Johnson Matthey
Inspiring science, enhancing life

Americas hydrogen and syngas technical training seminar

Feedstock purification

Dimitri Trufanov

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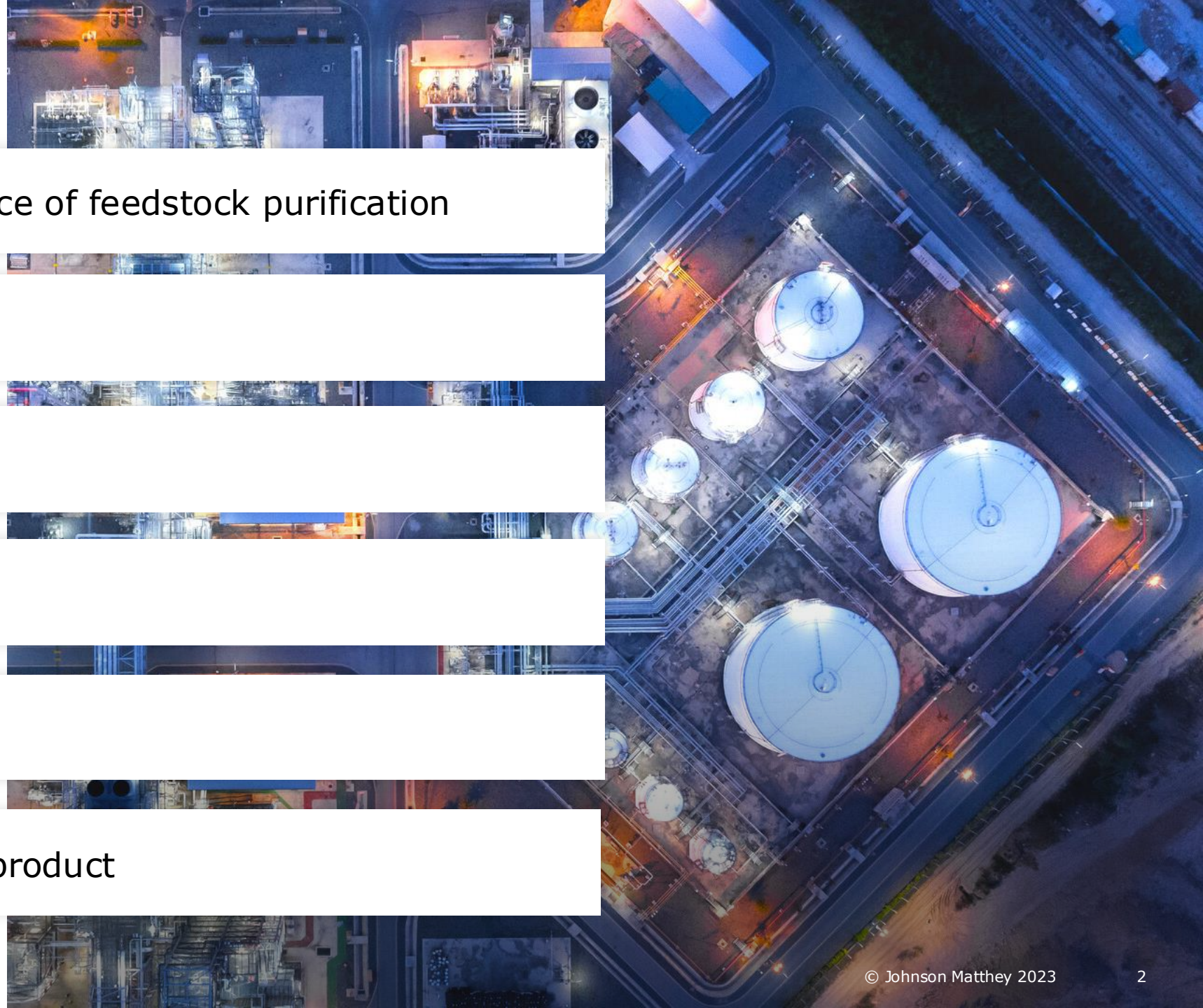

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Importance of feedstock purification

Preventing equipment damage and protecting catalyst lives

Impurities in a syngas plant feed can cause issues:

- sensitive catalysts can be poisoned (deactivated)
- **production constrained** due to decreased catalyst activity and shorter life
- equipment **contamination / corrosion** impacts process and safety
- some species can lead to unexpected **exotherms** and vessel failure
- unplanned **downtime**

Most affected catalysts:

- pre-reforming,
- steam reforming (SMR), and
- medium/low temperature shift

SMR hot spots caused by poisoning

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Purification challenges depend on hydrocarbon feed type

Type	Composition	Poisons	
NG / LNG	Mainly CH_4, small amount of C_2, C_3, N_2 and CO_2	S level:	Low (typically 2-20 ppmv)
		Type:	Usually simple (mercaptans; H_2S)
		Other:	Olefins and COS
NG Condensates or LPG	Similar to NG, with higher levels of heavier hydrocarbons	S level:	Low
		Type:	COS, H_2S
		Other:	Chlorides
Naphtha	Light straight run through to cracked heavy naphtha	S level:	High (typically 100-200 ppmw)
		Type:	Can be difficult (thiophenes)
		Other:	Chlorides, olefins and metals
Refinery Off Gas	Hydrogen rich feed, potentially higher levels of unsaturated hydrocarbon	S level:	Depends on source
		Type:	Can be difficult (thiophenes)
		Other:	Chlorides, olefins and acetylenes

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Selecting the right purification stages to meet your requirements

Hydrocarbon purification requirements vary depending on the feed and flow scheme

Feed

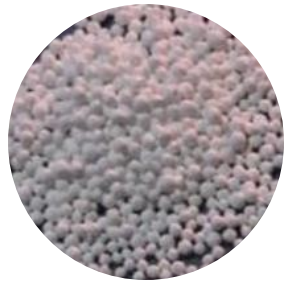
+

hydrogen

HDS

KATALCO
41- and 61-series

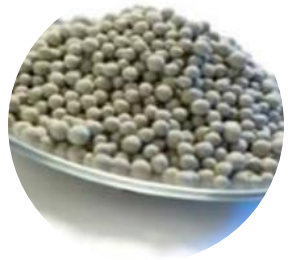
Converts organo-S, organo-Cl and olefins



HCl absorption

KATALCO
59-series

Removes HCl by chemical reaction



H_2S absorption

KATALCO
32-series

Removes H_2S by chemical reaction

Ultra-purification

PURASPEC™ solutions,

KATALCO
79-series

Polishes out trace sulfur

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The first layer of defense

Hydrodesulfurization (HDS) solutions

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Selecting the right purification stages to meet your requirements

Hydrocarbon purification requirements vary depending on the feed and flow scheme

Feed

+

hydrogen

HDS

KATALCO
41- and 61-series

Converts organo-S, organo-Cl and olefins

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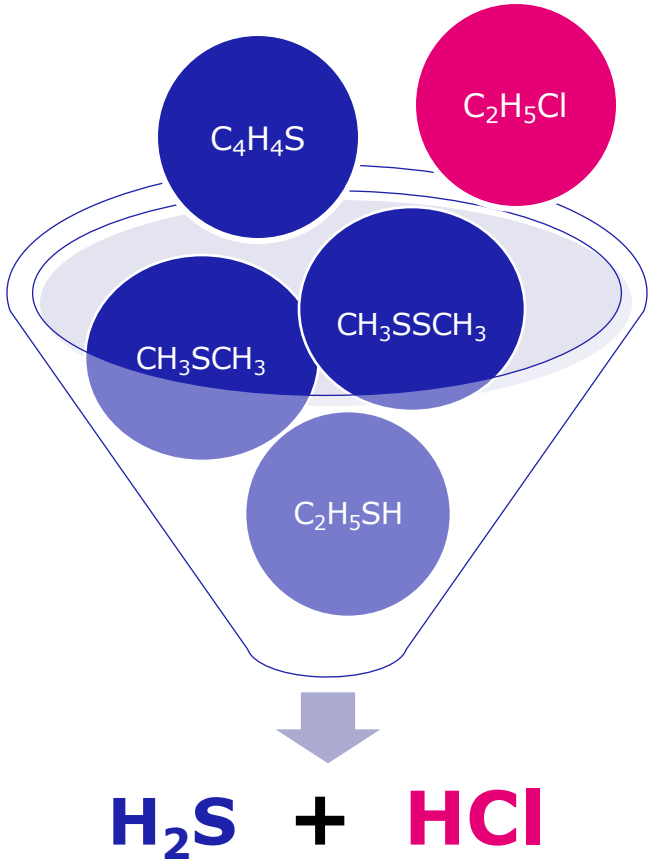
Simplifying the poison with hydrodesulfurization

