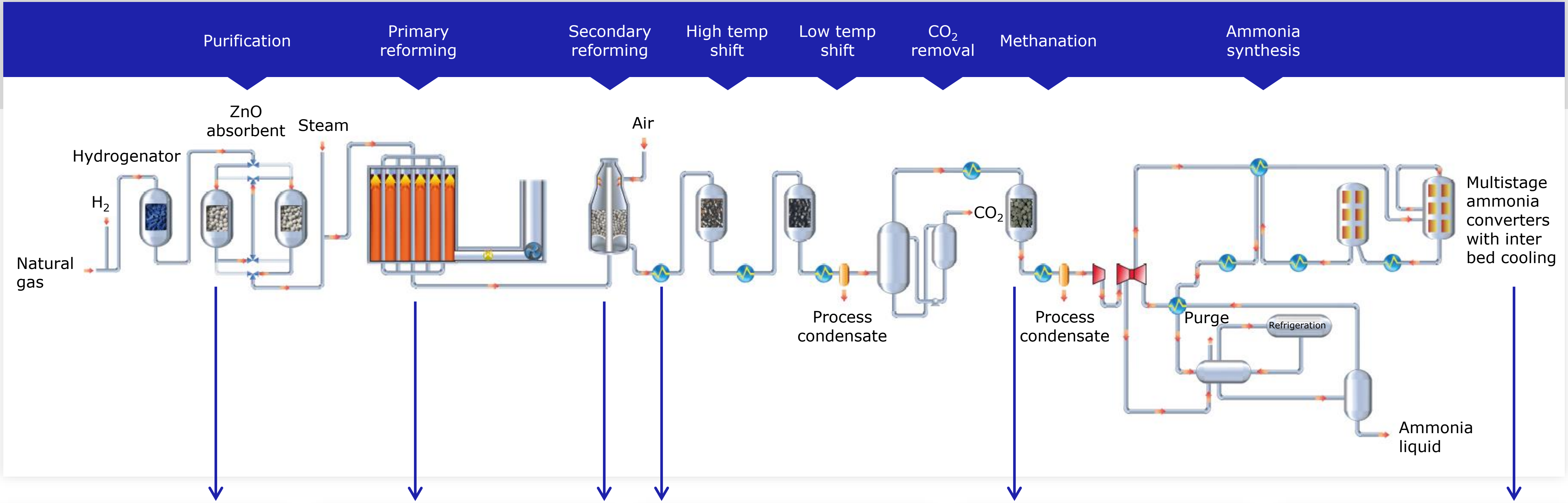
Johnson Matthey
Inspiring science, enhancing life

Americas hydrogen and syngas technical training seminar

Shift Process

Eddie De Amorim and Paulo Karavatakis

JM ammonia plant catalysts - specially designed for adding efficiency and reliability throughout flowsheet



Purification

Reduce S/Cl to **ultralow** levels for **enhanced** downstream **catalyst life**

Steam reforming

Leading catalyst and **services**, for **reliable conversion** of CH_4 to H_2

Water gas shift

Innovative solutions to **extend useful life** and **minimize pressure drop (p.d.)**

Methanation

Leading catalyst to **minimize p.d.** and **save energy**

Ammonia syn

Active catalyst for **max. NH_3 conversion, use at lower synthesis pressure**

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Water gas shift basics

$CO + H_2O \Leftrightarrow CO_2 + H_2$ $\boxed{+\ \text{Heat}}$ $\Delta H = -41.1\ kJ/mol$

Reversible reaction

Equilibrium limited

Exothermic (forward reaction)

