Americas hydrogen and syngas technical training seminar

Water gas shift -low temperature shift and medium temperature shift

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Agenda

01 LTS reaction & chemistry

02 LTS & MTS Comparison

03 Catalyst features & challenges

04 Poisons & Methanol

05 Reduction

Water gas shift basics

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

Reversible reaction

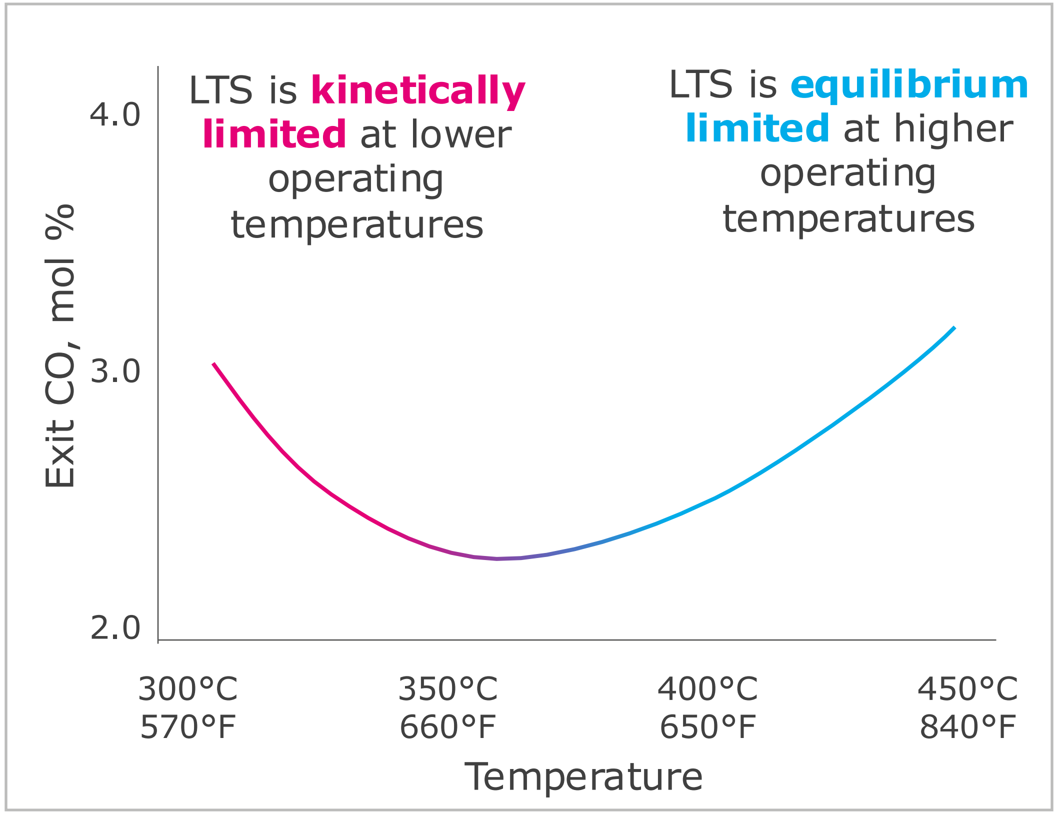
Exothermic (forward reaction)

- 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



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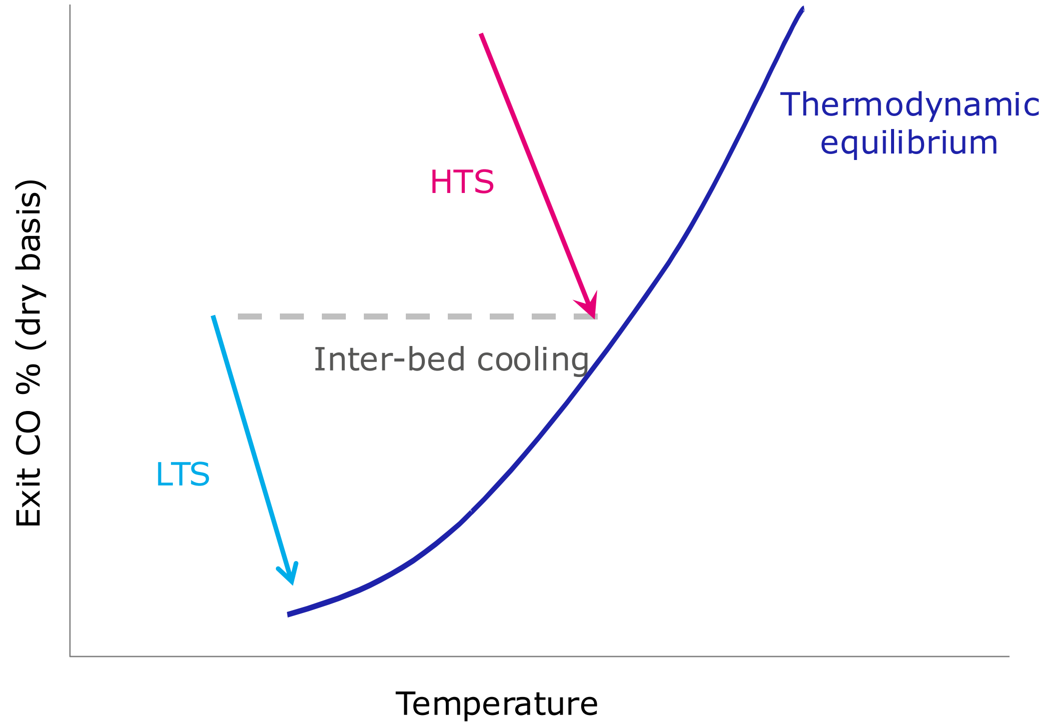
WGS equilibrium



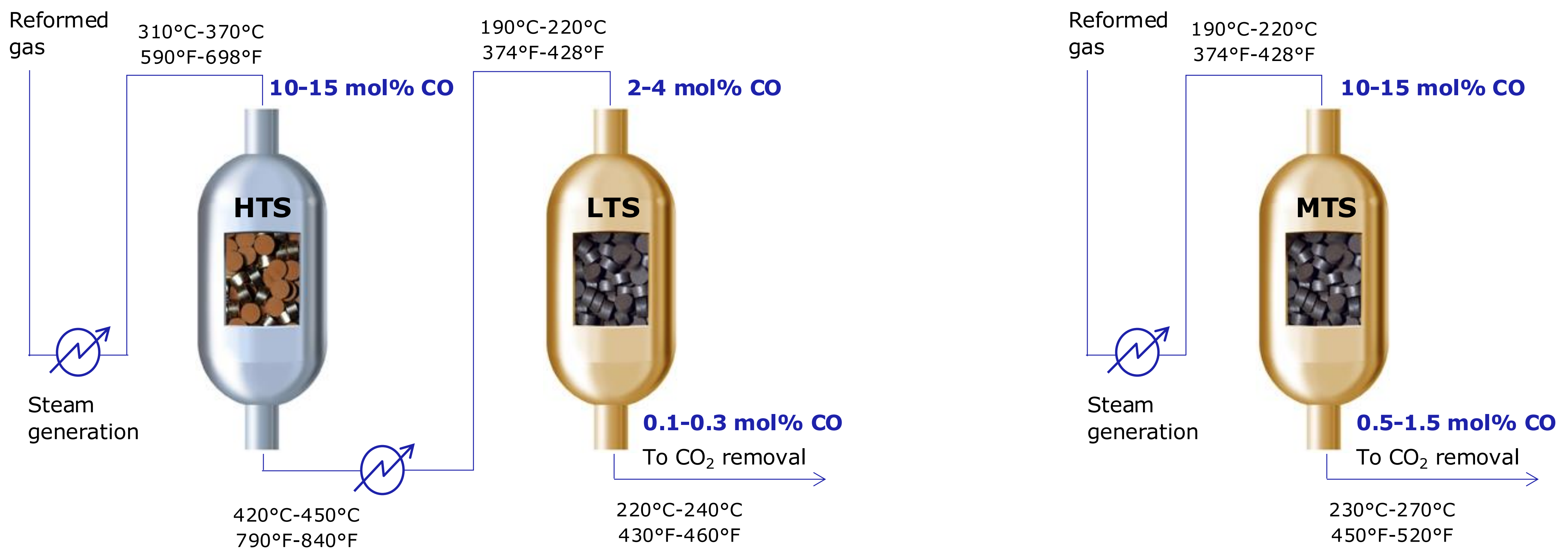
The WGS reaction is exothermic.