KATALCO HDS catalysts converts a wide range of organo-compounds to H_2S and HCl



- Organic sulfur compounds are not readily absorbed by ZnO
- **Organic sulfur and chloride compounds are severe poisons** to sensitive downstream catalysts
  - Pre-reforming catalyst
  - Primary reforming catalyst
  - LTS catalyst
- Converting organic sulfur to H_2S is beneficial. H_2S is absorbed by ZnO
- Organic chlorides are also converted to HCl, which can then be absorbed by the chloride guard

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Converting organic components for ease of removal

Organic sulfur removal

Organo-sulfur + H_2 → H_2S + Hydrocarbons

Organic chloride removal (if present)

Organo-chloride + H_2 → HCl + Hydrocarbons

Common HDS catalyst solutions

CoMo and **NiMo** catalysts are used in most syngas HDS duties

CoMo is more common and more **cost effective**

NiMo is preferred for elevated **olefin** levels and high **carbon oxides**:

- MeOH plants with CO_2 recycle / addition before HDS
- Plants with high CO_2 levels in natural gas feed
- Feeds with higher olefin levels

Typical composition	**CoO or NiO** 4 wt%	**MoO_3** 12 wt%	**Alumina** balance
General form	2.5 mm diameter shaped extrudate		
Features	High porosity for high activity		

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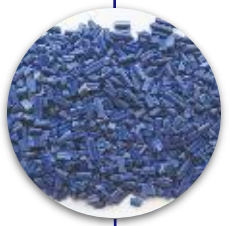
Johnson Matthey portfolio of HDS solutions

HDS catalyst selection

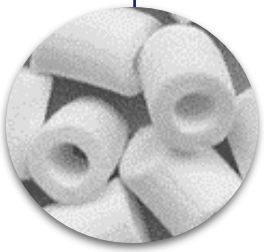
Ni Mo

Co Mo



KATALCO 61-1T

Designed for feeds with high COx and hydrogen (risk of methanation)



KATALCO 61-3N

An option for beds which are at risk of fouling from carbon

KATALCO 61-2F

Higher activity catalyst for low temperature applications and undersized units

KATALCO 41-6T

Standard HDS catalyst suitable for most applications

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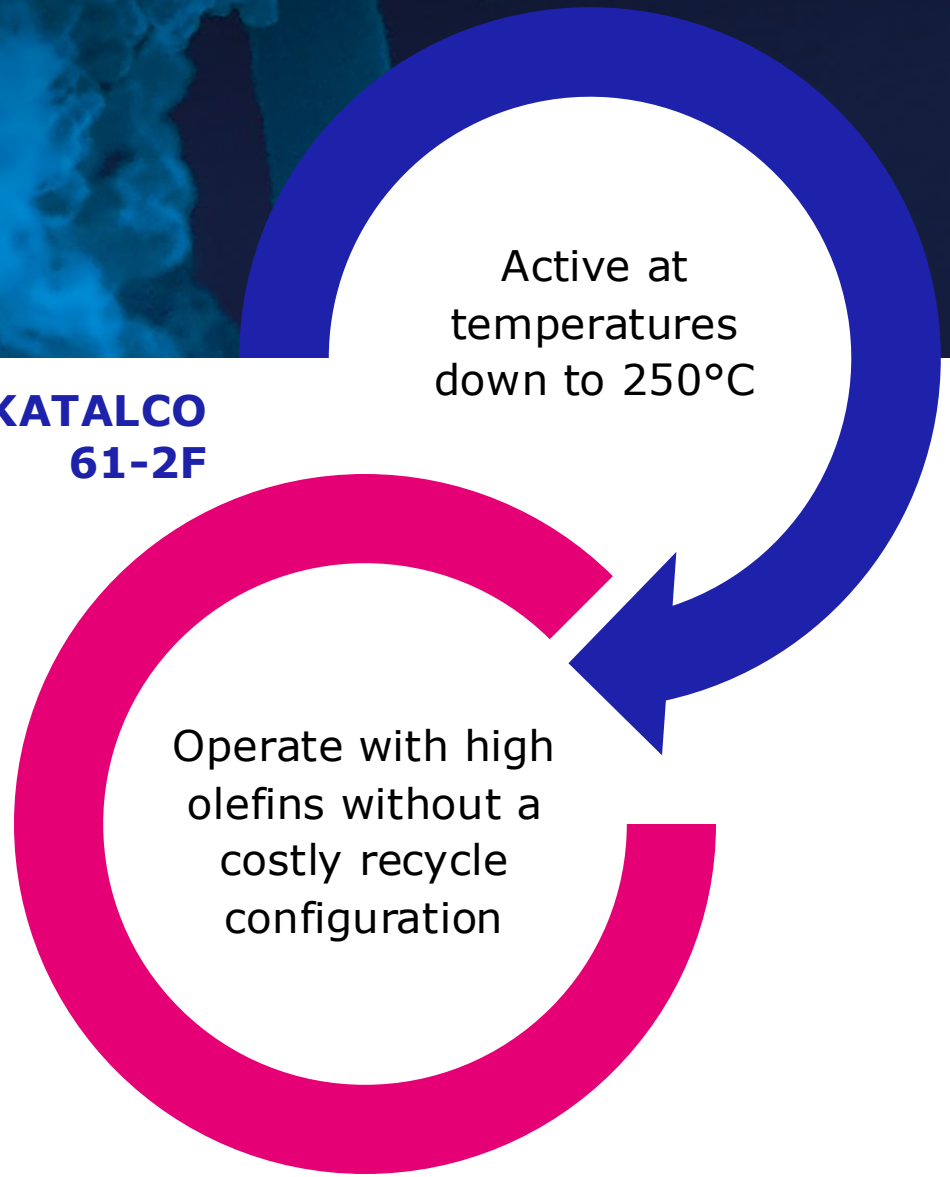
Case study: Managing high olefins without costly recycle systems

Lower temperature operation with KATALCO 61-2F

Standard HDS	
Inlet temperature	300°C/570°F
Olefins in feed	5.1 mol%
Exotherm	100°C/180°F
Exit temperature	<400°C/750°F
Feed required to be recycled back	**44%**

KATALCO 61-2F	
Inlet temperature	250°C/480°F
Olefins in feed	5.1 mol%
Exotherm	150°C/270°F
Exit temperature	<400°C/750°F
Feed required to be recycled back	**0**



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Gradually declining performance of a resilient catalyst

Causes of HDS deactivation

- Carbon fouling
- Carbon formation
- Iron scale
- Heavy metals
- Sintering

Rising pressure drop, channelling of gas flow, and catalyst deactivation can result in lower feed rates or cause the premature slip of impurities