- Lower temperature
- Increased CO converted
- Increased hydrogen produced

Equimolar

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

Low temperature favors H_2 production

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Agenda for today

01 **HTS**

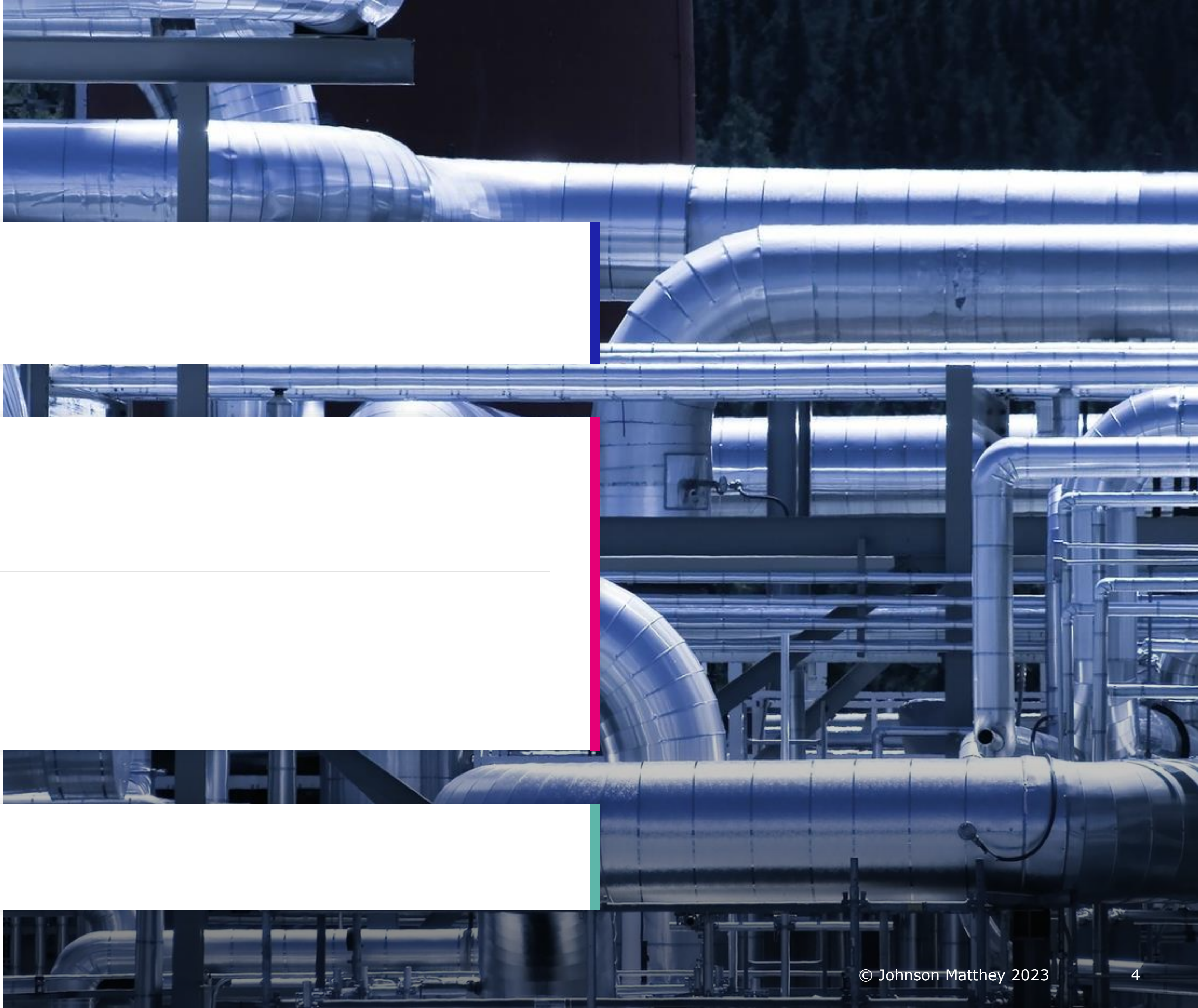
Catalyst features

02 **LTS**

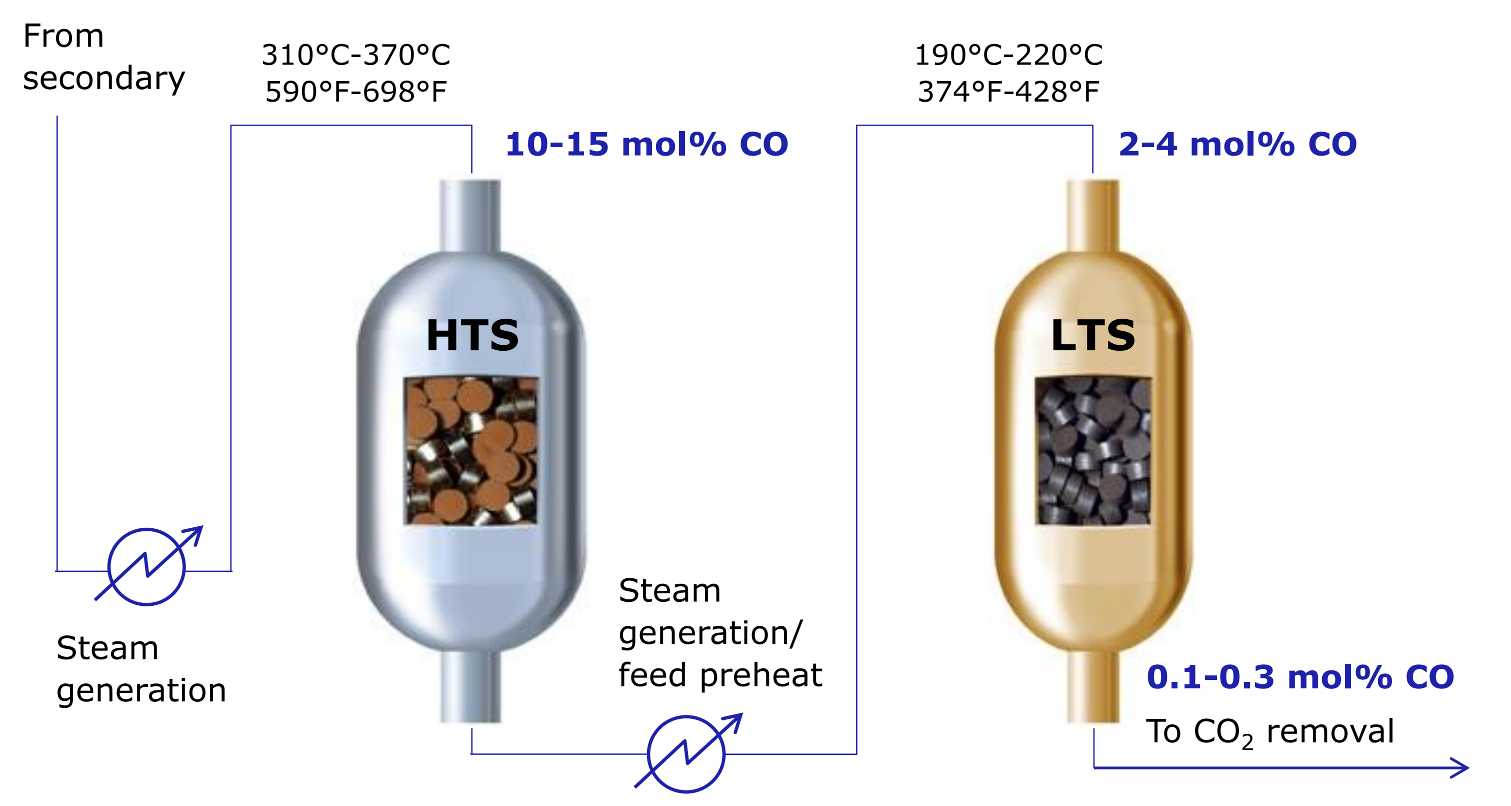
Catalyst features

Poisoning
- Sulphur
- Chloride

03 **Pressure drop**



HTS and LTS



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

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High temp shift catalyst

Eddie De Amorim

JM

HTS

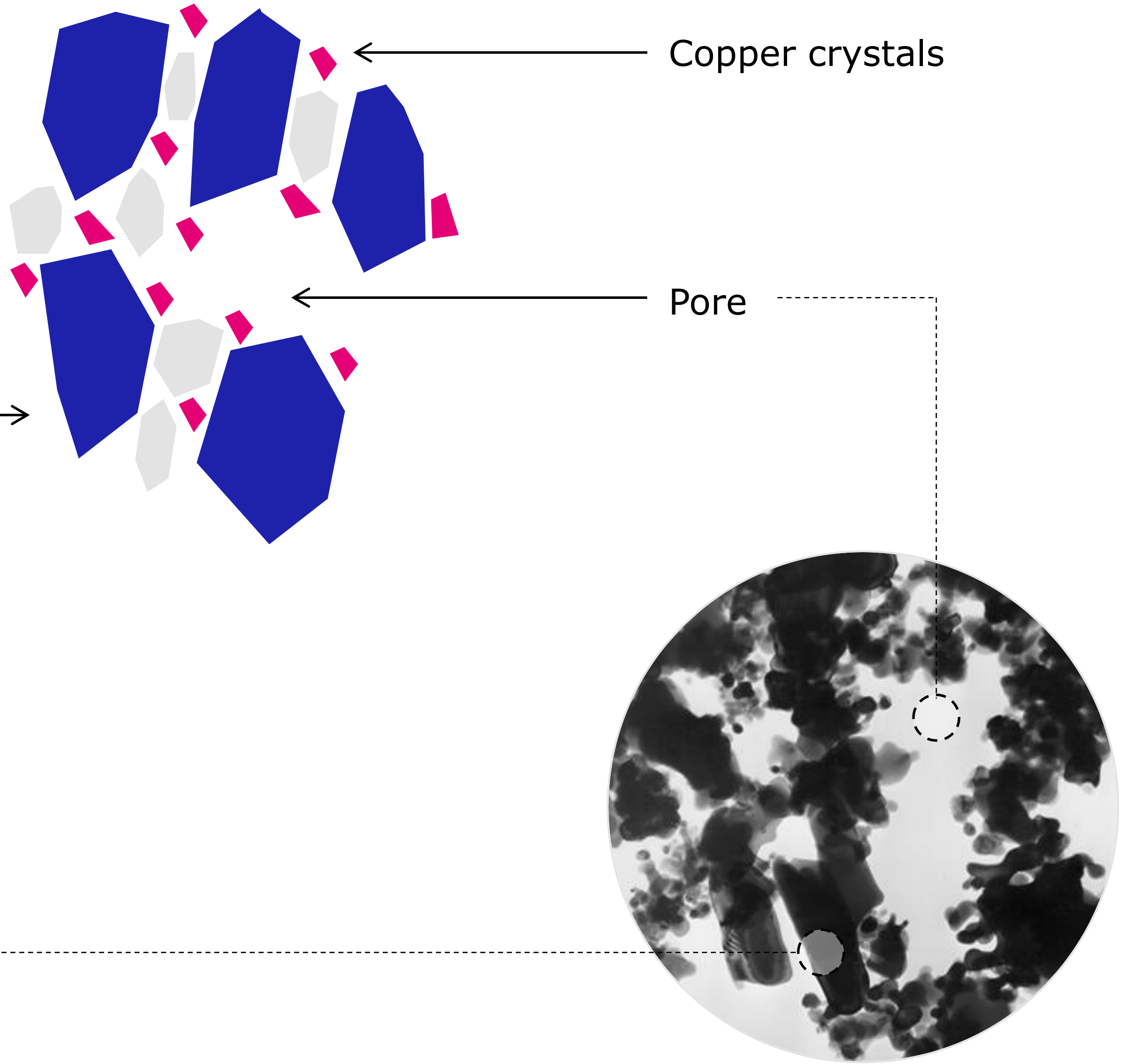
Catalyst features

Modern HTS catalysts require

High and stable activity

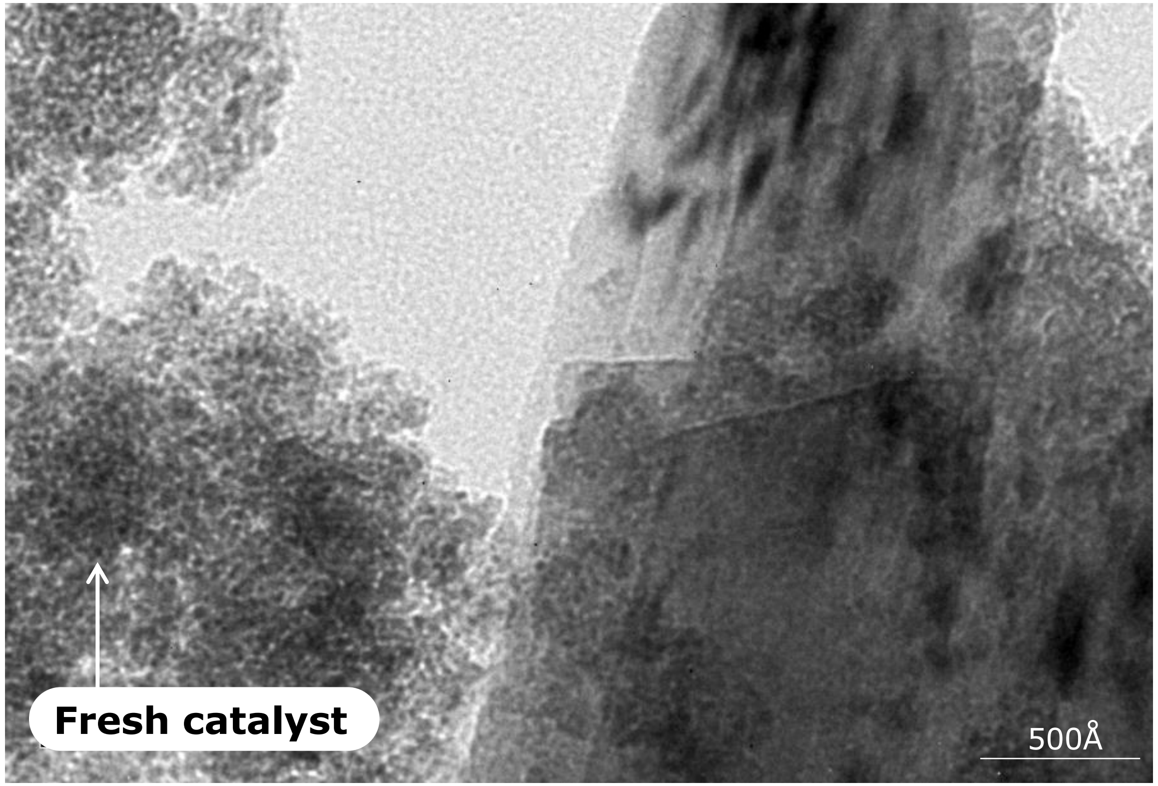
High strength

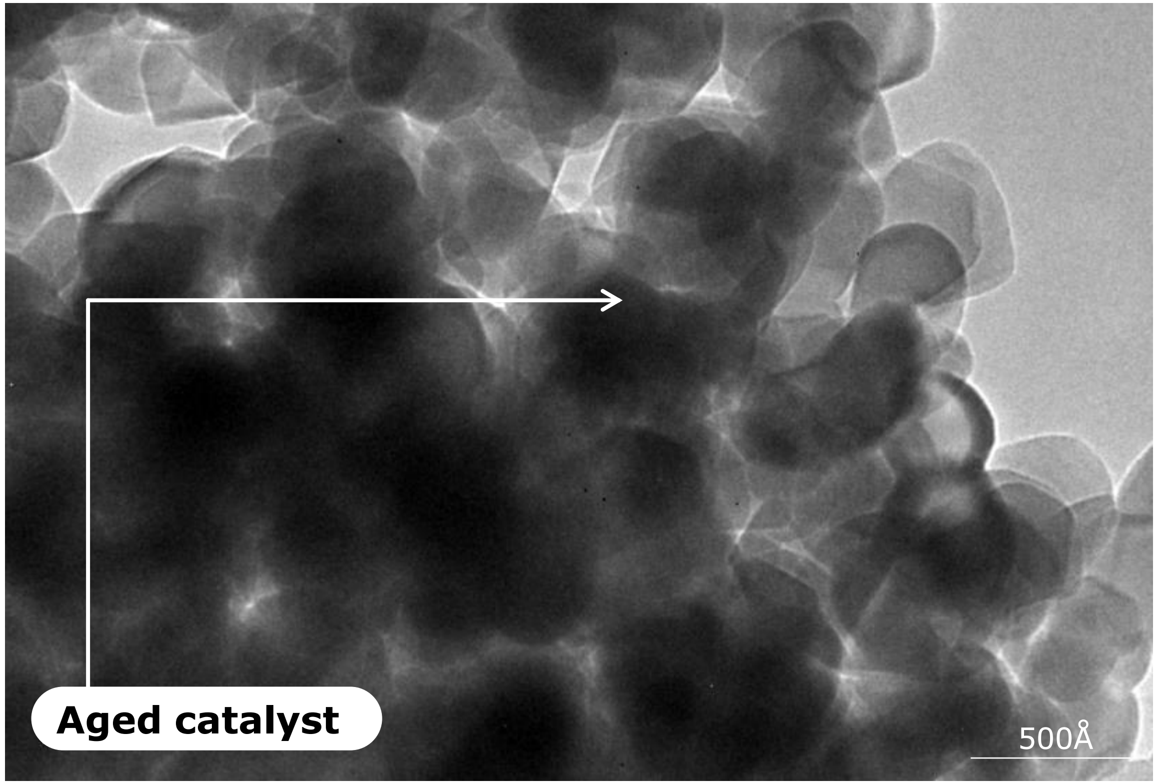
HTS



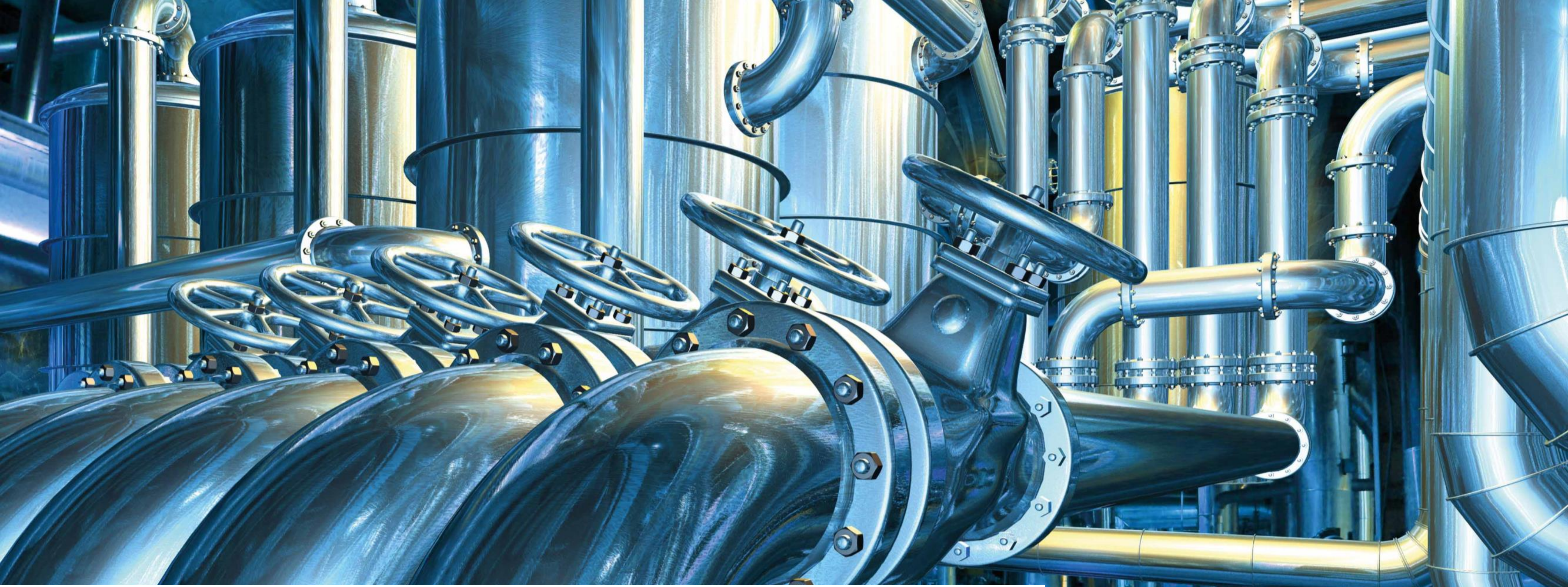
HTS

Catalyst microstructure





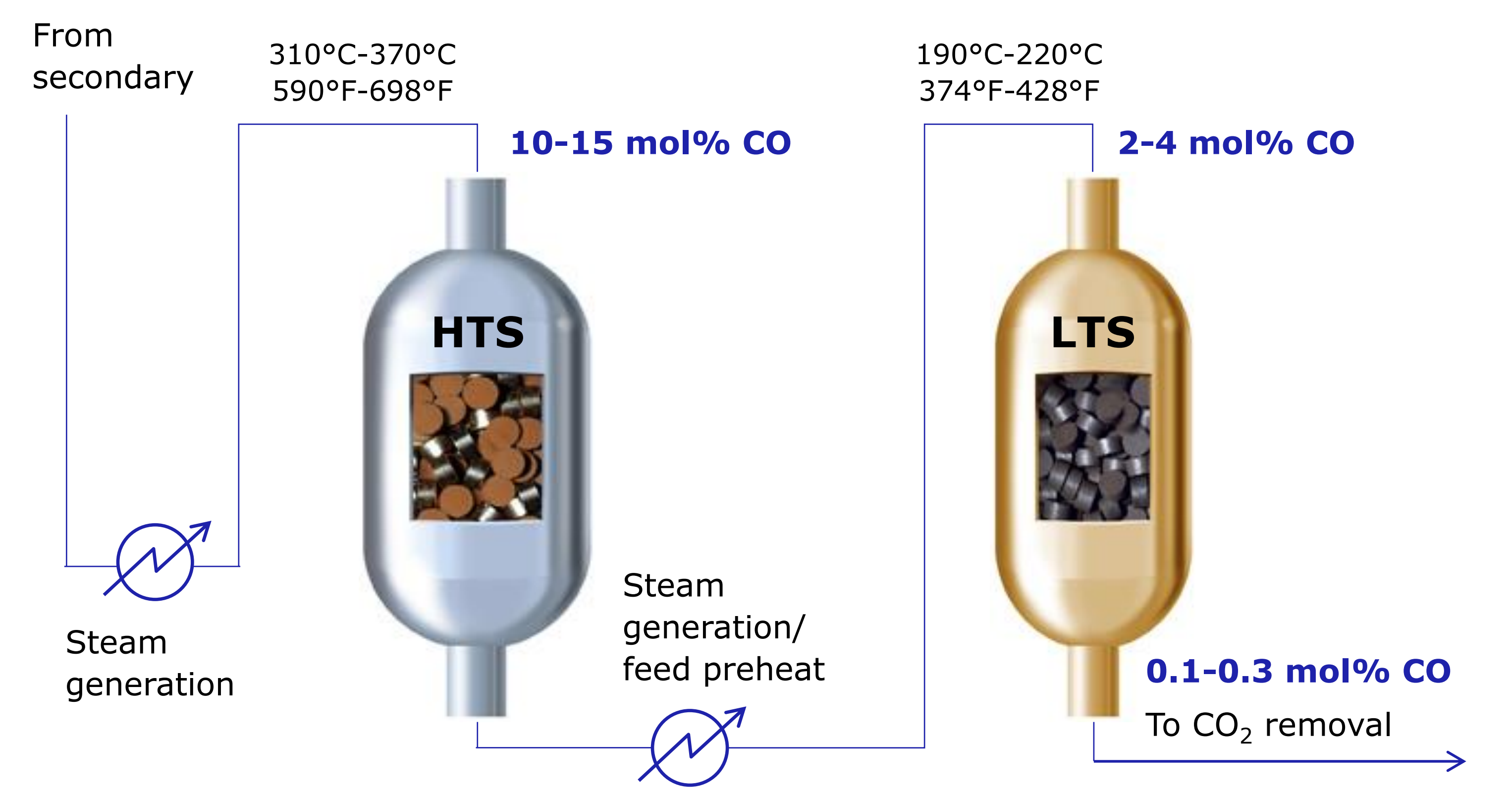
Same magnification



Low temp shift process

Eddie De Amorim

HTS and LTS



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

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LTS/MTS

Catalyst features

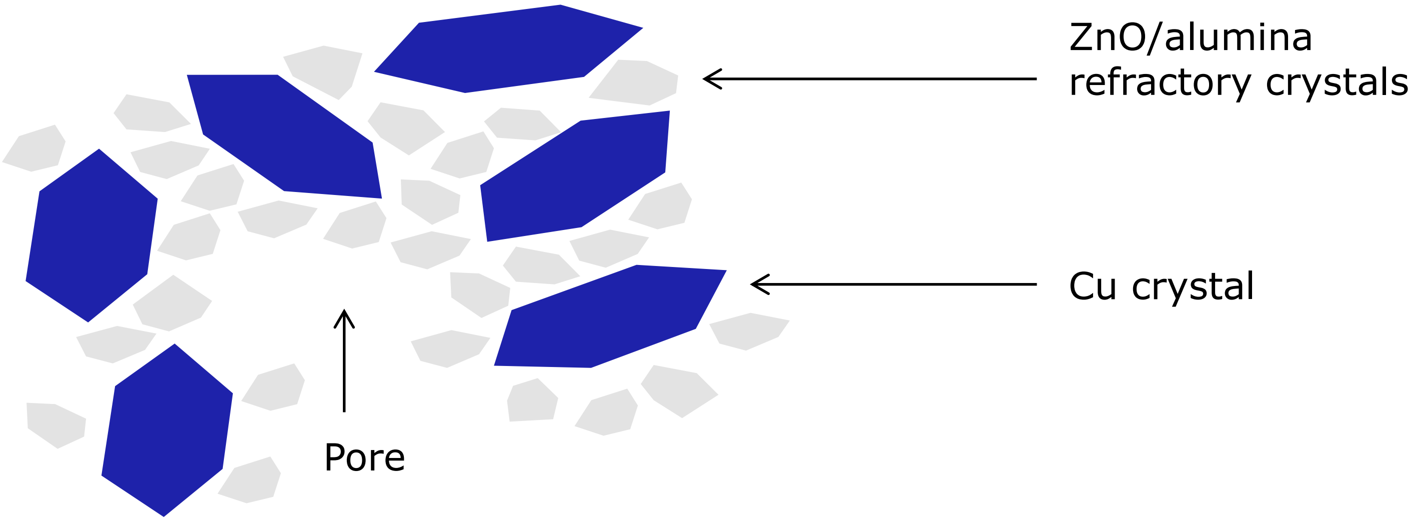
Cu/Zn/Al formulation

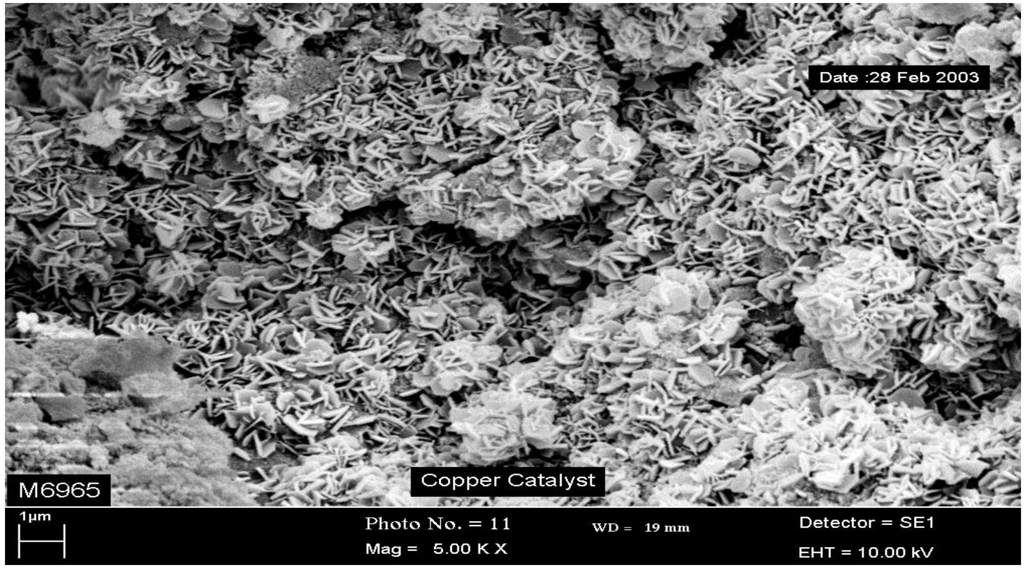