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

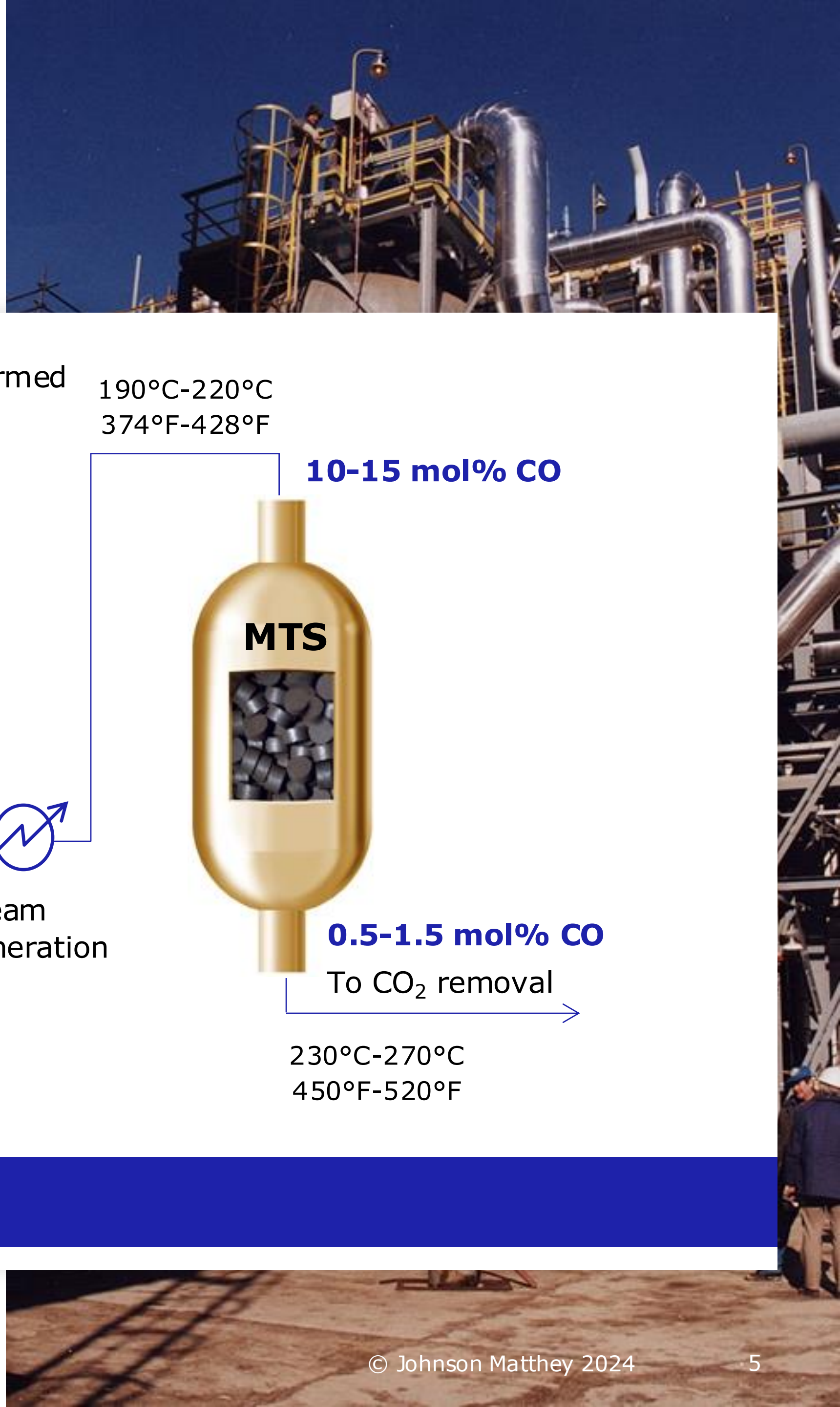
Higher conversion can be achieved by cooling the process gas, and reacting further to a lower equilibrium of CO.

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

LTS and MTS



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



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Advantages and disadvantages of MTS verses HTS in hydrogen plants

Advantages

Enabler for low steam:carbon ratio, avoids issues with over-reduction as faced with Fe based HTS catalysts

Reduction in feed rate (~3%) due to higher conversion lower CO slip, but a small increase in feed + fuel due to smaller PSA purge

Lower CO to PSA

Greater heat recovery in waste heat boiler to achieve lower inlet temperature, thus increased steam export

Disadvantages

More expensive heat recovery, larger BFW heaters required

CuZn based MTS catalyst is more expensive than Fe based HTS catalyst

Potentially shorter lives of CuZn MTS catalyst, as MTS catalysts are affected by both poisoning and sintering effects

