Johnson Matthey
Inspiring science, enhancing life

Americas hydrogen and syngas technical training seminar

Fundamentals of steam reforming

Danielle Covelli

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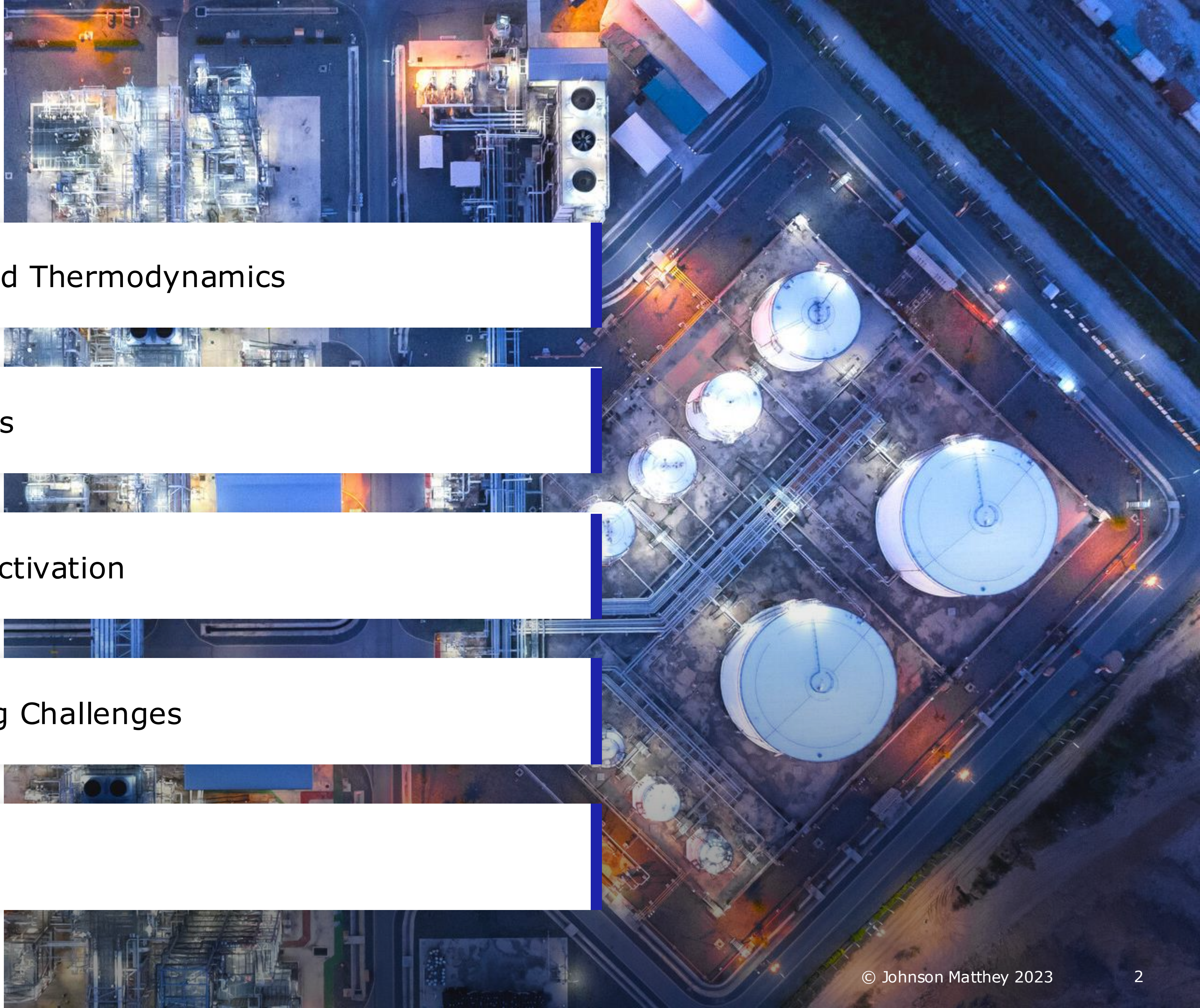

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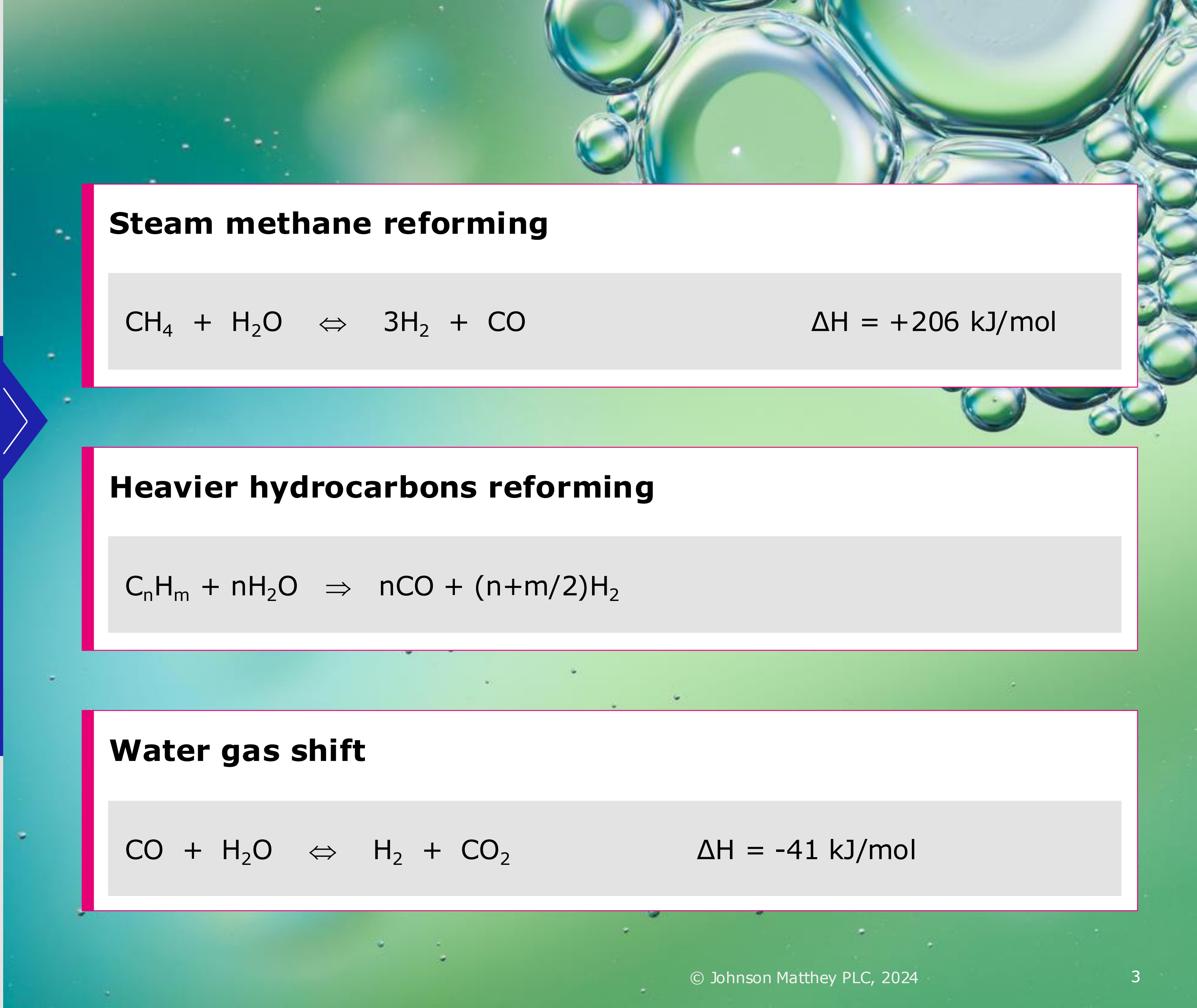
The core of hydrogen and syngas production

Steam reforming is the dominant process used for the creation of synthesis gas (syngas) for ammonia, methanol, hydrogen and hydrogen/carbon monoxide (HyCO) production.

The main reactions in a steam reformer are:



Steam methane reforming

$CH_4 + H_2O \Leftrightarrow 3H_2 + CO \quad \Delta H = +206\ \text{kJ/mol}$

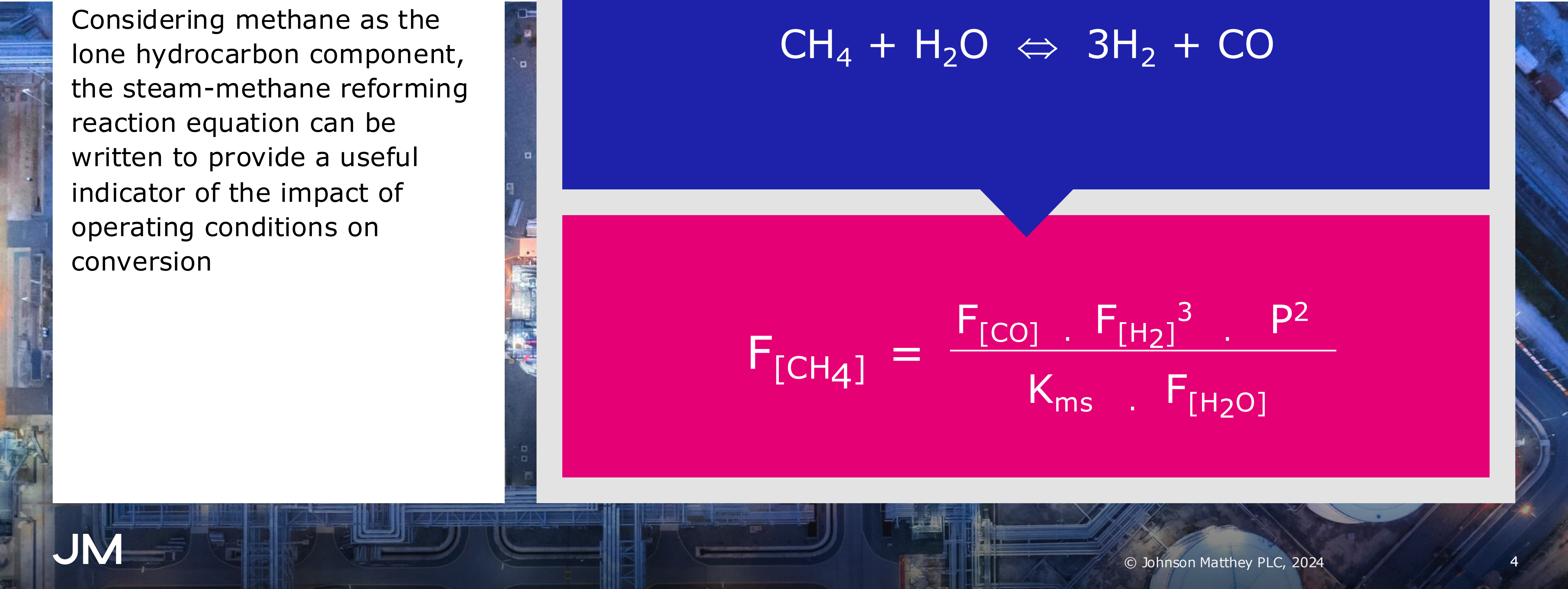
Heavier hydrocarbons reforming

$C_nH_m + nH_2O \Rightarrow nCO + (n+m/2)H_2$

Water gas shift

$CO + H_2O \Leftrightarrow H_2 + CO_2 \quad \Delta H = -41\ \text{kJ/mol}$

Reaction stoichiometry and thermodynamics



Reaction equation

Considering methane as the lone hydrocarbon component, the steam-methane reforming reaction equation can be written to provide a useful indicator of the impact of operating conditions on conversion

$$CH_4 + H_2O \Leftrightarrow 3H_2 + CO$$

$$F_{[CH_4]} = \frac{F_{[CO]} \,.\, F_{[H_2]}{}^3 \,.\, P^2}{K_{ms} \,.\, F_{[H_2O]}}$$

Higher pressures have a negative effect on conversion

Increasing pressure

Increasing S:C ratio

Increasing temperature

01

Effect of increasing pressure

Reduces conversion as indicated by an increase in methane slip

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Plant economics dictate higher pressure (20 bars)

$$F_{[CH_4]} = \frac{F_{[CO]} \,.\, F_{[H_2]}^{3} \,.\, \mathbf{P^2}}{K_{ms} \,.\, F_{[H_2O]}}$$

Conversion is favoured by higher steam:carbon ratios

Increasing pressure ←

Increasing S:C ratio →

Increasing temperature →

02

Effect of increasing steam:carbon ratio

Increases conversion resulting in a decreased methane slip

Often dictated by plant design (2.4-5.0 mol/mol)

$$F_{[CH_4]} = \frac{F_{[CO]} \,.\, F_{[H_2]}^{3} \,.\, P^2}{K_{ms} \,.\, \mathbf{F_{[H_2O]}}}$$

