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Johnson Matthey
Inspiring science, enhancing life

Americas hydrogen and syngas technical training seminar

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High temperature shift

Agenda

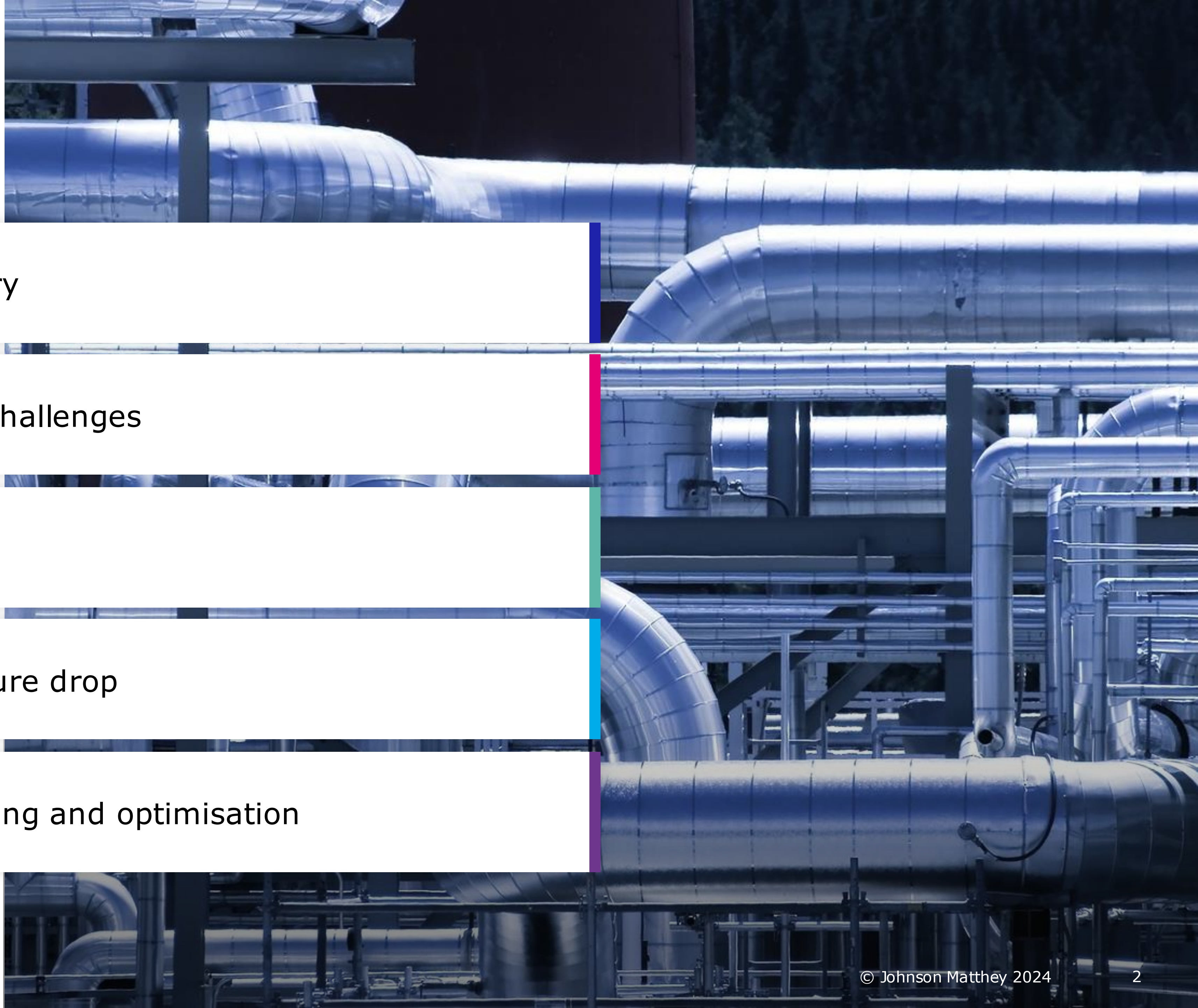
01 HTS, flowsheet & chemistry

02 HTS common issues and challenges

03 HTS catalyst solutions

04 HTS options for low pressure drop

05 HTS performance monitoring and optimisation



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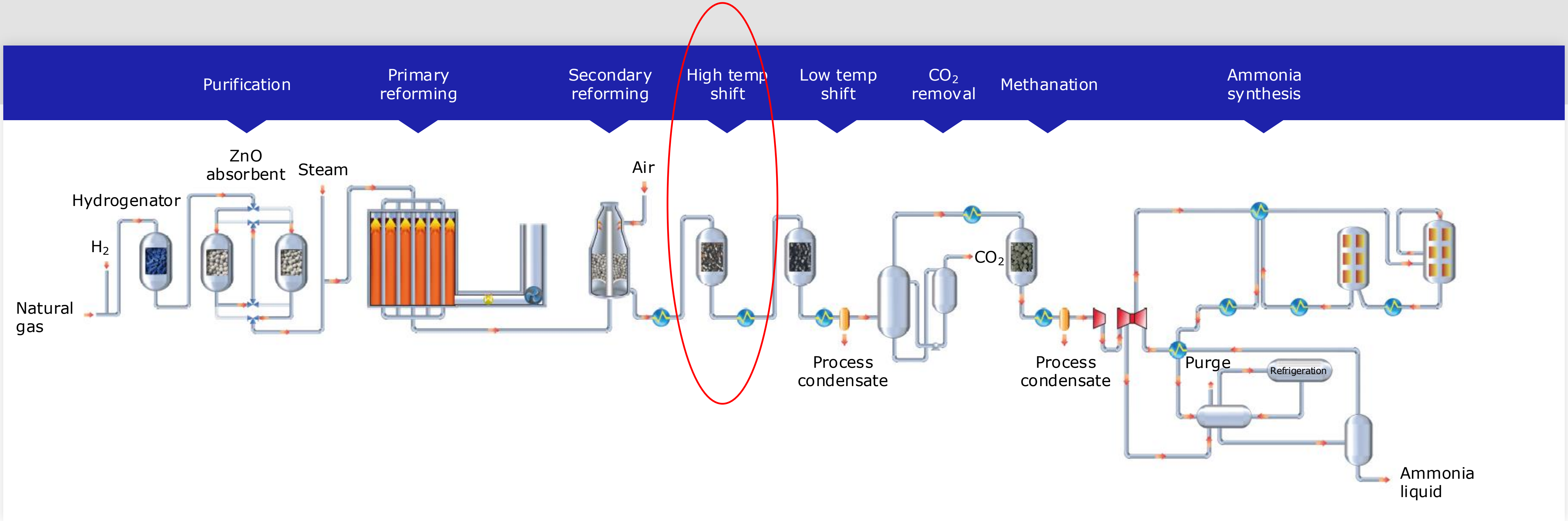
WGS is an important section of hydrogen and ammonia plants for maximising efficiency



