

JM

# Improvements to water gas shift process

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With a growing population supplies of natural resources are under ever-increasing pressure, their sustainable use has never been higher on the agenda. Against this backdrop, Johnson Matthey (JM) seeks to improve the efficiency, effectiveness and sustainable impact of their products, enabling JM customers to achieve high productivity by making more for less.

Through a new patented solution JM has used expertise in purification science and engineering skills to develop an innovative new shift product which extends LTS life allowing ammonia plants to increase their process reliability and production efficiency.

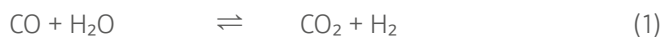
## Introduction

The choice of shift catalyst and how they operate are vital to the economy and efficiency of an ammonia plant. It is essential that the shift catalysts produce the lowest possible exit concentration of carbon monoxide in a stable and predictable manner. The catalysts need to be able to withstand the challenges presented in real plant operations for an increasing period of years between planned shutdowns.

The water-gas shift reaction and attributes for good catalysts are discussed in this paper, plus an introduction to new purification technology developed for use in the HTS reactor to further improve the performance of a LTS catalyst.

## Water gas shift reaction

The water gas shift reaction plays a major role in ammonia plant design and operation. Good performance of the shift catalysts, and attainment of a close approach to equilibrium thus minimising the CO slip from the catalyst system which is critical to the efficient and economic operation of the plant and ensures maximum hydrogen production from the hydrocarbon feedstock. The water gas shift or shift reaction (1) is highlighted below.



The reaction is exothermic and high conversions are favoured by low temperature and a high steam ratio. Ammonia plants usually operate a two-stage system – a High Temperature Shift (HTS) followed by a Low Temperature Shift (LTS) – with a suitable form of inter-bed cooling, as in Figure 1.

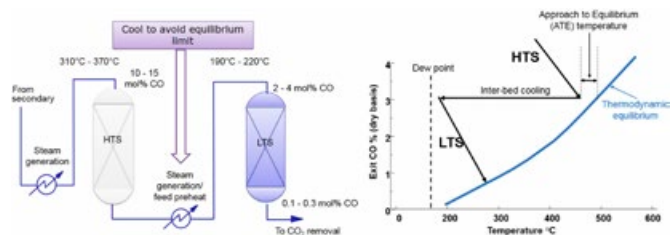


Figure 1 – Typical arrangement of WGS system in an ammonia plant

## HTS catalyst duty

The HTS is a Fe-Cu-Cr catalyst that is relatively insensitive to poisons. HTS catalysts have lower activity and must be operated at higher temperatures (typically 350-470°C) the gas stream leaving the HTS reactor therefore contains a substantial amount of carbon monoxide (usually 2-3%).

The HTS catalyst sits immediately downstream of high temperature reforming systems and heat recovery (boilers and superheaters). The heat recovery equipment is highly stressed which can cause failure leading to leakages and deposits onto the HTS bed. The HTS is the first catalyst bed downstream so can be fouled by refractory or metal dusting debris that may be emitted from the high temperature recovery equipment. The fouling impact of this on HTS can be mitigated using both high voidage inert hold-down media and a high voidage shaped HTS pellet such as **KATALCO™ 71-5F**. (Figure 2).



Figure 2 – **KATALCO 71-5F** shaped HTS

Shaped **KATALCO 71-5F** offers 12% lower pressure drop than the conventional tablet with increased strength. The shape offers additional voidage to accommodate any deposits that may foul the HTS bed lowering the rate of any resultant pressure drop increase on the HTS from deposits.

Also on top of the HTS bed high voidage inert **DYPOR™ 607** can be used to protect the top of a catalyst

bed by both capturing boiler solids and by preventing the impingement of liquid droplets onto the catalyst itself. JM market this solution as **SHIFTSHIELD**, Figure 3.

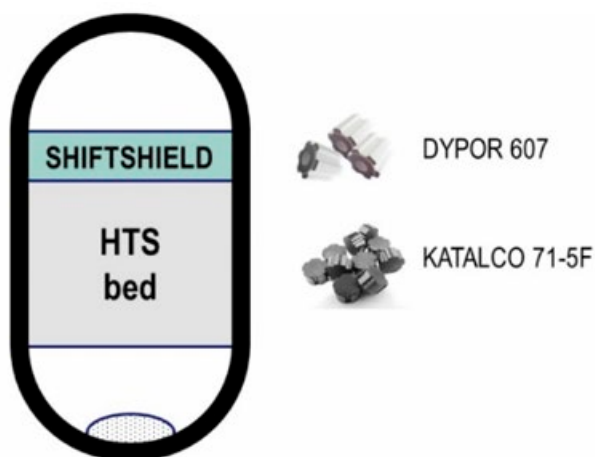


Figure 3 – High voidage inert DYPOR media

Below the HTS bed the use of similar inert media is well established in shift reactors as Johnson Matthey's **STREAMLINE** low pressure drop solution. **STREAMLINE** was originally developed in response to several high temperature (HT) and low temperature (LT) shift reactors exhibiting high pressure drops. On investigation it was discovered that a high portion of the vessel pressure drop was associated with the area around the collector. This was confirmed by detailed computational flow modelling. (Figure 4).