Higher temperatures also promotes conversion

Increasing pressure ←

Increasing S:C ratio →

Increasing temperature →

03

Effect of increasing temperature

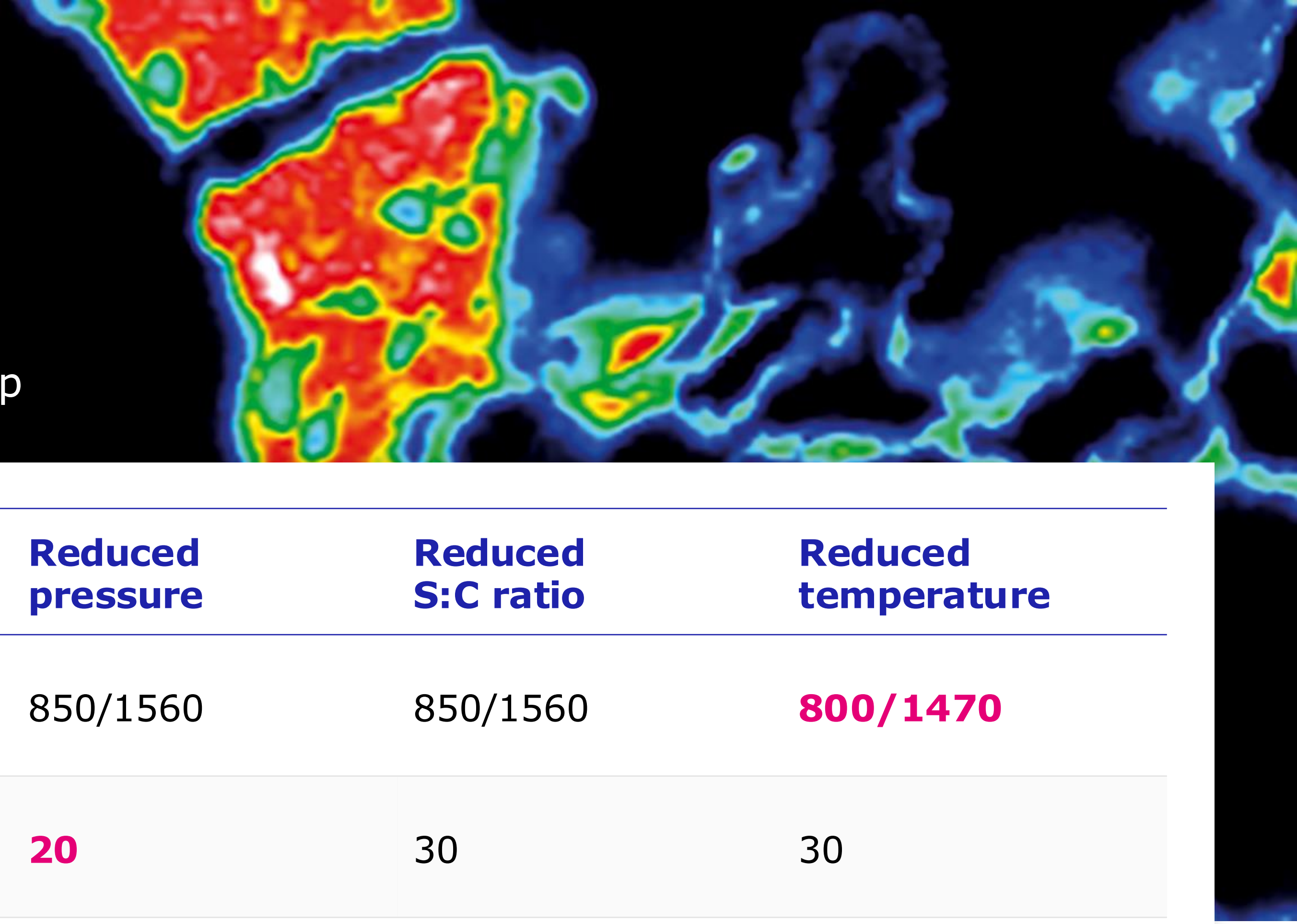
Decreases methane slip

Limited by tube metallurgy

$$F_{[CH_4]} = \frac{F_{[CO]} \,.\, F_{[H_2]}^{3} \,.\, P^2}{K_{ms} \,.\, F_{[H_2O]}}$$

Reaction Stoichiometry and Thermodynamics

A qualitative analysis of the impact of pressure, steam:carbon ratio and temperature on methane slip



	Base case	**Reduced pressure**	**Reduced S:C ratio**	**Reduced temperature**
Exit T (°C/°F)	850/1560	850/1560	850/1560	**800/1470**
Exit P (bar)	30	**20**	30	30
Inlet S:C (mol/mol)	3.5	3.5	**3.0**	3.5
CH_4 slip (mol%)	**5.4**	**3.4**	**6.7**	**9.3**

Reaction Stoichiometry and Thermodynamics

Effect of **feedstock composition**

Heavy feeds give lower methane slip, at constant conditions

Equilibrium moves to right:

$$CH_4 + H_2O \Leftrightarrow 3H_2 + CO$$

	ROG	**NG**	**LPG**	**LSR Naphtha**
C:H ratio	1:6	1:4	1:2.5	1:2.1
CH_4 slip (mol%)	6.7	5.4	4.3	4.0

Steam reforming catalysts

Catalyst for reliable operation

Leverage our expertise to drive performance

- Sintering resistant
- Carbon formation resistance
- Activity
- Pressure drop
- Heat transfer
- Robustness

The choice of steam reforming catalyst is extremely important and has a significant effect on the reformer and performance

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The catalyst has a direct impact on plant rate, tube life, methane slip and the formation of carbon

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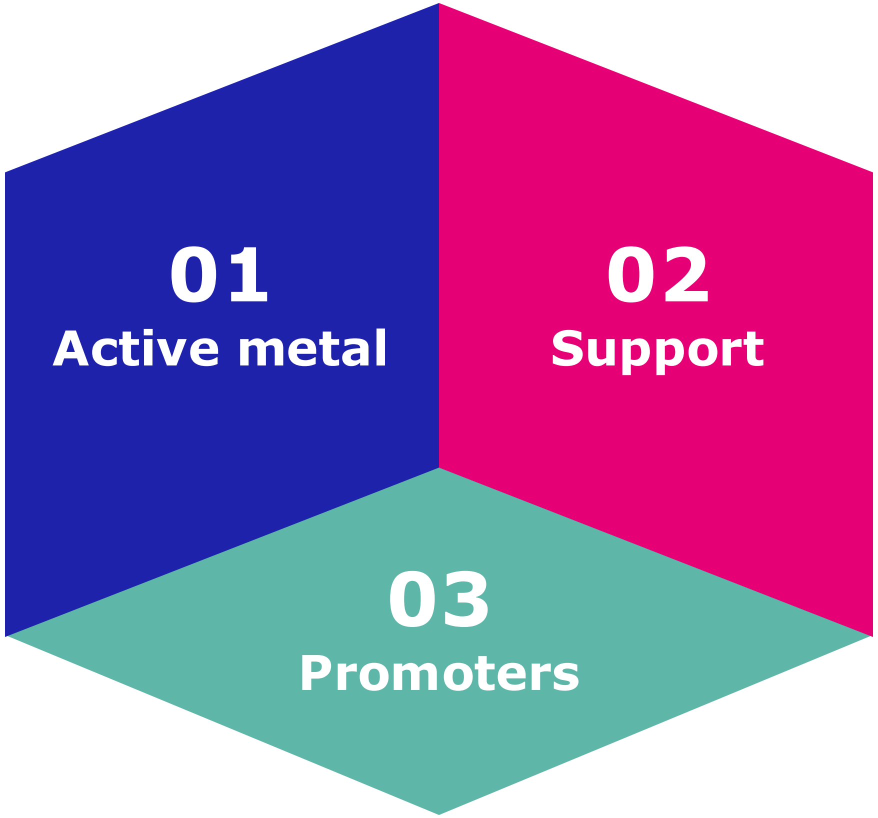
The main components of steam reforming catalysts

Inspiring science, enhancing performance



Steam reforming catalysts are comprise of:

- Active metal(s)
- Active metal needs to be dispersed onto a substrate
- Promoters to prevent carbon deposition

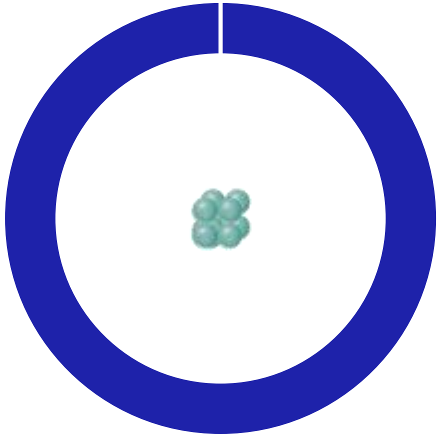
Johnson Matthey is a leader in steam reforming catalysts for the production of ammonia, methanol, hydrogen and HyCO

We have over 80 years of experience in steam reforming catalysts design and have led developments in the market with breakthroughs such as introducing potash promotion for carbon formation protection and deployment of structured catalysts for step out performance

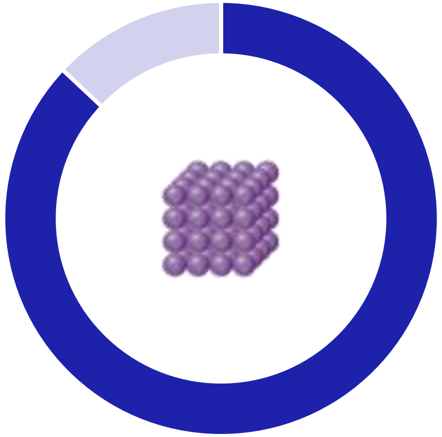
Metal dispersion is also important for activity

Dispersion with varying surface:volume ratios

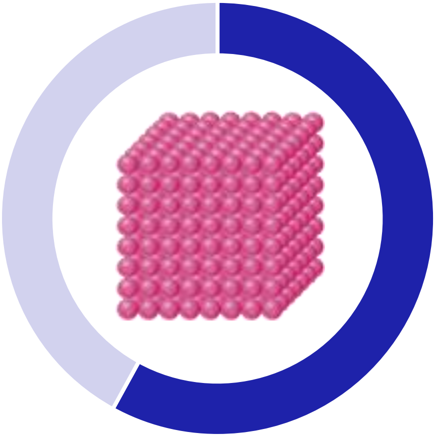
100%



87%



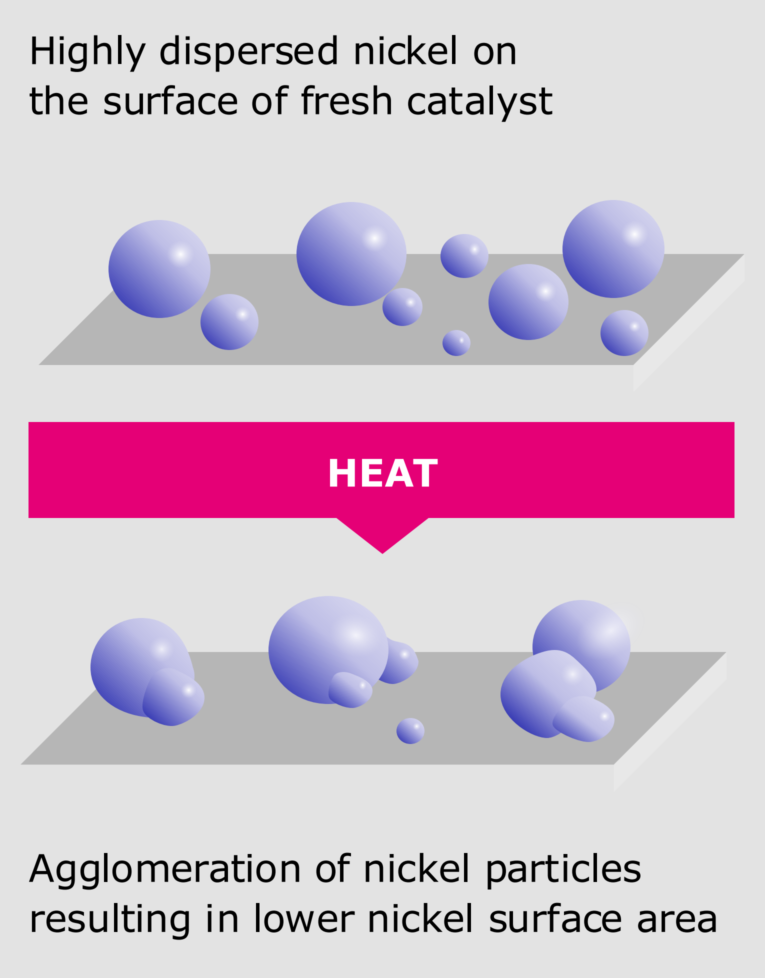
58%



Metal distribution

- Bulk of metal crystallite contributes little to catalyst performance
- Need small metal particles with high surface/volume ratio or dispersion
- Maintaining high nickel dispersion is important for sustaining the catalyst activity

Thermal stability helps maintain activity through the catalyst life



Highly dispersed nickel on the surface of fresh catalyst

Agglomeration of nickel particles resulting in lower nickel surface area

During operation, the metal crystallites of the catalyst undergoes **thermal sintering, causing** agglomeration of nickel particles and loss of active surface area, meaning a reduction in activity

Catalyst often supplied with high surface area/metal dispersion to take in account of sintering process