The WGS produces approximately 10-20% of the hydrogen

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Water gas shift basics

$CO + H_2O \Leftrightarrow CO_2 + H_2$ + Heat ΔH = -41.1 kJ/mol

Reversible reaction

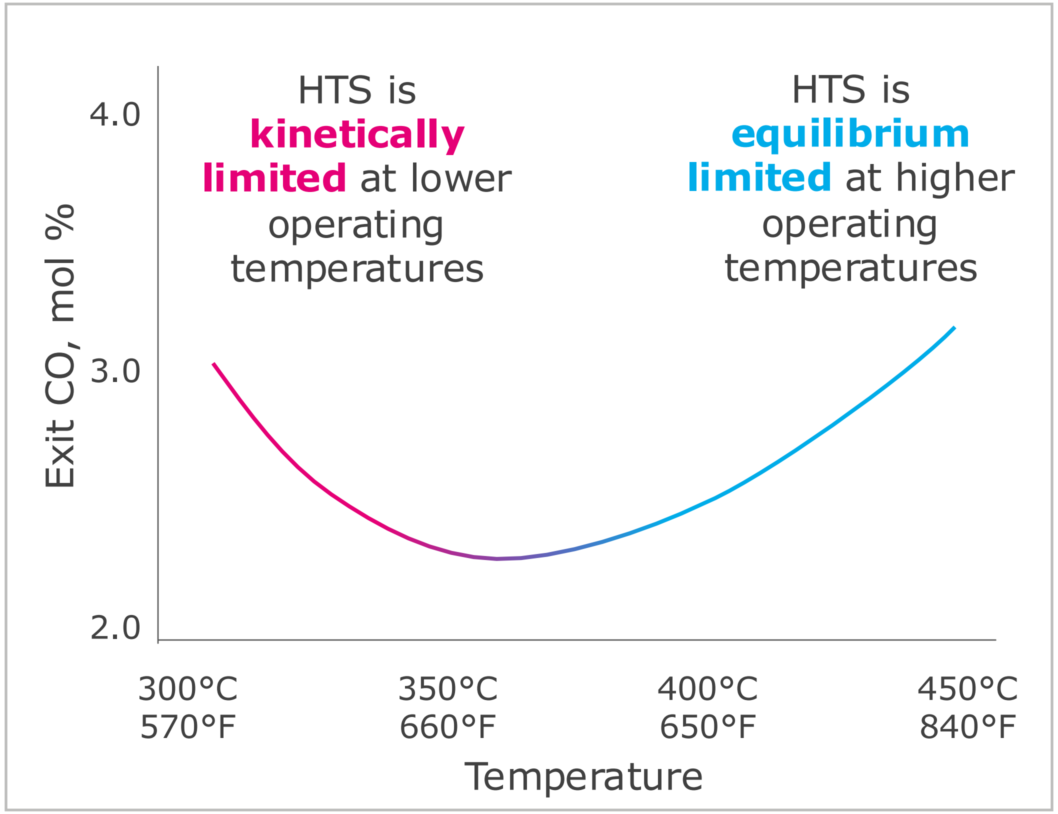
Exothermic (forward reaction)

- Lower temperature
- Increased CO converted
- Increased hydrogen produced

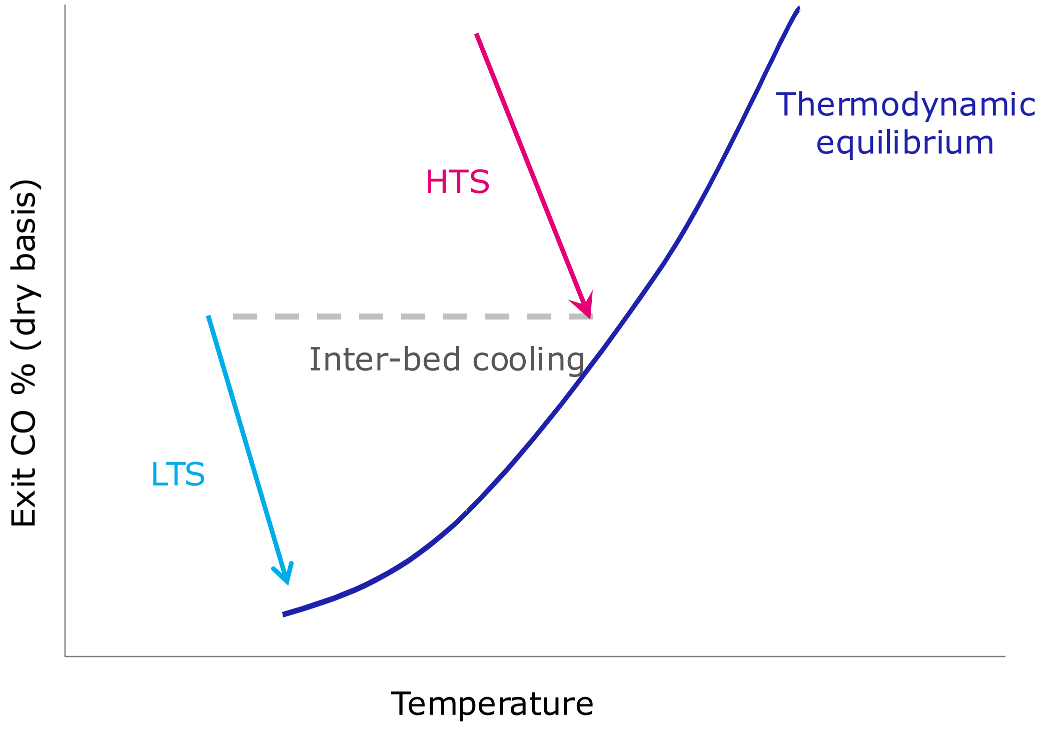
Equimolar

- Pressure - no effect on equilibrium
- Excess steam – more hydrogen produced

Low temperatures allow a more favourable equilibrium position, but kinetics help drive the rate of reaction at lower temperatures