Requirements to reduce the catalyst before putting into operation

More CO2 in the fuel gas

LTS/MTS

Catalyst features

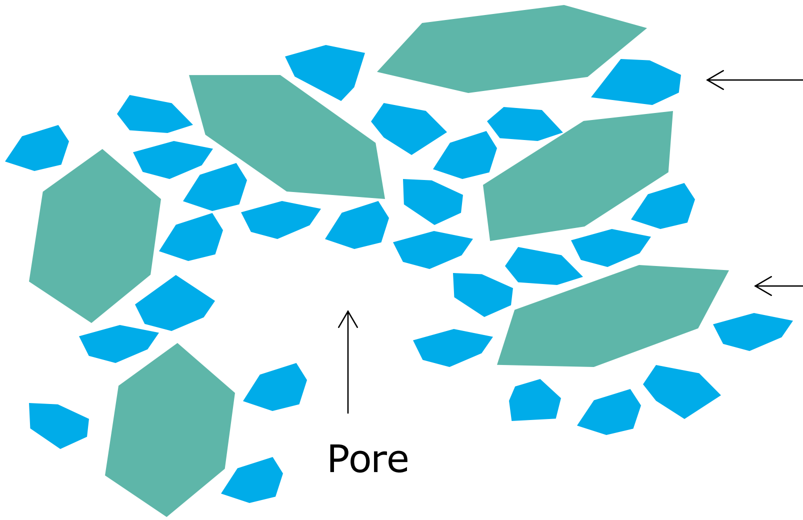
Cu/Zn/Al formulation

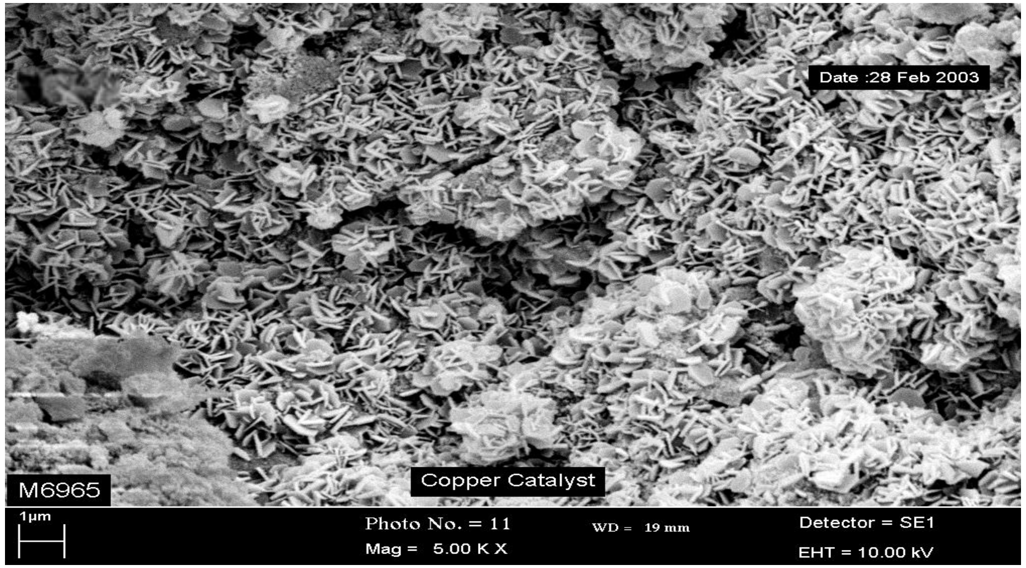
High and well dispersed Cu content

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



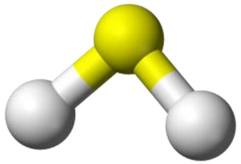


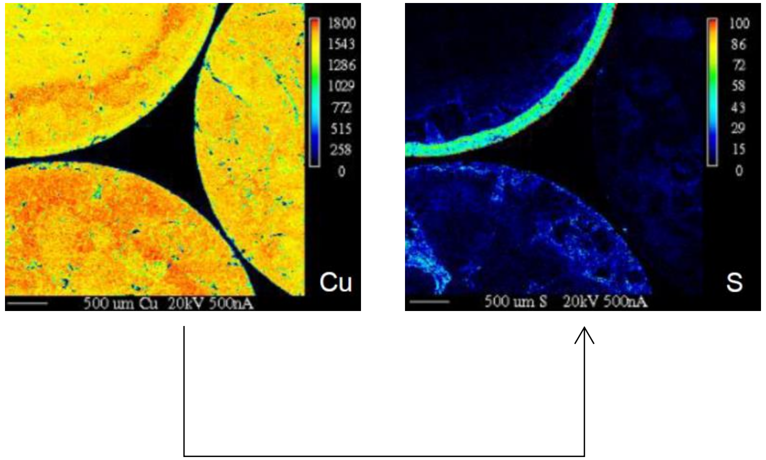
Common challenges with the LTS/MTS operation

Poisoning	• Poisons such as sulfur and chlorides in the feed can lead to faster catalyst deactivation. • Poisoning leads to frequent catalyst changes and unplanned shutdowns.
Pressure drop increase	• Pressure drop increase occurs from plant upsets such as wetting and condensation • Increased pressure drop can impact throughput
Condensate and wetting	• LTS and MTS generally operate with inlet temperatures close to dew point • Condensing on the bed can wash poisons into the bed
Increased methanol by-product formation	• At higher temperatures, by product methanol can be formed • This can lead to contamination of the vent gas and export CO…

