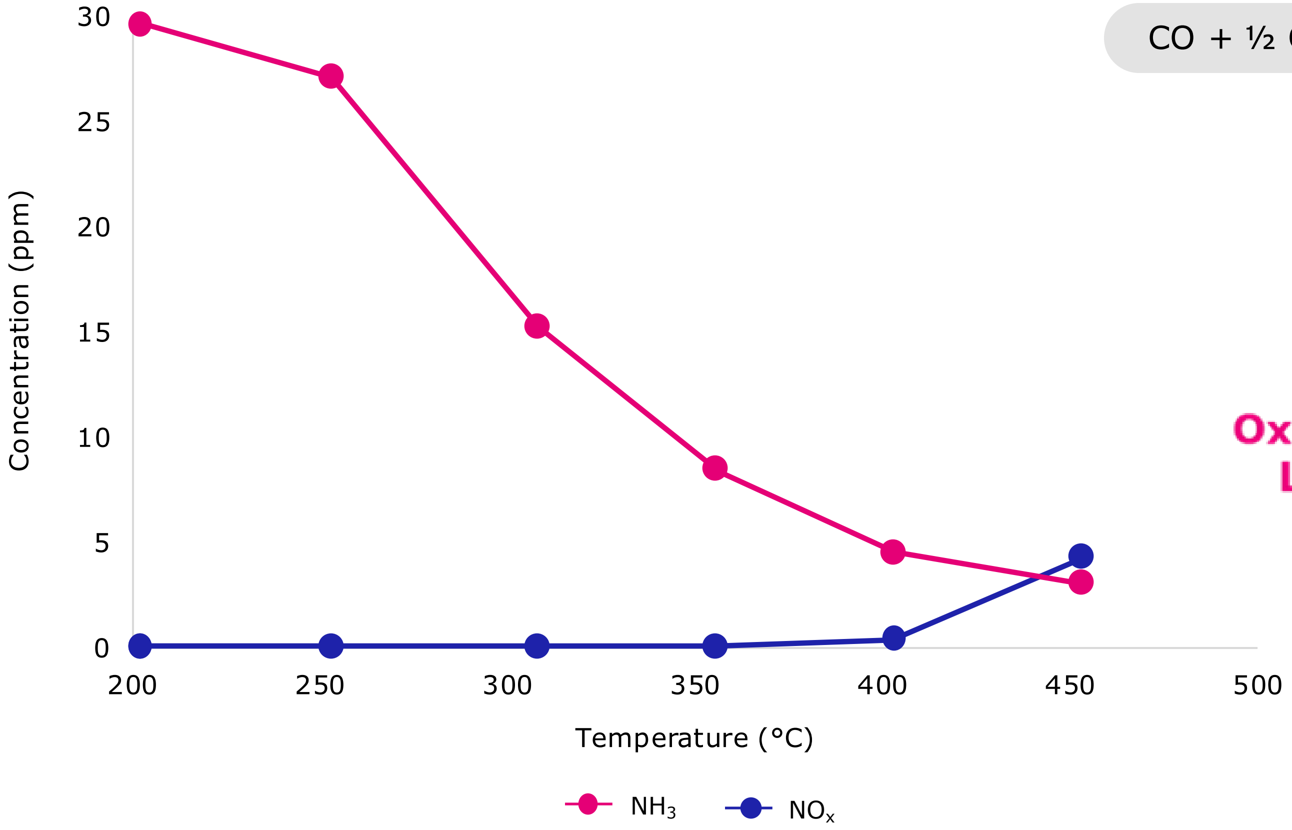
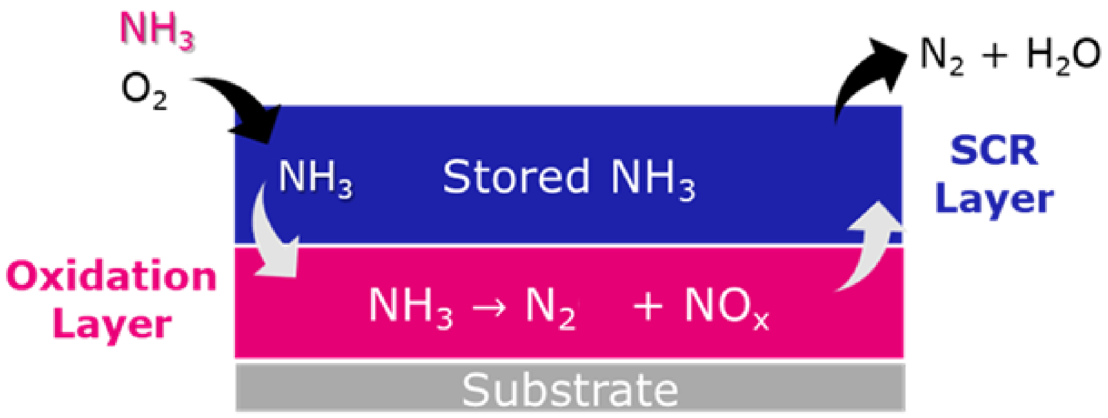
Advanced ASC performs both oxidation function and SCR function (selective to N_2) simultaneously