High and well dispersed Cu content

Strong ZnO/alumina refractory phases

Inhibition of Cu sintering by the ZnO/alumina phases

For LTS, control of Cu activity plus special promoters increase selectivity





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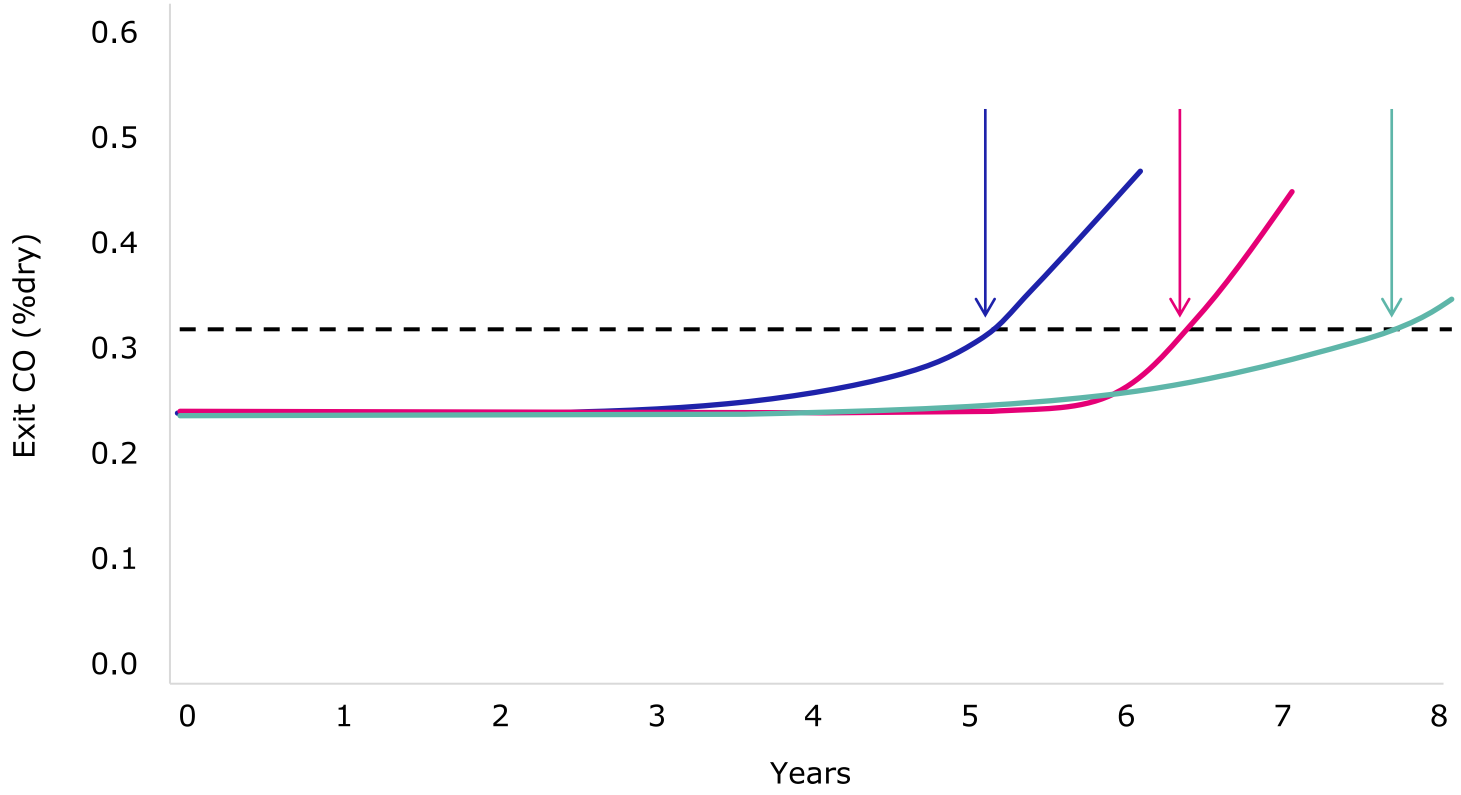
LTS

Benefit of activity vs poisons improvements

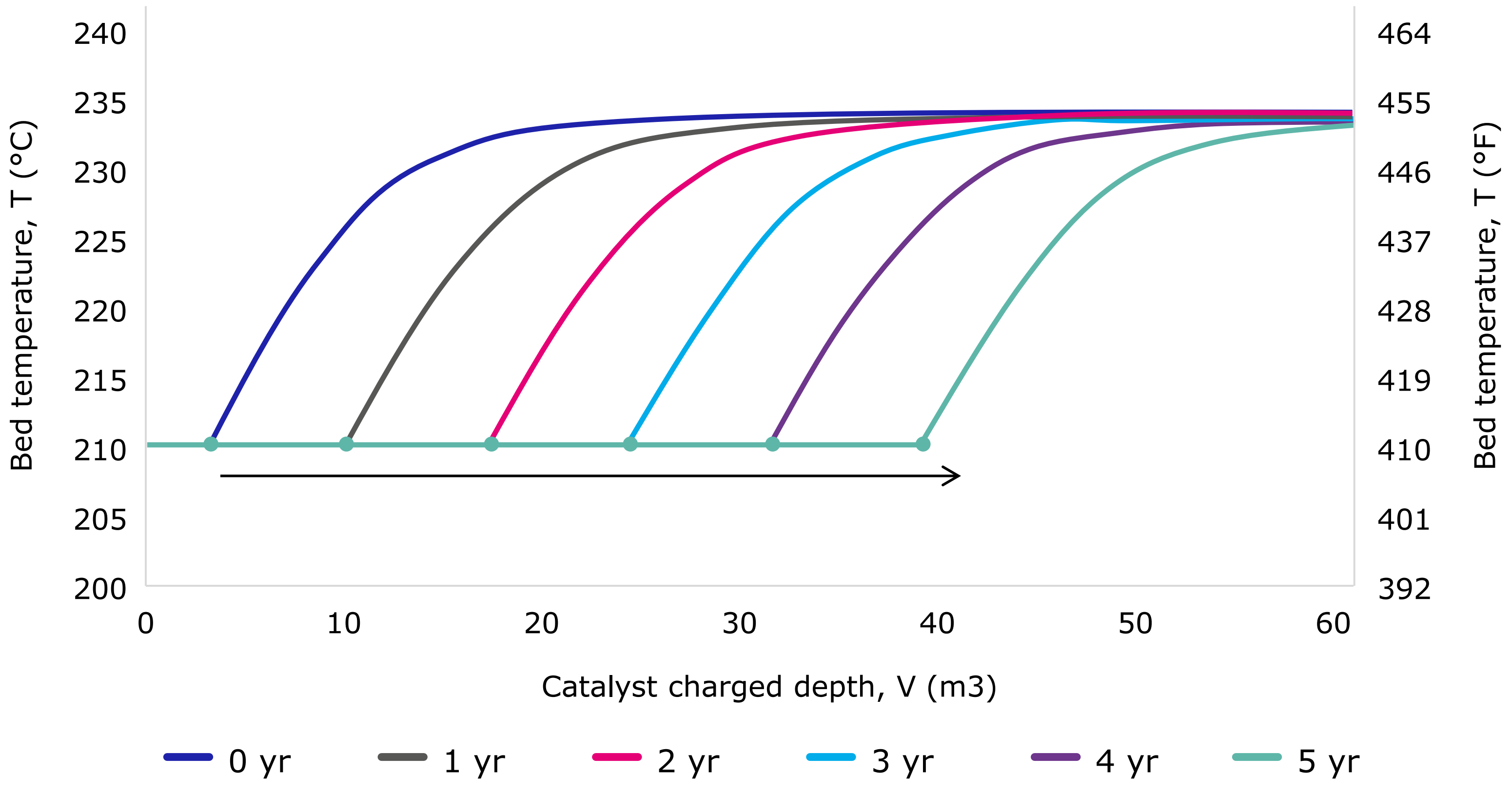


Activity	Poisons	Life
100%	**100%**	**5 years**

Poison resistance can often have more value than activity

LTS poisoning

LTS poisoning profile



Useful life **largely governed** by poisoning

No reaction occurs in the **poisoned volume**

The **poisoned volume** extends deeper into the bed over time

Poisons retained by the **catalyst prevent** poisoning further down the bed

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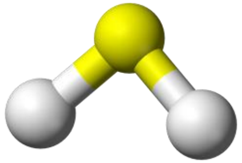
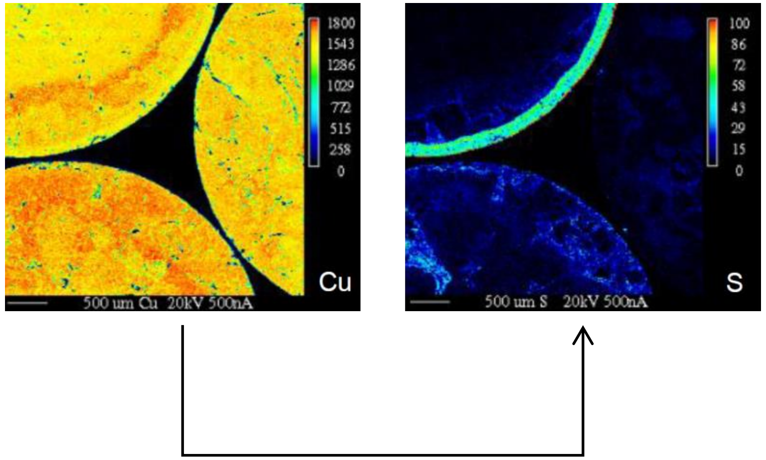
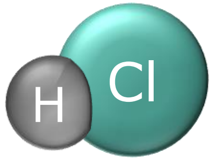
Two very different catalyst deactivators

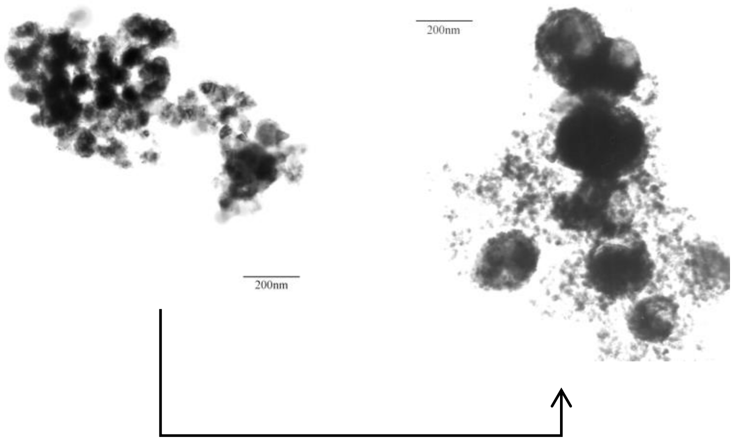
16
S
32.065





17
Cl
34.453





Feedstock

Process air

Insufficient purification

Lubricating oils

Water additives

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Two very different catalyst poisons