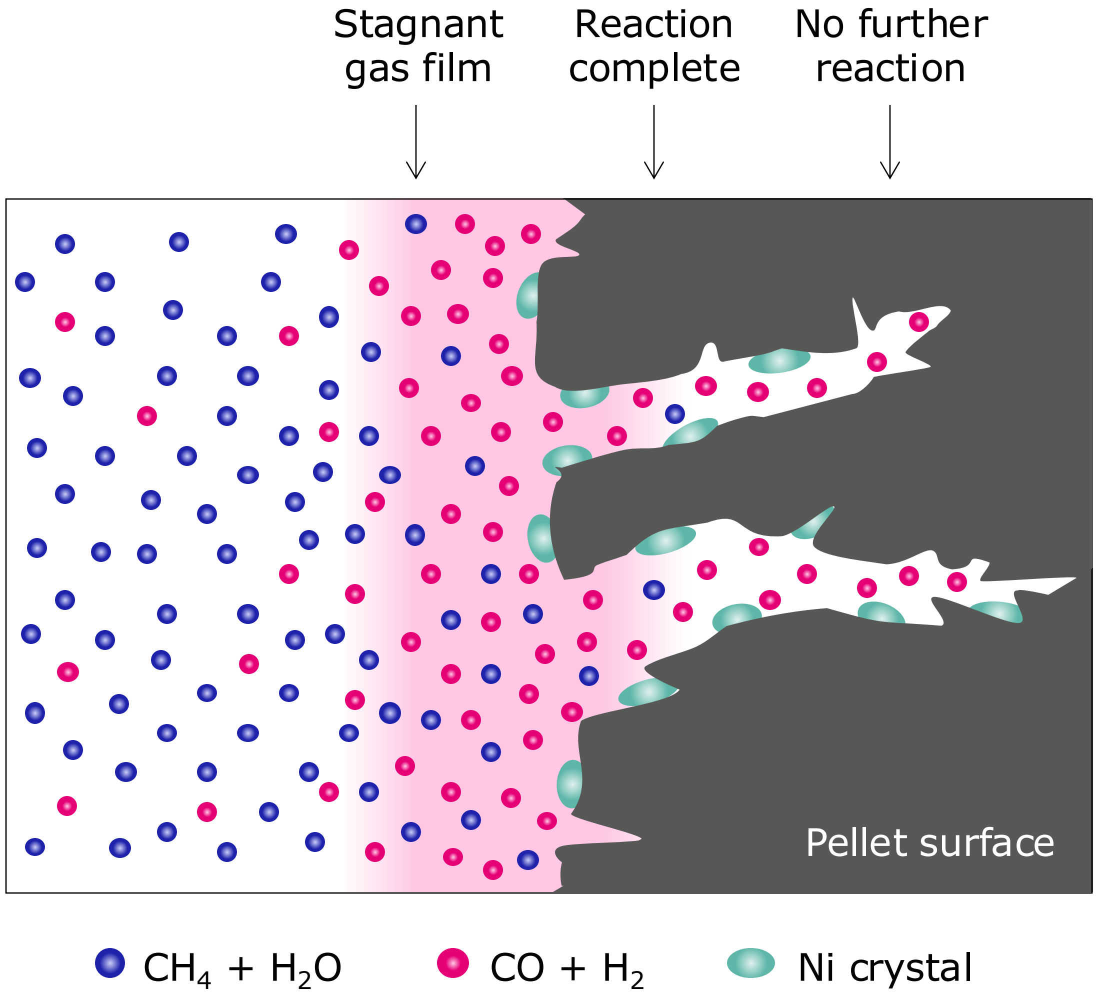
Metal-support interaction can minimise sintering rate

The importance of geometric surface area

Catalyst activity is proportional to **geometric surface area** (GSA) of the catalyst, which is the total pellet surface area per unit volume of the catalyst bed

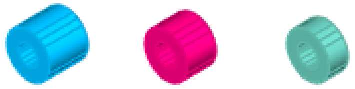
The majority of the steam reforming reaction happens at the **surface** of the pellet, where the reaction is very fast. Diffusion through the **gas film** is slow and little reaction happens in the pores

Improvements in GSA can also be achieved by **textured surfaces**, however textured surfaces promote turbulence and thus also impact on pressure drop and heat transfer



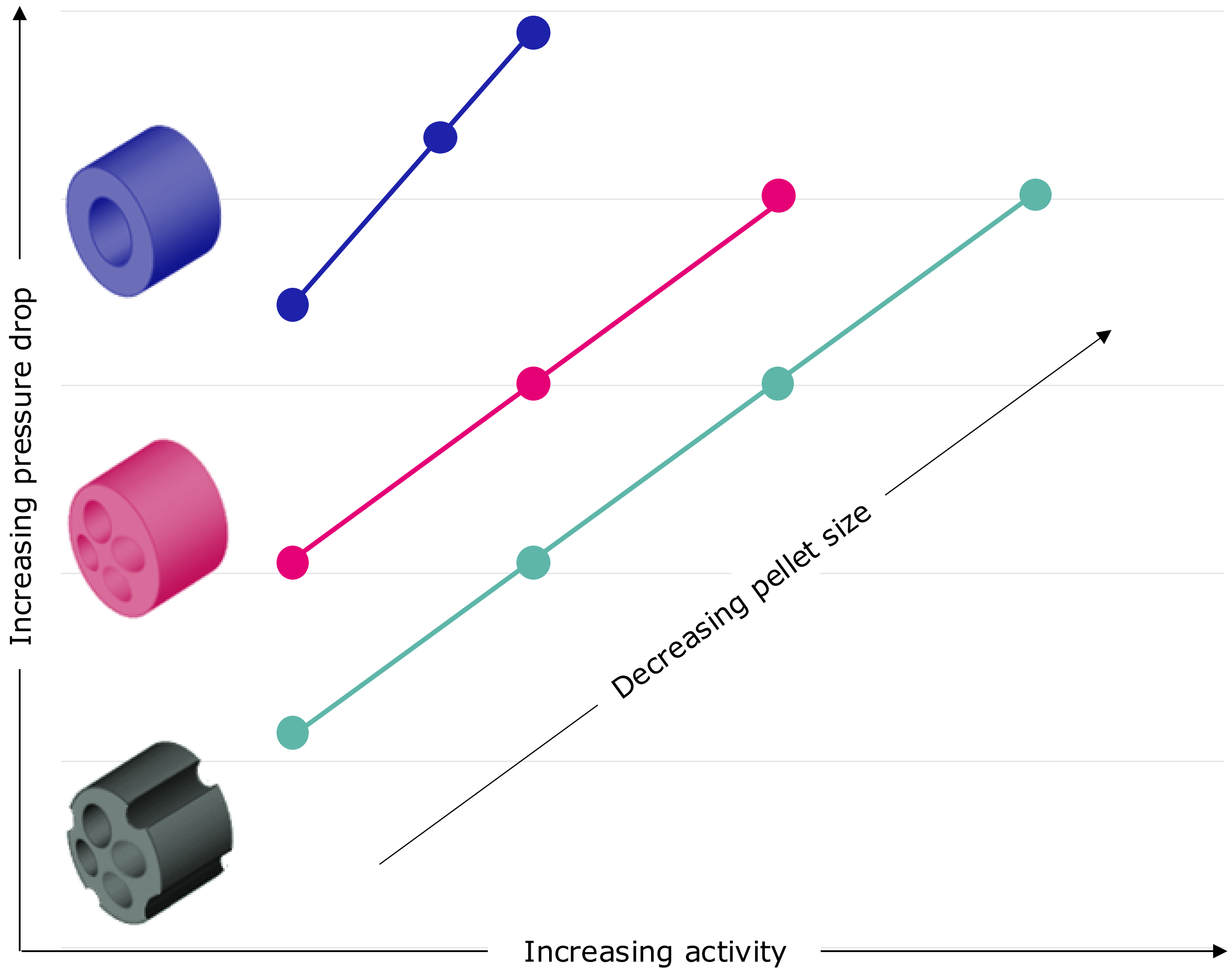
The effects of pellets size and shape

Pellet **size** is a trade-off between GSA and pressure drop. Smaller pellets have higher GSA but generally yield higher pressure drop



Relative length	**1.0**	**0.6**	**0.4**
Relative GSA	1.0	1.4	1.7
Relative pressure drop	1.0	1.3	1.5

Catalyst pellet **shape** designs have overcome the inherent limitations of the ring shape pellet



Catalyst damage and deactivation

Pressure drop

Start of run and growth during operation

- Pellet shape
- Pellet size
- Packing characteristics of pellet
- Texture of pellet surface
- Catalyst loading
- Breakage characteristics of pellet
- Number of thermal cycles

Pressure drop is largely dominated by the **voidage** in the catalyst bed which is defined by the pellet size and shape

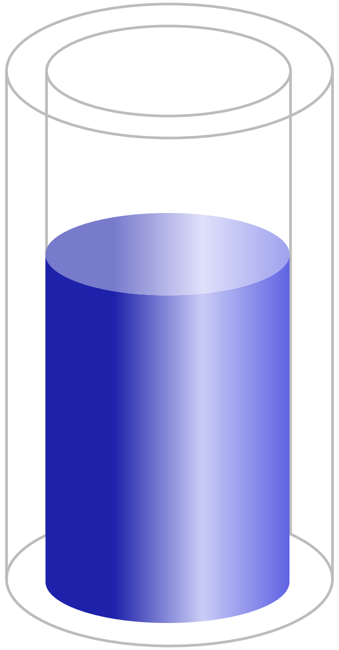
How the catalyst packs during loading and prevention of breakage during loading are also important for the **start of run pressure drop**

The catalyst breakage characteristics and the number of thermal cycles impact the rate of **pressure drop growth during operation**

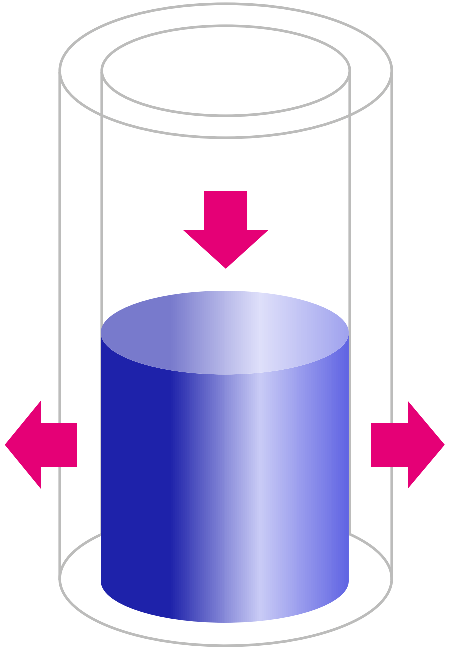
Thermal cycles lead to pellet breakage and pressure drop increase

The number of thermal cycles will impact the rate of pressure drop growth

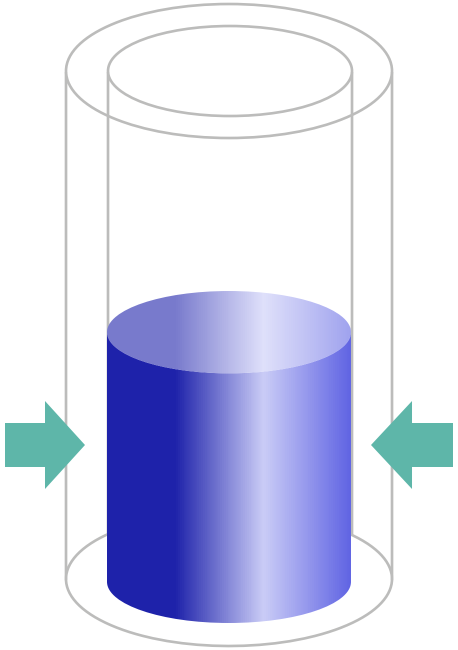
01 Catalyst is loaded in the reformer tube when the unit is cold



02 On heating the reformer tube expands, and the catalyst settles



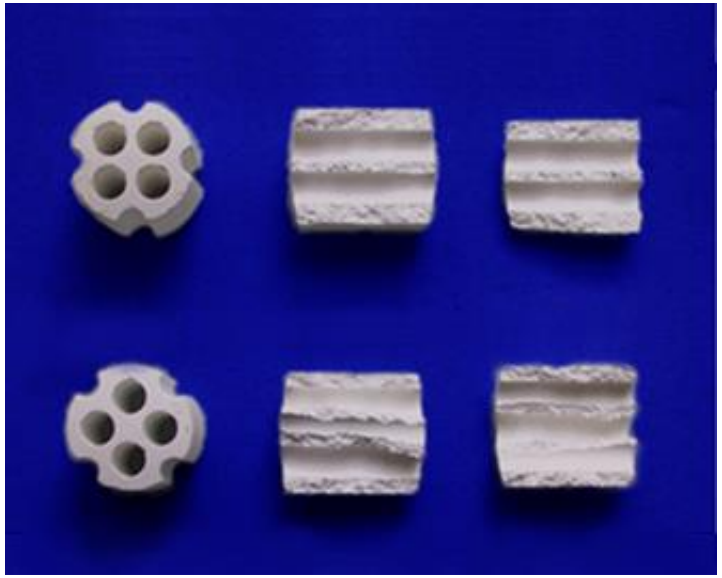
03 On cooling, the reformer tube contracts, crushing the catalyst