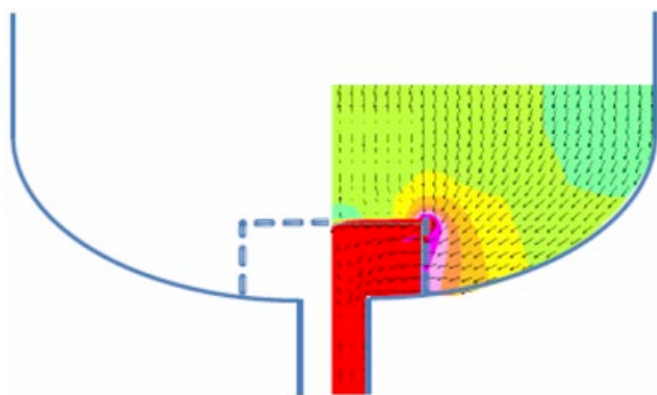


Figure 4: **STREAMLINE** flow modelling of shift reactor

The specific size grades of **DYPOR**, used as a support media, vary depending on the vessel configuration and particle size of material being supported. JM have a proprietary **STREAMLINE** software program which is configured for a full range of vessel collector designs. Figure 5 shows a **STREAMLINE** model of a vessel with a dished bottom collector, along with plant data showing the 60% reduction in pressure drop that resulted from the deployment of **STREAMLINE** on this vessel.

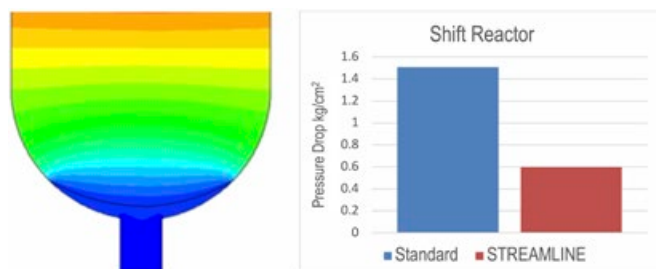


Figure 5: Case study **STREAMLINE** flow simulation and results

An enhancement to **STREAMLINE** technology is now available as discussed later, utilising **PURASPEC 2272** as a high voidage support media, which also provides LTS protection from chloride poisons.

## LTS

The efficiency of ammonia plants depends critically on the ability of the LTS catalyst to convert the maximum amount of CO to H<sub>2</sub>. For every molecule of CO passing through the LTS there is not only the loss in production of H<sub>2</sub> via equation 1, but also a further loss of three molecules of H<sub>2</sub> in the methanation of CO, (2) and further loss when this extra methane is purged from the synthesis loop.



## LTS catalyst composition

A catalyst is designed to increase the rate of reaction but does not change the thermodynamic equilibrium concentration of reactants and products for the actual operating conditions. The catalyst must, therefore be formulated for long-term reliable operation at, or near, equilibrium conditions.

LTS catalyst is copper (Cu) distributed on a mixed support of zinc oxide (ZnO) and alumina (Al<sub>2</sub>O<sub>3</sub>). The LTS catalyst is supplied as a mixture of oxides, and the copper oxide (CuO) is in a form that can be easily and quickly reduced into the active form. The Cu crystallites formed in this way must not sinter and lose activity during service, the active Cu phase and catalyst structure should also be unaffected, as far as possible, by traces of poisons in the process gas stream.

The properties of the LTS catalyst are critically dependent upon the formulation and manufacturing process rather than on the bulk chemical analysis. The importance of the correct control of formulation and preparation conditions are key in obtaining the correct LTS structure to give a catalyst that offers long-term stable activity and mechanical properties, thus avoiding pressure drop increase.

Energy-dispersive x-ray spectroscopy (EDX) is an analytical technique used by JM for the elemental analysis or chemical characterisation of catalysts. It relies on an interaction of some source of x-ray excitation and a sample, its characterisation capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum. Figure 6 shows the structure of **KATALCO 83-3X** catalyst using EDX.