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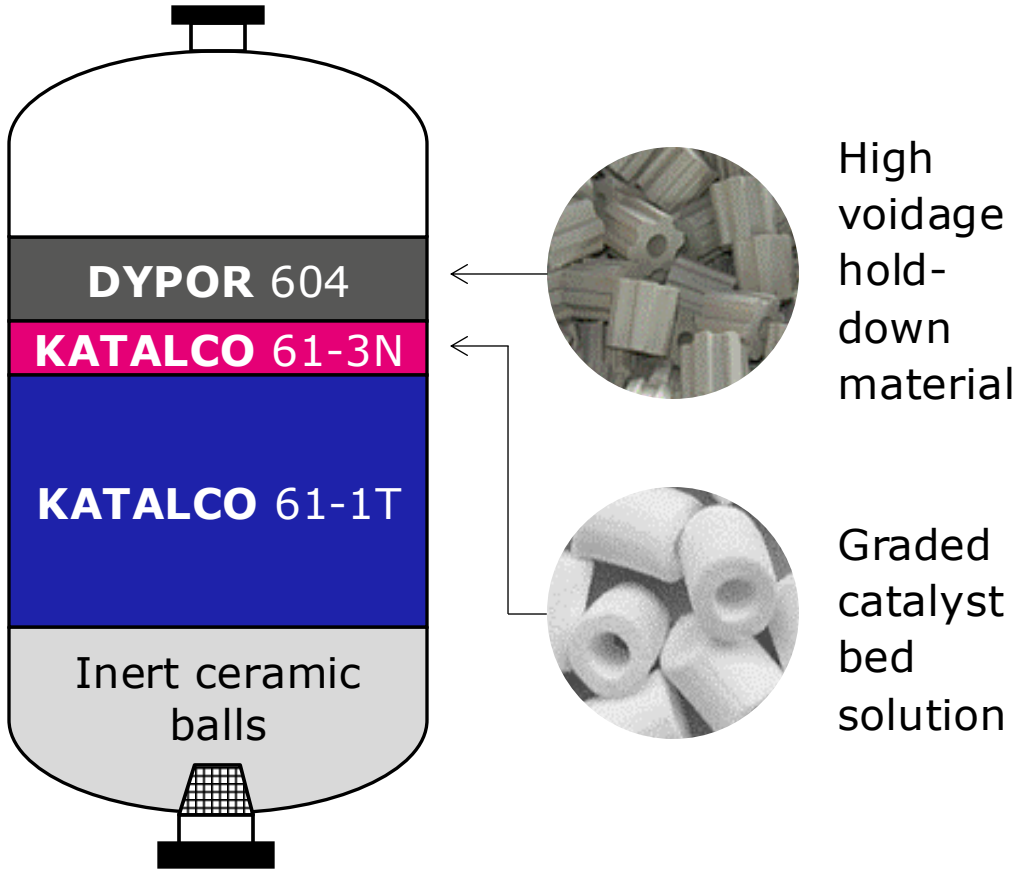
Handling fouling and increased bed pressure drop

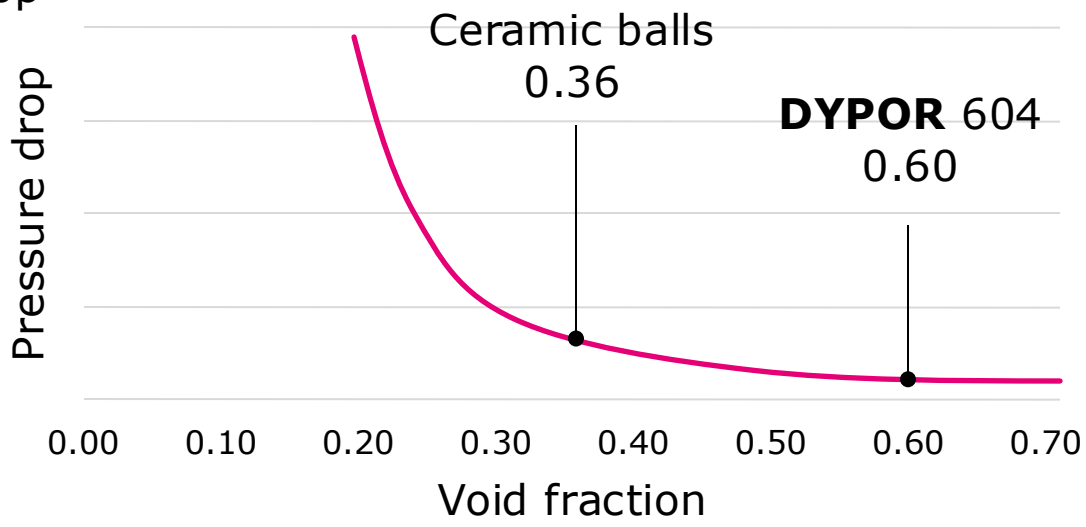
Tailored catalyst and support loading to maximize long-term performance

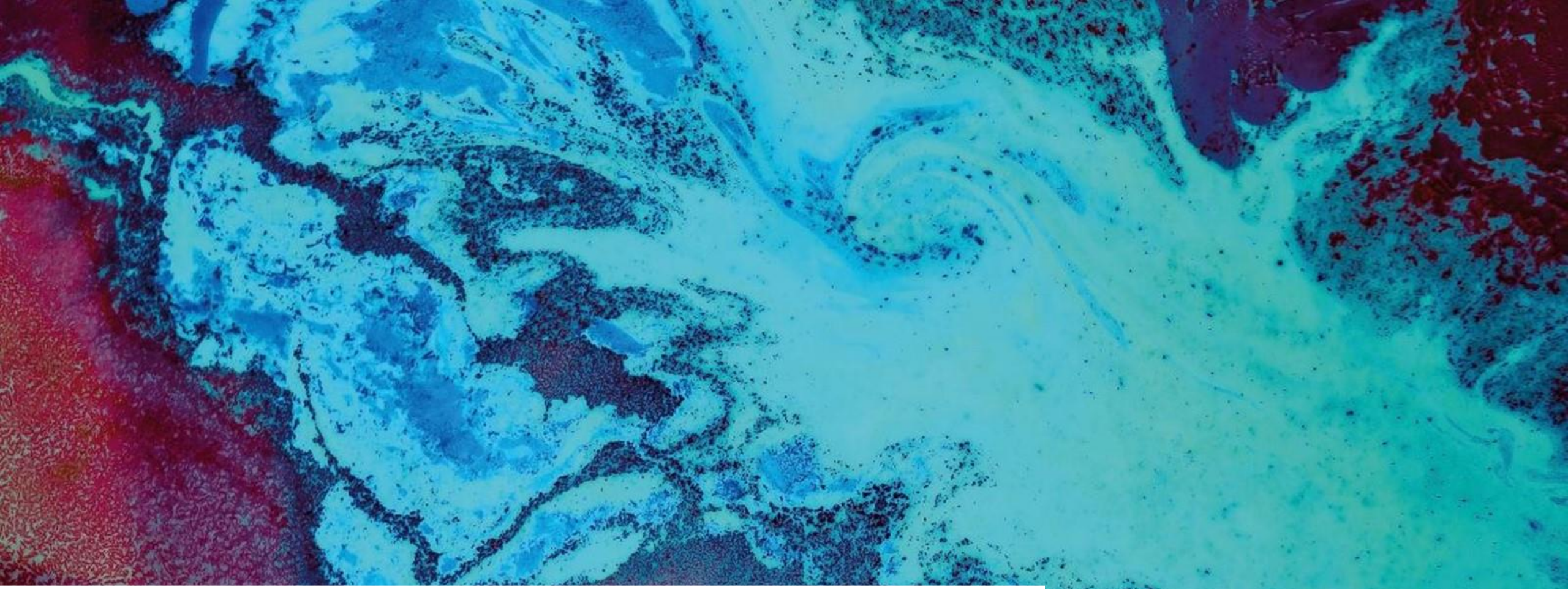


1. Ceramic balls as hold-down material:

Fouling => reduction in voidage => **rapid increase of dP =>** limit throughput

2. Shaped hold-down material with higher voidage, such as **DYPOR** 604, helps maintain a low pressure drop





Protecting against the corrosive impacts of chlorides

Cl removal absorbents

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Protecting against the corrosive impacts of chlorides

Feed

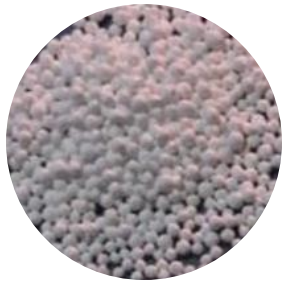
+

hydrogen

HDS

KATALCO
41- and 61-series

Converts organo-S, organo-Cl and olefins



HCl absorption

KATALCO
59-series

Removes HCl by chemical reaction

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Chlorides (halides) are a severe poison for downstream catalysts

Molecular: increased rate of sintering

Catalyst: The downstream shift Cu-based catalysts scavenge chlorides very effectively and get poisoned

Equipment: HCl (especially in the presence of water) cases corrosion in existing metal pipework

Economics: Incremental production loss due to lower water gas shift efficiency

- Chlorides are highly mobile at the reforming operating temperatures
- Chlorides migrate as far as the Cu-based shift catalysts (or methanol synthesis catalyst)

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Why not use ZnO for Cl removal?