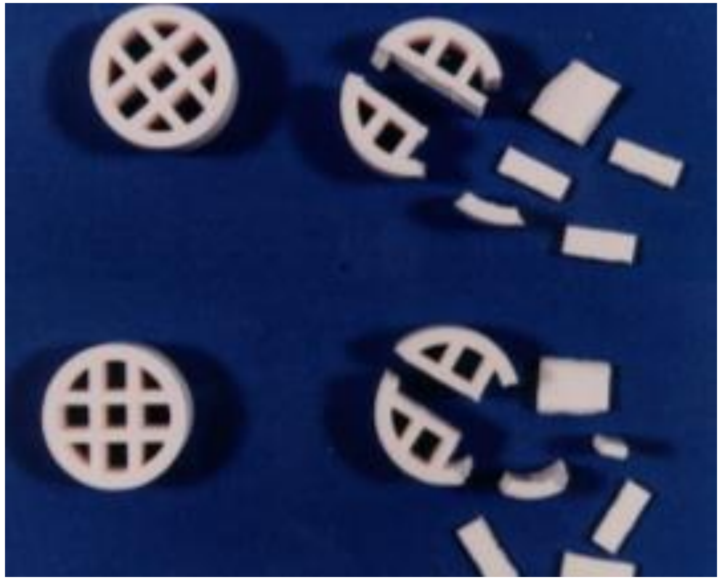


Designing the catalyst to minimise pressure drop growth

Most pellet shapes are designed to withstand the harsh steam reforming conditions, but no shape can withstand the forces of **thermal cycling**

Shape design must take this into account by ensuring that **pellet fragments** created during pellet breakage minimise small pieces





Carbon deposition mechanisms

Hydrocarbon cracking: $C_nH_{2m} \Leftrightarrow nC + mH_2$

Higher rates of carbon formation promoted by:

Higher concentration of hydrocarbon

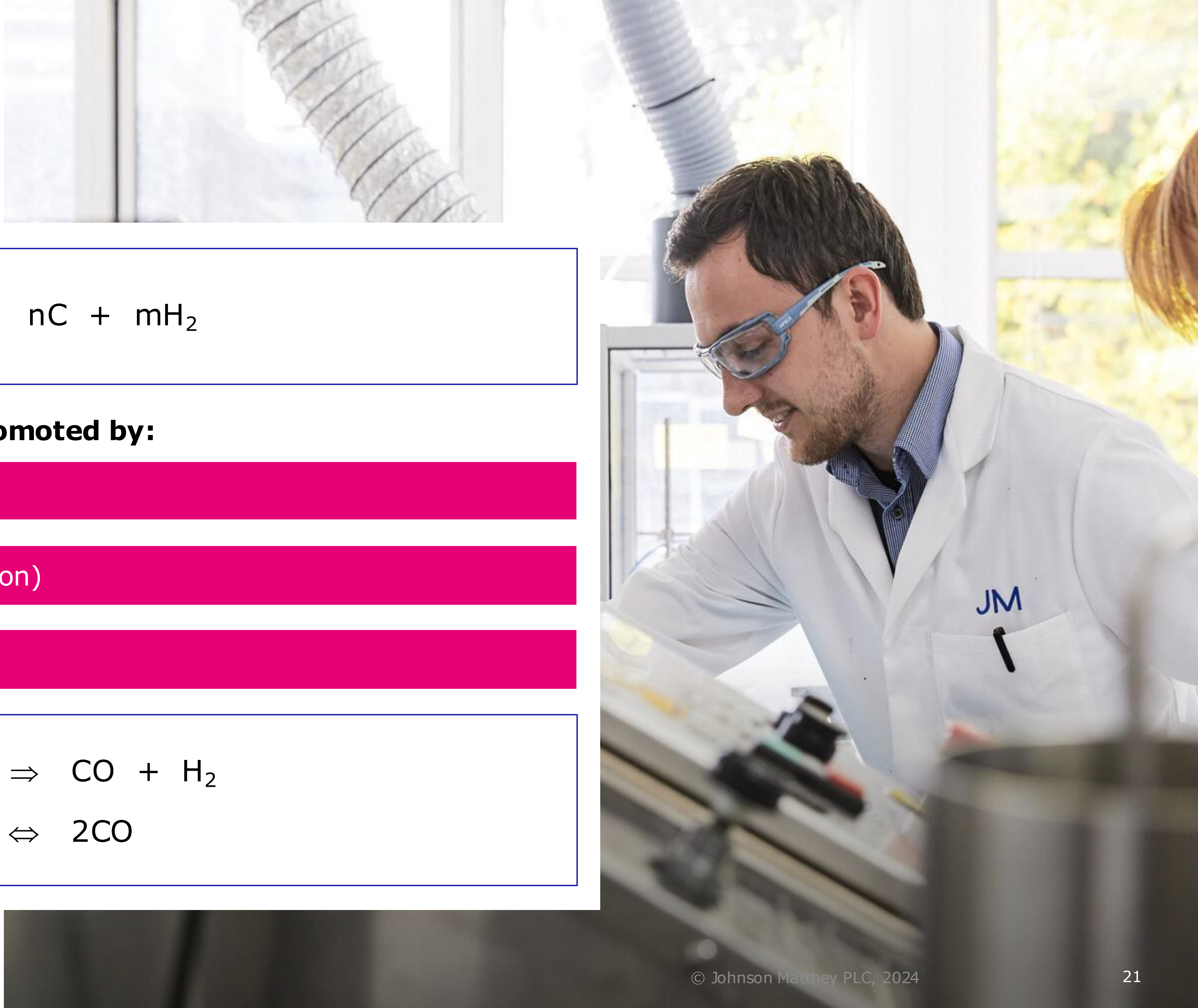
Higher temperatures (Arrehnius equation)

Lower partial pressure of hydrogen

Carbon gasification:

$$C + H_2O \Rightarrow CO + H_2$$

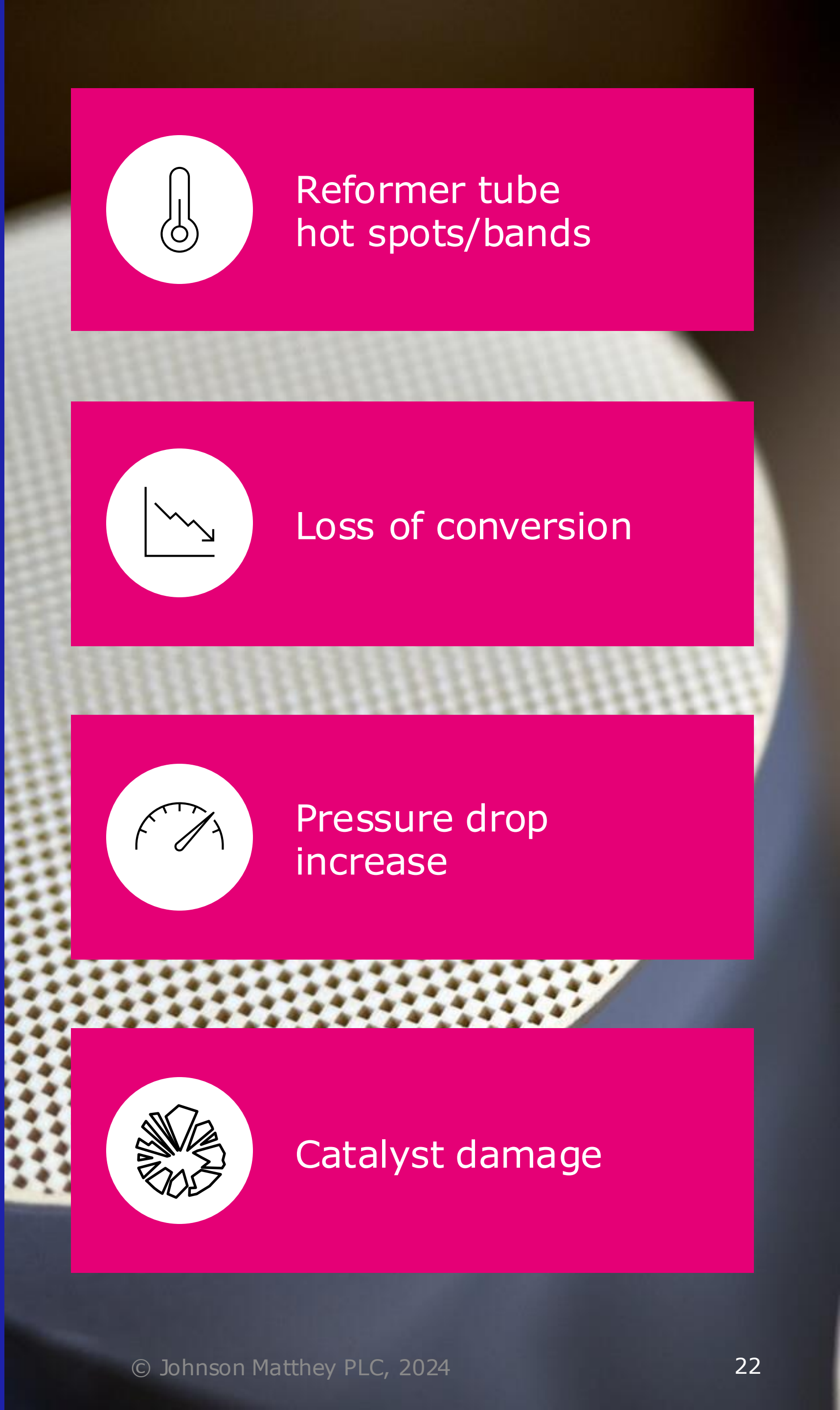
$$C + CO_2 \Leftrightarrow 2CO$$



Causes and consequences of carbon deposition

Causes of carbon deposition issues

- **Heavier feed components**
- **Low steam flow**
- **Catalyst deactivation**
- **Burner problems**
- **Maldistribution**
- **High operating temperatures**



- Reformer tube hot spots/bands
- Loss of conversion
- Pressure drop increase
- Catalyst damage