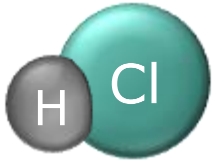
Two very different catalyst poisons

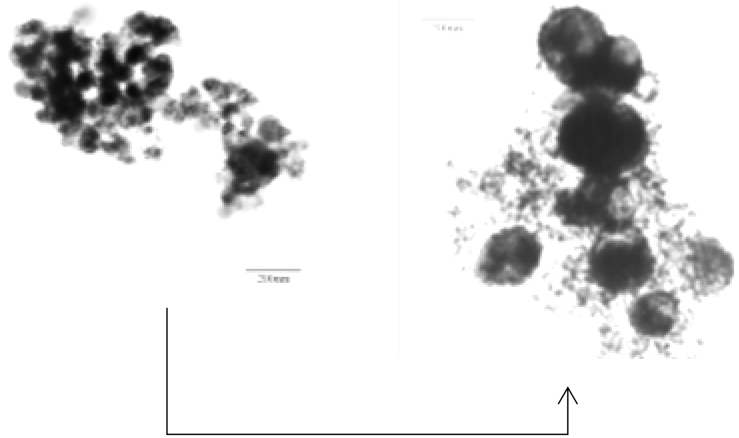
16
S
32.065





17
Cl
34.453





Feedstock

Process air

Insufficient purification

Lubricating oils

Water additives

Sulphur is the most common poison

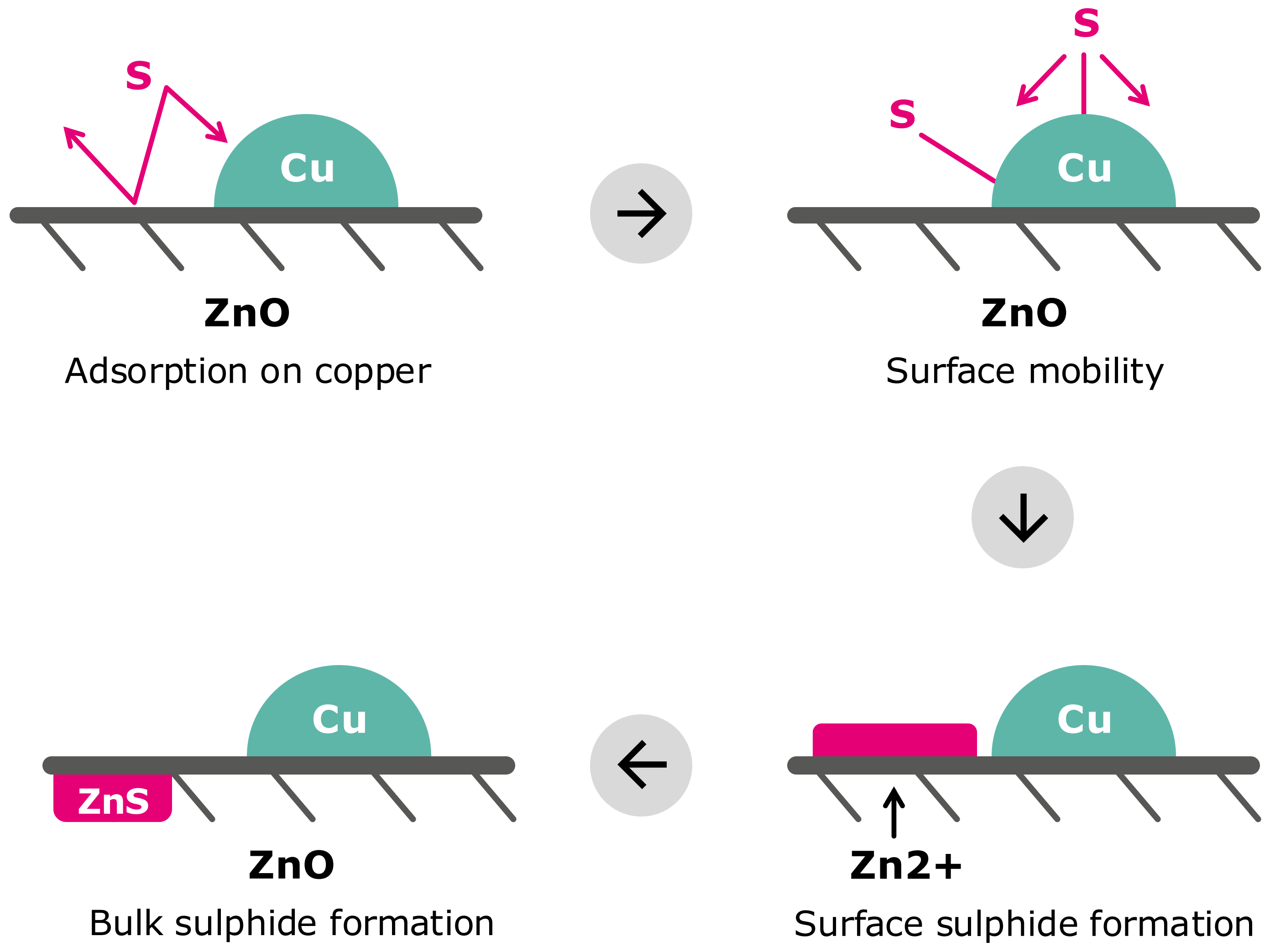
16
S
32.065

S reacts with Cu surfaces forming **CuS**

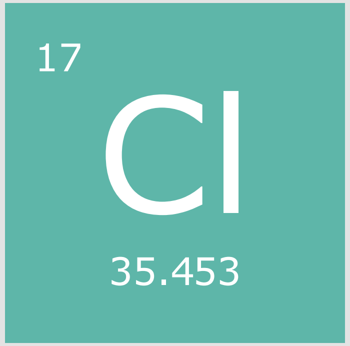
S surface **mobile**

ZnS thermodynamically stable

Bulk sulphide ZnS the stable endpoint within catalyst



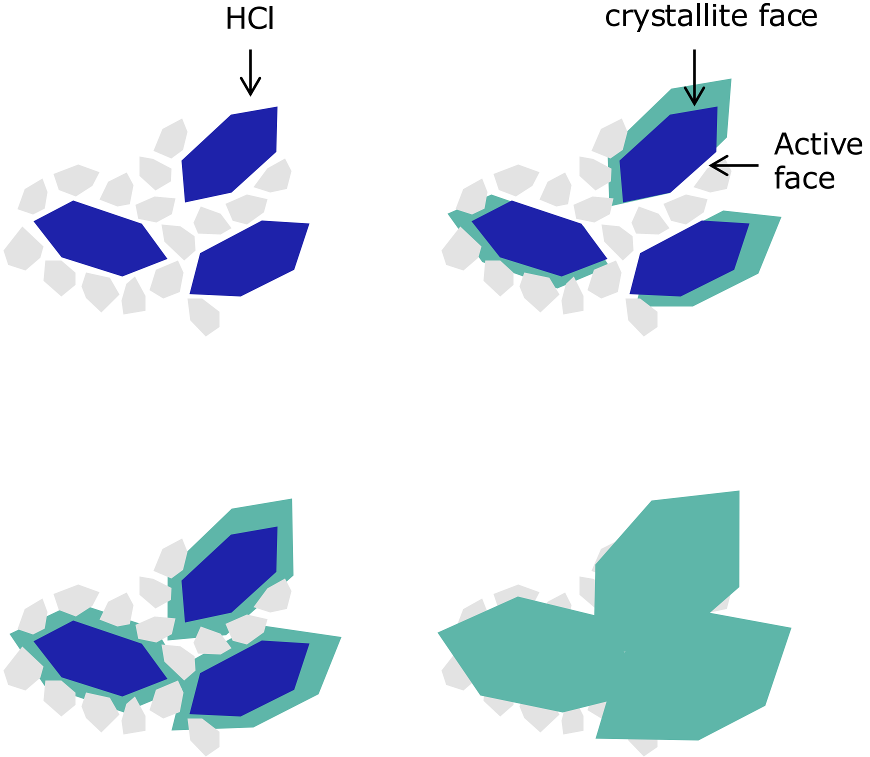