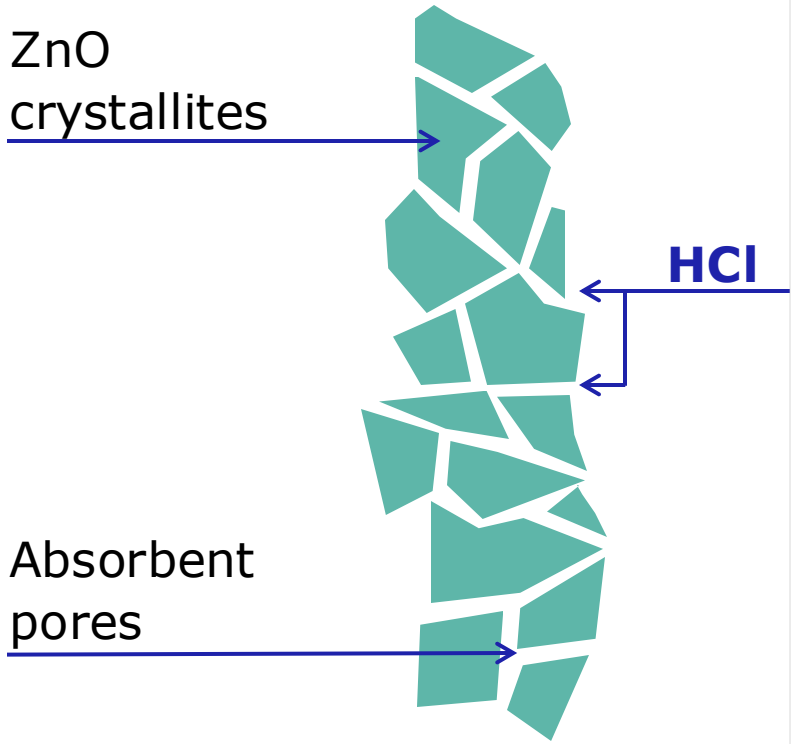
Weakens H_2S absorbent ($ZnCl_2$ sublimes at operating temperature)

Possible downstream Zn and Cl contamination

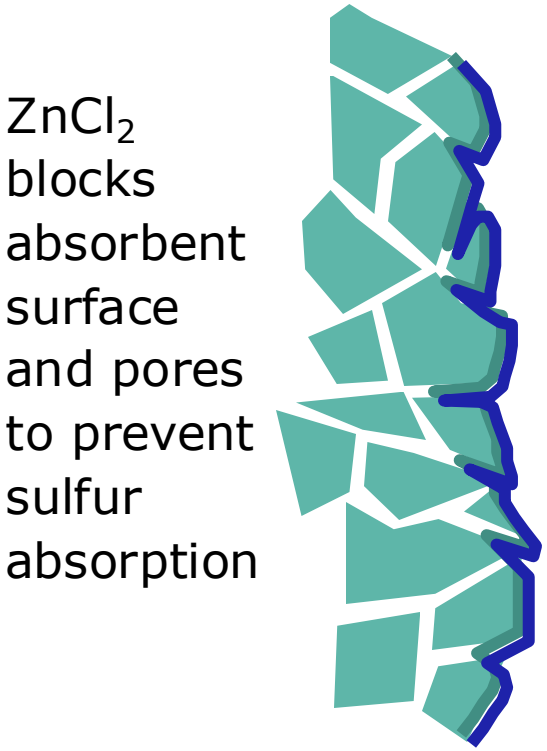
Potential Cl slip

Significant loss of ZnO capacity for sulfur

1 Fresh ZnO

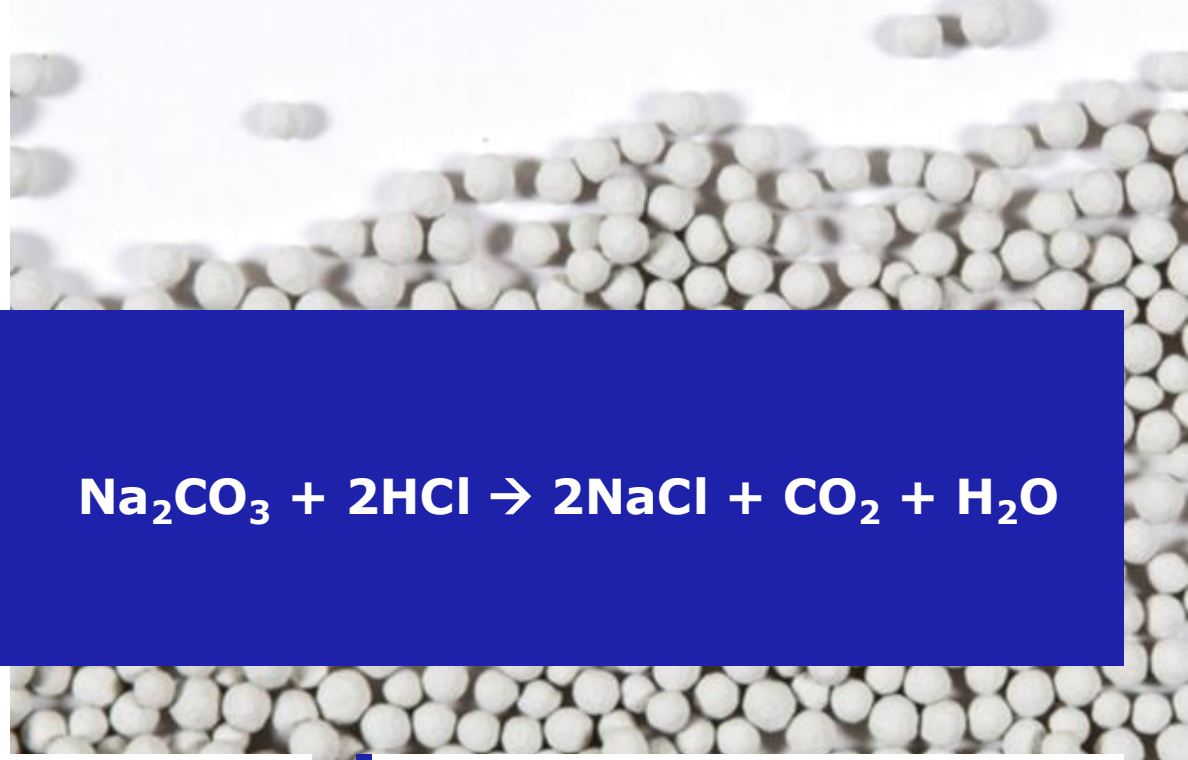


2 Poisoned



Introducing KATALCO 59-4

Designed for cost-effective HCl removal



KATALCO 59-4 is a proprietary chemical absorbent which contains an optimized level of alkali promoter to **lock up** chloride via an irreversible reaction:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

Low and stable pressure drop due to high particle strength

Cost effective chloride removal

Reliable performance and long predictable lives

Excellent performance over a wide range of operating conditions, between 480°F and 750°F