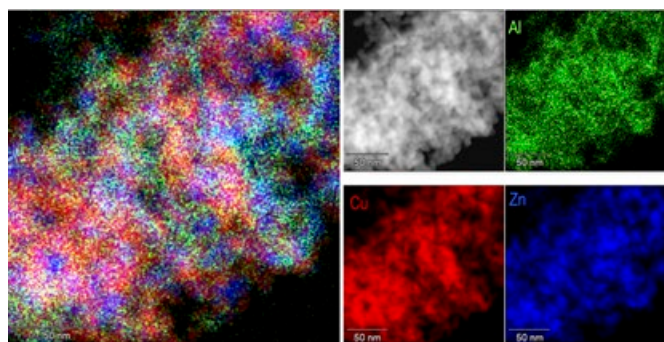


Figure 6: EDX analysis of **KATALCO 83-3X** showing elemental mapping of catalyst structure

To achieve a long and active life the copper metal crystallites (red) must be small and well separated from each other by even smaller, yet thermally stable, zinc/alumina refractory oxide crystals (blue/green). To obtain the necessary catalytic behaviour the scale of this science is measured in nano-meters (10<sup>-9</sup> meter). Bulk analysis of the LTS catalyst cannot be used as a basis of assessment or comparison of LTS catalyst since it yields no information on the fundamental properties or mechanism for operation such as:

- Quantity or size of the copper crystallites producing catalytic action
- The micro-structure for poisons resistance
- The form of the alumina, which in turn affects the strength and stability of the catalyst.

Through this leading science JM can manage the formulation and manufacture of the LTS catalyst with stringent controls to achieve the optimum structure balancing good activity, thermal stability and the ability to withstand the effect of poisons hence enhancing life.

## Activity and life

The current formulation of **KATALCO 83-3** LTS catalysts is a careful balance between poisons resistance, stability, selectivity and activity that is manufactured to achieve a high dispersion of Cu crystallites within the ZnO/Al<sub>2</sub>O<sub>3</sub> structure. The ZnO/Al<sub>2</sub>O<sub>3</sub> refractory crystallites add strength to the catalyst while providing a stable support maintaining the high dispersion of the active Cu sites and therefore inhibit the Cu crystallites from sintering thus maintaining activity and life.

After stabilising in-service, the LTS catalyst needs to display stable performance throughout it's working life – meaning uniform activity, retained strength and good capacity for poisons. The relative effects of increasing poisons resistance and activity of LTS are shown in Figure 7.

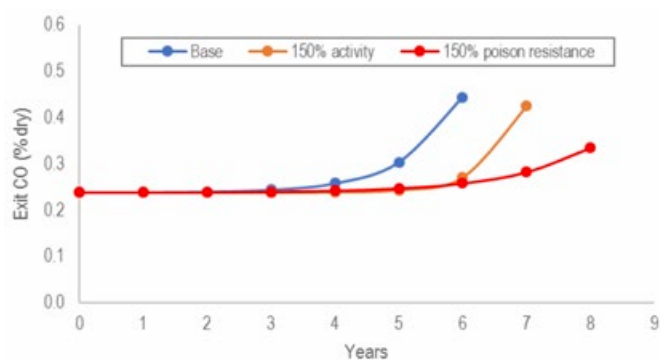


Figure 7: Increasing poisons resistance or activity – effect on LTS performance

If a level of 0.3% CO slip is considered as being end of run (EOR) condition, then, as can be seen from Figure 7 from a base case of current LTS technology, - increasing LTS activity to 150% could increase service life to 6 years whereas a 150% increase in poisons resistance extends the life to over 7 years.

## Operation of LTS catalyst

Considering what this understanding of catalyst science and LTS composition means in operation, typical use of LTS catalyst comprises of three stages:

- catalyst is loaded, reduced and started-up without incident
- catalyst is operated with trace levels of poisons as would be expected with a normally operating purification system
- after many years of stable operation with CO at equilibrium levels and low pressure drop, the catalyst is discharged

During the operation of an ammonia plant there are trips, boiler leaks, and catalyst poisons that are an unavoidable part of plant operation, and the LTS catalyst must be designed to survive these.

**KATALCO** 83-3 catalyst series have an excellent reputation of doing this. The catalyst structure retains a high in-service strength which is especially critical to the operator as this is the strength of the catalyst in the in-service condition, once reduced and used in plant conditions. The attached benchmark data shows with in-service strengths measured on reduced catalyst using a crush machine housed in an inert atmosphere.

