

JM ProcessWise Webinar

Water gas shift improvements

March 2021

Questions and Answers

Please note that a number of similar and repeated questions have been combined.

Q1. How are the reaction conditions for the chloride guard at the HTS outlet (high temperature) vs LTS inlet (low temperature)? (any kinetic or thermodynamic limits?)

A1. The reaction that takes place in the chloride guard is effectively a neutralisation reaction, resulting in the formation of a stable alkali salt. This reaction is generally considered to be "irreversible". The reaction conditions at the base of the HTS will provide improved kinetics for the neutralisation reaction due to the higher temperature. JM's testing of the chloride guard material at HTS outlet conditions found high levels of pick-up of the absorbent in a challenging high space velocity environment, the thermodynamic limit very much favours formation of the salt resulting in very low ppb Cl-slip at equilibrium.

Q2. Does JM offer a pre-reduced LTS catalyst?

A2. Johnson Matthey does not normally offer a pre-reduced LTS catalyst. We can provide guidance, advice and estimated reduction times to allow you to effectively plan the reduction process. The time taken for reduction can be minimised by (within reasonable and safe limits) 1) charging a smaller volume of catalyst, if short loading is possible 2) increase the carrier gas flowrate during reduction and 3) Carefully increasing the hydrogen concentration during reduction, whilst keeping within safe temperature limits. Please ask your JM representative for more information.

Q3. Our plant 1200 T/d, TKIS technology started in 2015 , we plan to increase the ammonia plant capacity , at existing of HTs and LTS what is the max. load (% increase) ?

A3. Given the individual nature of each plant's operation, it is difficult to know the precise plant limitations without more information. Johnson Matthey's revamp studies have helped dozens of syngas plant customers around the world to better understand their plant, its limitations and how to overcome these. Johnson

Matthey would be delighted to discuss our references and experience and how we could help your plant, please contact your representative for more information.

Q4. What will be the impact of BFW in case of internal leak or at more extend a flooding case for HTS Cat.

A4. JM HTS catalyst is robust to liquid water, **KATALCO**[™] 71-6 particularly so. However, boiler feed water can contain substances which will solidify on the top of the catalyst bed, agglomerating it together and covering the catalyst active sites. This will increase the pressure drop across the vessel and reduce the volume of active catalyst. In some cases this "cake" can almost completely cover the top of the catalyst bed, resulting in serious maldistribution of the process gas. In very serious cases, prolonged contact with liquid water can cause the catalyst to break down and agglomerate together, resulting in very severe pressure drop issues. In many cases this will make the catalyst difficult to remove at the next change-out. If the vessel is flooded with water, it is important to ensure care is taken on re-start to ensure that the catalyst is dried out slowly. If the temperature is increased too quickly, the liquid water in the catalyst pores can undergo rapid phase change to steam with a pressure build up within the catalyst pellet causing it to "burst" apart, resulting in damage.

Q5. Can you speak about methanol and ammonia formation on shift catalyst? I am thinking about hydrogen plants, is there space to reduce ammonia and methanol formation levels at shift reactor outlet?

A5. Methanol is a key concern across the shift section as it reduces product make, affects CO₂ quality (for urea production or if sold) and means that the process condensate must be treated before it can be reused or disposed of. Methanol is formed across the high and low temperature shift catalysts due to the reactive nature of the gas and the copper in the catalysts, which catalyses the methanol synthesis reaction. Methanol make reduces as the temperature is reduced and as the steam content of the gas is increased. A really effective way to reduce methanol make across the LTS is to install Johnson Matthey's low-methanol catalyst, **KATALCO** 83-3X, which can reduce methanol make by up to 90%.

Ammonia can be formed in the "front end" of ammonia, methanol and hydrogen plants due to the presence of nitrogen (either in the feed natural gas or the process air) and the high temperatures seen in the reforming section.

Small amounts of amines can be formed if the ammonia formed in the reforming section reacts with the methanol formed across the shift section. These can cause undesirable odour problems in the vent. Reduction in methanol formation across the shift, for example by the use of **KATALCO** 83-3X, results in a beneficial reduction in amines formed.

Q6. What is used to measure the health of the bed during operation? Interested in knowing if operators have a direct measurement to assess the health of their Catalyst bed during operation? Does the JM solution show a change in those readings?

What are the best tools for monitoring the WGS catalysts?