WGS equilibrium



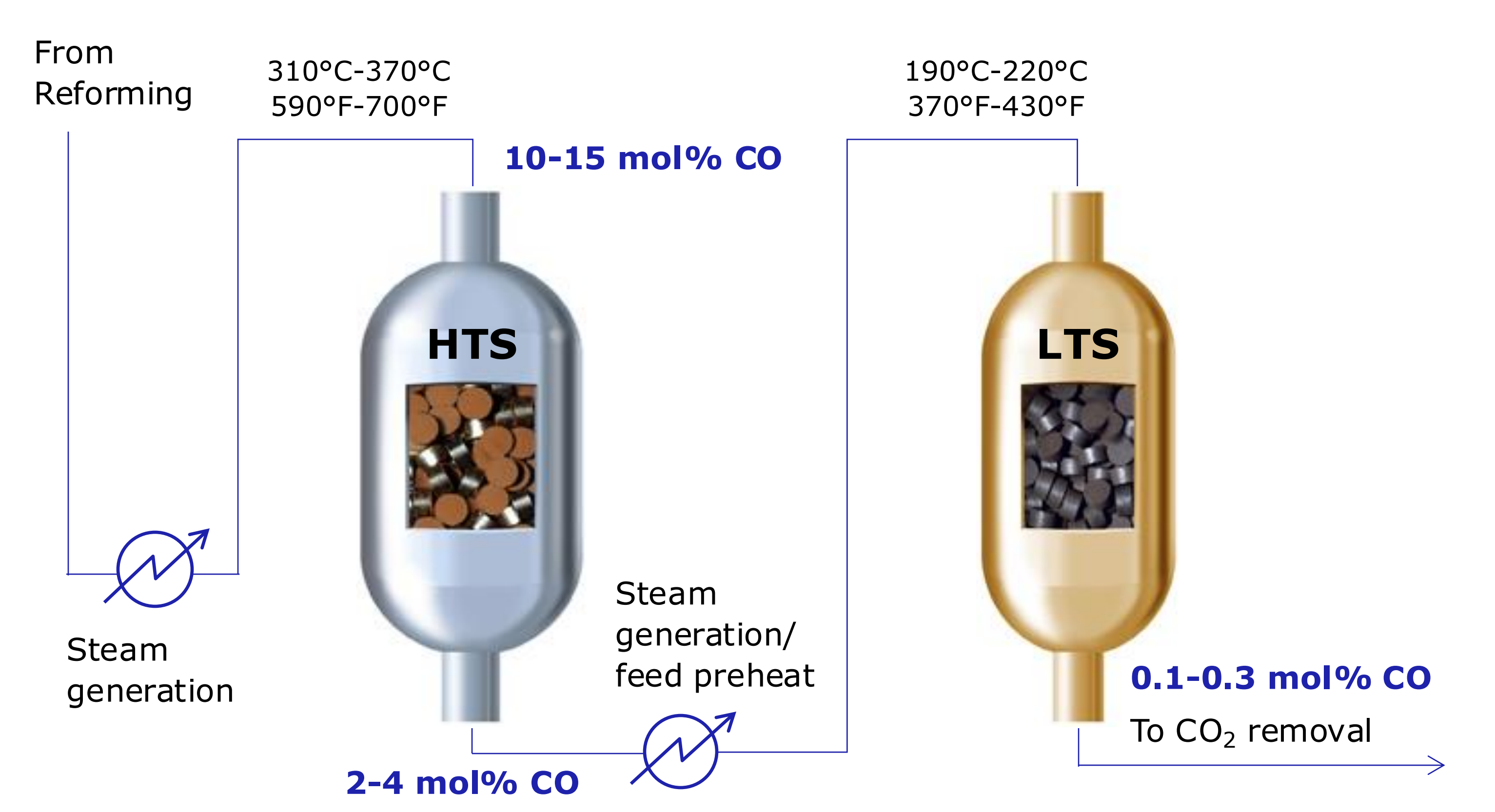
The WGS reaction is exothermic.

As the reaction approaches equilibrium, the rate of reaction slows.

Higher conversion can be achieved by cooling the process gas, and reacting further to a lower equilibrium of CO.

Hydrogen and syngas flowsheets have different WGS unit configurations depending on efficiency and downstream process requirements.

HTS and LTS



Reduce CO levels and increase H_2 make
$CO + H_2O \leftrightarrow CO_2 + H_2$ (exothermic)