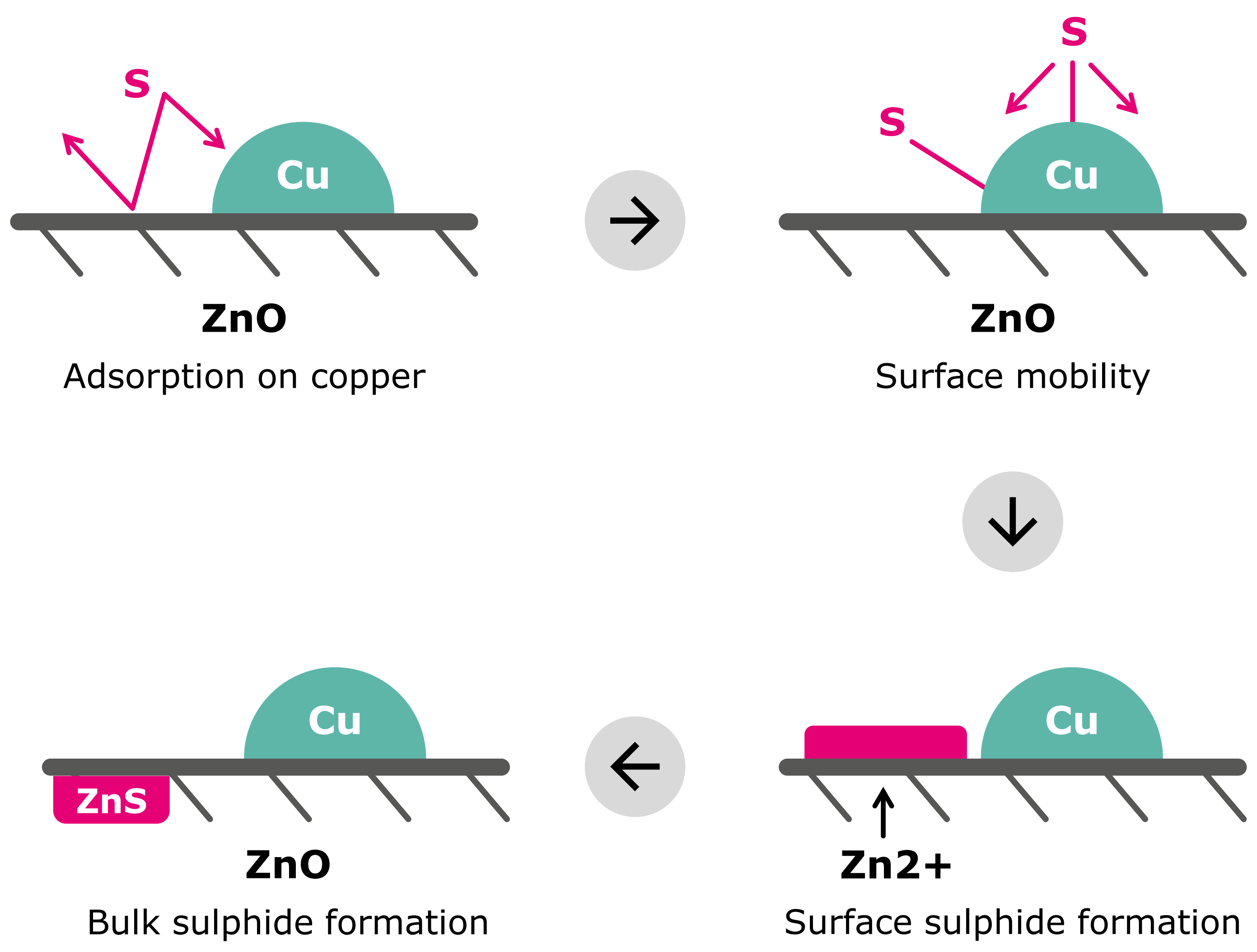
16
S
32.065

S reacts with Cu surfaces forming **CuS**

S surface **mobile**

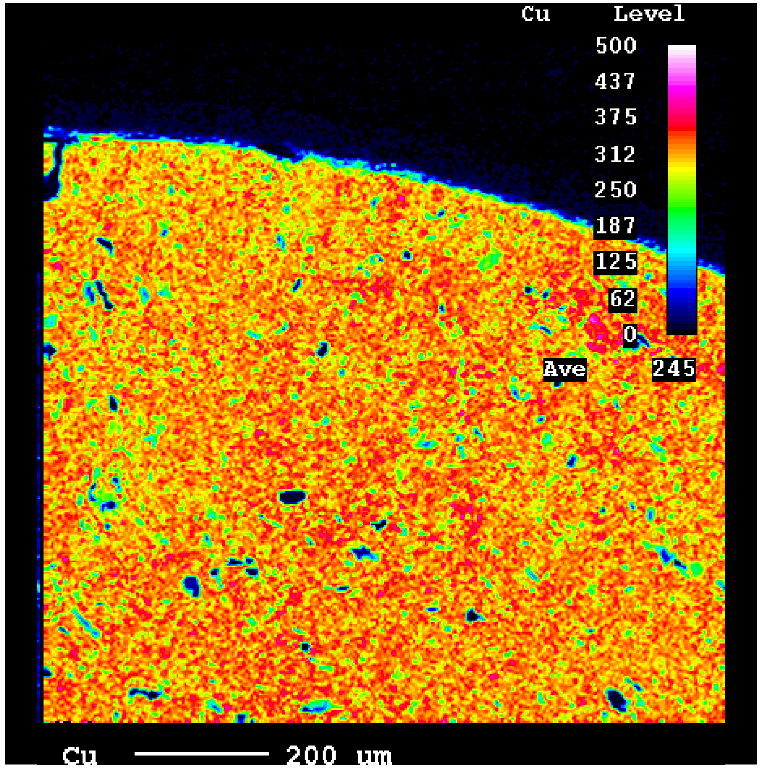
ZnS thermodynamically stable

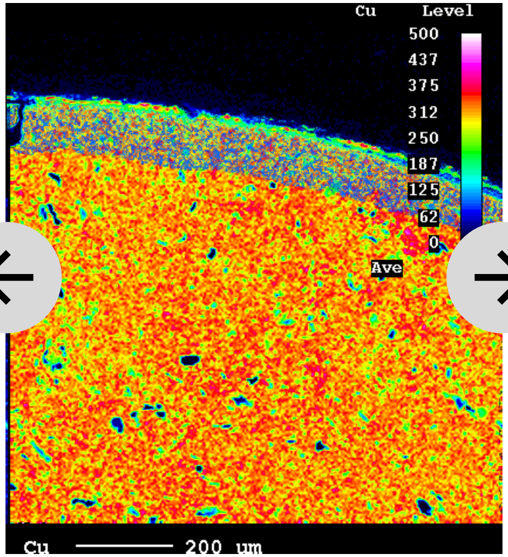
Bulk sulphide ZnS the stable endpoint within catalyst



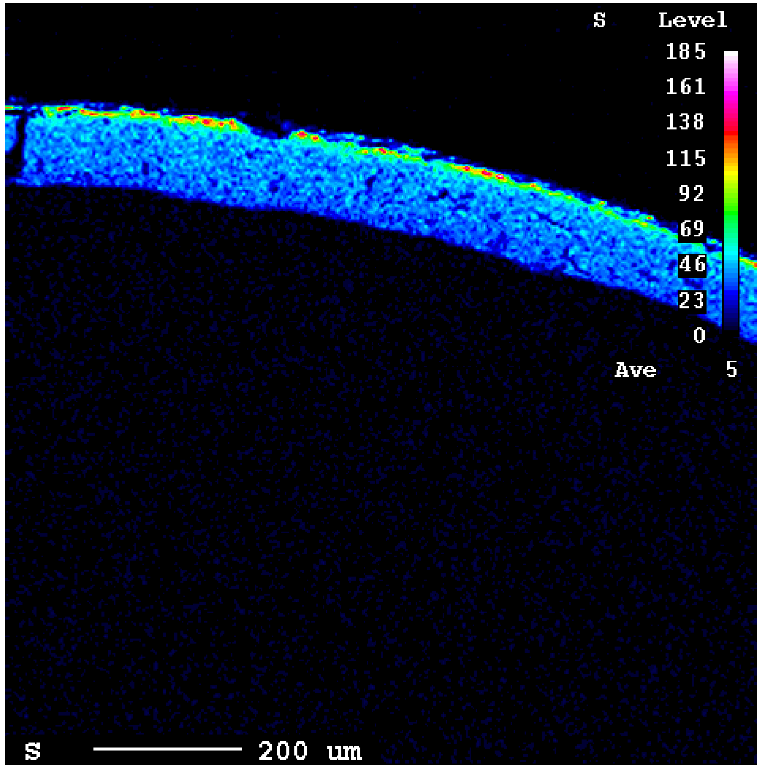
Sulphur poisoning

Copper





Sulfur



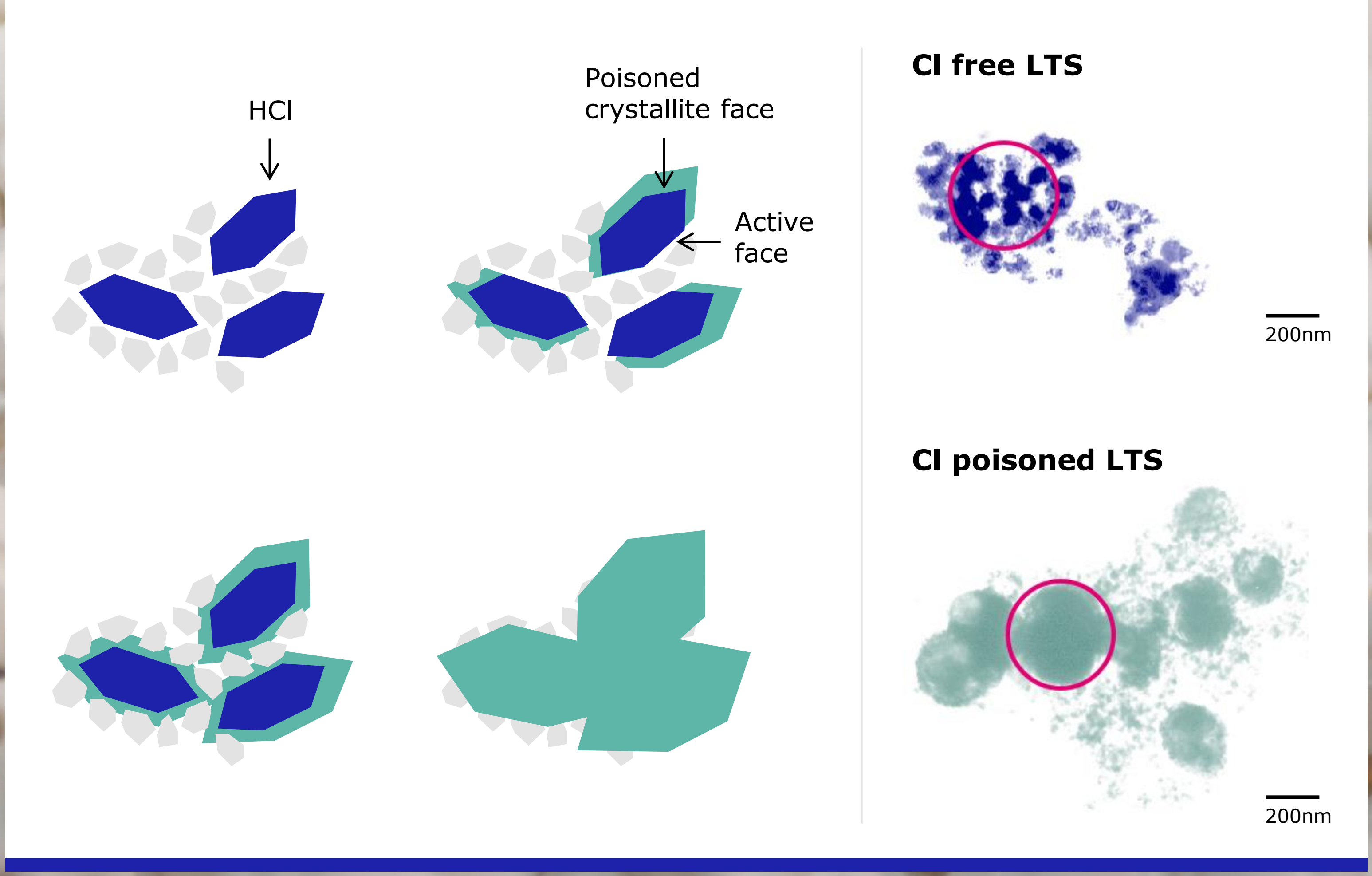
Chlorides strongly promotes sintering

17
Cl
35.453

Cl forms **CuCl**

CuCl mobile if **wetted so poisons can be washed deep into bed**

CuCl has **low melting point** promotes sintering



Chlorides strongly promotes sintering

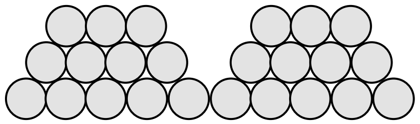
Tamman temperature, describes on-set of atomic particle migration