Chlorides strongly promotes sintering

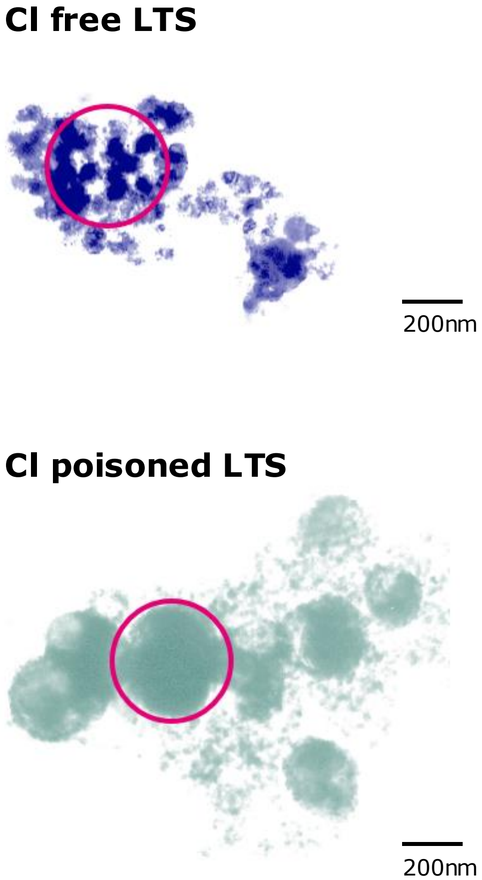


Cl forms **CuCl**

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

CuCl has **low melting point** promotes sintering





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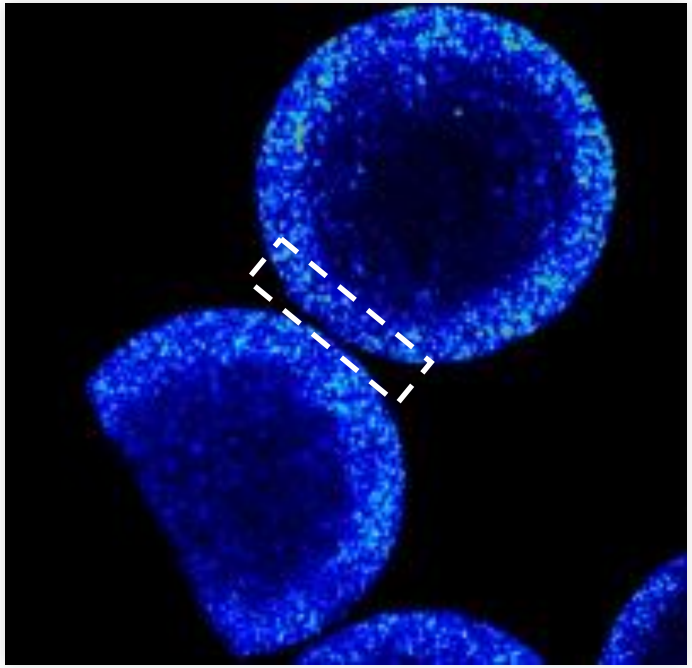
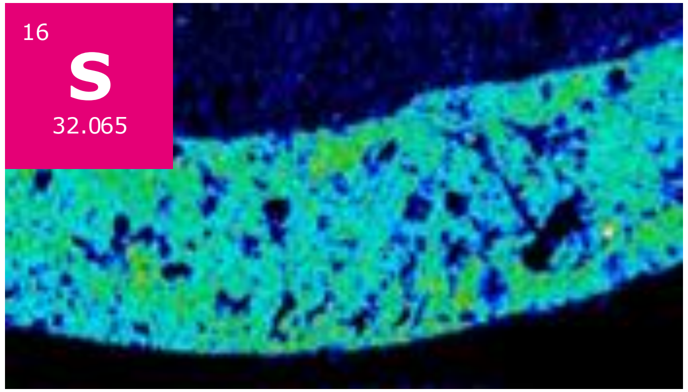
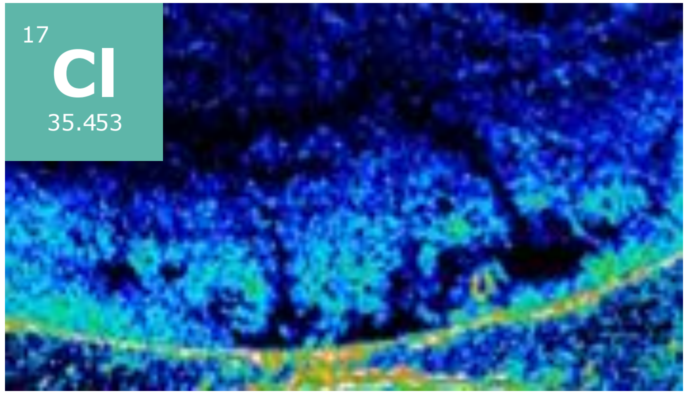
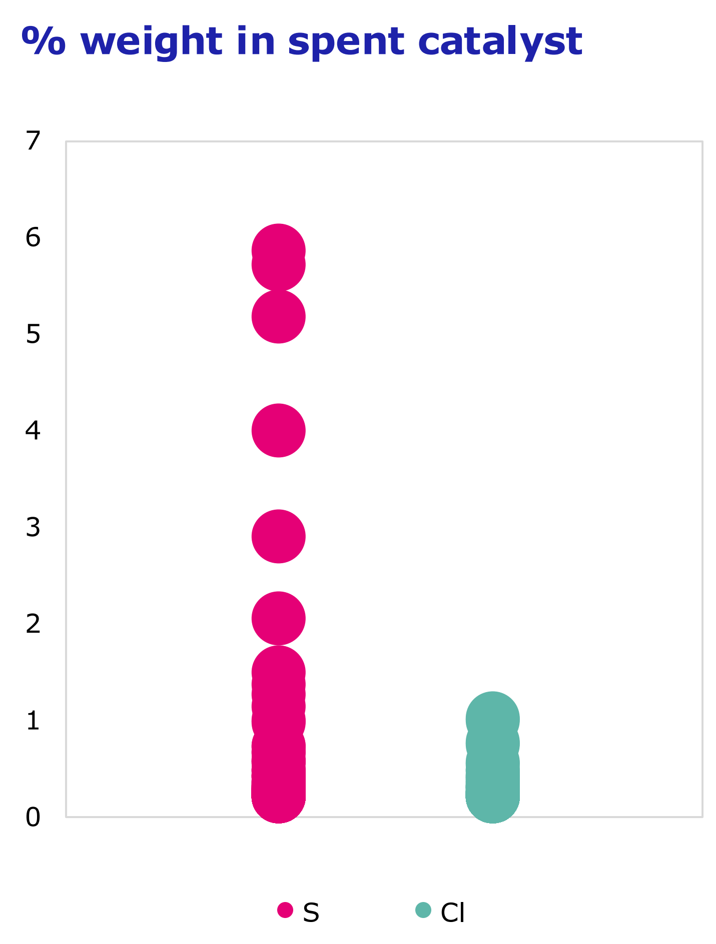
Self Guarding properties for S and Cl

Catalysts such **KATALCO** 83-3 and **KATALCO** 83-5 protect themself against poisons