Selective ammonia slip catalyst

$2NH_3 + {}^3/_2\, O_2 \rightarrow N_2 + 3H_2O$

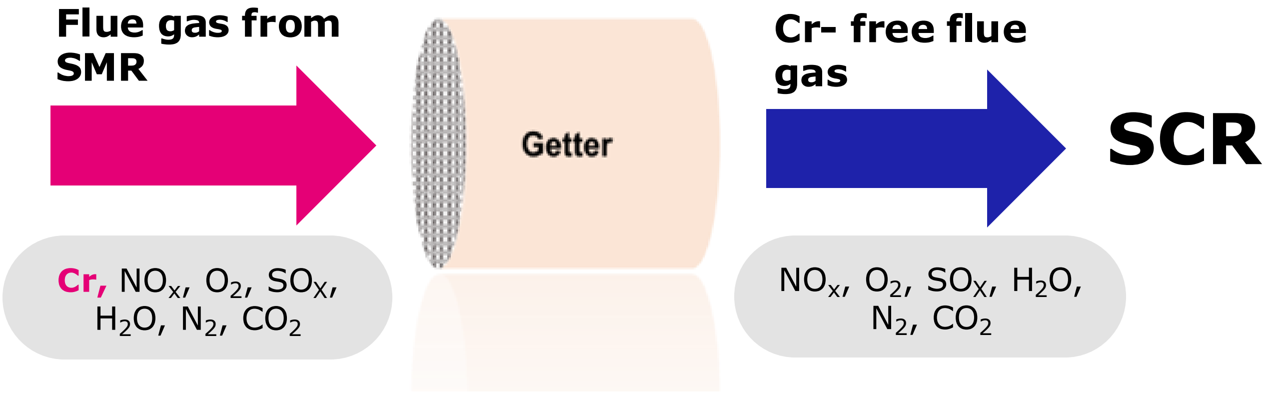
$CO + ½\, O_2 \rightarrow CO_2$





Chromium Getter

Identified solution to trap Cr vapour released from steel at high temperatures



Chromium Poisoning

Cr can deposit on downstream catalysts (SCR, ASC), killing performance efficiency

Hexavalent chromium is also carcinogenic

JM's solution

Cr getters (coated ceramic/metallic monoliths) can be positioned upstream of the SCR

94-99% Cr-capture efficiency proven at lab scale.