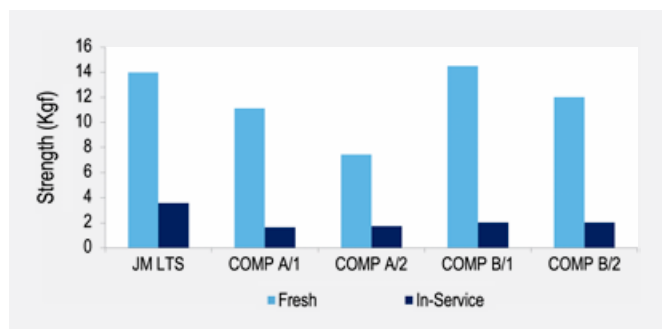


Figure 8: Relative strengths of LTS catalyst for both fresh and in-service conditions

These results show how for all LTS catalysts the reduced strength of pellets lower than for fresh oxidic. For JM LTS the in-service pellet strength is higher than competitive LTS pellets. This increased strength helps provide stable performance without increasing in-service pressure drop.

A further operational difference from the structural science of **KATALCO** 83-3 catalysts is the tolerance to catalyst reduction process conditions. The catalyst reduction itself is a transient process in which the CuO in the LTS is reduced to the active Cu metal, often in a recirculation loop. When a recirculating system is used there needs to be a continuous purge from the system to

prevent the level of contaminants from building up within the system. The oxidic LTS catalyst contains some complex copper-zinc basic carbonates and these decompose during reduction and release carbon dioxide (CO<sub>2</sub>). The amount of CO<sub>2</sub> in the recirculating carrier gas is one of the key parameters that determine the level of purging from the recycle loop.

There is a potential for the CO<sub>2</sub> in the recirculating gas to react with oxides in the LTS catalyst and damage its microstructure. The damage occurs primarily in the support phase of the catalyst, resulting in a weakening of the catalyst pellets. This is often observed as a higher than expected LTS pressure drop as soon as the plant is started up, which then increases rapidly during ongoing operation. Therefore, limits on the CO<sub>2</sub> partial pressure have been applied during some LTS catalyst reductions, with a figure of circa 1bara (15psia) being typical for some products. By optimising the catalyst formulation of **KATALCO** 83-3 series, JM have engineered a rugged stable support phase for the active sites, meaning it is an LTS catalyst less sensitive to the level of CO<sub>2</sub> in the reduction gas.

This has the economic benefit of reducing the cost of nitrogen or natural gas used during the LTS catalysts reduction, however, the main benefit is that it provides a larger operational envelope for catalyst reduction without risk of achieving a low catalyst activity. During LTS reduction, monitoring of the gas composition is often undertaken with temporary instrumentation and manual control of the purge flow. Therefore, a wider operating envelope within the period of less than ideal control is especially useful.

## LTS catalyst poisons

The two most virulent poisons for an LTS charge are sulphur and chlorides. They are the major source of LTS deactivation. The main catalyst poisons sources and their effects are summarised in Table 1.

Poison	Possible sources	Effect on LTS catalyst
Sulphur	Hydrocarbon feedstock	Covers active copper surface
	Lubricating oil	
	Air to secondary reformer	
	New HTS catalyst	
Chloride	Steam	Promotes copper crystal growth
	Quench water	
	Lubricating oil	
	Air to secondary reformer	

Table 1 – Main LTS catalyst poisons sources and their effects

## Sulphur

Catalysts start to be poisoned whenever an impurity in the process gas alters the surface structure or composition of the active metal. Sulphur, which is the most common of these poisons, deactivates LTS catalyst by a process of chemisorption onto the active copper surface followed by crystallite growth.

Hydrogen sulphide ( $H_2S$ ) can be absorbed as a layer onto active Cu surface at much lower partial pressures than required for bulk sulphides. As such Cu in LTS catalyst is very active for absorbing a surface layer of  $H_2S$  if present in the reacting process gas. However, since thermodynamic data predicts  $H_2S$  will react preferentially with ZnO rather than Cu it essential that an LTS catalyst is designed such that sulphur is rapidly transferred from the active Cu metal to ZnO before the Cu sinters.