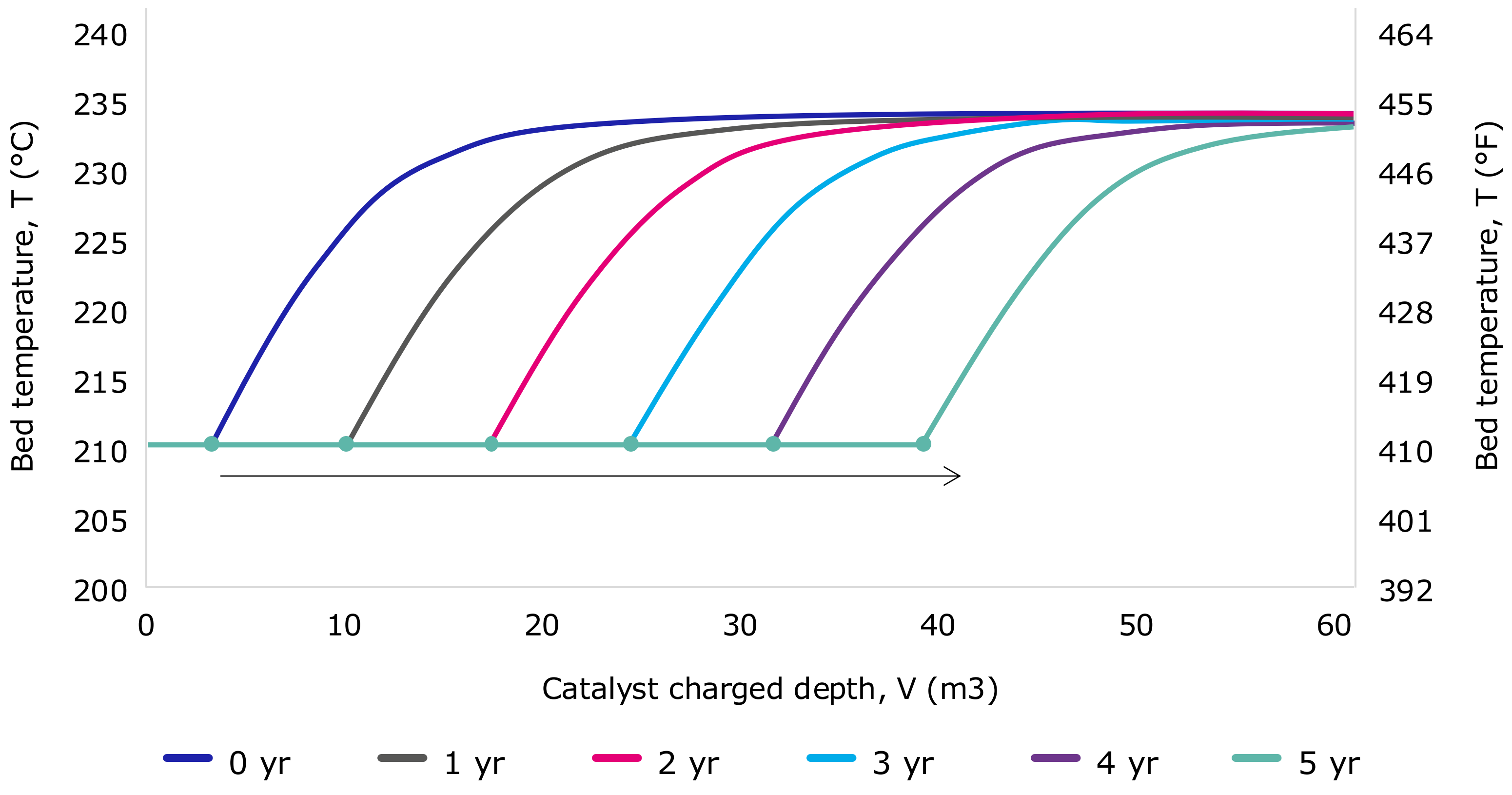






Catalyst poisoning

LTS poisoning profile



Useful life **largely governed** by poisoning

No reaction occurs in the **poisoned volume**

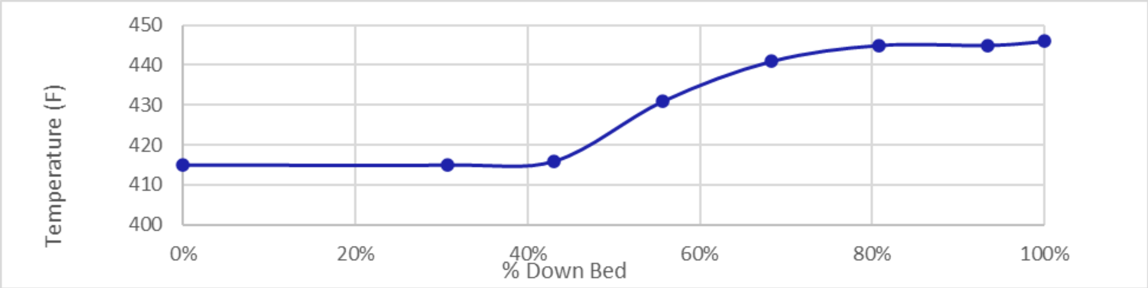
Poisons may be washed into the bed if **accidentally wetted**, which can impact performance

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

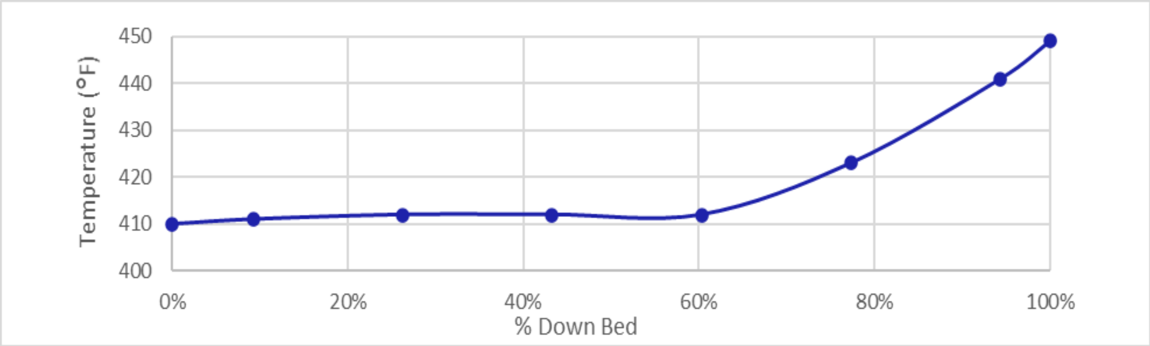
Thermal sintering may be observed in MTS or LTS units that are operated with long lives

Case Study: Longer lives due to self guarding properties of the catalyst

- Ammonia plant in North America with two similar Kellogg plants without guard
  - One plant: **KATALCO** 83-3
    - Lasted 4 years
  - Other plant: competitive catalyst
    - Needed replacement after 2.4 years due to high CO slip
- Operator saved US$700,000 in replacement costs compared to the previous competitive charge.



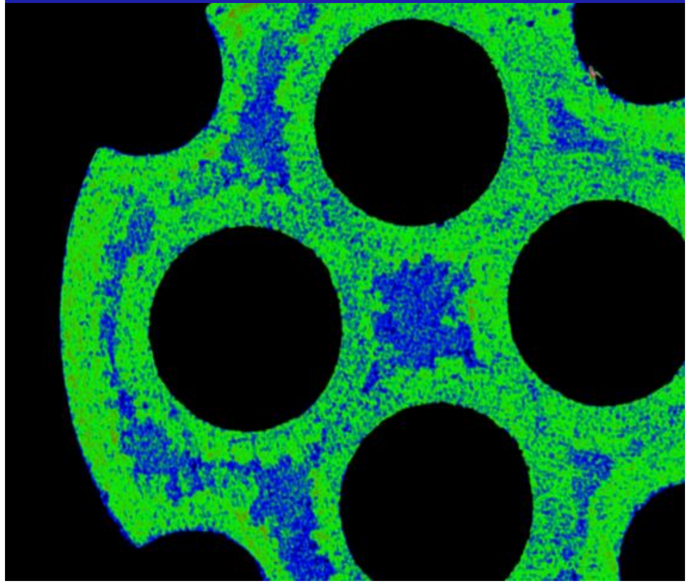
KATALCO 83-3 temperature profile after 3 years on-line

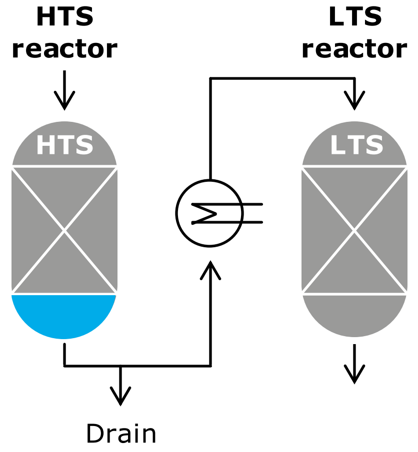


Temperature profile of competitive catalyst after 2 years on-line

Reducing risk of Cl poisoning and transient wetting

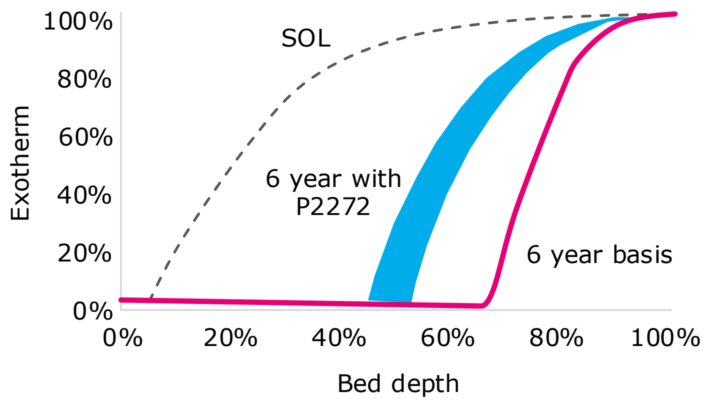
PURASPEC 2272:
Protection for Longer LTS Life