$T_{tamman} = ½\ T_{melting\ point}\ [^oK]$

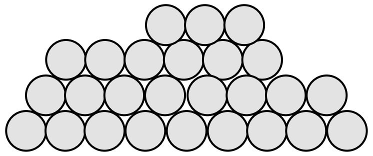
Particle migration

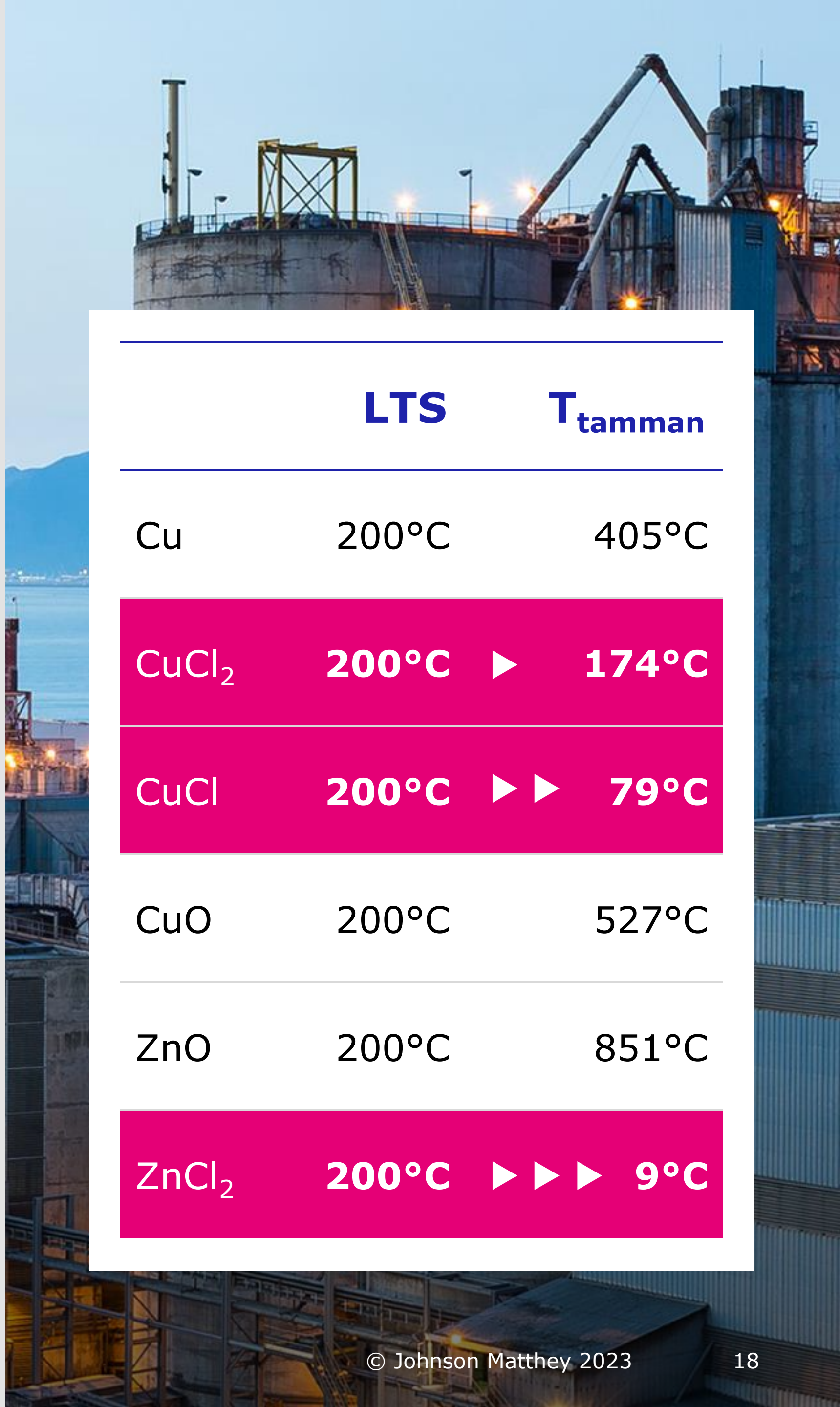
Particle migration

Particle collision



Particle merging





	LTS		T_{tamman}
Cu	200°C		405°C
$CuCl_2$	**200°C**	▶	**174°C**
CuCl	**200°C**	▶▶	**79°C**
CuO	200°C		527°C
ZnO	200°C		851°C
$ZnCl_2$	**200°C**	▶▶▶	**9°C**

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Chloride poisoning

Competitor solution

Speciality guard

Top 15% of bed not used for shift reaction

Reduced **LTS activity** of bed

Designed **for Cl retention**

Low S retention

Additives required to give **materials strength**

JM solution

Self guarding

Entire bed available for shift reaction

Maximised **activity of bed**

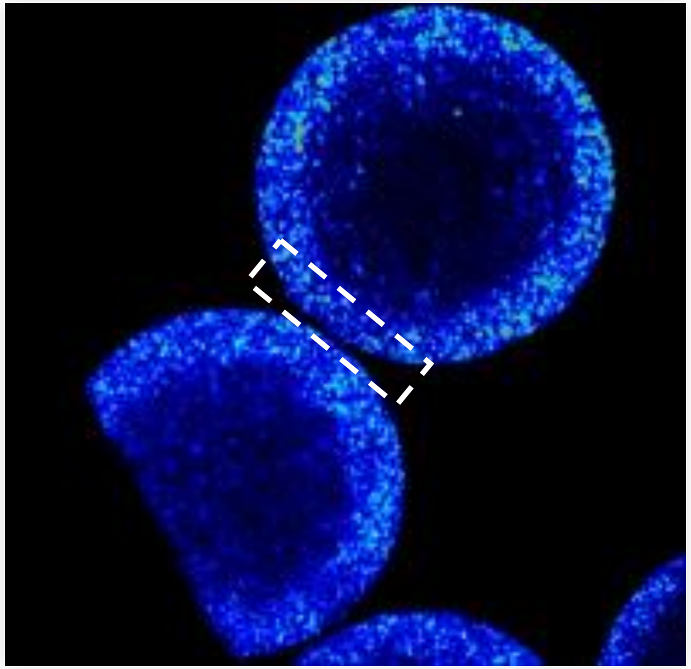
Equivalent Cl retention

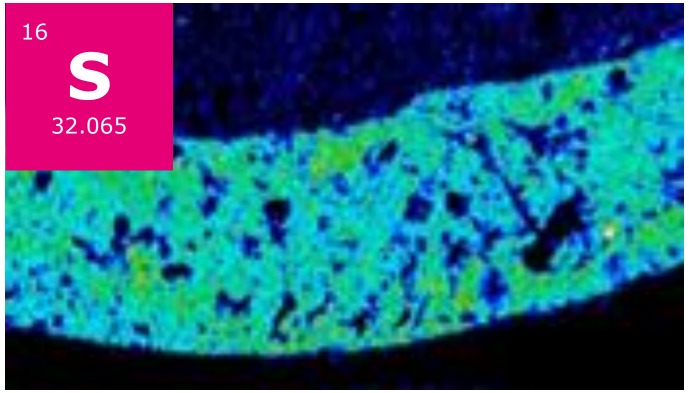
Very high S retention

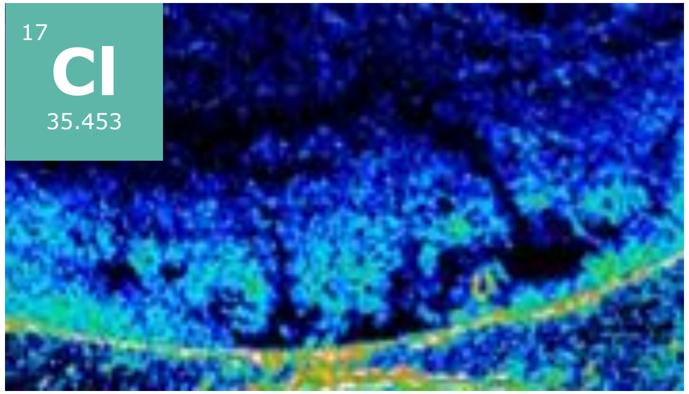
Strength inherent in product

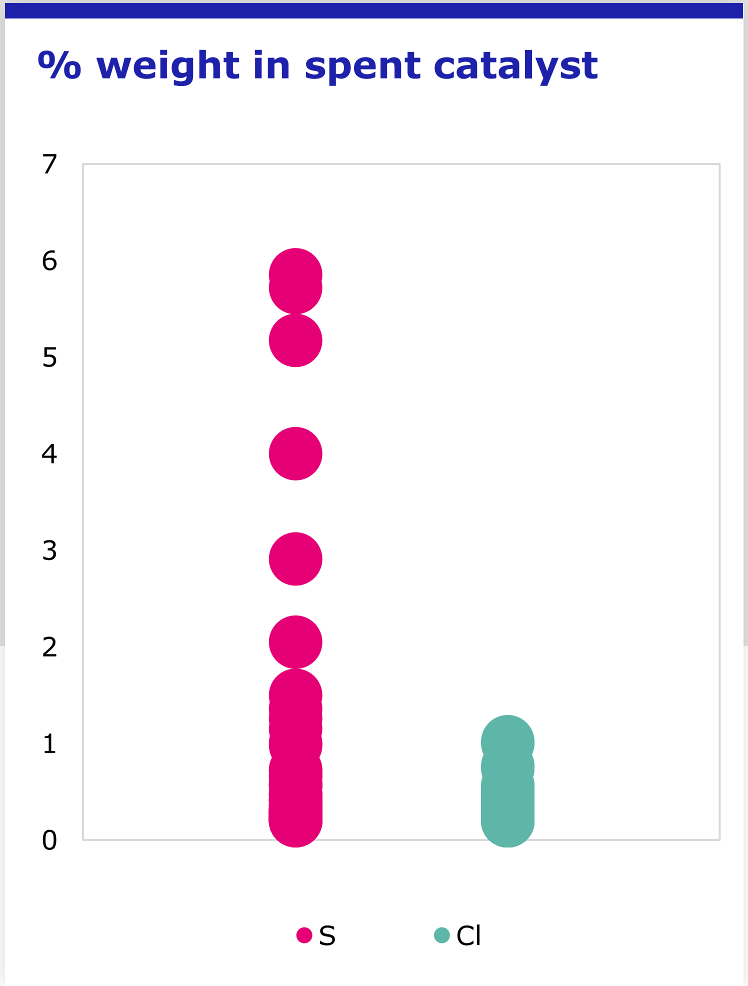
KATALCO 83-3 - self guarding for S and Cl

Analysis of pellets









PURASPEC 2272

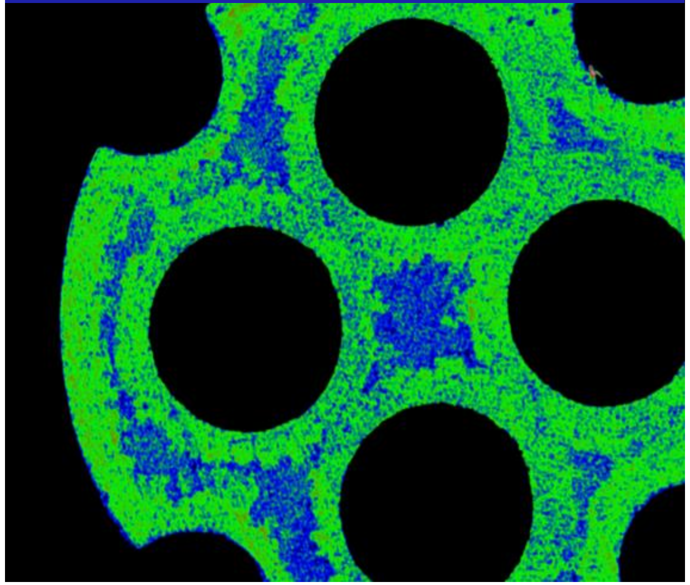
More protection longer LTS life; less risk from transient wetting

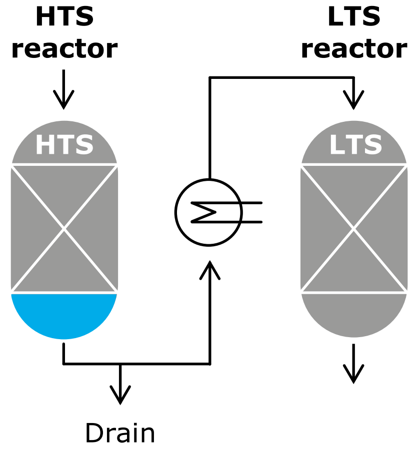
Increased profitability
Good catalyst performance **(assurance)**

Positive impact:
All of the time

JM

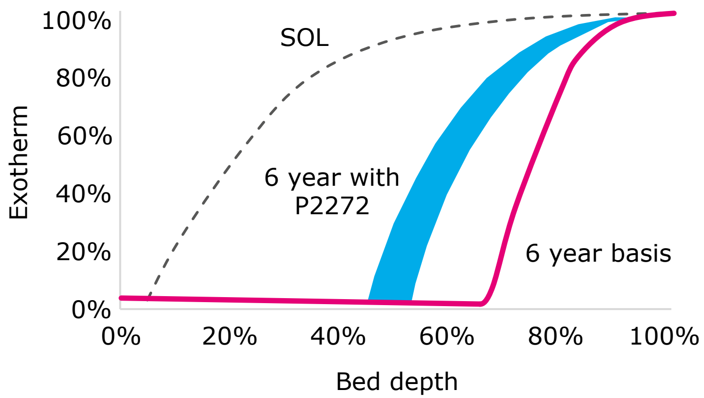
PURASPEC 2272:
Protection for Longer LTS Life



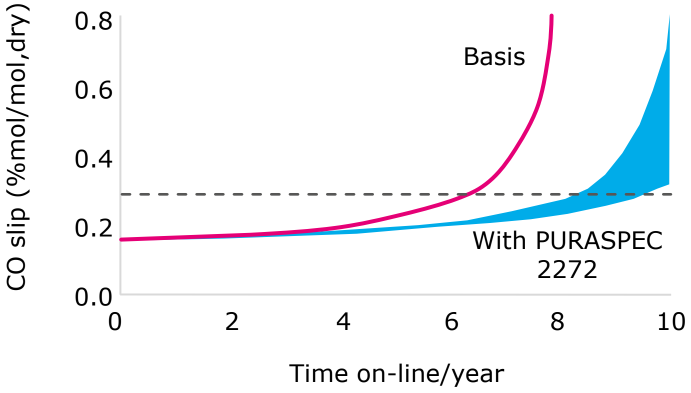


	HTS exit PURASPEC™ 2272	LTS inlet - traditional
Process	**450°C/840°F**	**195°C/380°F**
Dewpoint	180°C/355°F	180°C/355°F
Dewpoint margin	**270°C/484°F** No risk Cl migration	**15°C/27°F** Risk Cl migration