Chloride removal to **very low levels**, <0.1 ppmv

Simple to install and **operate**

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Effective removal of H_2S from feeds

ZnO for H_2S removal

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Effective removal of the most common impurity: H_2S

Feed

+

hydrogen

HDS

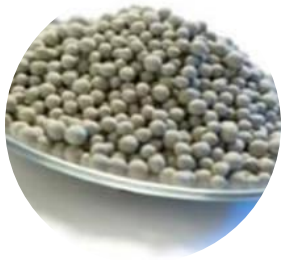
KATALCO
41- and 61-series

Converts organo-S, organo-Cl and olefins

HCl absorption

KATALCO
59-series

Removes HCl by chemical reaction



H_2S absorption

KATALCO
32-series

Removes H_2S by chemical reaction

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Finding the right sulfur removal solution

ZnO is a highly effective absorbent for trapping H_2S

Reactive ZnO phases react with H_2S:

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

Locks up sulfur in ZnS phase, preventing release of the sulfur under changing operating conditions

Thermal decomposition of lower mercaptans:

$$RSH \rightarrow H_2S + \text{olefin}$$

$$2MeSH \rightarrow 2H_2S + CH_4 + C$$

H_2S is removed by chemical reaction

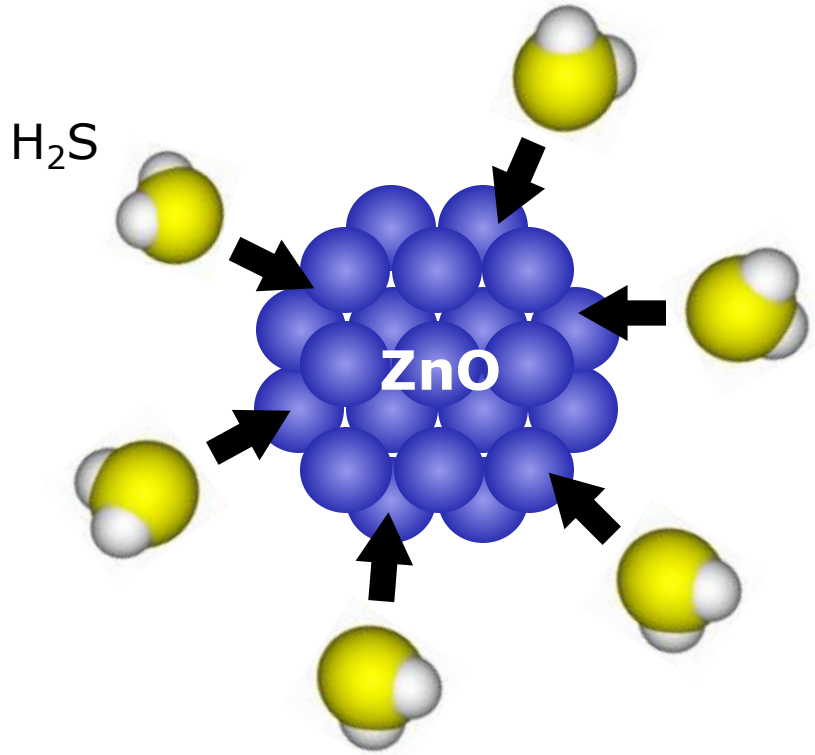
Absorbent properties needed for protection

Performance is not solely determined by the ZnO content

Maximum S pick-up requires:

- High **bulk density** provides more ZnO per unit volume
- High **porosity**
  - Allows access of H_2S to center of catalyst pellet
  - Porosity maintained as ZnO is converted to ZnS
- Highly **accessible surface area**
  - Sharp sulfur absorption profile at high space velocities

JM has continually developed the **KATALCO** 32-series of absorbents for over 60 years to provide a portfolio of ZnO products to meet every need



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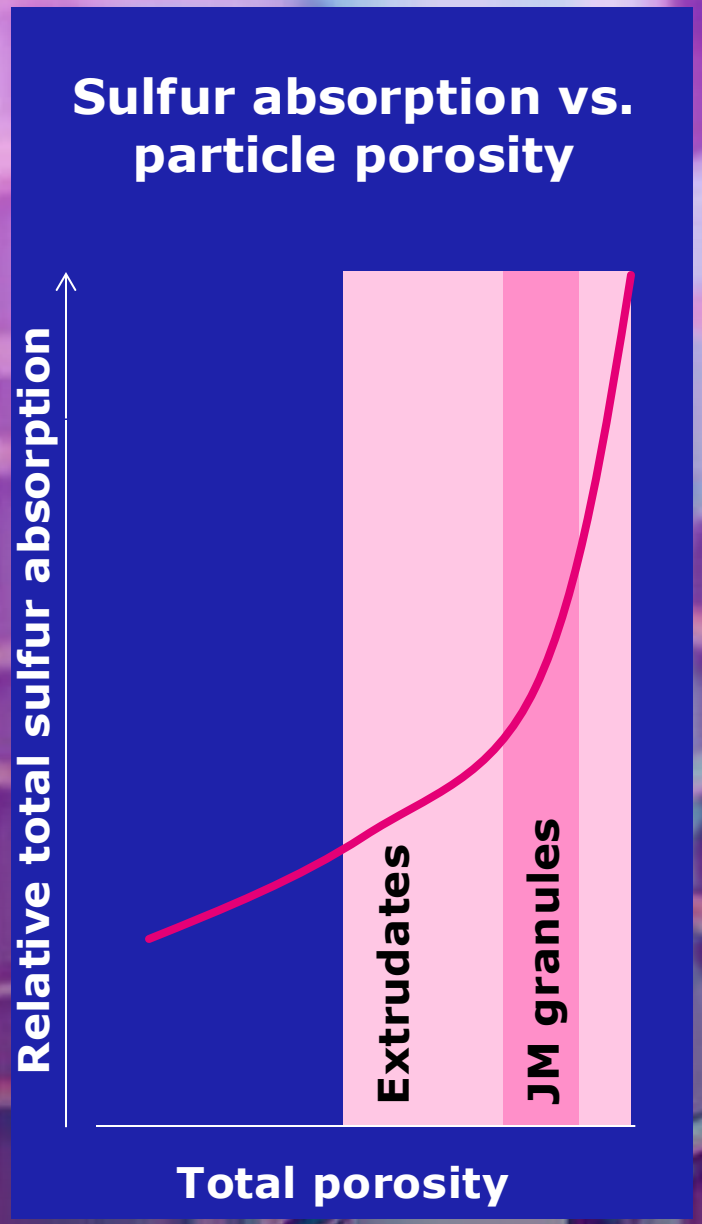
Balancing porosity, density, and strength

Sulfur absorption capability is very sensitive to porosity
So, the **optimal window of porosity** is small

JM granulated ZnO is more porous than extrudates
So, sulfur can access the whole pellet

Protecting pellet strength is critical. So, cement reinforcement makes them **stronger** than extrudates