Types of carbon deposition

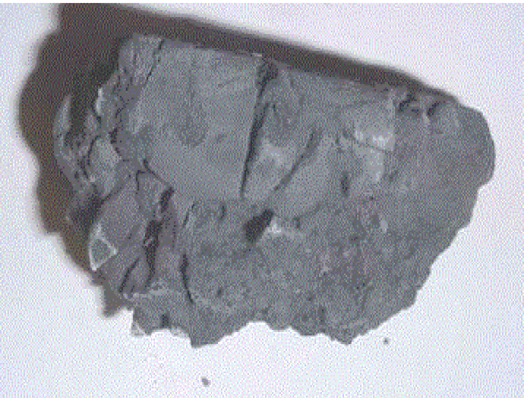
Whisker carbon

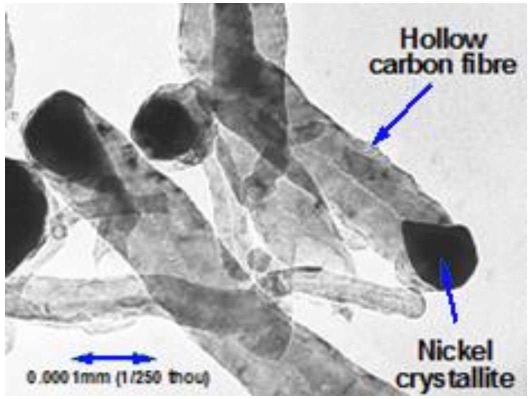
Catalytic cracking

Carbon dissolves in Ni metal crystallites

Tubular “whiskers” form containing Ni crystallites

Filaments are strong and can damage catalyst pellets





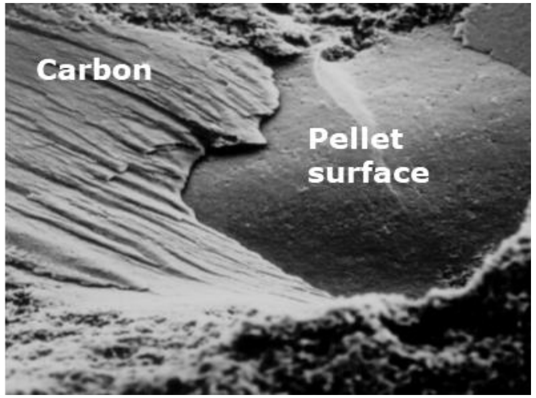
Pyrolytic carbon

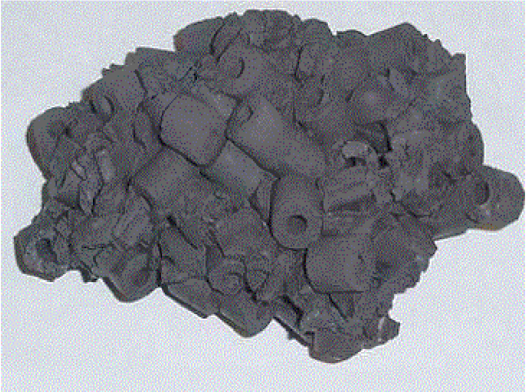
Gas phase thermal cracking

Deposits across catalyst surface

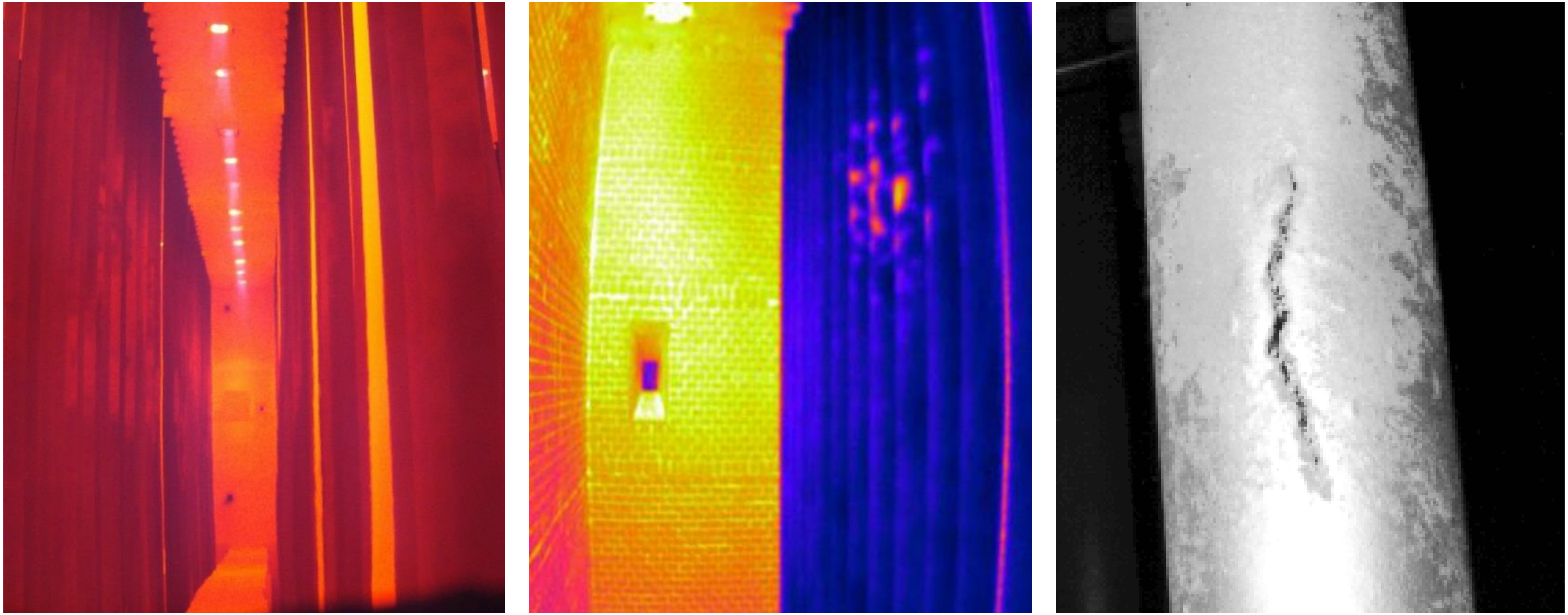
Covers active surfaces

Reduces catalyst activity

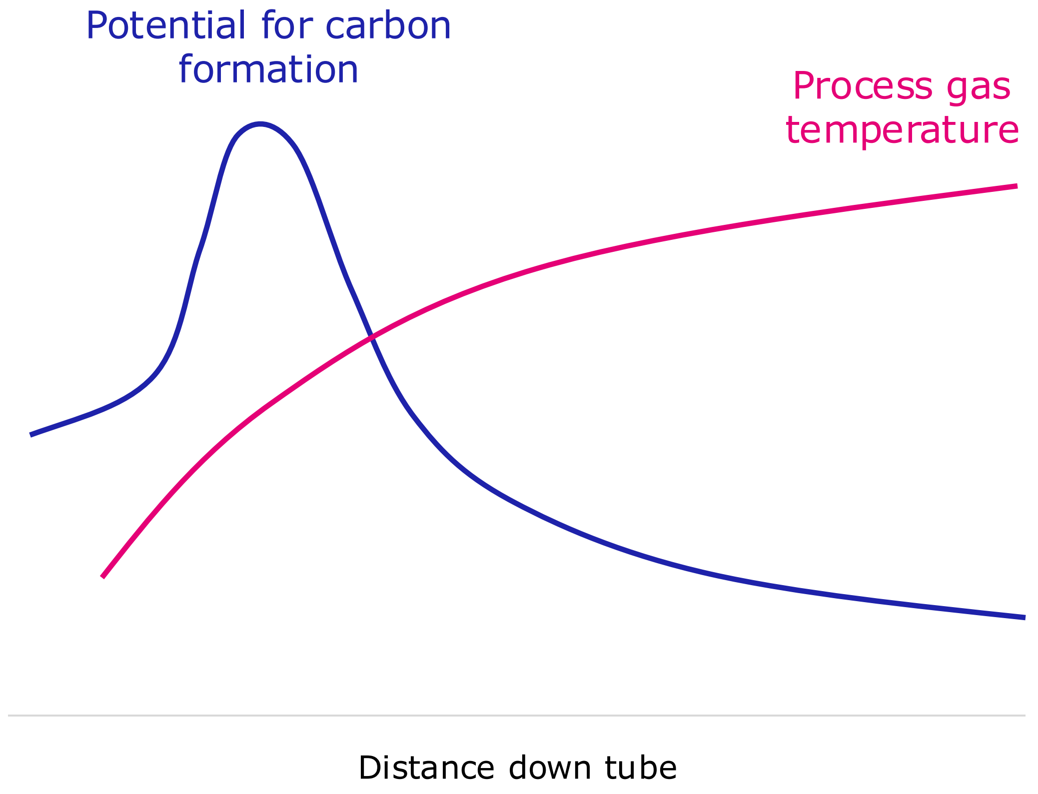


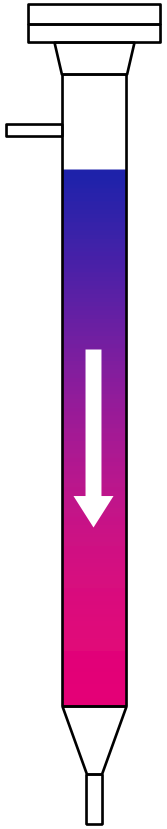


Concerns for tube life



Meeting the different needs across the length of the reformer tube

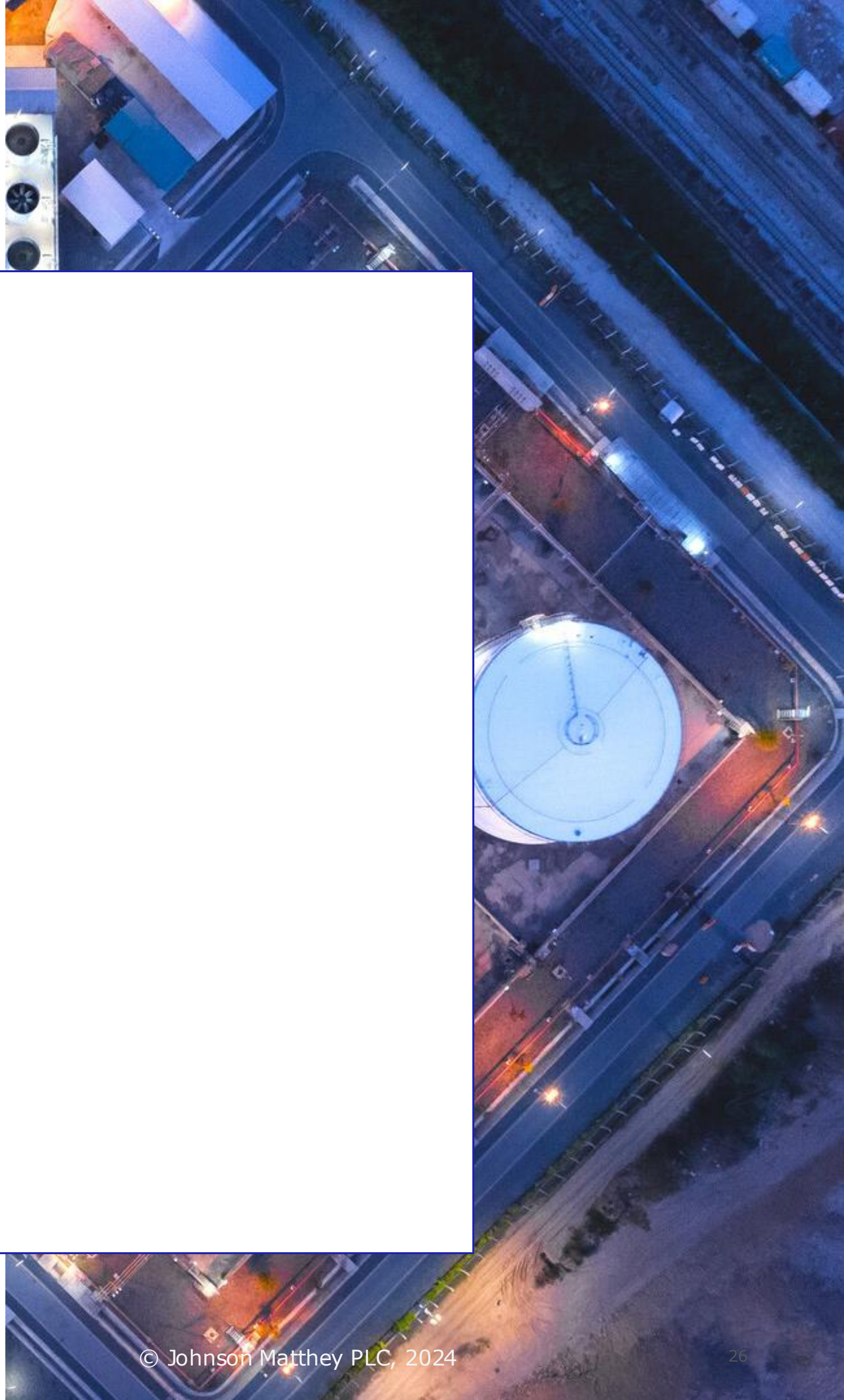




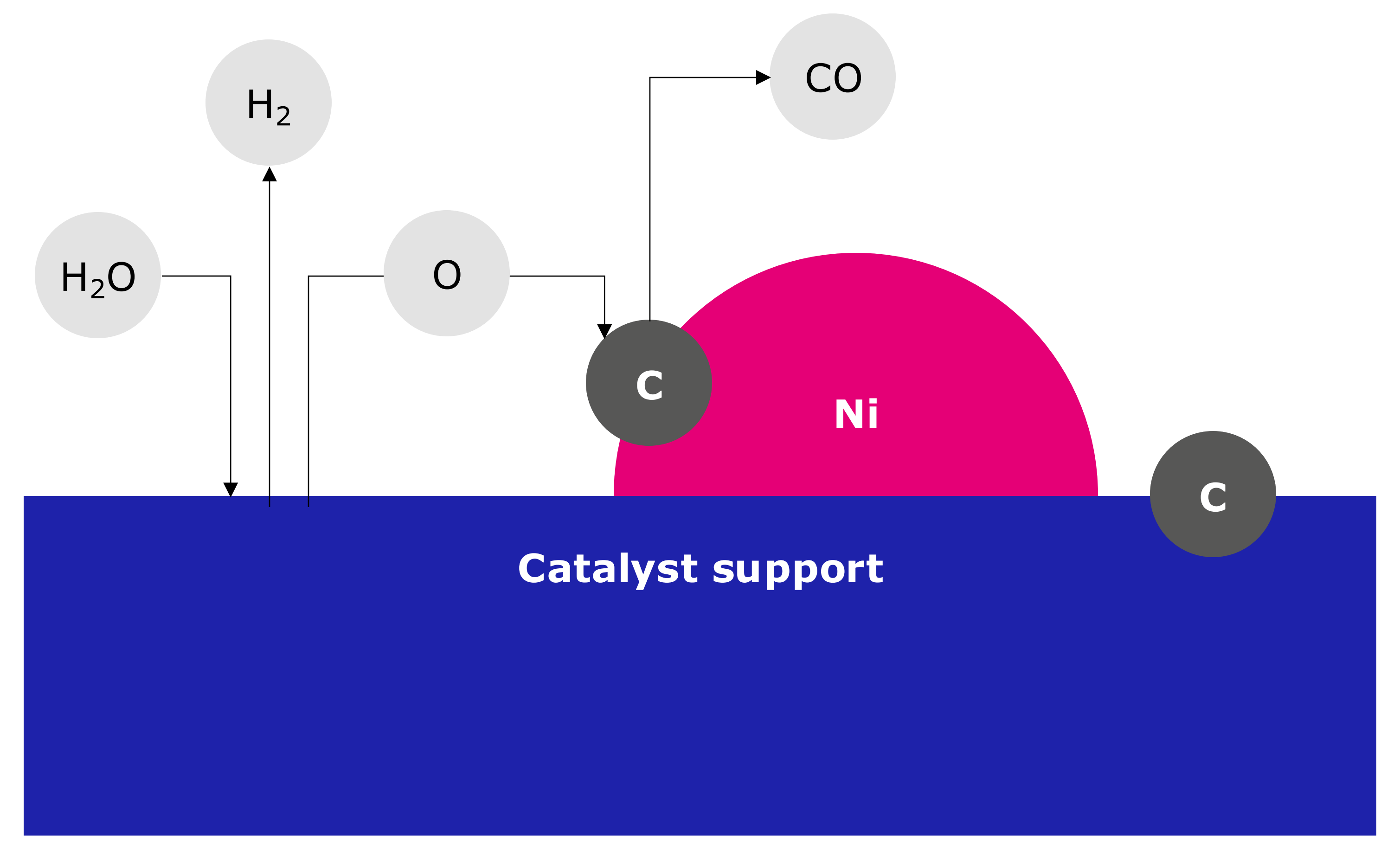
Alkalised catalyst are used for preventing carbon formation near the inlet of the tube, but cannot be used at higher temperatures due to concerns of accelerated potash migration

Further down the reformer tube, temperatures increase but there is less potential for carbon formation due to lower concentrations of heavier hydrocarbons and higher concentrations of hydrogen. Thus, **non-alkalised catalyst** can be used in this section of the tube