JM

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Durable Chromium Getter Technology Developed and Proven Under High Cr Flux Conditions (Condensate)

No Cr-Getter

99.4% Cr-Capture Efficiency	
	Cr Content
No Getter	712 µg/kg (ppb)
With Cr-Getter	4.3 µg/kg (ppb)

0 hrs

100 hrs

Testing Time High Cr Flux

50 hrs

300 hrs

With Cr-Getter

JM

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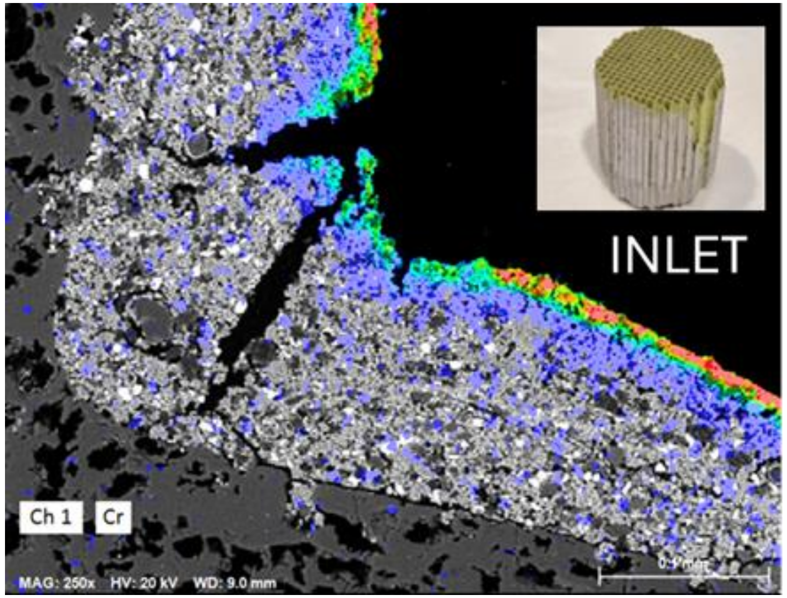
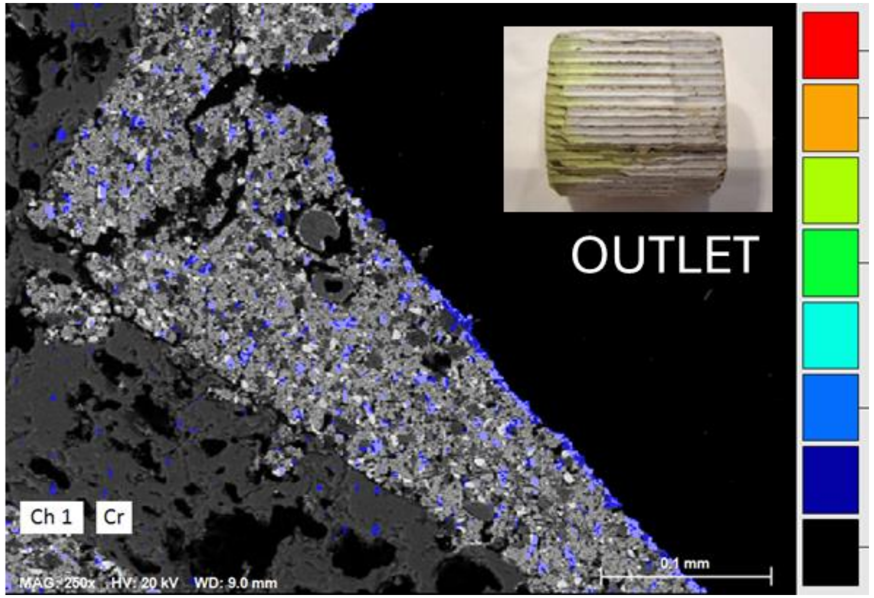
Durable Chromium Getter Technology Developed and Proven Under High Cr Flux Conditions (Evidence from SEM/EDX)





Cr Trapping at Inlet Face (~5mm) as Designed = Longer Lifetime

Upstream Cr Trap should improve performance and extend catalyst lifetime

Cr Getter must be upstream of NH_3 injection as Cr can act as oxidation catalyst

High capture efficiency and suitable sizing design should offer protection over catalyst lifetime

Improved SCR and ASC function from Cr protection should reduce aggregate emissions

JM

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Cr Getter Sizing Considerations