Slower LTS deactivation



LTS life extension



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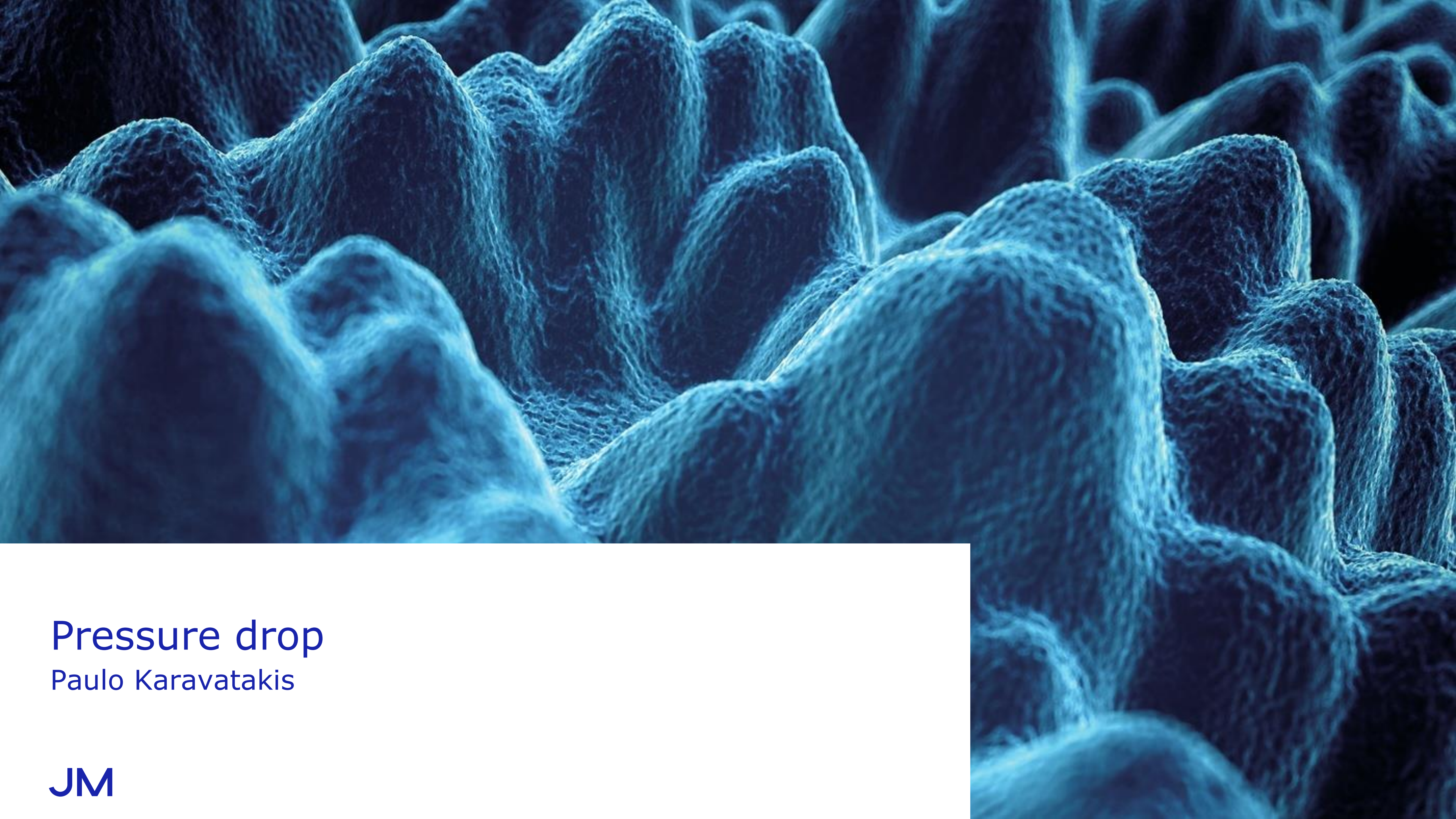
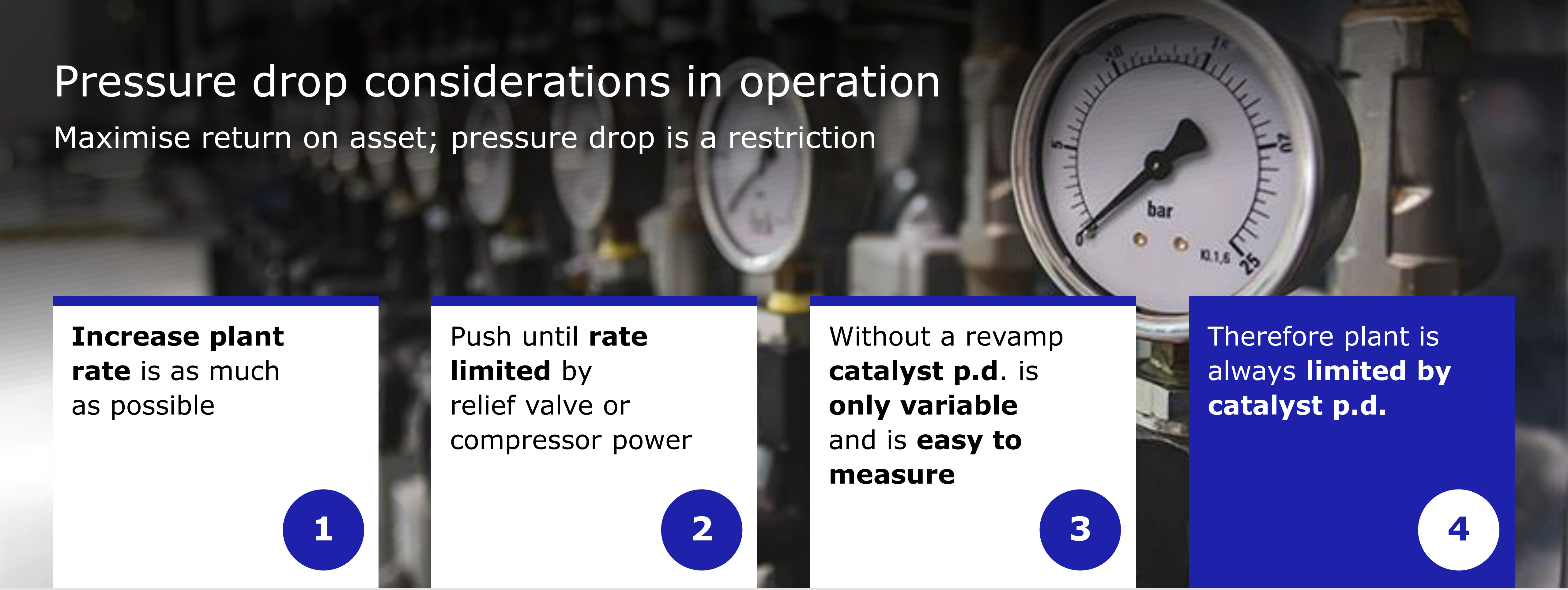


Pressure drop

Paulo Karavatakis

JM



Pressure drop considerations in operation

Maximise return on asset; pressure drop is a restriction

Increase plant rate is 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

Pressure drop – catalyst important

Range of tools and types to optimise

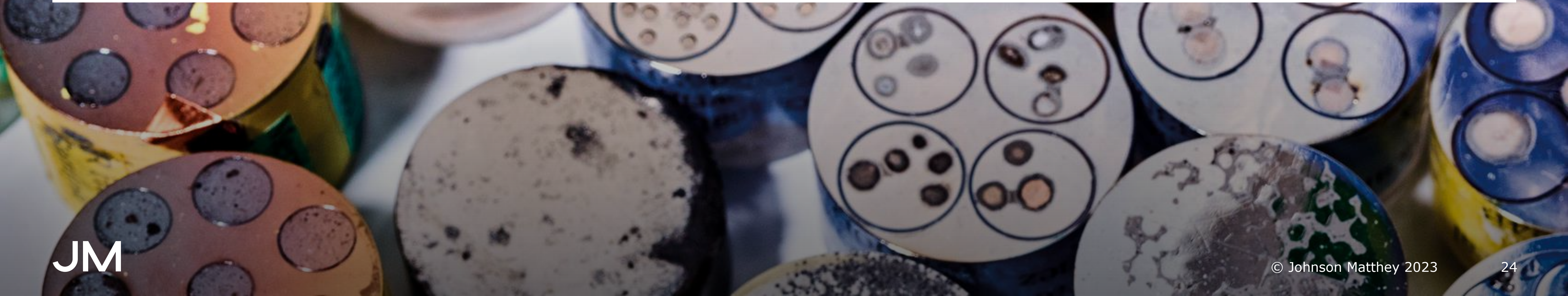
Catalysts must satisfy **operator** needs

Different sizes, catalyst **shapes** and **loading options –** available to **reduce catalyst p.d.**

Design tools for **value adding solutions**

Catalyst p.d	Flowrate
100%	100%
50%	104%
0%	109%

Assuming air compressor limit, matching 9bar p.d. from primary to Syngas machine suction



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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

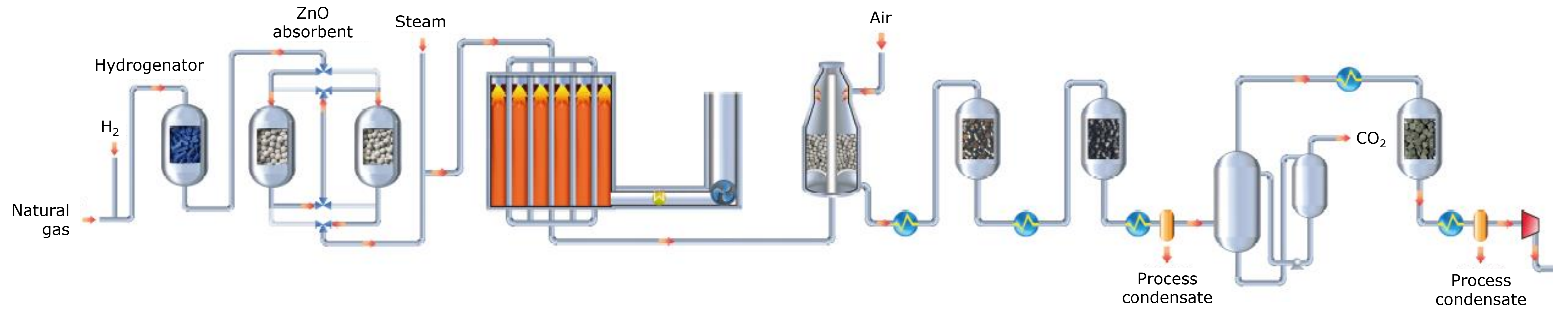
Strength in-service

Breakage characteristics

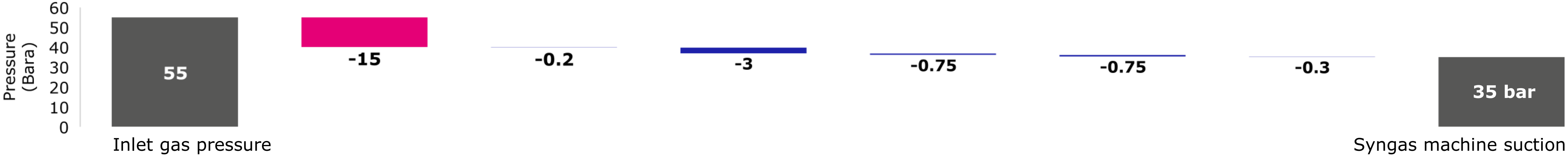
Operational stability

Transients/poisons

Pressure drop across the front end of flowsheet



	Exchangers, piping etc.	Purification	Reforming	HTS	LTS	Methanation
	75%	1%	15%	4%	4%	2%



Shift catalyst - pressure drop case studies

Increased or lost profitability impacts

Increased profitability

Good catalyst performance **(assurance)**

Positive impact:
All of the time

Lost profitability

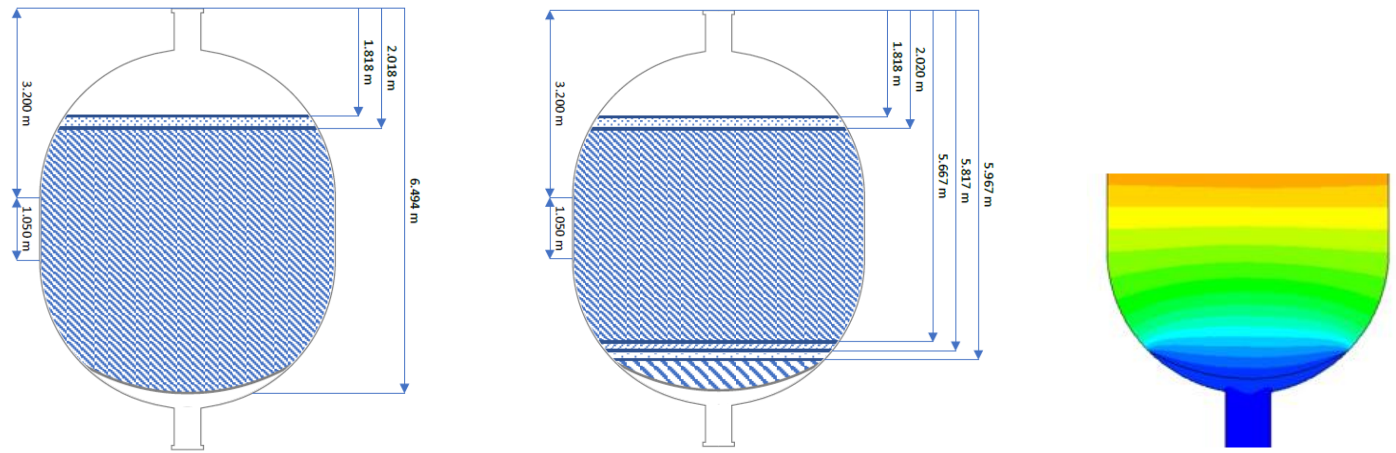
Poor catalyst performance **(risk)**

Negative impact:
Infrequent event

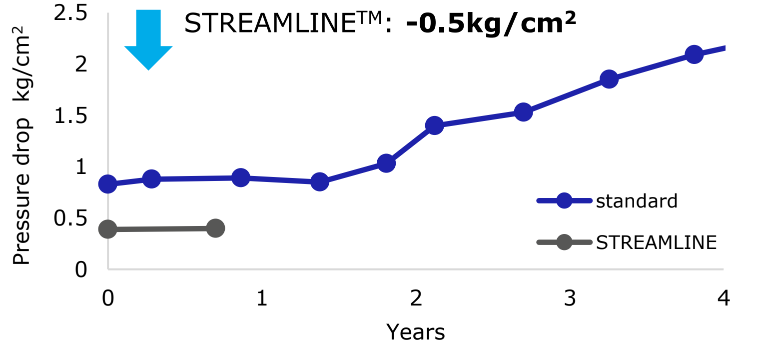
STREAMLINE solution to lower pressure drop