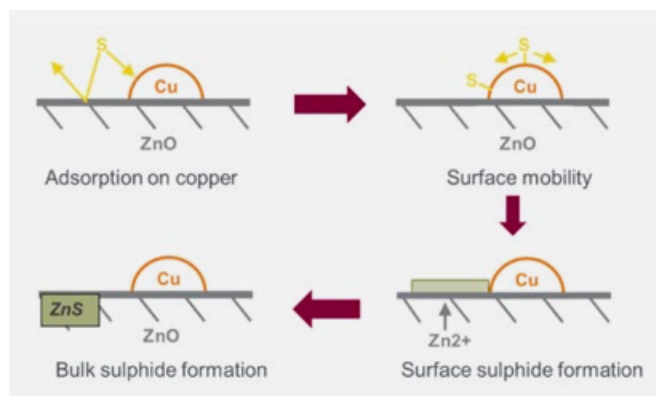


Figure 9 - Schematic mechanism for S capture within LTS

In a well formulated LTS, there is an excess of free ZnO meaning that  $H_2S$  presence is absorbed quickly at the top of the bed leaving the rest of the catalyst to operate satisfactorily. Absorption capacities of around 6% wt. have been measured in KATALCO 83-3 series LTS catalysts in plant use. The sulphur capacity relates directly to the surface of free ZnO present in a catalyst. Those containing less available ZnO can allow a given quantity of  $H_2S$  to penetrate deeper into the bed causing greater deactivation.

## Chloride

Chloride as a poison presents more of a challenge in the LTS reactor because of the low melting point and high solubilities in water of zinc, copper chlorides. Chloride can be redistributed through the catalyst bed by dissolution in condensed water or by vapour phase transfer of volatile chloride. Consequently, the absorption profile for chloride in the catalyst bed is not as stable as for sulphur and chloride can be distributed deeper into the bed. So, although the levels of chloride reaching the LTS bed are generally lower than sulphur the damage can be more harmful.

The levels of S and Cl vary from plant to plant depending on the prevalent conditions of poisons. Ranges seen on inlet LTS catalyst samples taken at the top of the bed over a wide range of over 150 plant samples, are shown in Figure 10.



Figure 10: Levels of sulphur and chloride measured in spent LTS catalysts

High surface coverages are often seen of both sulphur and chloride on discharged samples, often above 1 wt.% at the top of the bed. A long standing feature of JM LTS technology is that it is self-guarding in terms of both S and Cl. Figure 11 shows an EPMA (electron probe micro analysis) of spent KATALCO 83-3 series LTS showing the distribution of both S and Cl captured on the surface of the pellets.

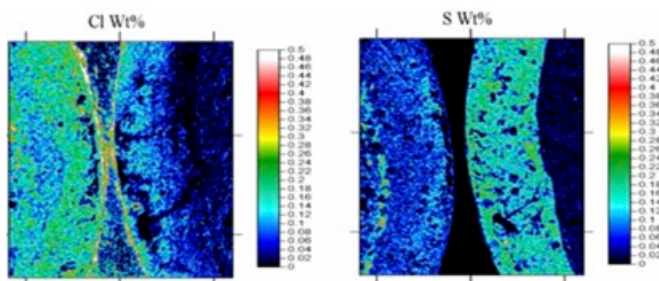


Figure 11: EMPA analysis showing mapping analysis for S and Cl on KATALCO 83-3 pellet surface

As shown in Figure 10, typical levels of chloride in spent LTS are much lower level than sulphur, however even these low Cl-levels have the potential to be much more damaging, for two reasons:

- Cl-solubility - both copper and zinc chloride are soluble in water, hence condensation on the catalyst during start-up, shutdown or normal operation can move chlorides further down the bed.
- Cl-induced sintering - low levels of chlorides can have a significant effect on LTS catalyst activity since they promote sintering.

To understand why the impact of Cl is so pronounced the effect of temperature on sintering of metals and oxides should be considered. Temperature is the dominant factor in controlling the rate of sintering of metallic and

oxidic species. Relationships have been evolved which utilise the melting point of the material concerned to estimate the magnitude of the sintering process at any given temperature. The Tamman temperature is calculated (in absolute units) as one half of the melting point of the metal or oxide. This gives an indication of the temperature at which metal or metal oxide atom lattices experience mobility, physically in terms of the driving forces for dissociation and diffusion of surface atoms.

Accordingly, sintering rates of a metal or metal compounds are significant and very high near the Tamman temperature; thus, the relative thermal stability materials can be correlated in terms of the Tamman temperatures, Table 2 below lists these for the LTS metals and their compounds.