A6. There are a few measurements that can be used to look at the performance of the catalyst during operation, bear in mind that these are all sensitive to plant changes, such as plant rate and so on:

1) The pressure drop across the bed is a key parameter as it can often affect the plant rate or efficiency if constrained. Additionally, if there has been a plant upset that results in a deposit of solids on top of the bed then this will be readily seen by a jump in the pressure drop. If there is poor gas distribution at the top of the bed that causes milling of the catalyst, this will also be seen in an increased pressure drop across the bed. It is difficult to diagnose the cause of the pressure drop increase without looking inside the vessel, but a sharp increase in pressure drop is a good indication that something has happened.

2) The temperature profile within the catalyst bed can be a good qualitative indication of the progress of the catalyst life. It is beneficial to have enough temperature measurement points within the bed to allow a representative temperature profile to be seen. There are modern multipoint solutions to temperature measurement, such as multipoint single sheath thermocouple technology which offers higher data resolution. For an HTS catalyst bed, at the start of life the temperature profile is sharp, the temperature rise occurs over a short volume of catalyst. The main deactivation mechanism of HTS catalyst is thermal sintering, what is seen over time is that the profile becomes lazier, the slope is longer taking more of the bed to complete the reaction. The main LTS catalyst deactivation mechanism is poisoning. The temperature profile should remain sharp over the life of the catalyst bed, but the "dead" zone of poisoned catalyst at the top of the bed slowly moves the reaction profile down the bed as the catalyst life is consumed by the poisons in the process gas.

3) The carbon monoxide concentration at the outlet of the bed should be monitored as this is a key parameter that will affect downstream processes. Normally by installed permanent gas analyser or laboratory analysis.

PURASPEC™ 2272 is designed to reduce the rate of deactivation of the LTS catalyst. This would be seen in that the LTS temperature profile will have a slower rate of progression through the LTS bed compared to a system operating at the same plant rate without **PURASPEC 2272**.

JM can provide regular evaluation and analysis of process data to monitor the performance and projected remaining life of the water gas shift catalysts, and the rest of the plant. Please contact your JM representative to discuss your requirements.

Q7. Does the inclusion of Cl guard following HTS limit or subtract from the catalyst charge for the HTS operation, and if so, how can that be resolved?

A7. No, the inclusion of **PURASPEC** 2272 does not reduce the volume of HTS catalyst in the vessel. Instead, it replaces the inert support material underneath the catalyst bed, maximising the use of the vessel volume. The change to PURASPEC 2272 will not affect the performance of the HTS catalyst.

Q8. If low temps are more favourable, why isn't the HTS run cooler?

A8. The shift catalysts are tailored to their operating conditions, which are a balance between equilibrium and kinetics. Lower temperatures are better for low equilibrium CO concentrations, but higher temperatures result in higher reaction rates and allow higher grade heat recovery in terms of plant design which can be important depending on the flowsheet. The faster the reaction is, the smaller the required catalyst volume. The HTS catalyst is designed to carry out the bulk of the water gas shift reaction and is robust and highly active over the wide temperature range seen in this duty (typically 330°C to 460°C (626°F to 860°F)). By comparison, the LTS catalyst is more of a "polishing" duty, and is designed to provide high activity even at the required lower operating temperature. It has a smaller required operating temperature range (typically 190°C to 230°C (374°F to 446°F)) and maintains a high catalyst activity over the required lifetime. There is a lower temperature limit on the operation of the HTS catalyst to ensure that the reaction kinetics are fast enough to complete the reaction in a reasonable catalyst volume. JM can also supply medium temperature shift catalyst, which typically operates in the range 270-330°C (518°F to 626°F) and can be appropriate for certain flowsheets as a single stage of shift conversion..

Q9. Please could you explain what is shiftshield?

A9. Additional protection against boiler leaks onto HTS catalyst can be gained through use of a layer of guard material. **SHIFTSHIELD** is a high surface area, high voidage inert hold down material that is ideally suited for capturing boiler solids that would otherwise damage the top layer of HTS catalyst. **DYPOR™** 607 hold down material has a fluted ring shape to provide high voidage and strength. This ensures a high surface area to allow maximum pick up of foulants such as boiler solids, whilst maintaining an open structure to prevent pressure drop build up.

Q10. What is streamline?