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

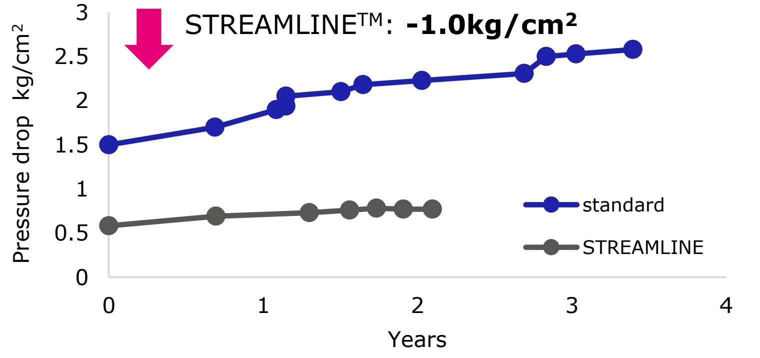
JM's proprietary design tools used to optimize



HTS - 2200mtpd



LTS - 3300mtpd



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Shift catalyst – pressure drop case study HTS

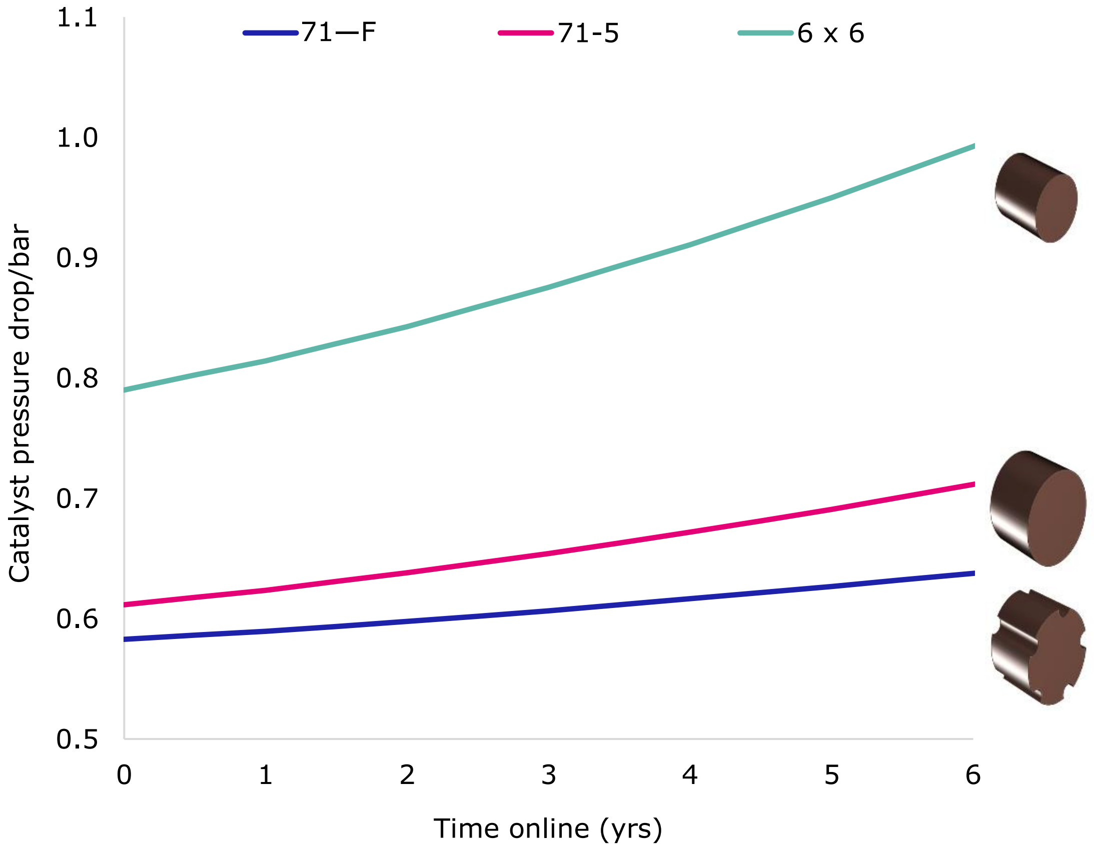
HTS – plant scale 3,300 tpd of ammonia, case at $1000/MT_{NH_3}$

Increased profitability

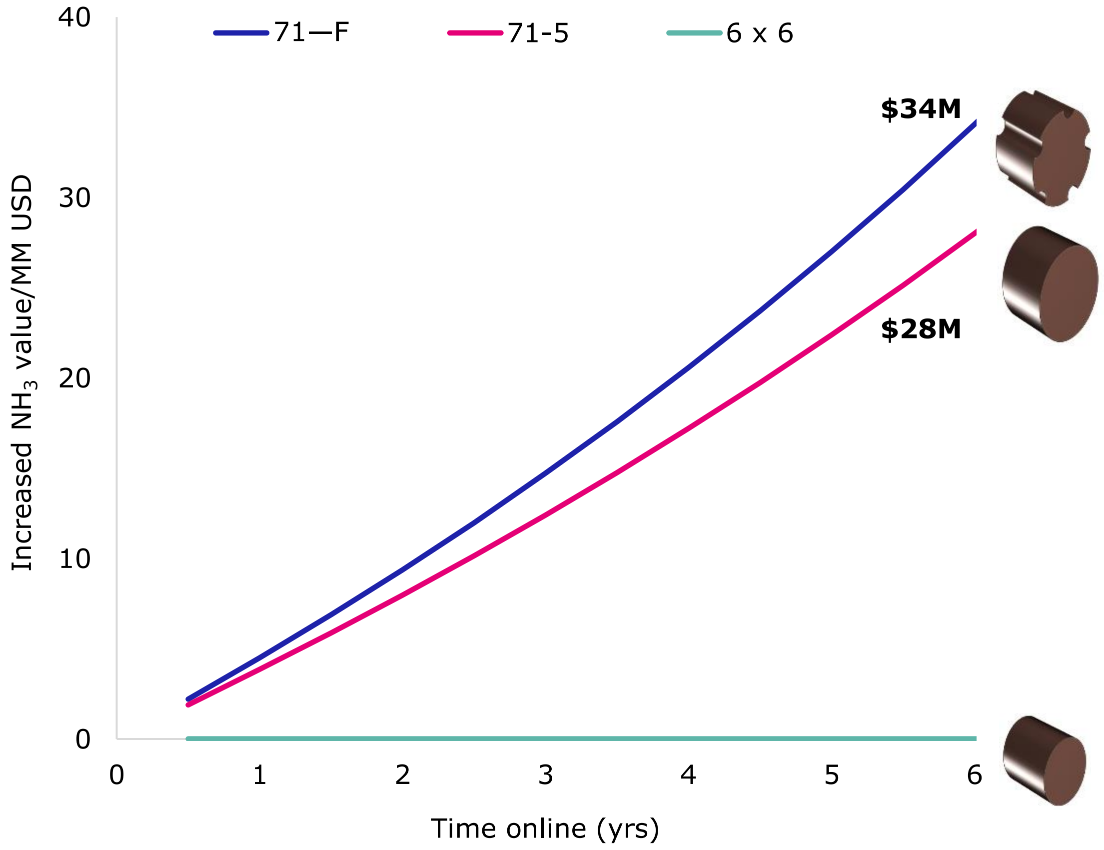
Good catalyst performance (assurance)

Positive impact: All of the time

p.d. predictions



p.d. benefit - increased throughput



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Shift catalyst – pressure drop case study HTS

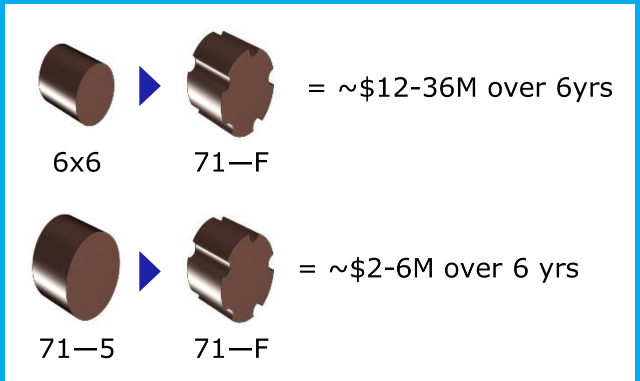
Increased profitability
Good catalyst performance **(assurance)**

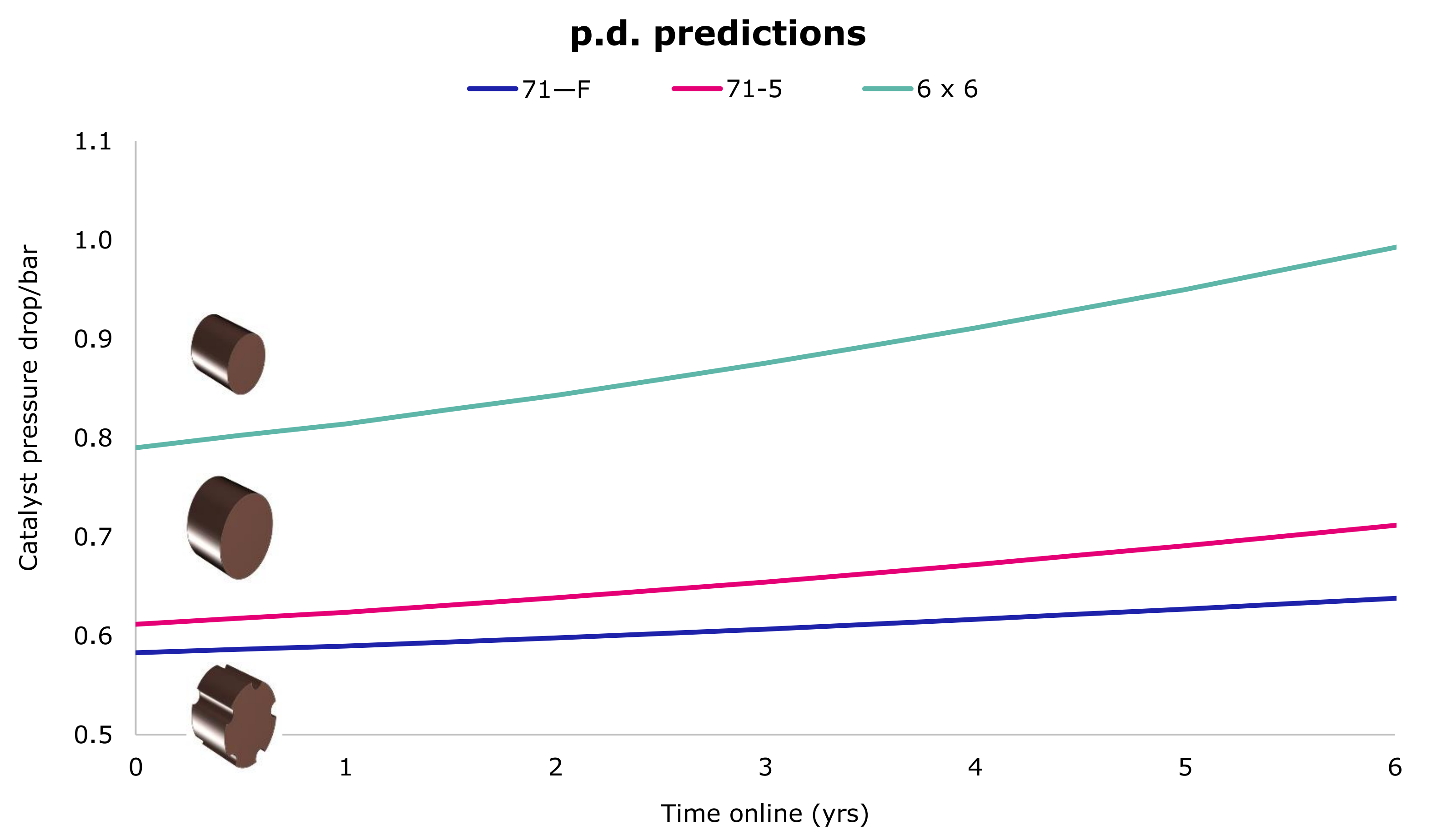
Positive impact: All of the time

HTS – plant scale 3,300 tpd of ammonia between $300/MT$_{NH_3}$ and $1000/MT$_{NH_3}$

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





Shift catalyst – pressure drop case study LTS

LTS – plant scale 1,200 tpd; considering product at $300/MT$_{NH3}$

Lost profitability

Poor catalyst performance **(risk)**

Negative impact: Infrequent event

Competitive LTS charge

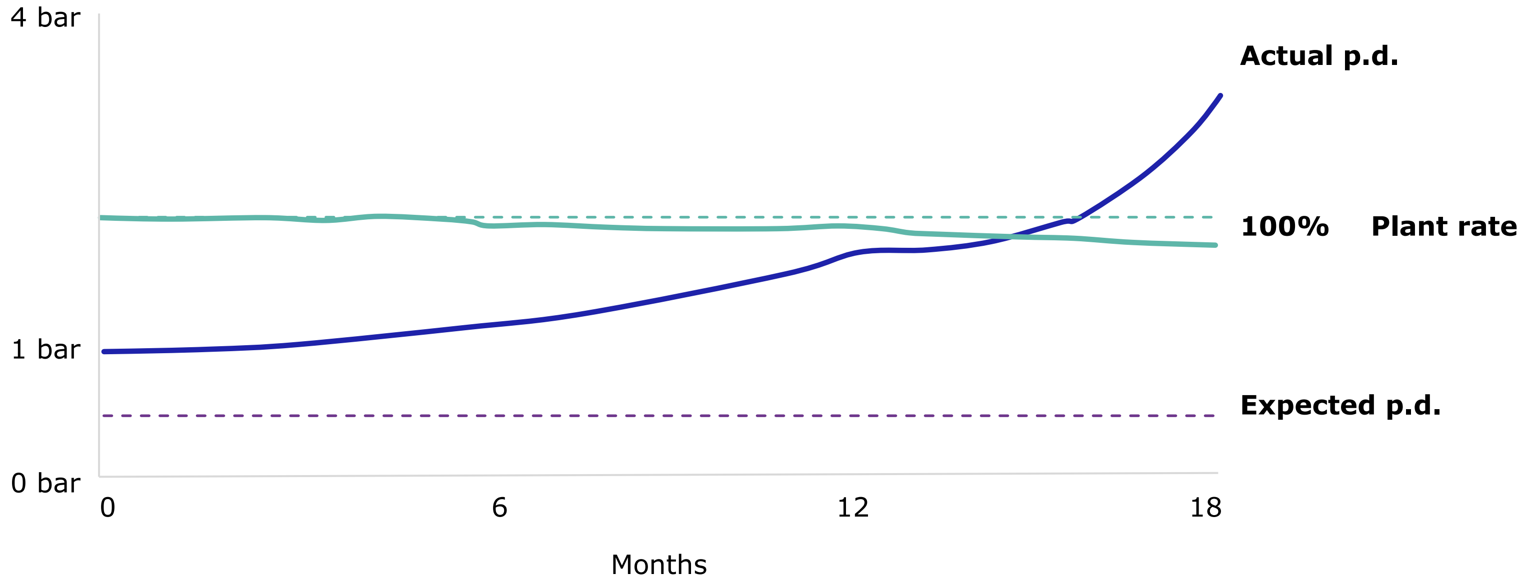
Purchase cost saving

Performance issues

- LTS pressure drop double expected SOR **@ 1bar**
- p.d. increased dramatically through life to **3.5bar**
- Caused rate restriction, changed at **18 months**
- Incident cost, estimated at **>$10M**

Why?