Compound	T <sub>mp</sub> (Melting point)		T <sub>Tamman</sub> (= 0.5 T <sub>mp</sub> °K)	
	°K	°C	°K	°C
Cu	1356	1083	678	405
CuCl <sub>2</sub>	893	620	447	174
CuCl	703	430	352	79
CuO	1599	1326	800	527
Zn	693	420	347	74
ZnO	2248	1975	1124	851
ZnCl <sub>2</sub>	563	290	282	9

Table 2: Melting point and Tamman temperatures for LTS metals/compounds

Sintering of LTS catalysts is strongly promoted by traces of chlorine in the feed, which react at operating temperatures with the active metal/metal oxide surface to produce a highly mobile chloride phases. Copper chlorides having a Tamman temperature of only 79–174°C compared to 405°C for copper metal and zinc chloride a Tamman temperature of only 9°C relative to 851°C for ZnO. As such the formation of copper and zinc chlorides provide a mechanism for loss of activity and poisoning by sintering, as shown schematically in Figure 12.



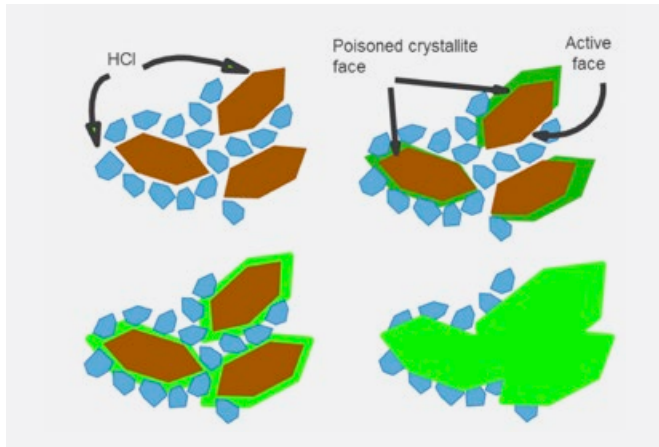


Figure 12: Schematic mechanism for Cl promoted sintering of LTS

### Case study – impact of wetting.

This case study illustrates the impact a wetting incident can have on LTS performance. An ammonia plant using competitive product strategy, including a Cl-guard layer (5% bed depth) over the main bed catalyst. After less than two years on-line the performance was good with low CO slip (<0.2%) and the reaction exotherm showed little signs of poisoning.

However, following a plant trip which resulted in the LTS being wetted, the CO slip increased to End of Run (EOR) conditions. Consequently, the reaction exotherm moved much deeper into the bed becoming less sharp. The Key Performance Indicators (KPI) over this incident are shown in Figure 13.

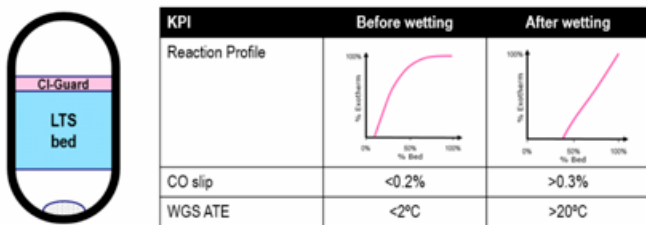


Figure 13: KPI showing performance of an LTS system before/ after a wetting incident

After the wetting damage the inefficient LTS performance significantly increased production costs. The plant therefore made an unplanned shutdown to change the LTS catalyst. An estimate of the production costs for this event was in the range \$1,000,000 – \$5,000,000.

### New purification technology for shift reactors

JM's latest development in technology combine strong purification expertise with the design of low pressure drop

systems for shift reactors to develop **PURASPEC™ 2272** - an 'adsorbing inert'.

**PURASPEC 2272** is a low pressure drop active adsorbent support media that replaces the inert support media at the bottom of the high temperature shift (HTS) reactor, (Figure 14), and captures chloride which would otherwise poison the low temperature shift (LTS) catalyst downstream.

### Development of PURASPEC 2272 absorbent

JM has used its expertise in purification science along with its proven **STREAMLINE** engineering skills to develop **PURASPEC 2272** – an innovative new product which combines the functions of a low pressure drop support with that of a chloride trap.

The development of **PURASPEC 2272** was made in JM's research facilities in Billingham, UK where the effectiveness of the alkali promoted absorbent was tested using with reactor temperature 430°C, pressure: 30 bar and steam : dry gas ratio: 0.5 short term 25 day high GHSV test was completed on its effectiveness as an Cl-guard at typical HTS exit test conditions.

The process gas used was representative of plant conditions H<sub>2</sub>, 55%; CO 4%, CO<sub>2</sub>, 16% and N<sub>2</sub> 25% containing only a low level of HCl at 9ppbv.

During the test no chloride was detected in the exit gas. After the test was completed the **PURASPEC** absorbent was recovered and analysed for C content – the inlet portion contained 330ppm similar to the level of Cl levels that would be found at the top of the LTS bed in a similar duration test. In long term operation within plants that saturation capacity of **PURASPEC 2272** is well above 1% chloride meaning it is expected to more than match %w/w Cl capture that takes place normally within the LTS bed.