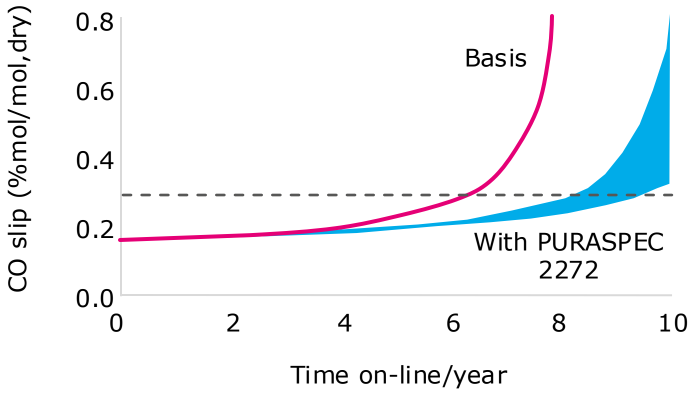


	HTS exit PURASPEC™ 2272	LTS inlet - traditional
Process	**450°C/840°F**	**195°C/380°F**
Dewpoint	180°C/355°F	180°C/355°F
Dewpoint margin	**270°C/484°F**	**15°C/27°F**
	No risk Cl migration	Risk Cl migration

Slower LTS deactivation

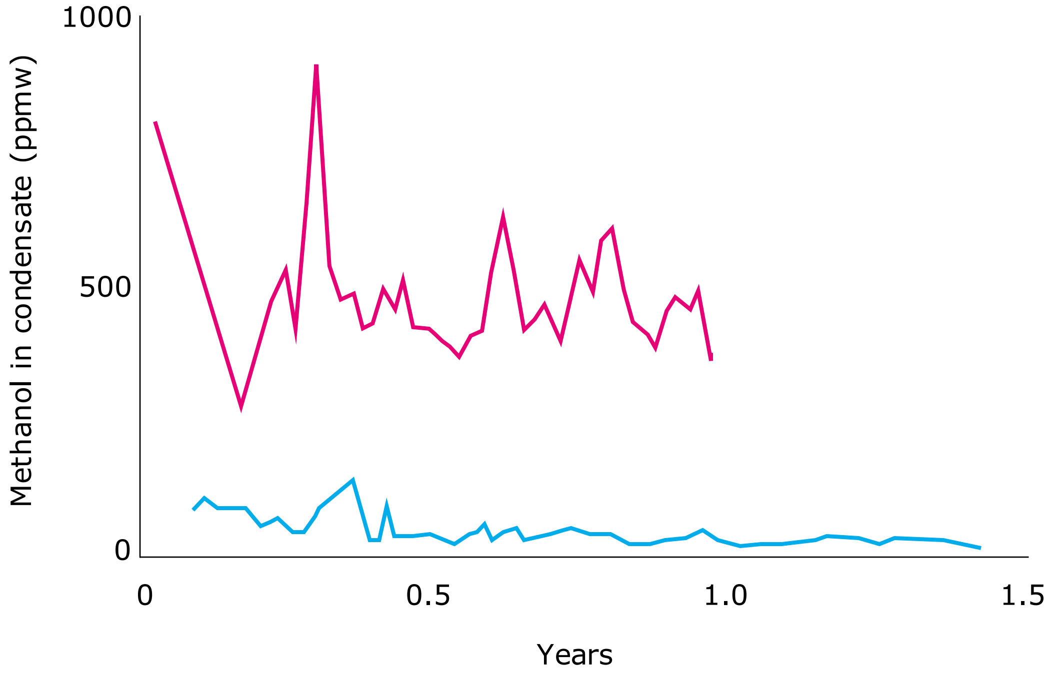


LTS life extension

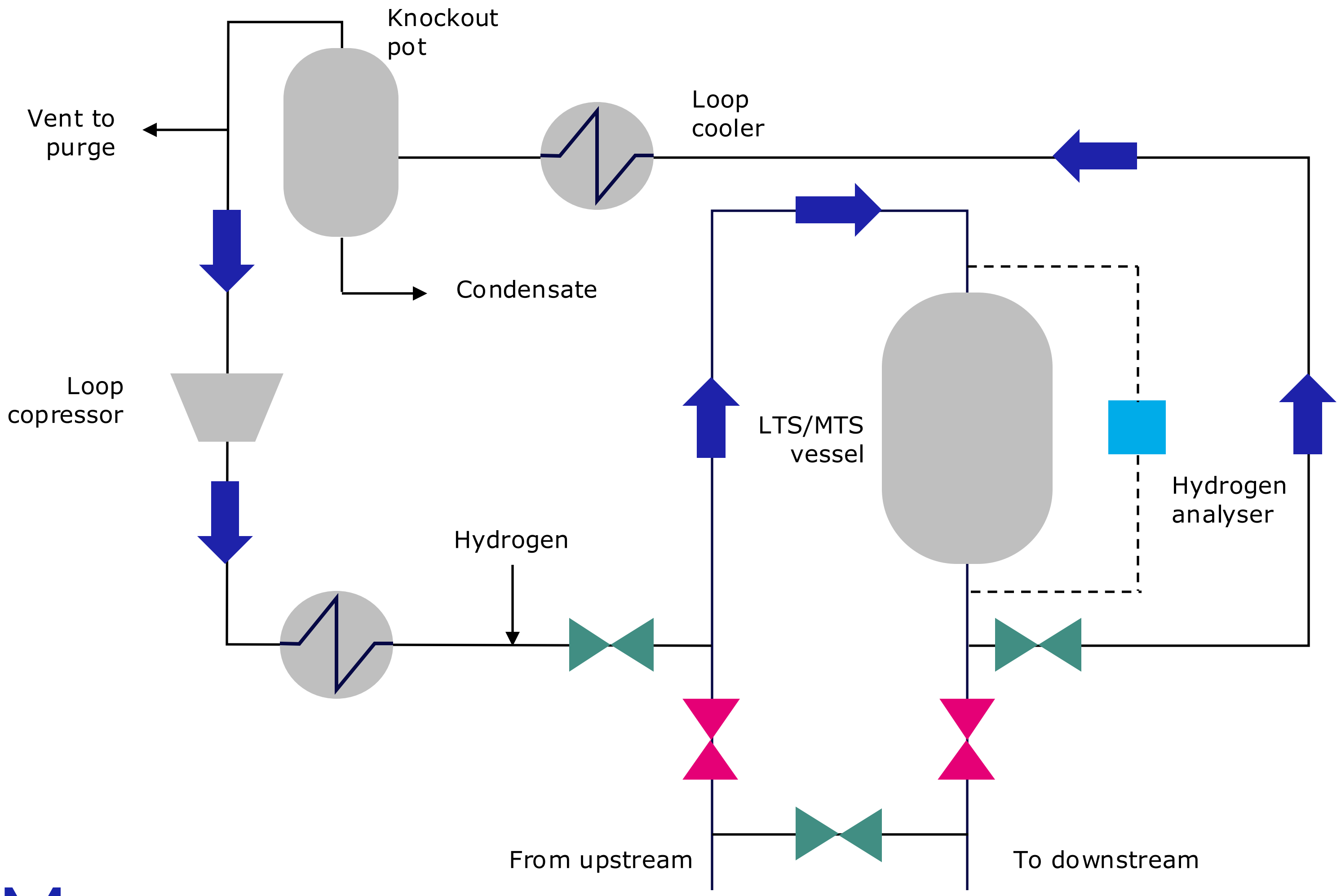


Byproduct methanol production can be an issue for some hydrogen and ammonia plants

- Methanol can be formed in the process condensate, especially at higher temperatures
  - Environmental issue
  - Process inefficiency
- Dedicated catalysts, such as **KATALCO** 83-3X, are formulated with promoters that have improved selectivity and **suppress methanol formation by up to 90% without impacting shift activity**
- Promoters are also effective at retaining trace poisons



LTS/MTS catalysts needs to be reduced before putting into operation



Catalyst is supplied in the oxidic phase and needs to be reduced to the active phase.

The reduction reaction of CuZn based LTS/MTS is very exothermic, hence it needs to be done under controlled conditions before putting into operation.

Important factors for reduction are:

- Good gas distribution, >300 $Nm^3/h/m^3$ of catalyst
- Good control and measurement of hydrogen addition
- Management of peak temperature, 230°C/450°F

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LTS and MTS catalyst activation

- Drain low points and purge lines
- Start inert gas flow/circulation