- Catalyst structural issue in reduction?
- Chloride suggested as contributor??



Poor pellet integrity results in fused pellets and reduced voidage

Water gas shift

LTS catalyst – highly active, strong robust catalyst

KATALCO 83-3X

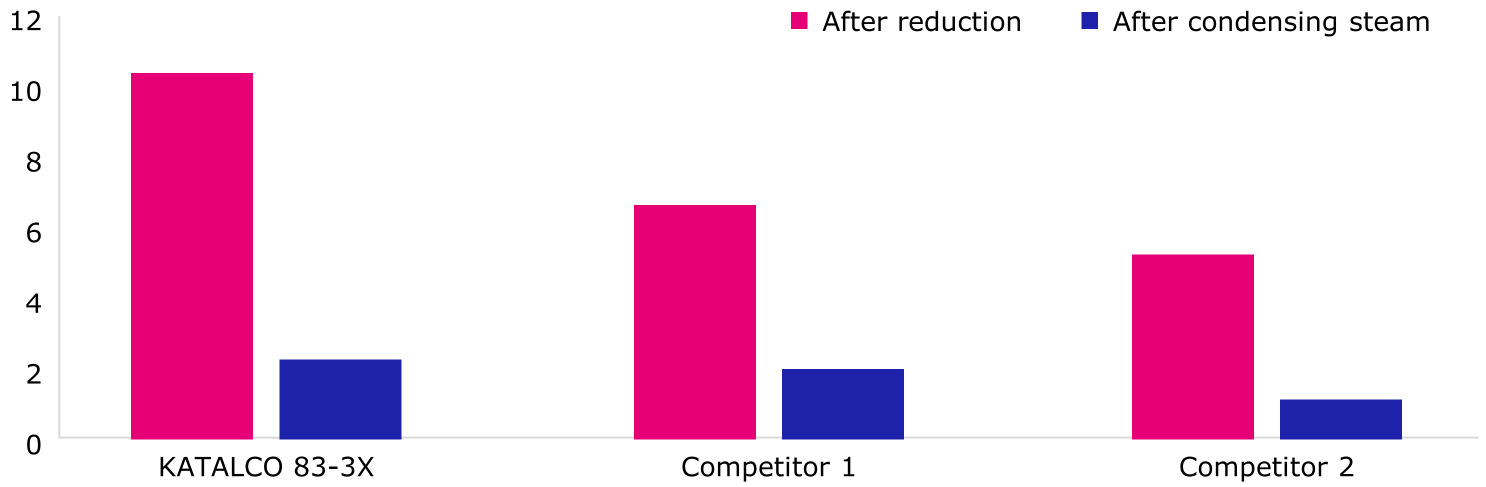
Robust LTS - optimum catalyst structure

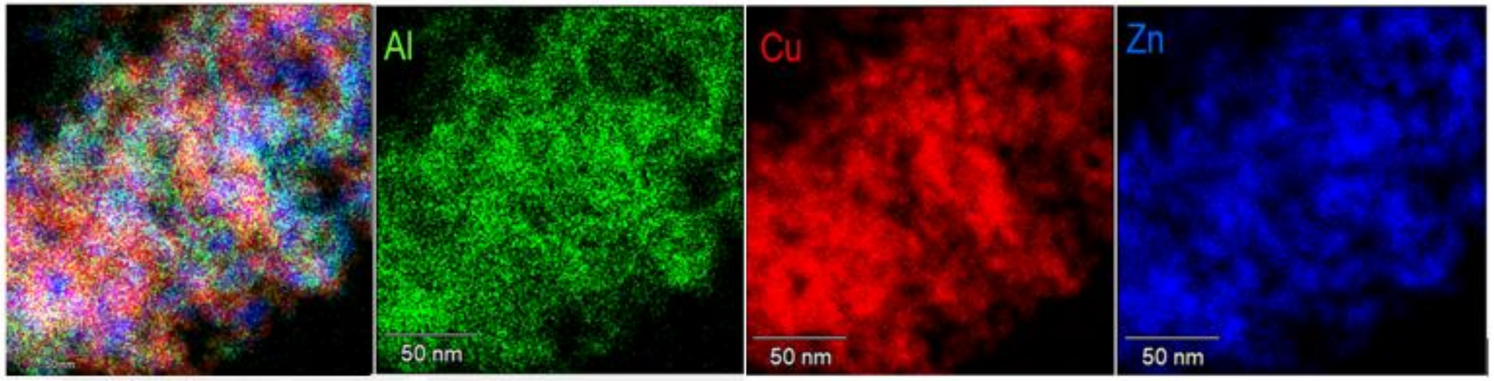
'Good skeleton' of Zn-Al refractory crystals

Supports Cu, provides intrinsic strength

Relative strength after simulated condensing incident

HGS (KgF)





Strength, Al, Zn

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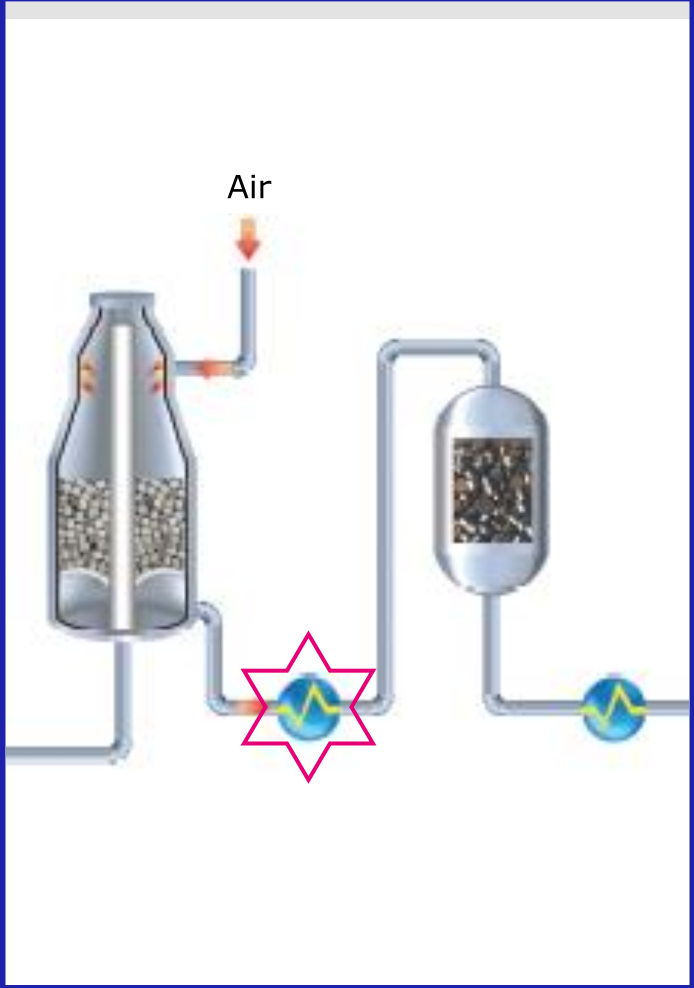
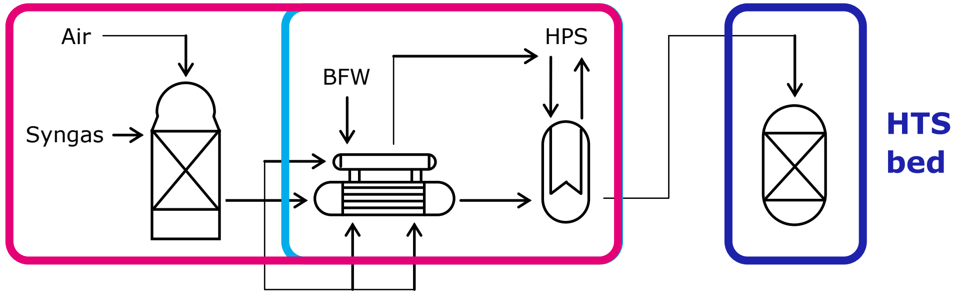
HTS challenging duty



Upstream HP boilers and superheaters

Upstream refractory systems



Issues

Wetting

Leaks

Fouling

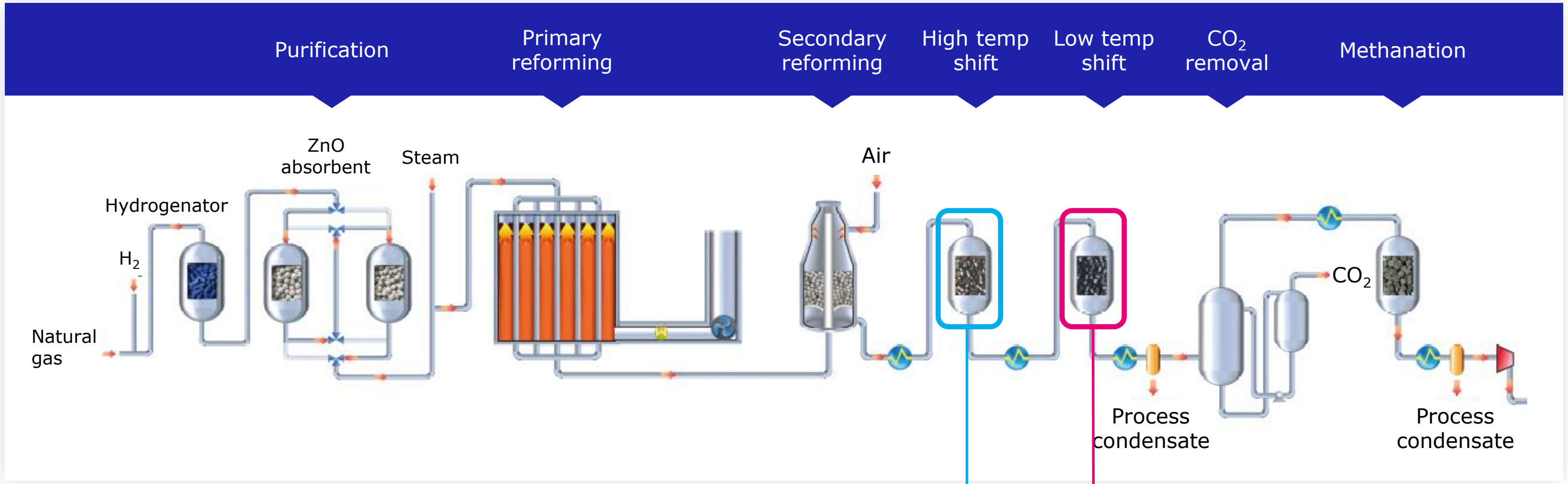
Refractory/metal dusting debris

Overreduction

Weakened pellet

Pressure drop solutions in WGS

Leading water gas shift solutions



HTS

Unique patented **F-shape**

Strongest HTS available

Lowest p.d. in-service

LTS

Market leading LTS

Strongest LTS available

Most stable p.d. in-service

Summary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Trusted solutions for the ammonia industry
www.matthey.com
Johnson Matthey
Inspiring science, enhancing life


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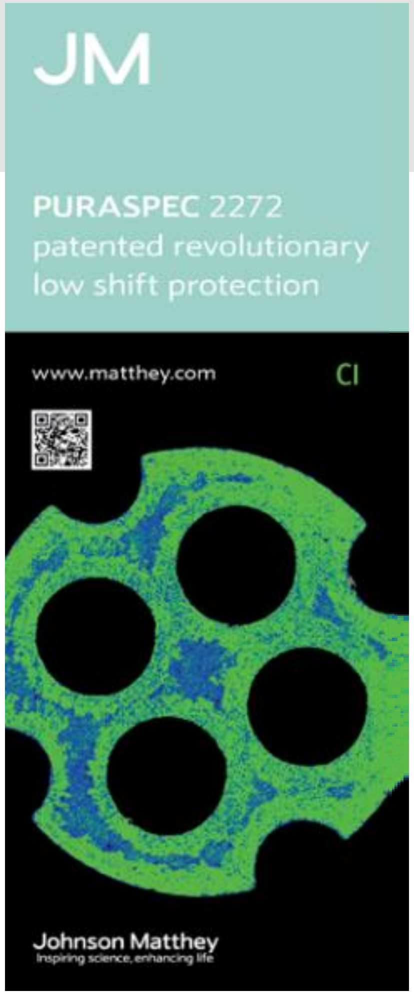
Shaped HTS for lowest PD & highest strength
www.matthey.com
Johnson Matthey


JM
Leading LTS stays strong lowest pressure drop
www.matthey.com
Johnson Matthey
Inspiring science, enhancing life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Reliable ammonia production has never been more important
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