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Maximizing sulfur pickup

Challenges in obtaining optimum porosity in ZnO formulations

Sulfur absorption (ZnO → ZnS) causes lattice expansion

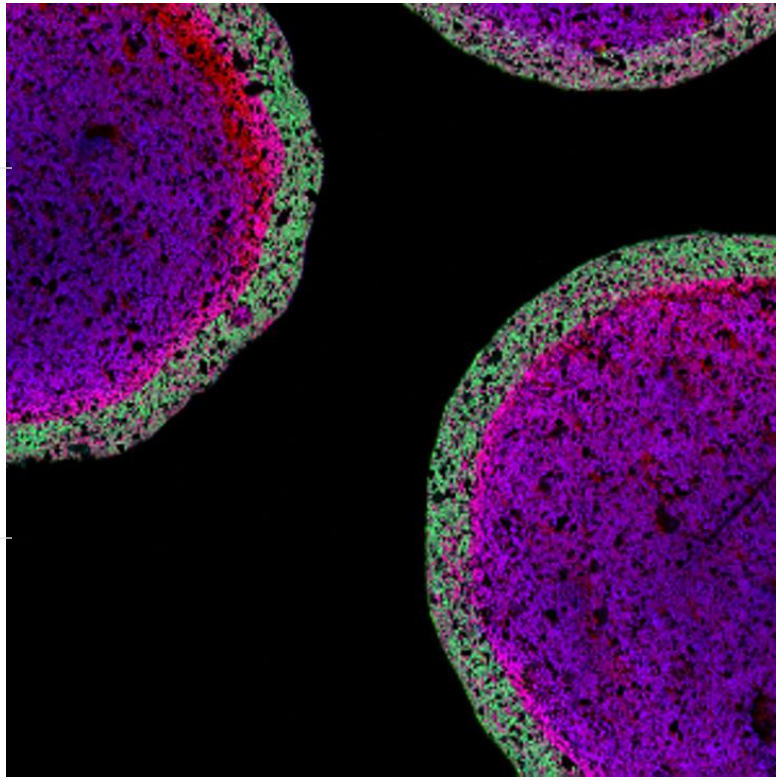
ZnS molar volume is higher

Lattice expansion causes pore blocking

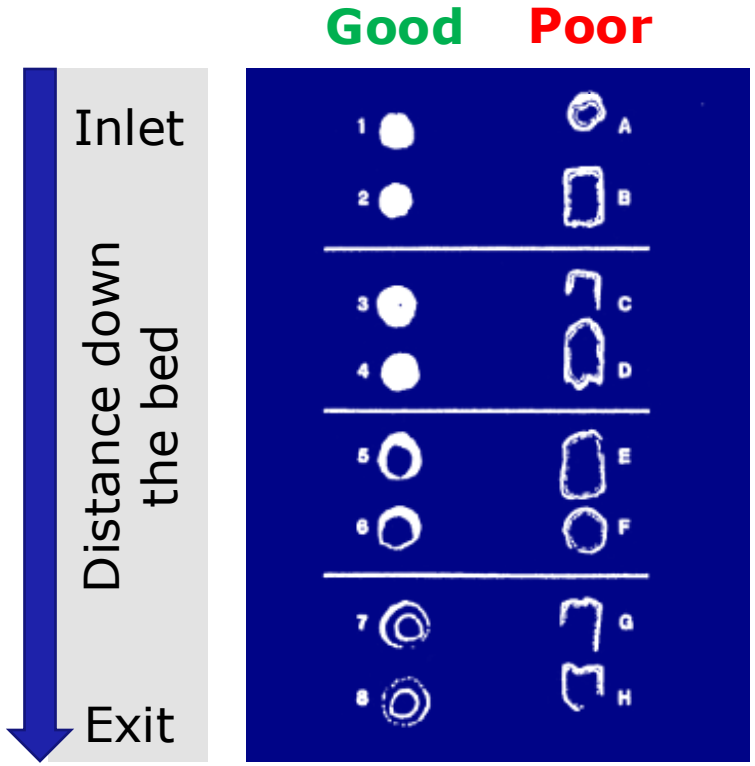
Actual pick up is < theoretical

Rate of absorption limited by pore/lattice diffusion

Very low porosity formulations suffer from poor sulfur pick up



Radiographs of pellet profiles



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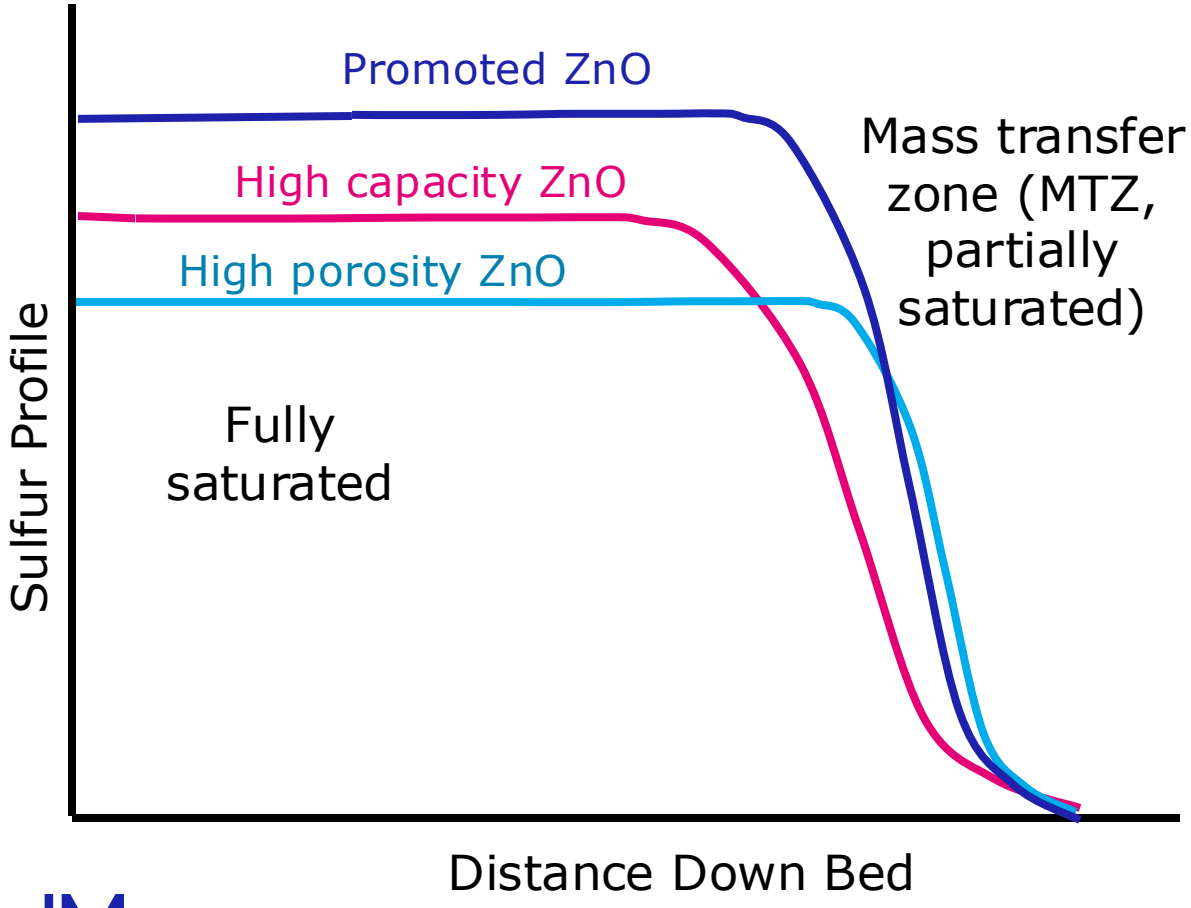
Performance, confidence, and reliability

More than 900 JM absorbent loads world-wide



KATALCO 32-4 A well-established ZnO, optimized to provide a balance between capacity, porosity and cost.

KATALCO 32-5 Denser by design giving a higher capacity that enables longer bed lives and reduced lifecycle costs.

KATALCO 32-6 Highest sulfur capacity for longest cycle length. Reduce changeout costs and enhance protection against sulfur spikes.