- Heat bed, normally 50°C/h (90°F/h)
- Test injection of hydrogen before strike temperature, typically below 100°C (210°F). Confirm good measurement and control of hydrogen.
- Slow heat rate as when bed gets to 120°C (250°F) to 25°C/h (45°F/h)
- With bed at 160°C, inject 0.5-1.0% hydrogen
- When temperatures stabilize, increase hydrogen to 2.0-2.5%, do not exceed maximum bed temperature of 230°C (450°C)
- Water produced by reaction must be drained from loop
- Reduction will pass through bed, reduction complete when no more reaction and no more hydrogen being consumed, normally reduction takes 36 hours
- Preference for soak after completion, ~4 hours

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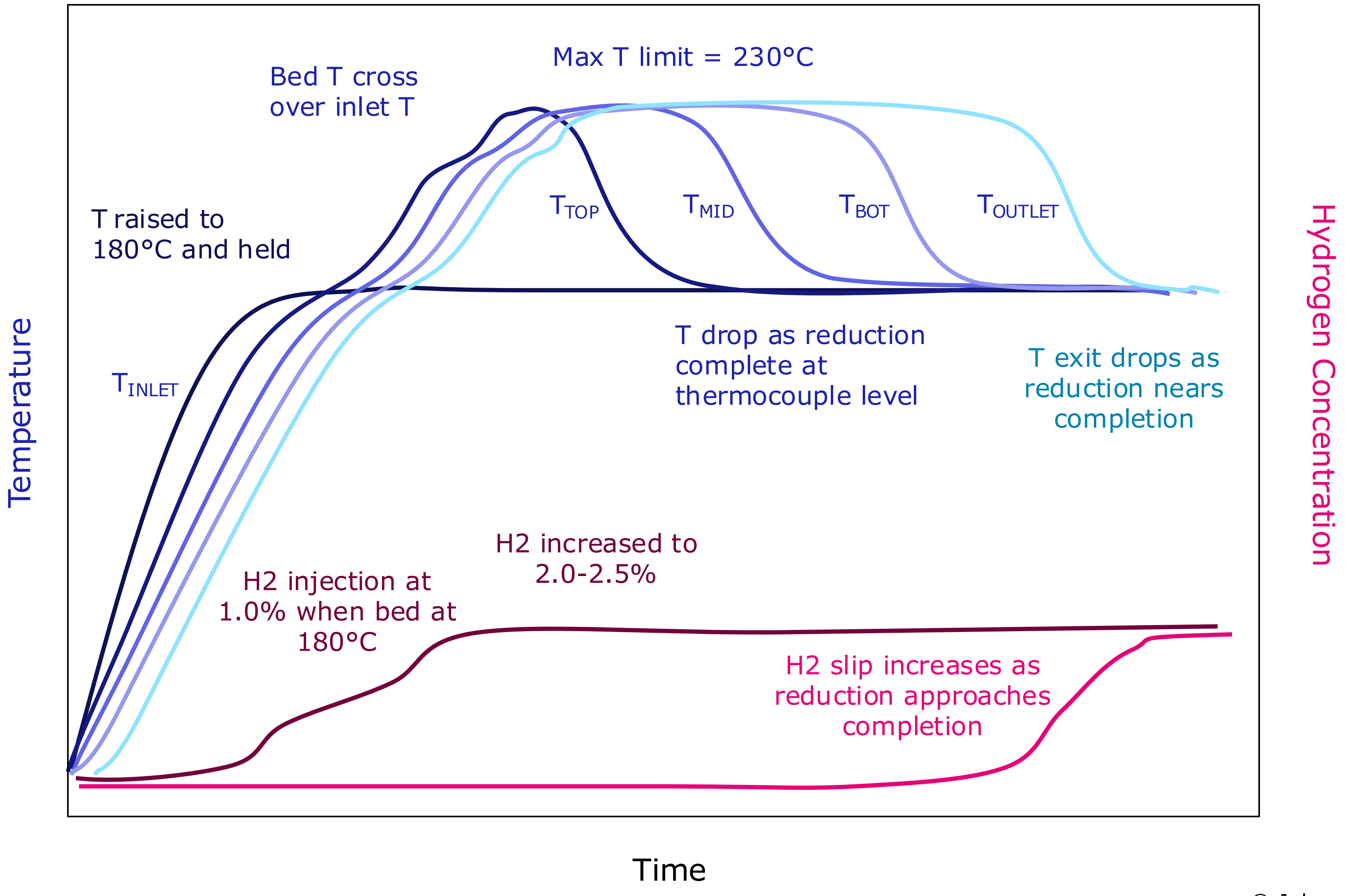
LTS/MTS catalyst reduction monitoring



Summary

- LTS/MTS enable more hydrogen production through the water gas shift reaction
- The reduction reaction of the CuZn based LTS/MTS catalyst is very exothermic, and hence needs to be done under controlled conditions before putting the bed into operation.
- The main deactivation mechanism for LTS/MTS is poisoning.
- Regularly monitoring the rate at which the top of the bed is being deactivated through poisoning is good practice.
- Due to the low operating temperatures, care is needed to avoid condensing on the bed. Wetting the catalyst can wash poisons through the bed and impact performance.
- Promoted catalysts reduce byproduct methanol formation.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