### PURASPEC 2272 – Cl-guarding support media

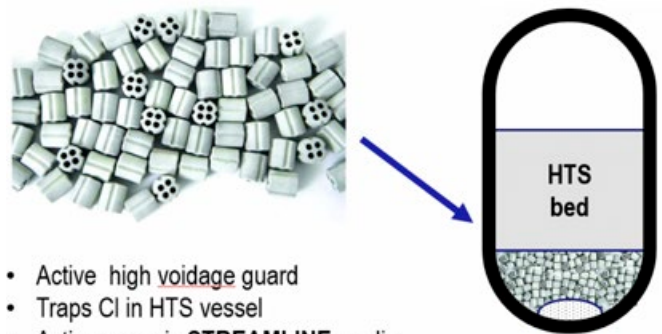


Figure 14: Location for installation of **PURASPEC 2272** at HTS exit

**PURASPEC 2272** is a patented solution which provides protection by helping to stop chlorides from reaching the LTS catalyst. Chlorides are very soluble and so are mobile when wetted. This means that condensation on a LTS catalyst can distribute chlorides throughout the bed and have a severe impact on catalyst performance.

### Wetting risk - Dewpoint consideration

To achieve the lowest CO slip LTS catalysts are run close to dewpoint. Hence as shown figure 15, dewpoint at the top of the LTS traditional location for a dedicated Cl-guard above catalyst (B) is typically below <25°C. The location for **PURASPEC 2272**, at the bottom of the HTS vessel (A), gives a much greater safety margin.

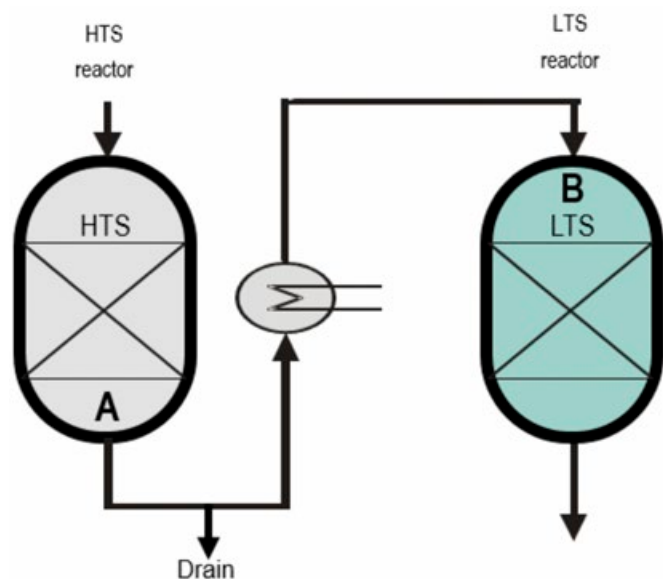


Figure 15: Locations for a Cl-guard in the shift section

The use of **PURASPEC 2272** at a location below the HTS gives several benefits:

- dewpoint margin is above 200°C
- chlorides are kept out of LTS reactor
- should wetting occur, chlorides can leave from a drain rather than enter LTS

The first reference for the technology is a 1360 MTPD Kellogg ammonia plant, operating at 120% of design capacity with parallel design HTS and LTS vessels in each vessel the catalyst was supported via a conventional arrangement of ceramic balls above a semi-elliptical outlet collector, Figure 16

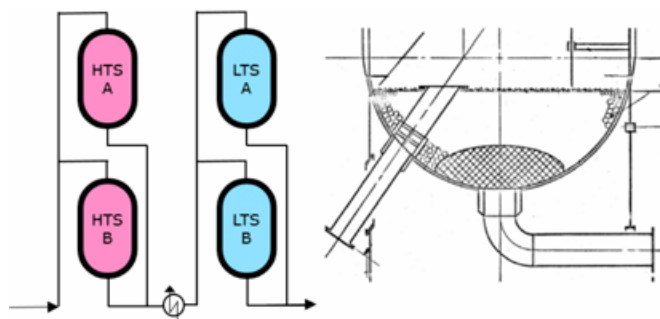


Figure 16 – Arrangement of HTS/LTS and outlet collector

JM were able to analyse the pressure drop profile through the catalyst bed and support media using their proprietary **STREAMLINE** software, JM were able to analyse the flow regime through the catalyst support balls, Figure 17.