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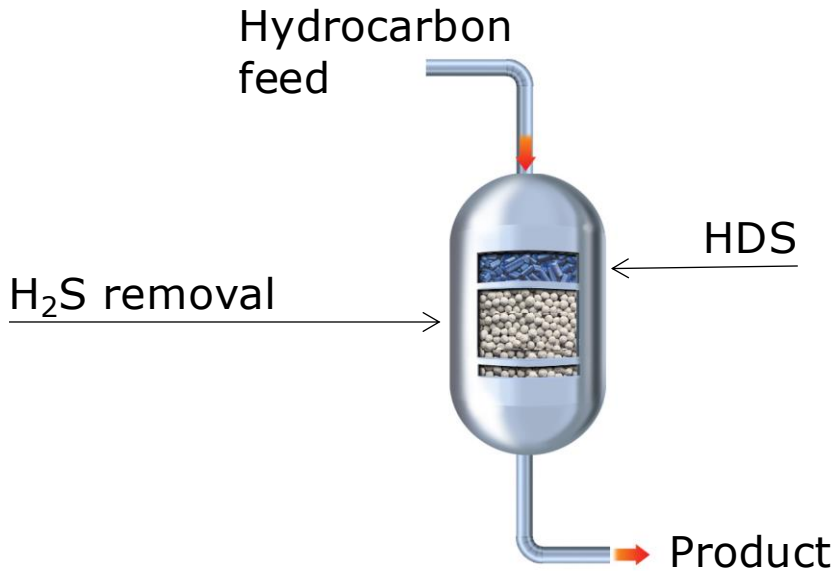
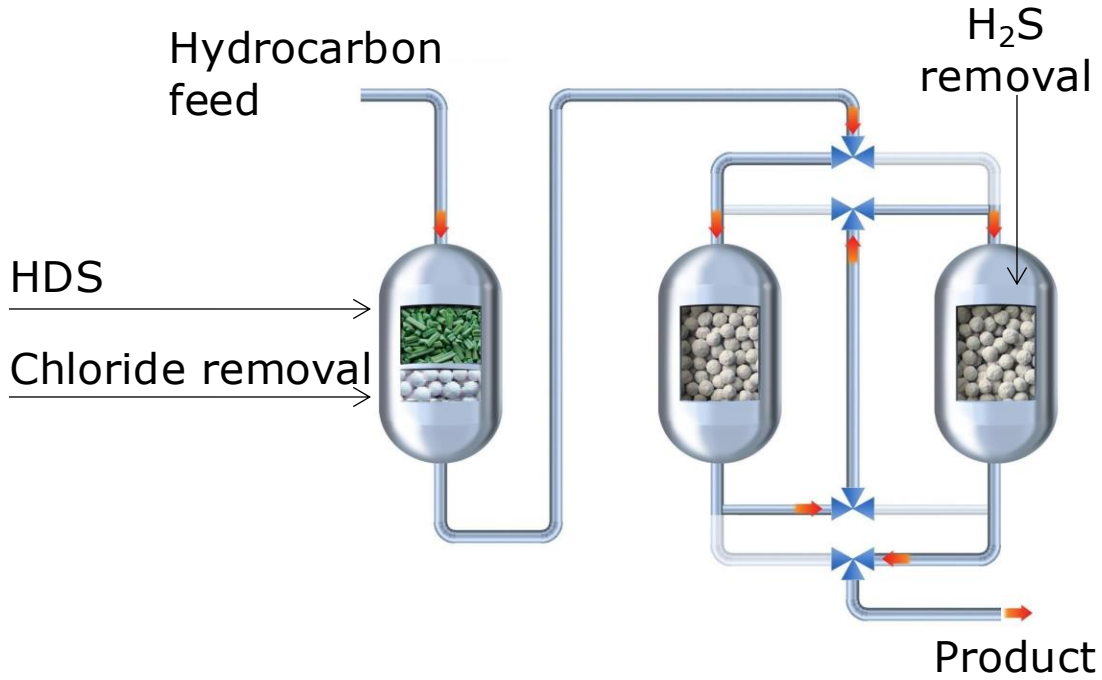
A range of flow schemes, vessel designs, and operating needs





Sulfur removal: single bed

Use of single bed:

- **Low and predictable** sulfur level (typically)
- Bed is sized to operate for a whole number of **turnaround cycles**
- Requires high-capacity absorbent with **sharp MTZ**: *maximizes bed utilization*

Sulfur removal: lead / lag

Upstream reactor can be operated with H_2S slip to **maximize sulfur pick-up in lead bed**

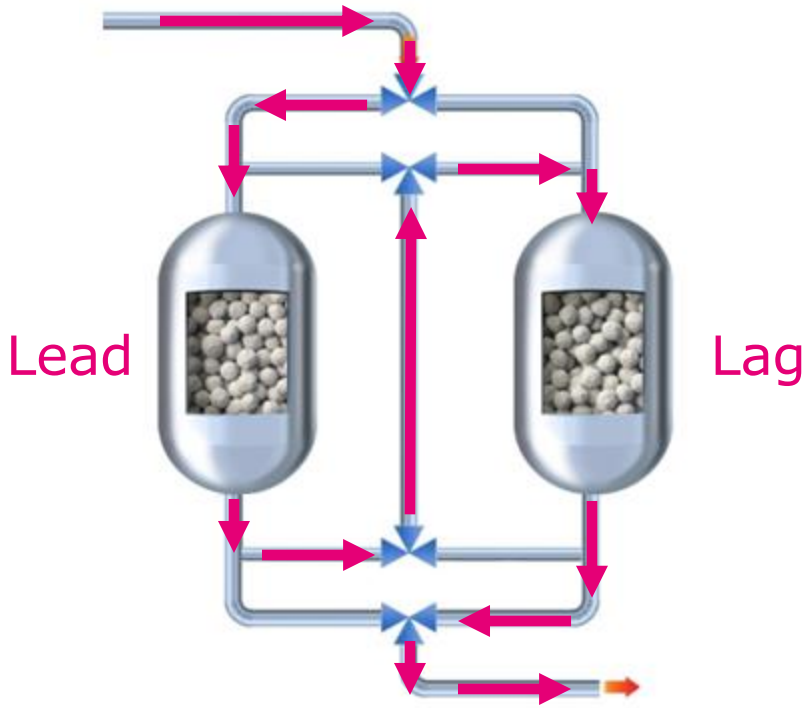
- Outlet = 80 - 90 % of inlet

Lead bed **changed out online**

- Lag bed used alone
- Lead bed re-commissioned in the lag position (interchangeable)

Requires **high-capacity absorbent**

- Maximizes bed utilization
- Slacker mass transfer zone (MTZ) is irrelevant



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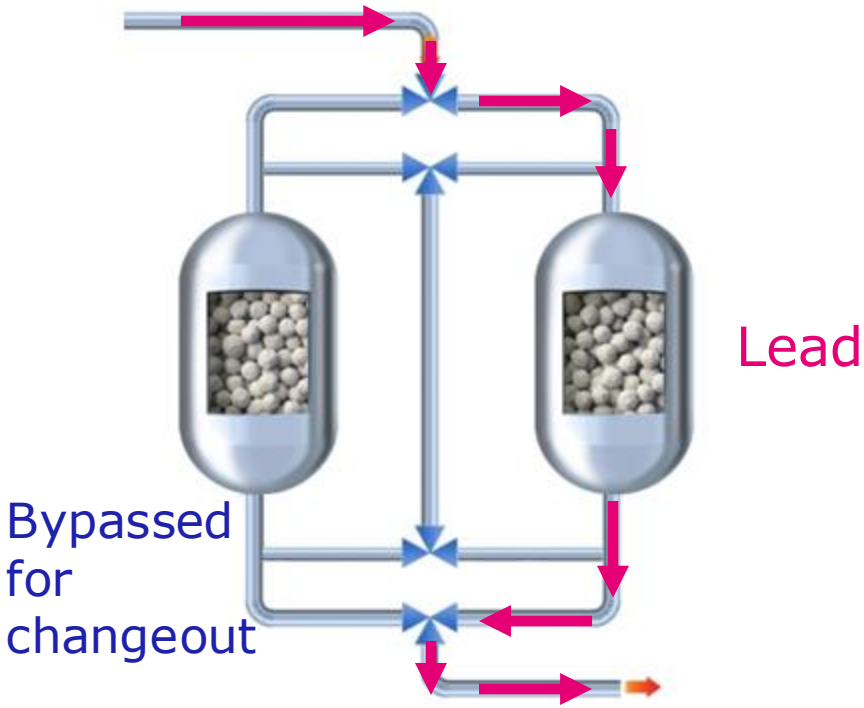