A10. JM developed **STREAMLINE** to help plants with high pressure drop across reactors. High pressure drops are often found to be due to either poor design of exit collector arrangement or increased plant rate. **STREAMLINE** is a simple modification that, in many cases, gives a rapid return on investment. **STREAMLINE** is a package comprising of 3 steps, 1) JM flow modelling study to identify sources of pressure drop in the vessel, 2) design a proven solution based on a novel support material 3) provide installation assistance B9

Q11. What is difference between **KATALCO** 71-5 and **KATALCO** 71-6?

A11. Both **KATALCO** 71-5 and 71-6 are iron-based HTS catalyst products, with added promoters to boost performance. **KATALCO** 71-5 is our robust, high activity HTS catalyst, with many years of proven strong performance in service. **KATALCO** 71-6 is our premium HTS catalyst product which is more resistant to boiler leaks, it has higher strength in service and has the highest activity of any HTS catalyst on the market.

Q12. What are the best tools for monitoring the WGS catalysts?

A12. See answer 11.

Q13. For the LTS, what dew point margin should we have, do you have a recommendation?

A13. For LTS catalyst, the typically recommended margin to dewpoint at the inlet is 15-25°C, 27-45°F.

Q14. Whats the typical approach to equilibrium value for HTS and LTS catalyst at SOR/EOR condition?

A14. At start of run (SOR) we would expect that the approach to equilibrium (ATE) for both HTS and LTS catalyst would be close to zero (0°C or 0°F). As the catalyst moves towards end of run (EOR), we would expect that the inlet temperature would be increased to compensate for the natural deactivation of the bed. This increase in temperature will improve the reaction kinetics and move the ATE back towards zero. Once the bed has reached a temperature limit (process or catalyst), and the outlet CO concentration is approaching the downstream process limit, it is considered that the bed has reached the EOR. It is worth bearing in mind that the ATE will also be affected by plant rate (lower rate, lower ATE) and process gas composition, such as steam ratio. These factors should also be considered when judging if the catalyst is approaching EOR.

Q15. What is the split proposed loading for the chlorine guard and the 83-3 catalyst?

A15. JM's LTS catalysts, **KATALCO** 83-3 and 83-3X are self-guarding and no active catalyst volume needs to be replaced with a guard. The **PURASPEC** 2272 guard which sits in the base of the HTS does not require catalyst volume to be reduced, it replaces the existing inert support material but adds extra Cl removal meaning Cl is prevented from entering the LTS

Q16. We have Cl absorbent layer under the HDS, is it better to have here or under the HTS?

A.16 Chloride can enter the plant through the feed gas, the process air intake, and in some cases through the steam system. Therefore, to ensure maximum protection for the LTS and to maximise life, both the chloride absorbent **KATALCO** 59-3 under the HDS (hydrodesulphurisation) and the chloride guard **PURASPEC** 2272 under the high temperature shift are recommended. **KATALCO** 59-3 will clean the natural gas feed and protect all catalysts in the plant, particularly the steam reforming catalyst, from chloride in the feed. **PURASPEC** 2272 will protect the LTS from chlorides from all sources, including in the process air (a particular problem if your plant is located near the sea), chlorides in the steam and any residual chlorides from the feed gas.

Q17. What is the typical height of the dead zone of the sintered/poisoned LTS catalyst?

A17. The poisoned volume at the top of the LTS will depend on the concentration of poisons such as sulphur and chloride in the feed, the length of time the catalyst has been in service and the plant rate. The LTS catalyst is generally considered to have reached end of life when the poisoned volume has grown so large that the reaction is only just complete within the remaining active catalyst volume. JM can track the movement of this dead zone and project remaining catalyst life, please contact your JM representative for more information.

Q18. What's the s/c ratio required for HTS and LTS?

A18. There is a lower limit on the steam to carbon ratio (S:C, S/C) to protect the HTS catalyst from over-reduction. The active form of the catalyst is an iron oxide species, and if the catalyst is subjected to overly-reducing gas conditions this can be reduced to iron metal. This will weaken the catalyst, resulting in pressure drop increase, as well as cause the formation of unwanted byproducts. The typical minimum recommended S:C ratio is around 2.8 -3.0, but there are a number of other factors that can affect this. If you require more information and guidance, please contact your JM representative who will be able to provide more detail for your plant conditions. There is no LTS catalyst lower limit on the steam to carbon ratio, but a reduction in the steam content of the gas will likely increase the outlet CO concentration due to the change in equilibrium position and will increase the methanol make across the catalyst.