Hot bands due to carbon formation



Recovering from an incident



After a carbon deposition incident, conditions will get worse without action

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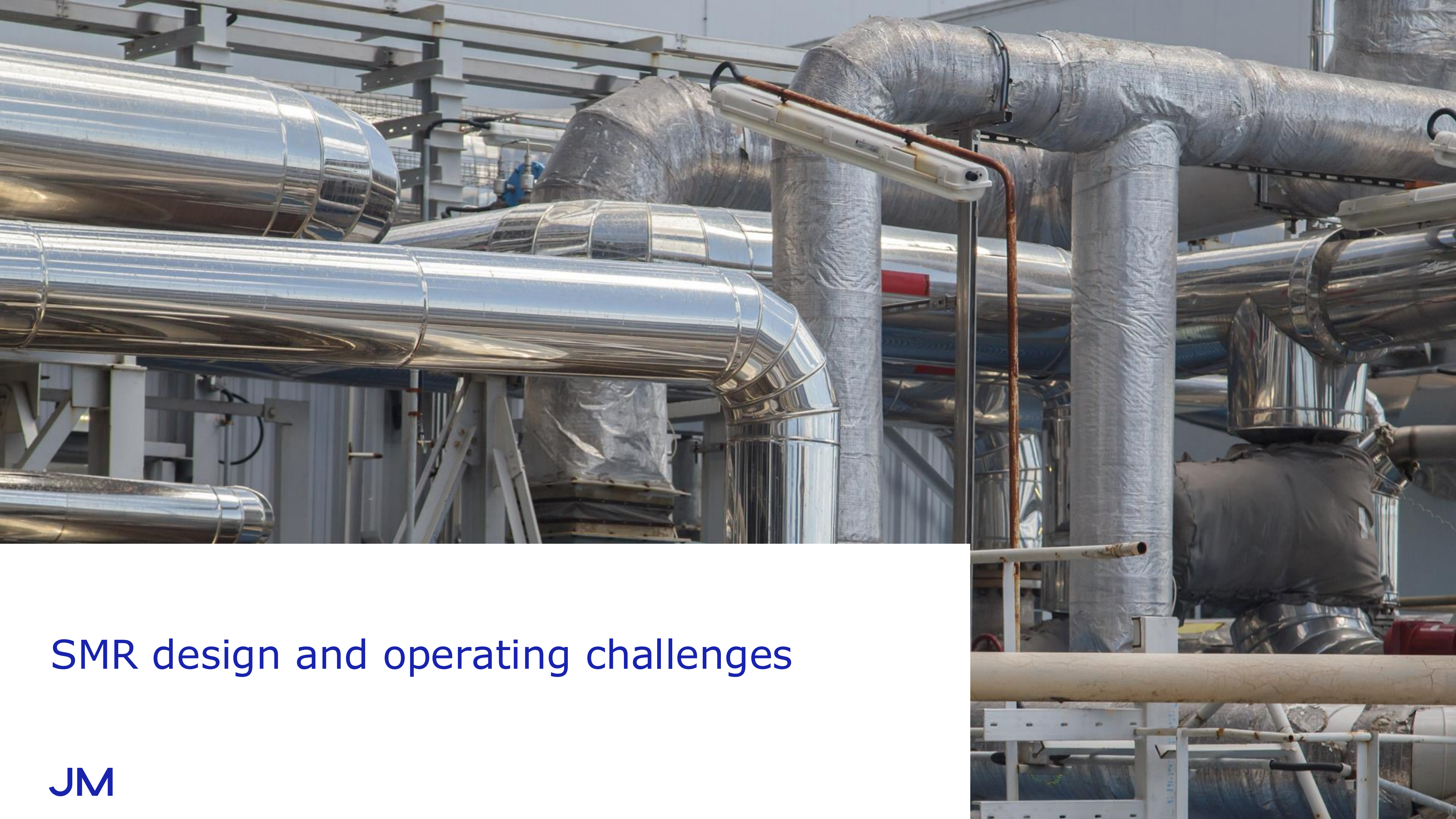
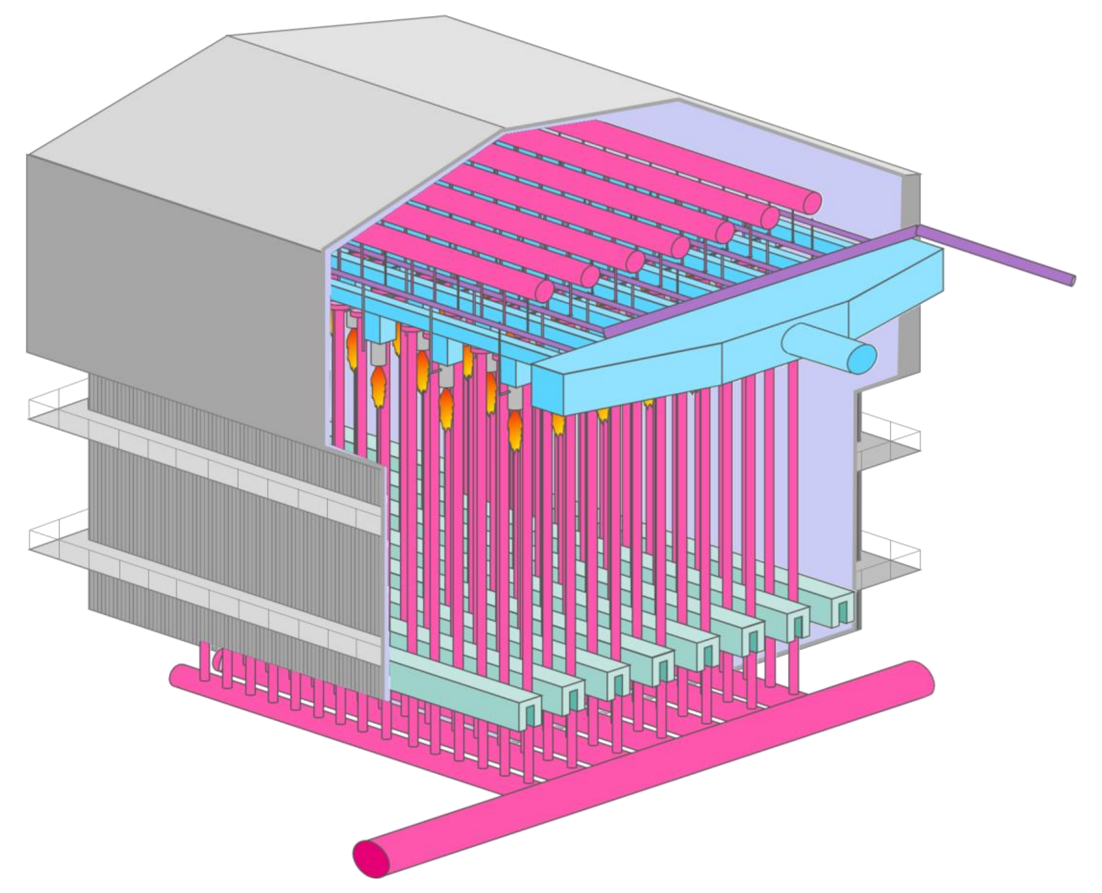
In some cases, it is possible to remove the carbon through gasification with steam

- Isolate hydrocarbon feed
- High rate of steam flow#
- High temperature
- Nitrogen to facilitate monitoring



SMR design and operating challenges

Challenges of uniformity in design



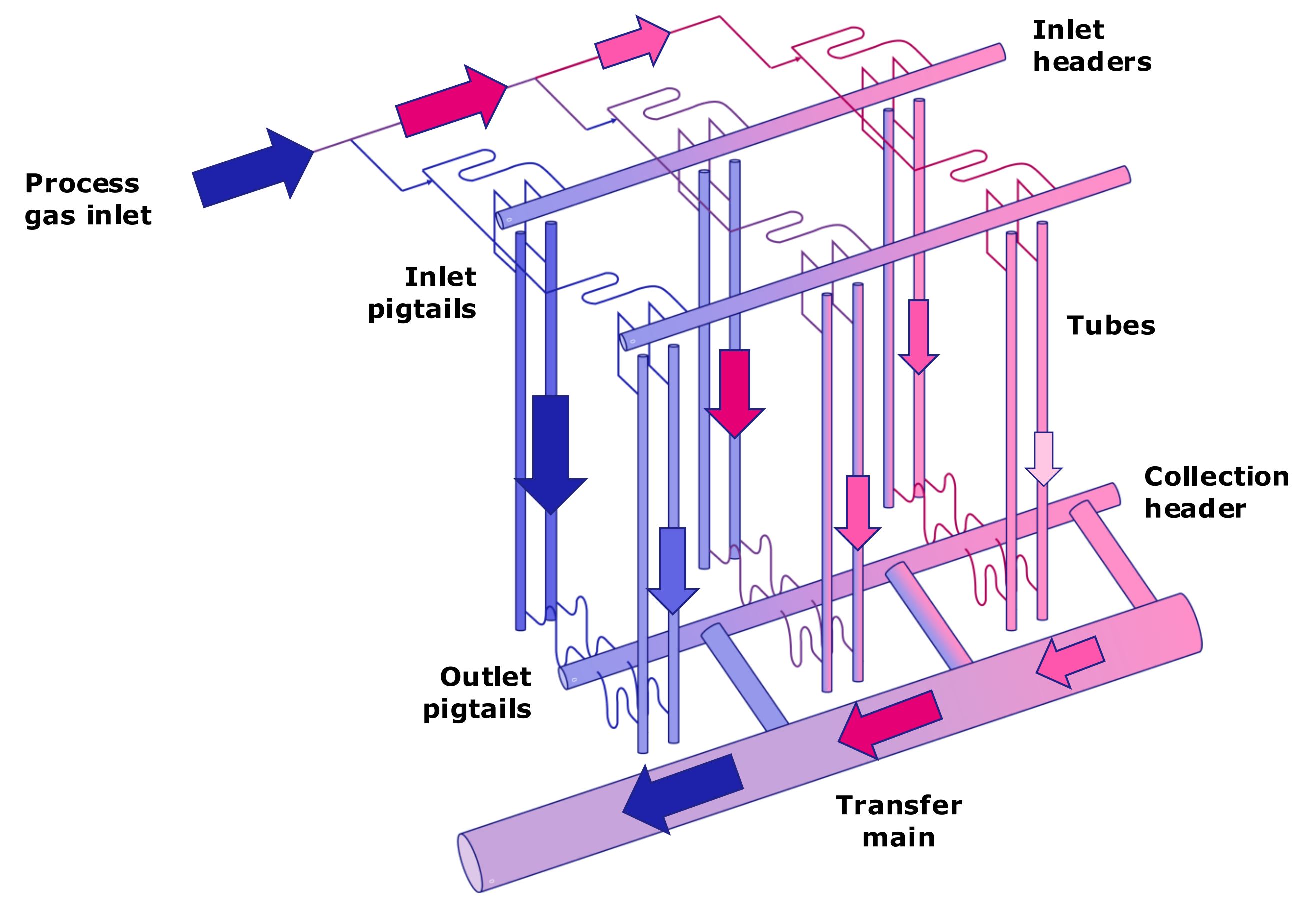
Process gas distribution

- Inlet manifold
- Pigtails
- Tube size
- Catalyst loading
- Outlet manifold
- Transfer main

Heat distribution

- Primary fuel system
- Makeup fuel system
- Combustion air
- Burners
- Flue gas
- ID/FD fans
- Tunnels
- Convection duct

Process gas maldistribution



Causes of maldistribution

- Design and construction leading to preferential gas flow
- Operation at low rates
- Low pressure drop across system

This leads to variations in conditions:

- Between tubes
- Between row in top fired reformers, or between cells in side fired reformers

Balanced firing

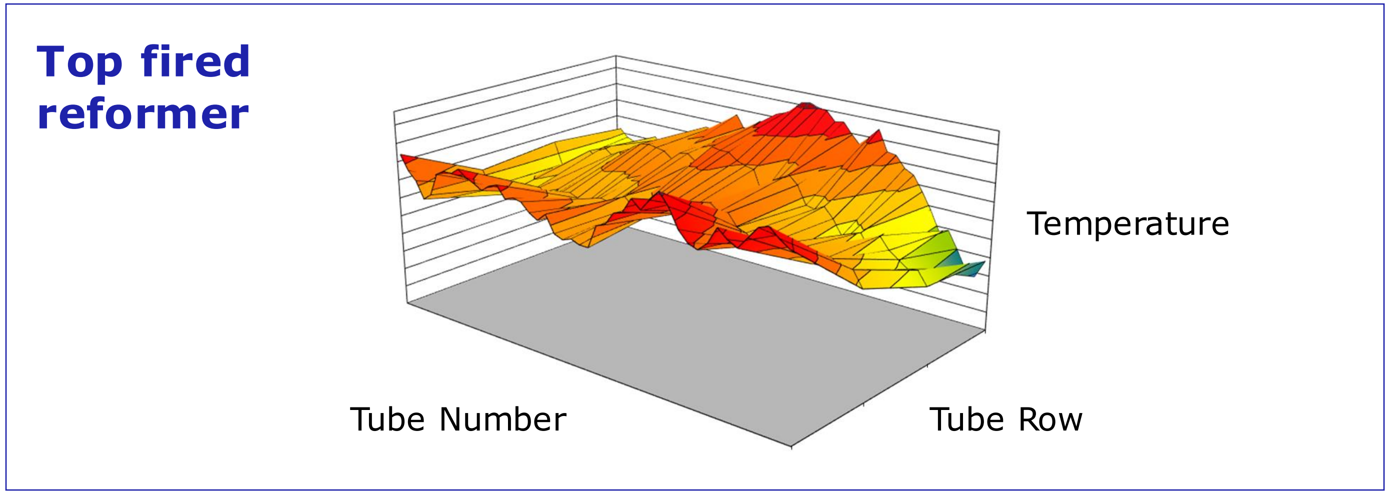
Potential for fuel, combustion air and flue gas maldistribution due to low pressures