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HTS

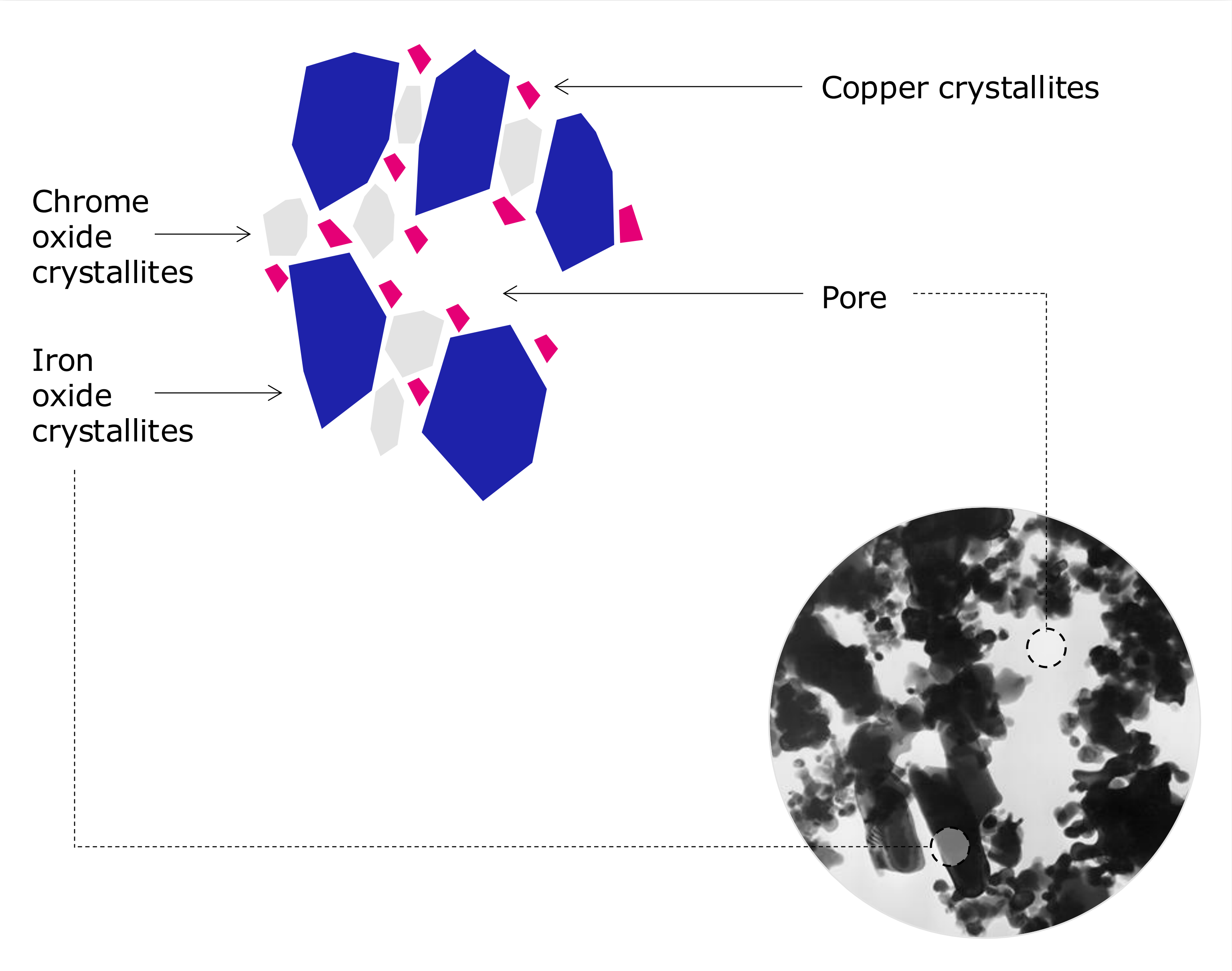
Catalyst features

Modern HTS catalysts require

High and stable activity

High strength

HTS



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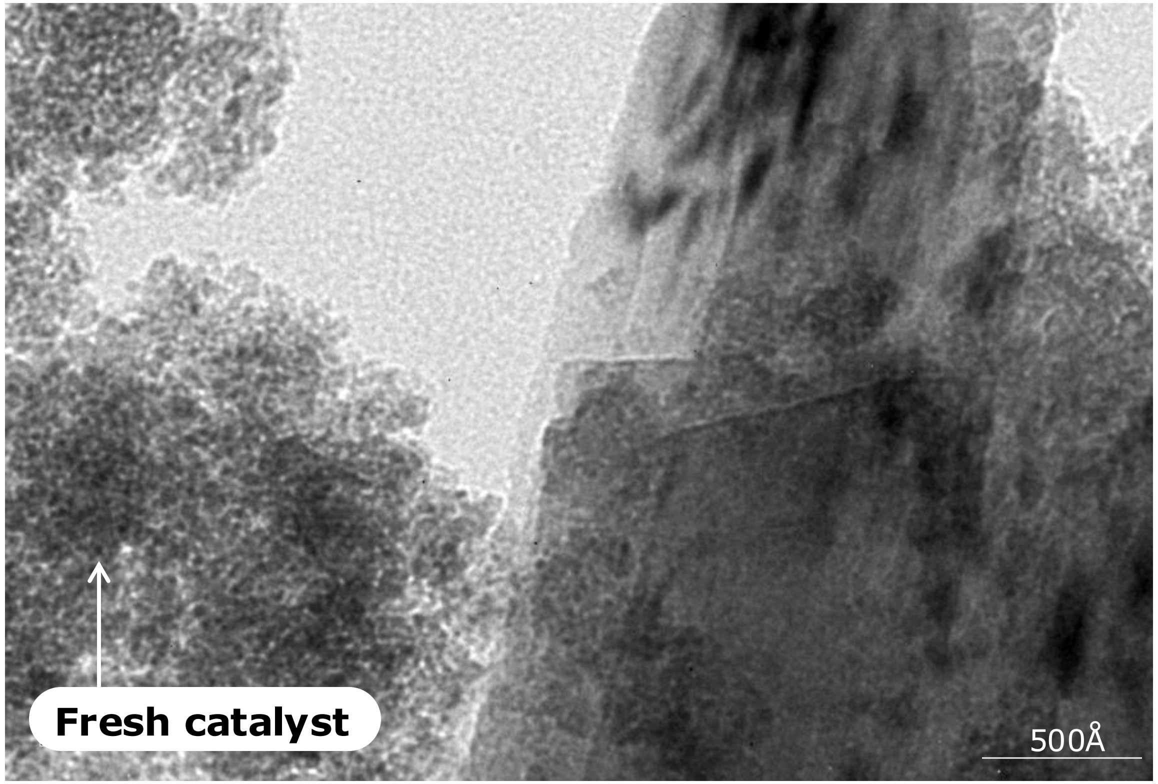
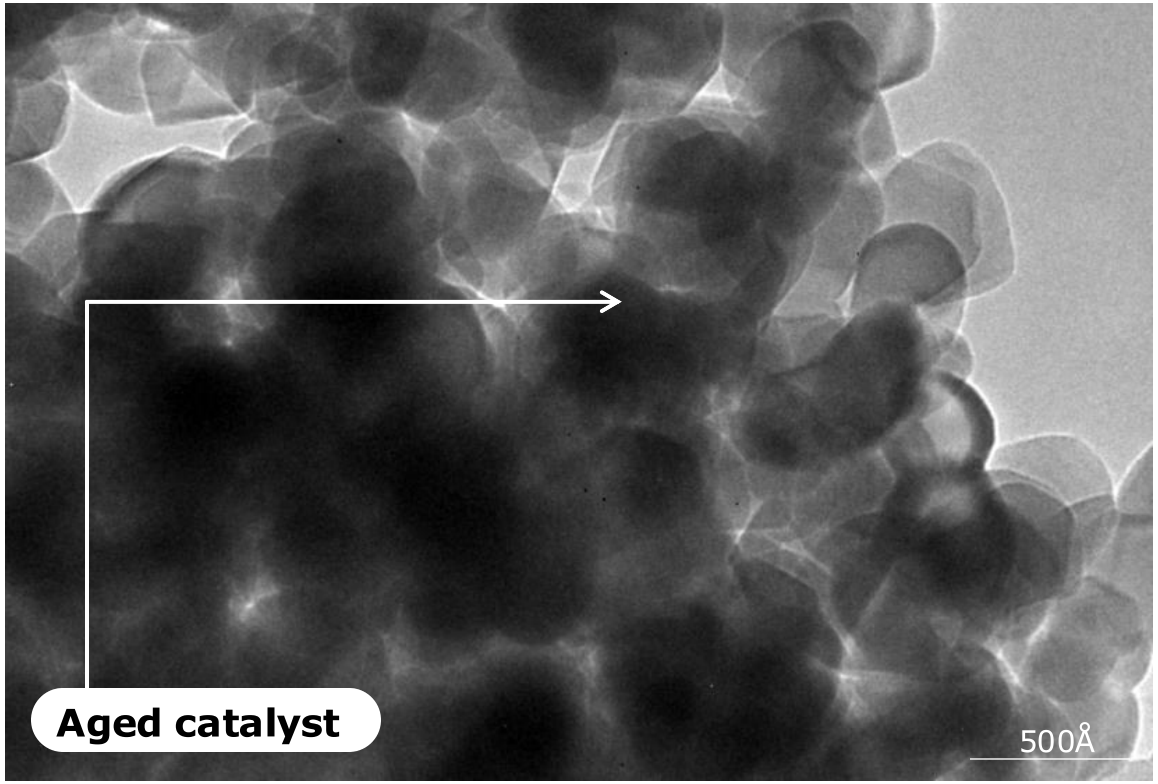
HTS deactivation mechanism