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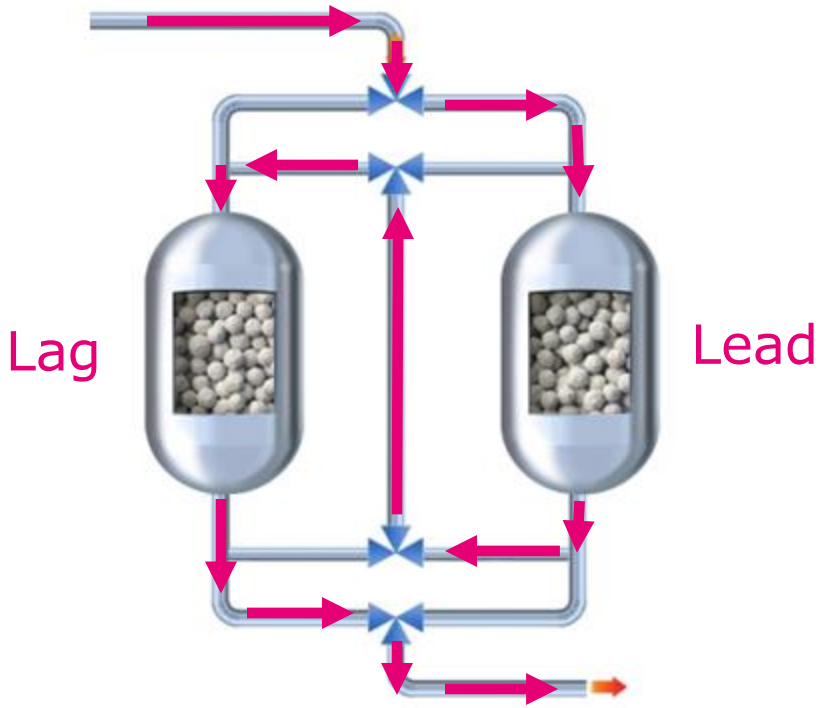

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Maximizing catalyst lives using deeper purification

Ultrapurification of sulfur

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Maximizing catalyst lives using deeper purification

Polishing sulfur to lower levels

Feed

+

hydrogen

HDS

KATALCO
41- and 61-series

Converts organo-S, organo-Cl and olefins

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Removes HCl by chemical reaction

H_2S absorption

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Removes H_2S by chemical reaction

Ultra-purification

PURASPEC™ solutions,

KATALCO
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Polishes out trace sulfur

JM

The challenges of reducing impurities to ultra-low levels

Stringent purification requirements for maximizing the performance of high-activity catalysts

Pre-reforming and steam reforming catalyst requirements	Sulfur	<0.1 ppmv: poison
	Chlorides	<0.1 ppmv: poison
	As/V/Pb/Hg	<5 ppbw: poison
	Olefins	<1-2 vol %: carbon formation
MTS/LTS catalyst requirement	Chlorides	<5 ppbv: severe poison
	Sulfur	<0.1 ppmv: poison

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*process gas feed (dry basis)

JM ultrapurification products to fit your plant design

Ultrapurification catalyst selection

No reduction required

Pre-reduction required

KATALCO 33-1

Multifunctional product with HDS, bulk sulfur removal and ultra-purification capability for light feeds

KATALCO 79-1

Dedicated ultra-purification product based on copper/nickel on ZnO for light feeds

PURASPEC 2084

Dedicated ultra-purification product suitable for a range of feeds

JM

Combined product

Johnson Matthey's **KATALCO** 33-1

1. High hydrodesulfurization (HDS) activity
2. High-capacity H_2S removal
3. And Ultra-purification (<5 ppb S exit)

All in a single catalyst solution

Key product benefits:

- No need for prematurely discharging HDS catalyst when reloading zinc oxide absorbents
- Lower sulfur slip vs. traditional sulfur removal absorbents
- Works with very low inlet sulfur concentrations, requires no sulfiding step and has full HDS activity from day one
- Simple catalyst loading, discharging and disposal

High density + High porosity = Max. access ZnO

JM

KATALCO 33-1 performance

Case study 1

Large North American syngas plant

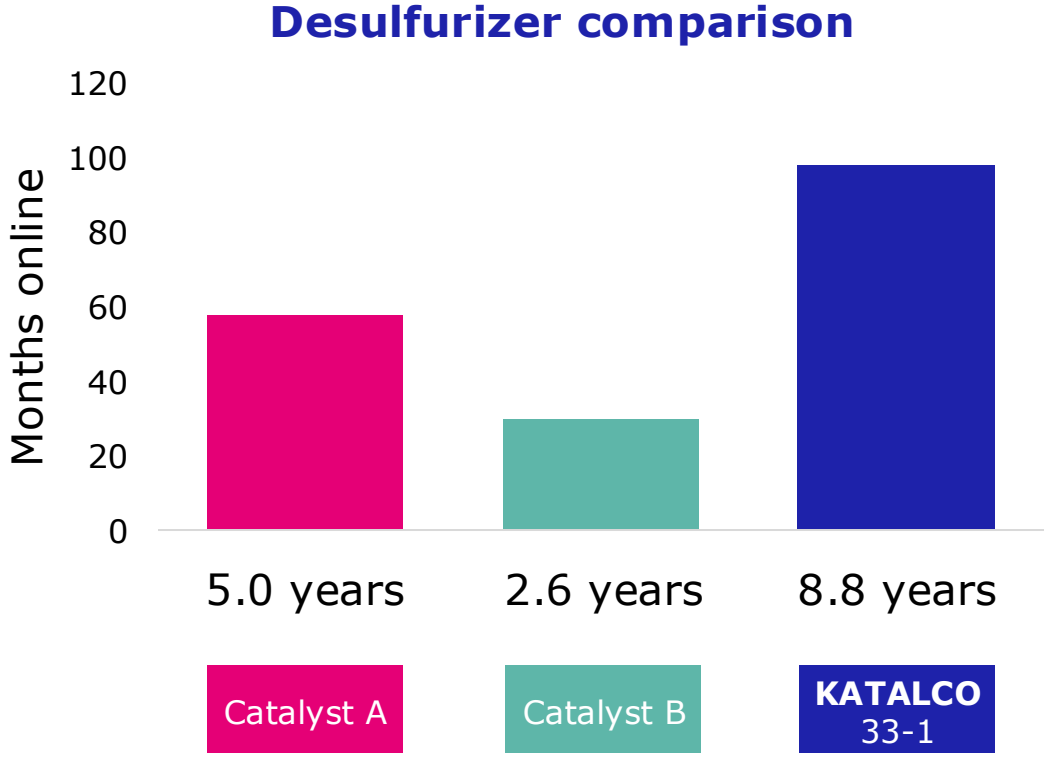
Previously installed two different purification charges containing competitive **HDS and ZnO** materials

Charges lasted **5 and 2.6 years,** respectively

After installing Johnson Matthey's **KATALCO** 33-1, the customer was able to utilize the higher overall sulfur capacity.

Resulting life: nearly 9 years

KATALCO 33-1 achieves longest life



JM provides a complete and trusted purification package

Process security from start-up to shut-down

1

Expertise in selecting the best HDS solution from CoMo and NiMo portfolio to target a range of feeds and operating conditions

2

Continued development of the 32-series of catalysts to provide a portfolio of ZnO products to meet every need

3

Ultrapurification for **optimum protection** to maximise the performance of downstream high activity catalysts

4

Unique 3-in-1 product combines high HDS activity, high H_2S capacity, and ultrapurification in a single catalyst solution

JM

Simple, effective solutions for impurities removal

Feedstock flexibility	Ability to operate with a wide range of feeds
Robust operation	Suitable for varying operating conditions
Long and predictable bed lives	Meet your major turnaround schedule
Downstream equipment	Preventing HS&E incidents and improve process safety
Technical support	Full technical team for purification expertise, modeling and guidance
Peace of mind	JM is a reputable supplier with product availability

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Johnson Matthey
Inspiring science, enhancing life

Thank You