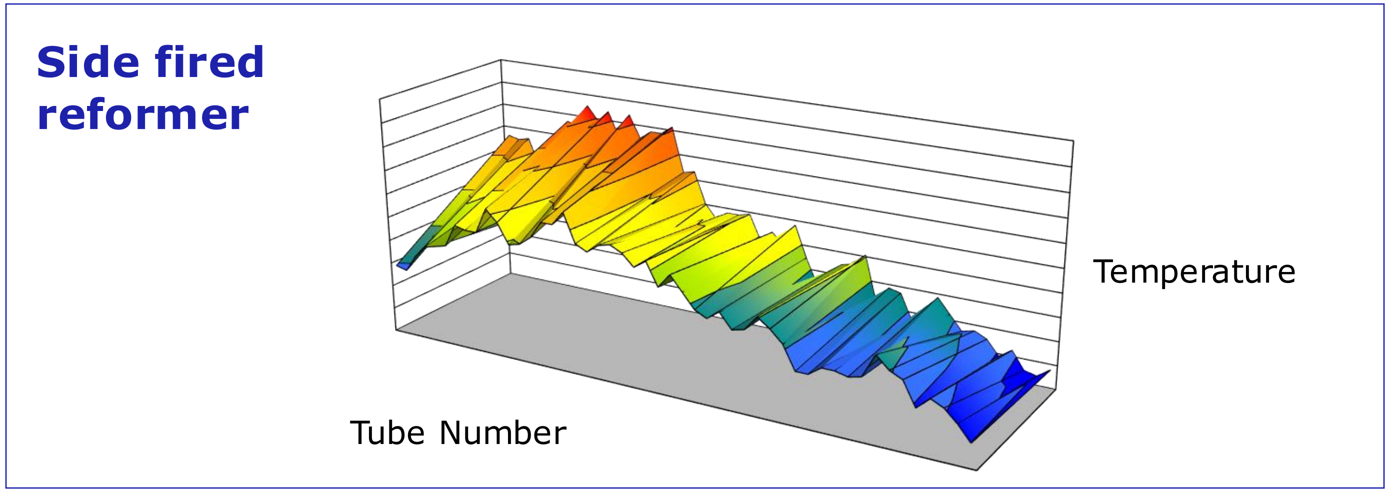
Fuel line pressures

Air damper setting

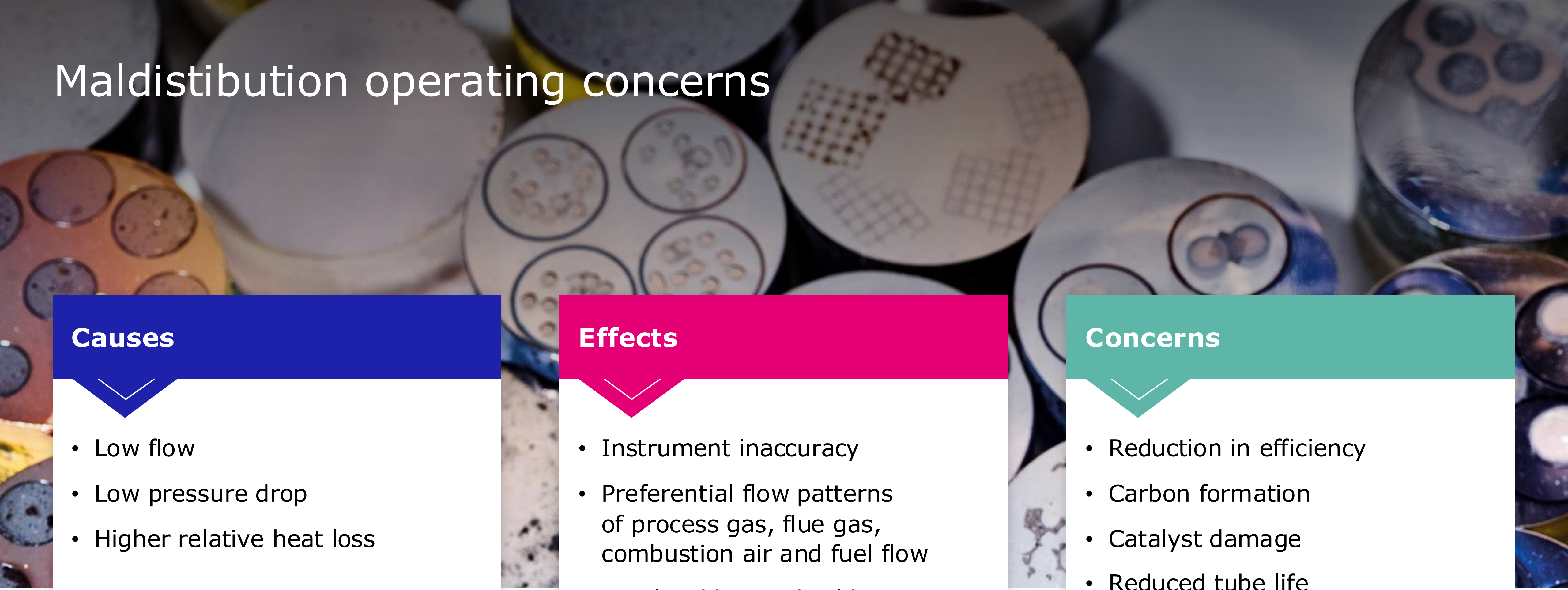
Flue gas tunnel condition

Burner adjustments
- Minimum turndown
- Isolation
- Flame detectors





Maldistibution operating concerns



Causes

- Low flow
- Low pressure drop
- Higher relative heat loss

Effects

- Instrument inaccuracy
- Preferential flow patterns of process gas, flue gas, combustion air and fuel flow
- Localised hot and cold zones
- Flame impingement
- High TWTs

Concerns

- Reduction in efficiency
- Carbon formation
- Catalyst damage
- Reduced tube life
- Coil failures

Loss of efficiency due to maldistribution

	Well Balanced	Poorly Balanced		
		Cell 1	Cell 2	Mixed Gas
Fuel Flow, %	100	55	45	**100**
Exit T, °F (°C)	1544 (840)	1596 (869)	1490 (810)	**1544 (840)**
Exit CH_4 Slip, mol% dry	2.3	1.5	3.7	**2.6**
ATE, °F (°C)	24 (13)	20 (11)	20 (11)	**29 (16)**

Operating good practice

Identifying an issue early, provides opportunities to be able to understand the root cause and correct the issue. The longer you operate with a problem, the more expensive resolving the issue may be.

• Feed flowrate	Daily
• Feed composition	Weekly
• Operating S:C ratio	Daily
• Reformer exit temperature	Daily
• Methane slip	Weekly
• Pressure drop	Daily
• Tube wall temperature (TWT)	Daily
• Hottest TWT	
• Spread in TWT	
• Visual assessment of tubes	Daily

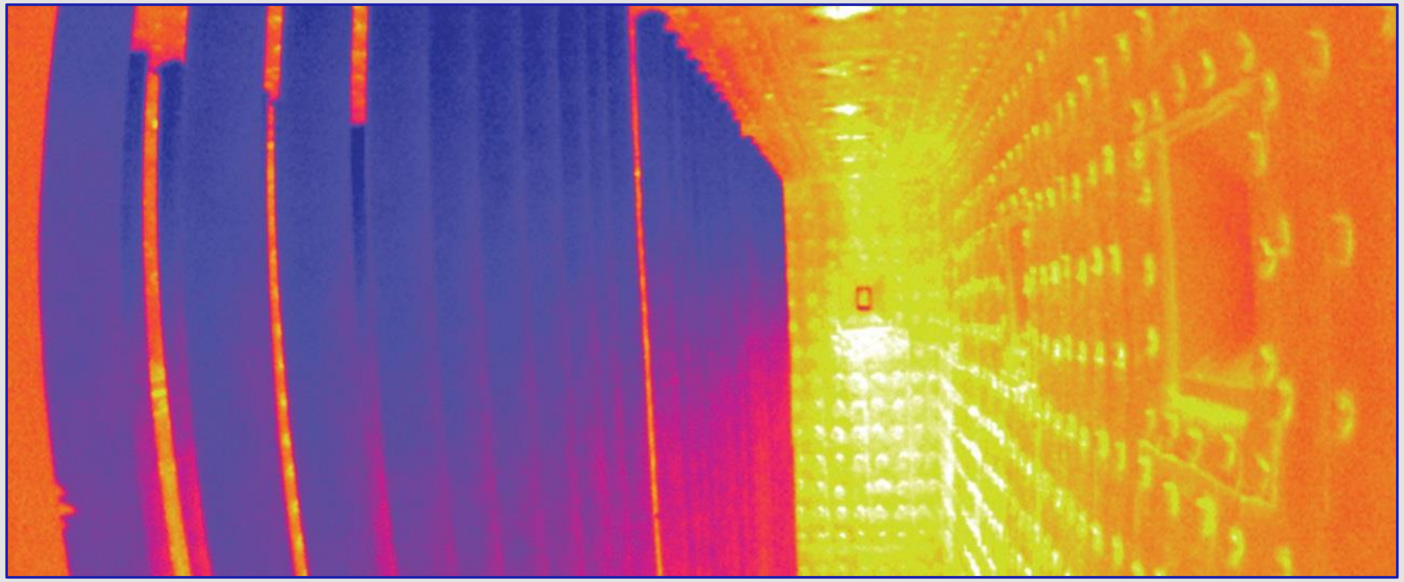
Monitoring high TWTs and signs of carbon laydown

Potential effects of low rates:

- Maldistribution of process gas or flue gas causing localized overheating
- Maldistribution of flue gas causing flame impingement
- Error in steam/feed flow meter and high heat loss

Measure and record TWTs regularly:

- High TWT give concern to tube life and premature failure
- Carbon formation will progressively get worse



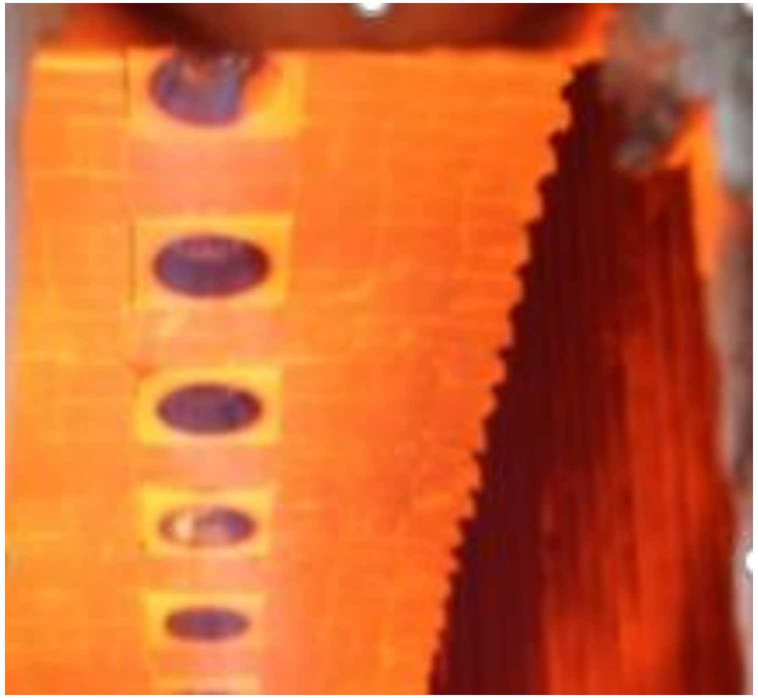
Visual inspection of the reformer

Tube appearance

Refractory condition

External hot-spots

Flame characteristics



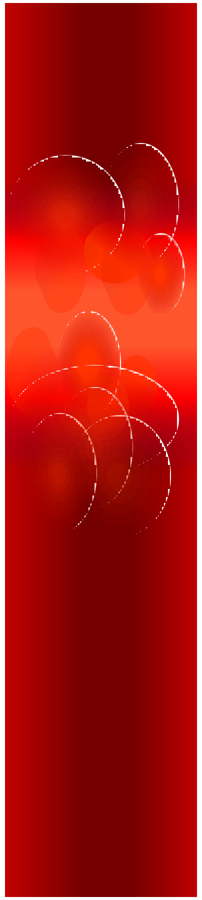
Tube appearance

The visual appearance of the tubes can be an early indication of problems and can be used to determine the root cause before the performance of the unit is significantly impacted.

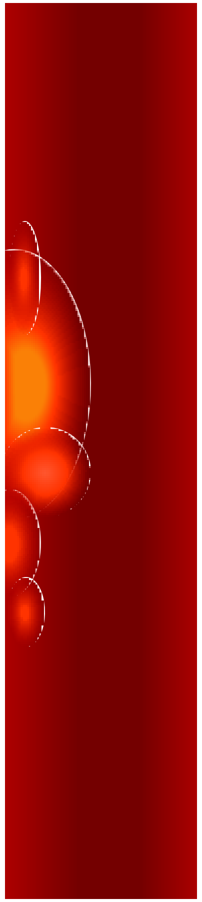
Hot bands – normally caused by catalyst poisoning or carbon formation.

Hot spots – suggest a localised mechanism, such as flame impingement or catalyst bridging.