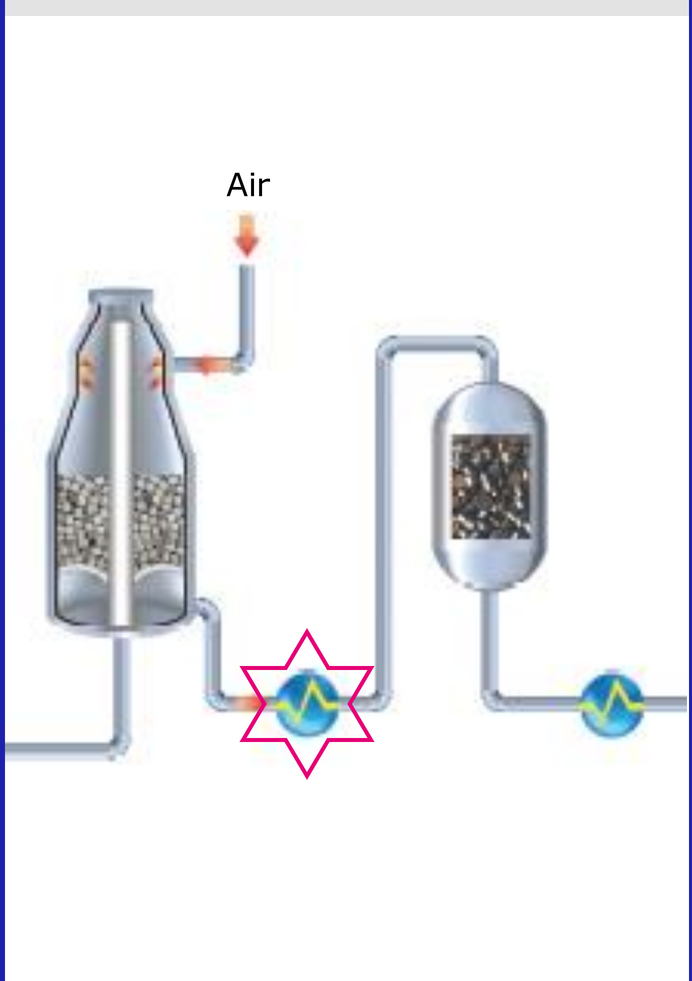
Catalyst microstructure





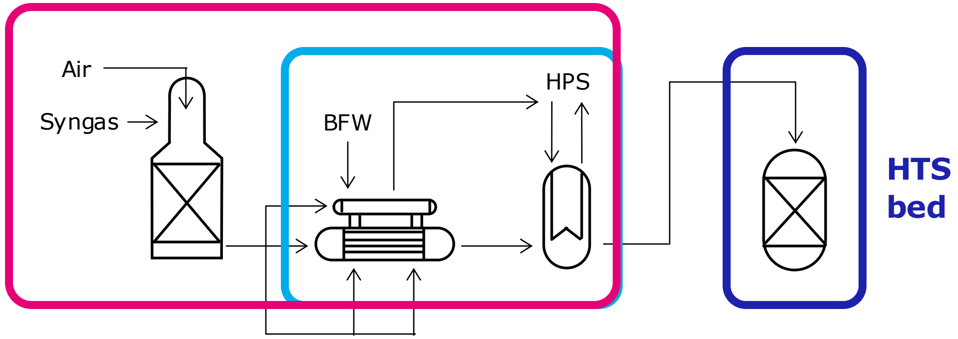
Same magnification

HTS challenging duty



Upstream HP boilers and superheaters

Upstream refractory systems



Issues

Wetting

Leaks

Fouling

Refractory/metal dusting debris

Overreduction

Weakened pellet

HTS wetting

Failure of a boiler tube adds water into HTS	• Varying degrees from small leak over time to larger water leak
May force immediate plant shutdown	• Process gas cooling may become inadequate • Complete flooding may occur, blocking gas flow
Catalyst can be severely impacted	• Initial shock from mass flow and abrupt temperature change creates large stress on pellet structure
Dry out of catalyst required	• Catalyst pores must be accessible to ensure all water is heated slowly and removed
Catalyst can be severely impacted by initial carryover and drying	• Pellet integrity can be compromised impacting pressure drop and activity