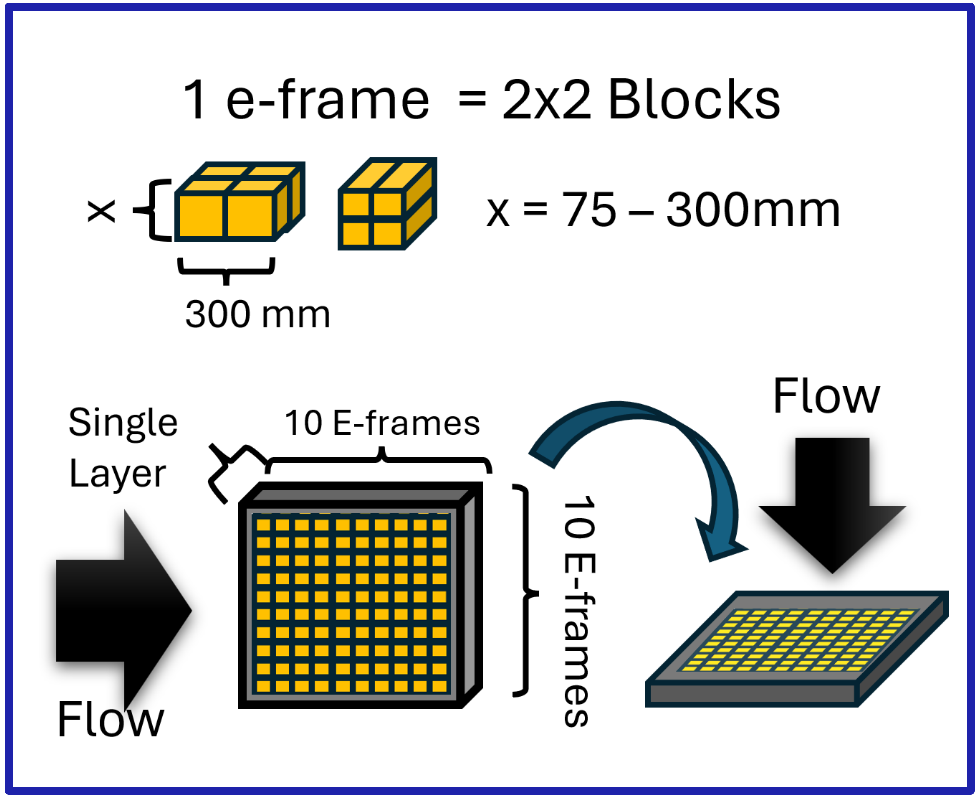
Key Parameters Dictating Size
Operating Temperature (550-750+ °C recommended)
Cr Slip Requirement
Available Cross Section & Total Volume
Guarantee period
Pressure Drop Requirement

Parameter	Sizing Example 1	Sizing Example 2	Sizing Example 3
Mass Flow Rate (kg/hr)	10,000 kg/hr	75,000	75,000
Temperature (°C)	550 °C	550 °C	750 °C
Reactor Cross Section (m^2)	10 m^2	45 m^2	45 m^2
Total Volume (m^3)	1.4 m^3	6.3 m^3	6.3 m^3
Predicted Pressure Drop (in H2O)	< 0.3 in H2O	< 0.4 in H2O	< 0.7 in H2O

Cr Getter Sizing Considerations

Key Parameters Dictating Size
Operating Temperature (550-750+ °C recommended)
Cr Slip Requirement
Available Cross Section & Total Volume
Guarantee period
Pressure Drop Requirement

Parameter	Sizing Example 1
Mass Flow Rate (kg/hr)	10,000 kg/hr
Temperature (°C)	550 °C
Reactor Cross Section (m^2)	10 m^2
Total Volume (m^3)	1.4 m^3
Predicted Pressure Drop (in H2O)	< 0.3 in H2O



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 (450°C-650°C) commercially available

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

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
- Cr-getters being developed to protect downstream catalysts

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