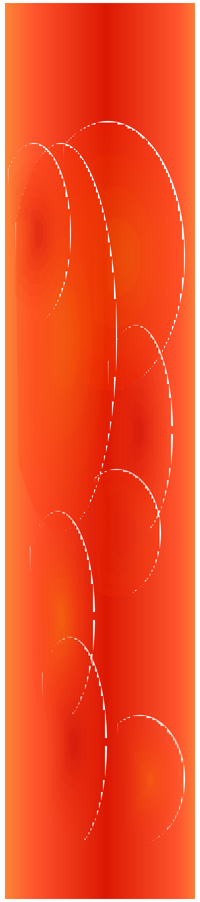
Hot tubes – an indication of a restriction of gas flow through the tube.



Hot bands



Hot spots



Hot tubes

Importance of TWT measurement

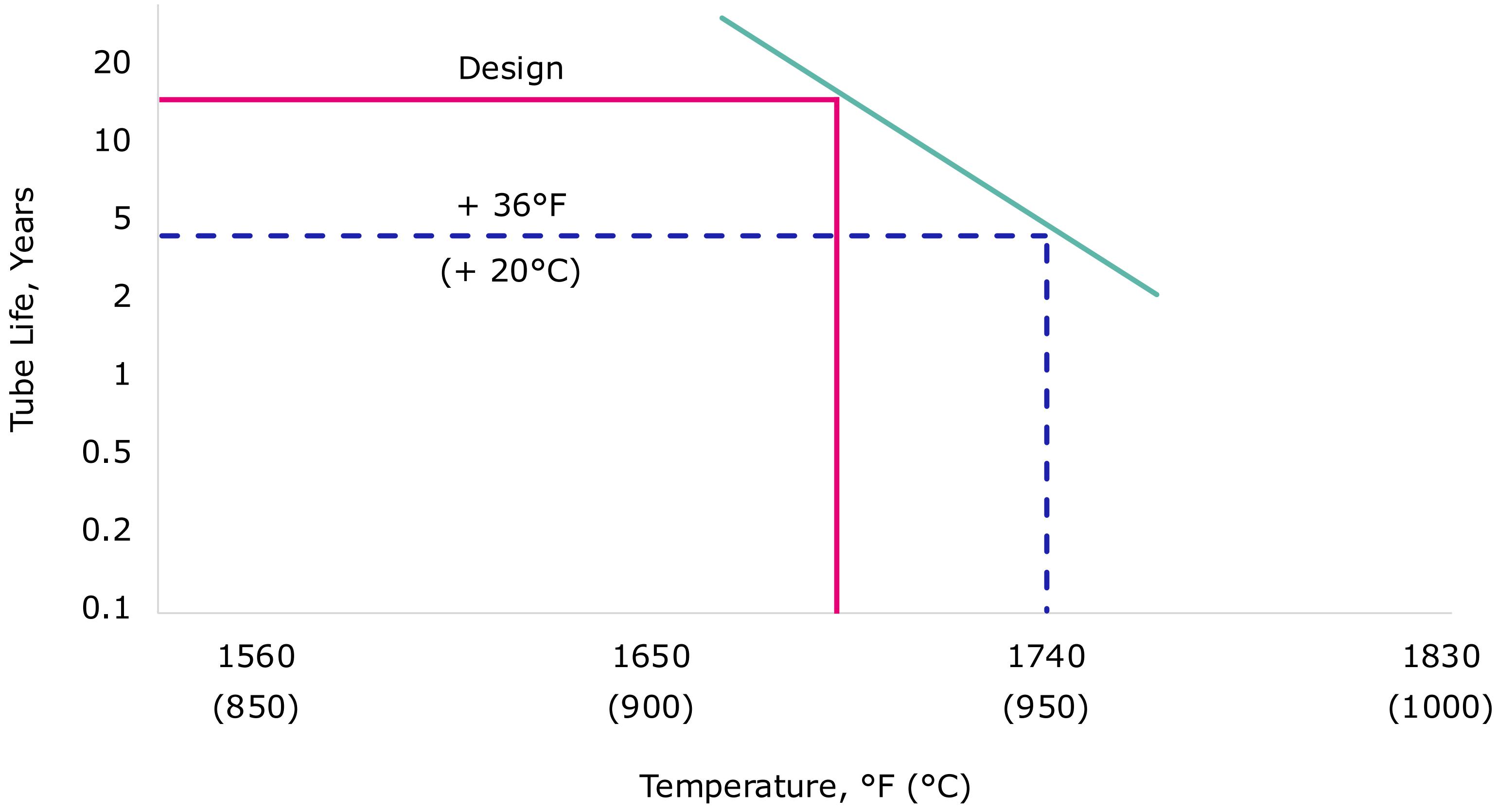
Tube repair/replacement is expensive – want to maximize life

Tube life is a function of time at temperature (for a given pressure)

Accurate measurement is vital

If measured **high**, might artificially **limit plant rate**

If measured **low**, tube life **shorter than expected**



*Note design temperature is at design pressure (normal operation is generally below design pressure)

Unmatched modelling capability

Johnson Matthey has one of the most advanced steam-reforming simulation tools

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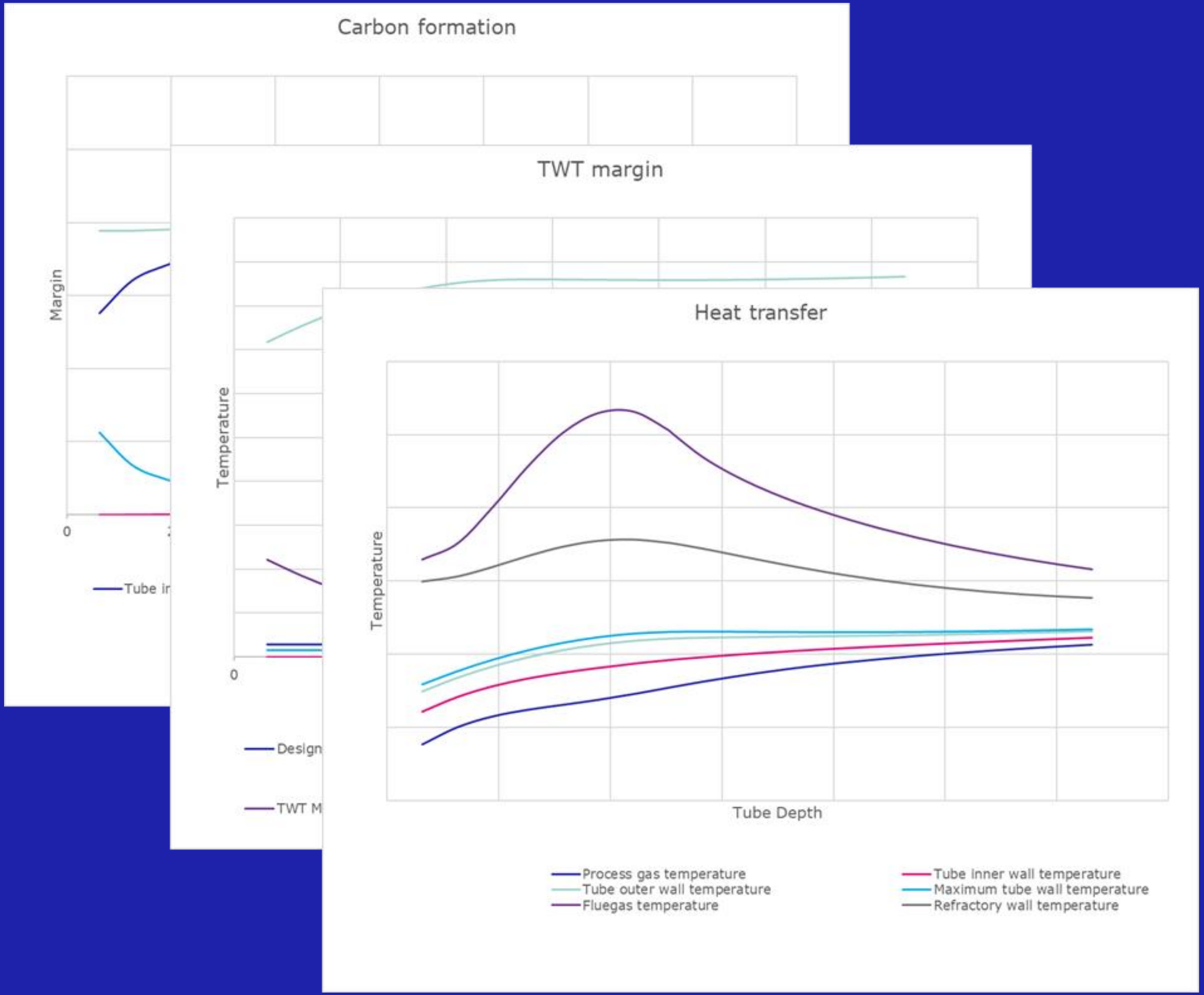
Includes a proprietary carbon formation model, which combines extensive analytical test results with years of plant operating data



Optimised catalyst solutions to achieve production targets

Overcoming plant bottlenecks

1. Improving efficiency
2. Increasing throughput
3. Reducing TWT and protecting tube lives
4. Reducing flue gas temperatures
5. Avoiding carbon formation
6. Simplifying reduction
7. Heavy hydrocarbon operation

Hydrogen and syngas plants come in many different configurations. The operation of each plant is unique and impacted by factors such as the gas feed, the plant rate, steam to carbon ratio and operating pressure and temperature.

Johnson Matthey has the strongest portfolio of alkalised and non-alkalised steam reforming catalysts that enable a wide variety of feeds and operating conditions.

A portfolio of over

30 **different steam reforming catalysts**

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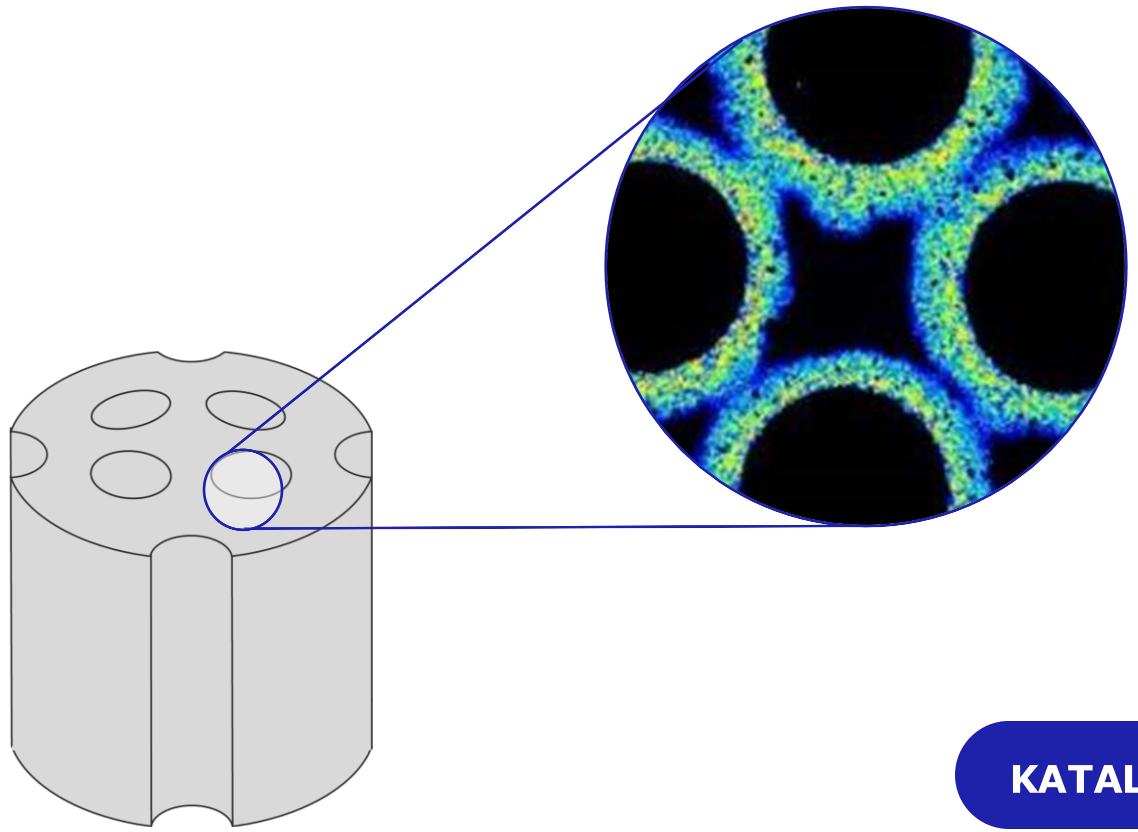
Continued innovation to maximise activity



KATALCO 57-6Q pellet

An innovation in steam reforming catalyst

Advanced manufacturing process

Optimizing active metal availability

Patented technology focused on putting Ni where it can achieve the highest rate of reaction

Protecting against volatility in metal costs

Summary

- The steam-methane reformer is one of the most important units on a hydrogen, ammonia and methanol plant.
- It is a complex unit due to the need for providing heat for the endothermic reaction, and for ensuring even heat distribution.
- Good operation of the upstream purification system is required to prevent poisoning of the catalyst, and careful management of the operating temperature, steam:carbon ratio and catalyst type is required to prevent carbon formation.
- Issues such as flame impingent and carbon formation can significantly reduce the life of the reformer tubes, and potentially lead to a tube rupture.
- Regular monitoring of the reformer is important to identify any issues early.

JM

Johnson Matthey
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