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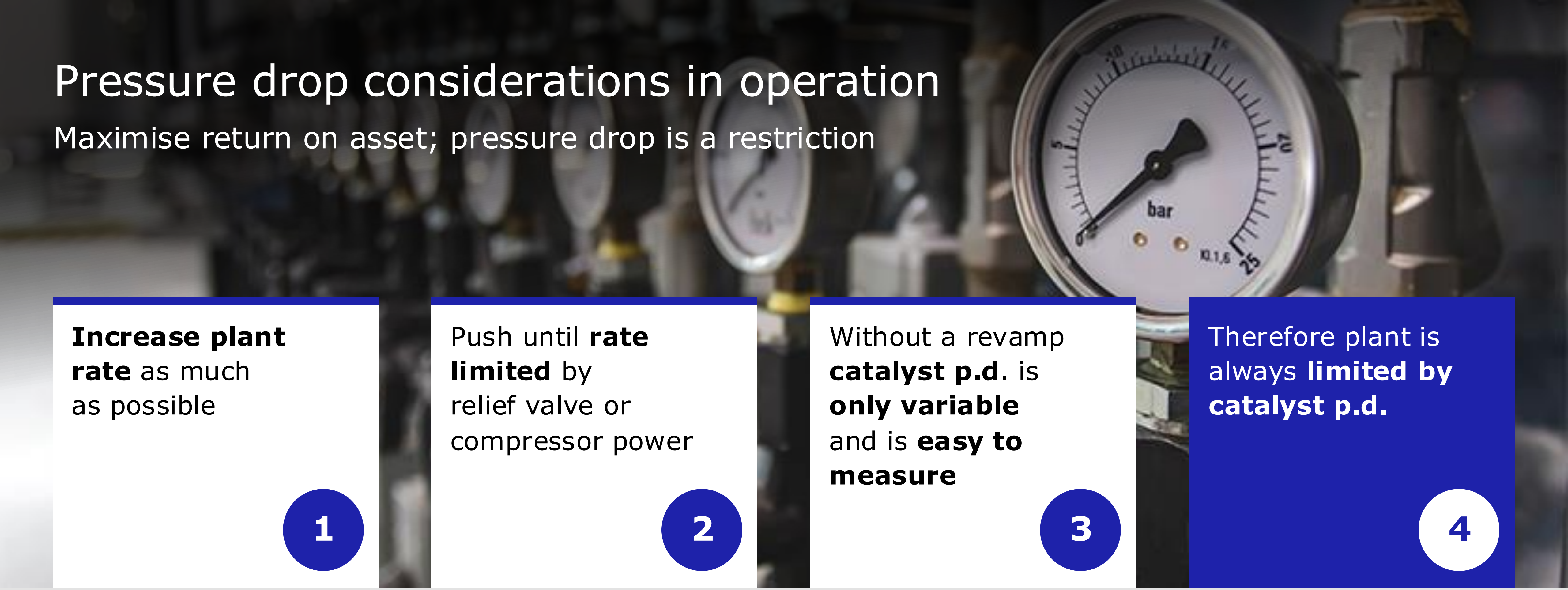
HTS over-reduction

Can occur at low steam to gas ratios	Typically S:DG <0.5 inlet HTS (~< 3.0 S:C ratio at reformer) Higher pressure plants more susceptible
Catalyst becomes over-reduced	Pellets weakened by reduction reactions Potential carbon laydown Catalyst break up can occur
Structural damage is irreversible	Step Change in dP
Side Reactions are enhanced	FT & methanation lead to hydrocarbons



Pressure drop considerations in operation

Maximise return on asset; pressure drop is a restriction

Increase plant rate as much as possible

1

Push until **rate limited** by relief valve or compressor power

2

Without a revamp **catalyst p.d**. is **only variable** and is **easy to measure**

3

Therefore plant is always **limited by catalyst p.d.**

4

Catalyst p.d. characteristics

Start as low as possible, increase as little as possible (stay low)

Start of run p.d.

Catalyst shape

Strength at loading

Loading care/control

Start-up/reduction

Support media loading

- e.g. **STREAMLINE™**

Rate p.d. change

Strength in-service

Breakage characteristics

Operational stability

Transients/fouling

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Established HTS catalyst offer

Established

Johnson Matthey's **KATALCO™** 71-series catalysts were introduced in 1998 and we currently have over 500 active references.

The **F shape** was commercialised in 2016 and it still remains the only advanced shaped HTS catalyst available on the market today.

Performance and reliabiliy

KATALCO 71-5F
Standard offer for low pressure drop, high performance and long lives

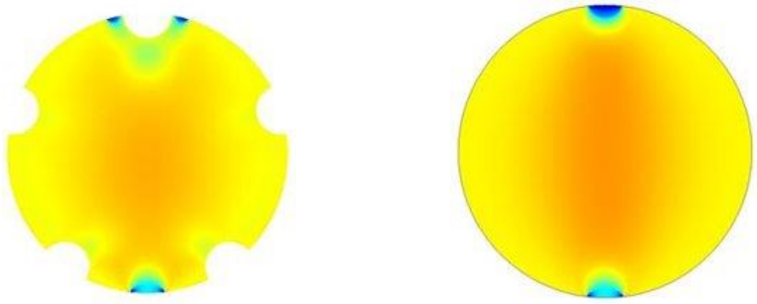
KATALCO 71-6F
Higher strength and activity. More resistant to wetting and over-reduction.

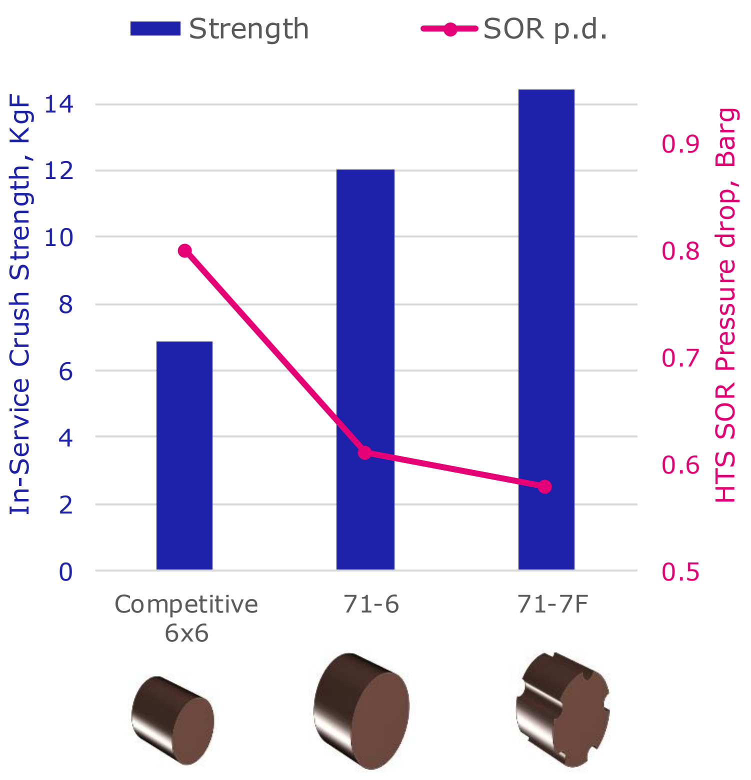
KATALCO 71-7F
Our latest HTS catalyst, Strongest HTS catalyst available and even better resistance to over-reduction.