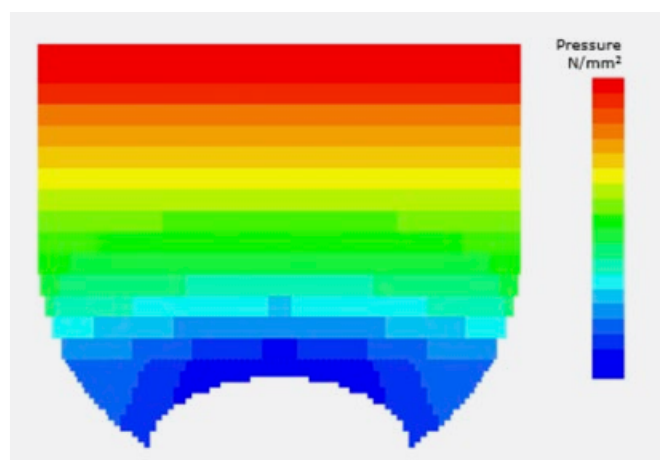


Figure 17 – STREAMLINE analysis of pressure drop gradient at HTS outlet collector

From this analysis the following improvements were developed for both the HTS/LTS reactors, Figure 18.

- HTS
  - DYPOR as **SHIFTSHIELD**
  - KATALCO 71-5F as the catalyst bed
  - PURASPEC 2272 support as Cl absorbing **STREAMLINE** media.
- LTS
  - KATALCO 83-3 as the catalyst bed
  - DYPOR support as **STREAMLINE** system.

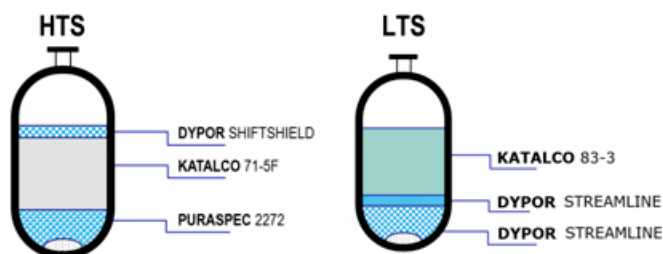


Figure 18 – Case study – improvements to HTS/LTS loadings

The anticipated improvement in LTS performance and life extension from using **PURASPEC 2272** is shown in figure 19, based on steady state operation.

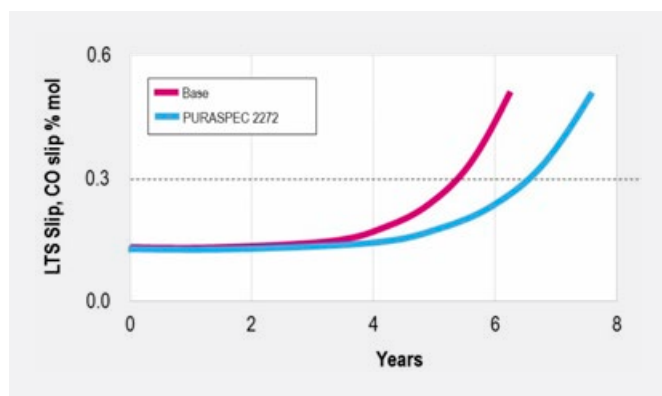


Figure 19 – Expected performance of LTS with **PURASPEC 2272**

In addition to this life extension by keeping some Cl safely guarded outside the LTS reactor then in the event of unexpected transient conditions in which condensation may occur at the top of the LTS bed the use of **PURASPEC 2272** provides significant protection against what would be a potentially damaging event.

Applications of **PURASPEC 2272** are increasing quickly since the launch at Nitrogen and Syngas Berlin in March 2019, the following references are already now in-service, with these customers benefiting from increased chloride protection for the downstream LTS.

Process	Capacity, mtpd	Region
Ammonia	1,600	FSU
Ammonia	600	Europe
Ammonia	1,400	FSU
Ammonia	1,200	Europe

Table 3: **PURASPEC 2272** references as Oct -2019

## Conclusion

Over many decades water gas shift technologies for both HTS and LTS have been improved, with the use of shape for pressure drop reduction in the HTS recent JM technology innovation.

JM's LTS technology for self-guarding catalysts has continued to evolve so catalysts offer ever longer lives with reliable performance, JM's catalyst science and manufacturing processes are key.

The LTS duty is vulnerable to being easily damaged by wetting and chlorides. JM's catalyst technology leads in terms of surviving wetting incidents due to product strength. The new Cl guard **PURASPEC 2272** adds a further new layer of protection to the LTS catalyst from chloride that can impact a bed if wetting inadvertent occurs.

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