Leading HTS catalyst products

KATALCO 71-7F

- Manufacturing process delivers higher strength
- Better survival in over-reduction conditions
- F-Shape lowers pressure drop and is 12% lower than the older generation cylindrical pellets
- The higher strength and careful design of shape enables a low pressure drop to be maintained through the life-time of the catalyst





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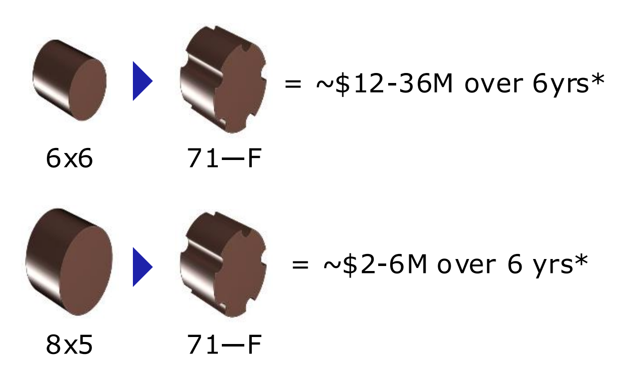
Shift catalyst – pressure drop case study HTS

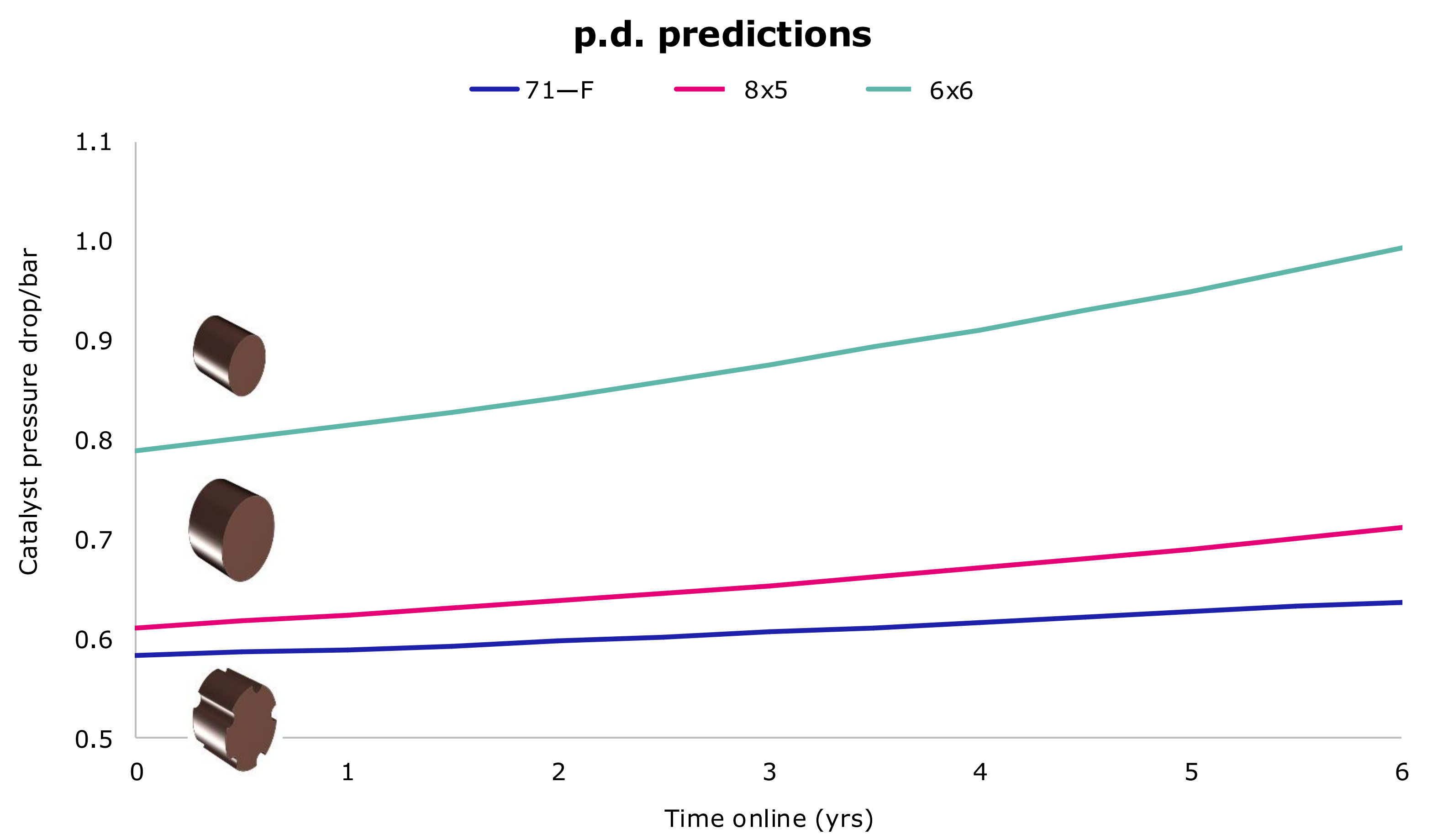
↑ **Increased profitability**
Good catalyst performance **(assurance)**

Positive impact: All of the time

Even **relatively small p.d.** differences allow strong returns due to combination of the **plant scale** and **ammonia production margin**

p.d. saving can **increase value** production



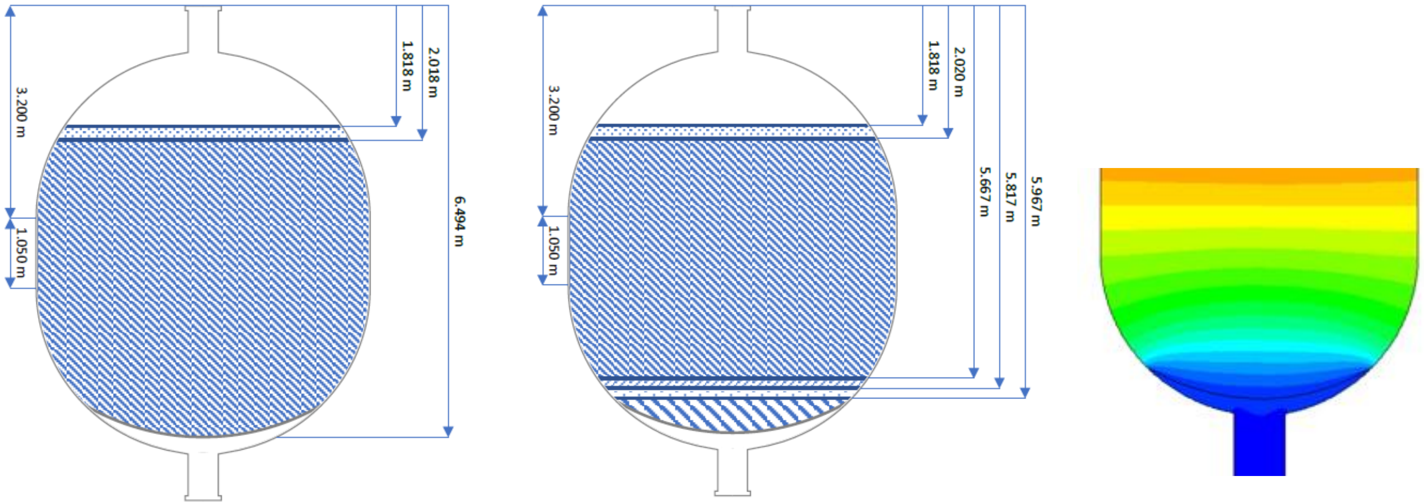


*HTS – plant scale 3,300 tpd of ammonia between \$300/$MTNH_3$ and \$1000/$MTNH_3$

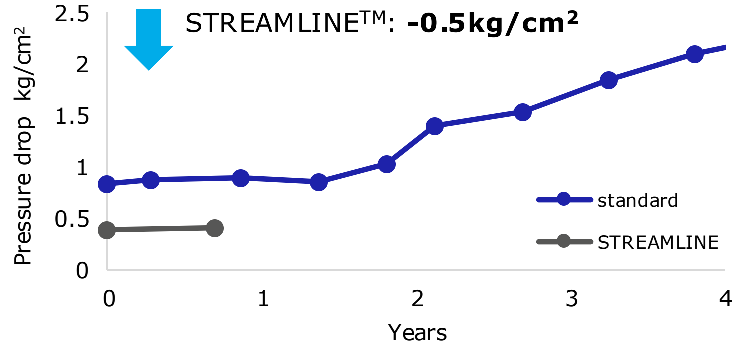
STREAMLINE solution to lower pressure drop

Engineered loading of supports in reactor; case studies in both HTS and LTS

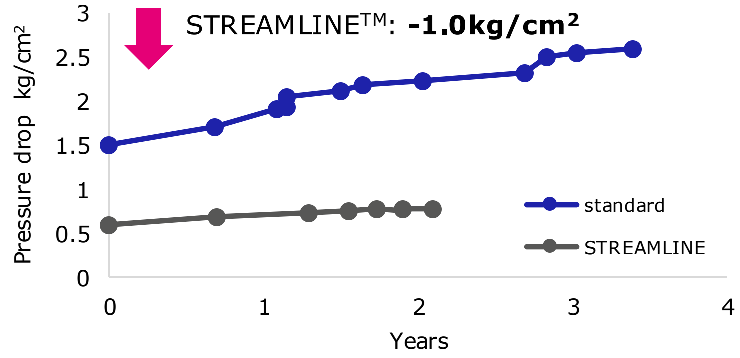
- Process gas accelerates towards the collector
- High gas velocities in the bed causes high pressure drop
- Modelling is used to determine areas providing the highest contribution to the pressure drop
- High voidage STREAMLINE solutions reduce velocities in these locations



HTS



LTS



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Performance monitoring and optimisation

In order to identify potential issues early, it is advisable to regularly measure, record and trend

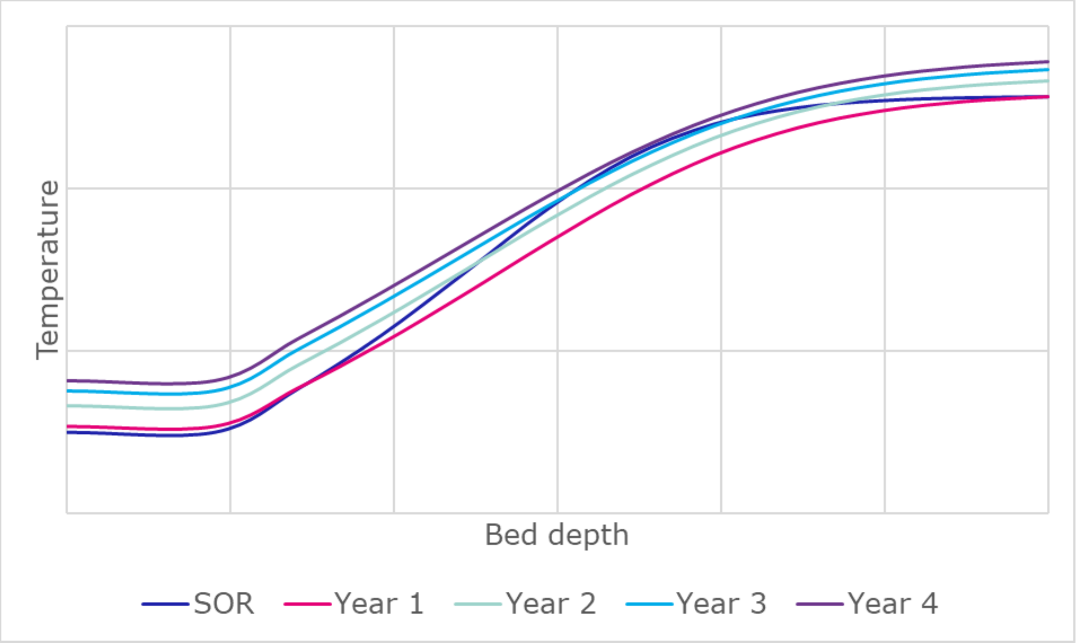
- CO slip
- Inlet and exit temperature
- Pressure drop

Optimising HTS operating temperature:

1. Operate at the lowest temperature, to maximise life of the catalyst, which provides the required CO slip
2. If the temperature profile suggests the reaction is not nearing equilibrium, then increase the inlet temperature by 5°C/10°F, and monitor CO slip over 24 hours.
3. If the CO slip reduces, then repeat step 2. Alternatively, if the CO slip increases or makes no improvement, then return to the previous condition.

Johnson Matthey can support with modelling of optimum operating conditions and catalyst life predictions.

HTS temperature profiles over the lift time of the catalyst with optimised inlet temperature



Summary

- HTS catalysts exhibit good resistance to poisons and the main deactivation mechanism is thermal sintering.
- Kinetic and equilibrium limitations are both factors in the HTS. Optimising the operating temperature over the life of the catalyst will help maximise the life of the catalyst and the conversion of CO.
- Wetting and fouling are also common problems for the HTS due to upstream units in the flowsheet. Regularly monitoring the KPI can help identify a problem early.
- Plants operating at aggressive steam to carbon ratios need to consider the risk of iron over-reduction
- Catalyst, hold down and support solutions can help reduce and maintain pressure drop in the HTS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