JM ProcessWise Webinar
Nitric acid webinar questions
July 2020

Questions and Answers

Q1. Are there any time limits for raising the temperature? For example: 10 minutes?

A1. Plant start up procedures need to take account of the manner in which each individual plant is designed. A time which is too long on one plant might be too short on another plant. JM is happy to discuss start up procedures on a case by case basis.

Q2. A black spot on gauzes was noticed during production campaign, plant tripped and restarted up again, then surprisingly black patch disappears. do you think it was Iron contamination?

A2. The attrition of the support rings is caused, primarily, by the thermal expansion (on start-up) and contraction (on shut-down) and so is virtually impossible to eliminate. There are several designs of circumferential devices which can be used to give better support to the gauzes and minimise the risk of tearing due to lack of support. Additionally, the gap resulting from the attrition increases the flow around the perimeter due to reduced flow resistance and this in turn causes increased consumption of the wires. Increasing the gauze density around the perimeter can help by ensuring enough strength in the gauzes at end of campaign to reduce the risk of tearing.

Q3. Any other solution other than the circumferential ring to stop attrition of support rings and thin tears?

A3. Correct, a lead-lag system would ensure that once the lead bed has started the breakthrough, the lag bed is brought online to treat the stream. It also serves the purpose of ensuring the maximum capacity of the lead bed is achieved.

Q4. Are there any negative impacts or risks of contamination from sea water cooling towers in close proximity?

A4. If cooling towers are located upwind of the process air intake, chloride can be drawn into the nitric acid plant. In addition to obvious concerns relating to the absorption columns, the presence of chlorides can, in theory, lead to increased metal losses. Sodium and chloride contamination on the gauze surface can adversely affect performance through blocking catalytic sites, potentially preventing or reducing the level of restructuring observed on the wire surface.

Q5. Are there any rules of thumb of start-up flows to the gauze, for example 50% of normal capacity 40% etc?

A5. Plant start up procedures need to take account of the manner in which each individual plant is designed. Something which is appropriate on one plant might be inappropriate on another plant. JM is happy to discuss start up procedures on a case by case basis.

Q6. Can we remove Rh_2O_3 by stopping the plant and reduce again gauzes with H_2?

A6. Rh_2O_3 is stable and, once formed, is difficult to remove. Whilst it can be reduced by hydrogen, full activity is unlikely to be restored due to other deterioration mechanisms.

Q7. Can you comment on ratio control vs temperature control, is there a benefit for either with regard to efficiency, total production, N_2O etc?

A7. Depending on the stability of the plant and magnitude of diurnal fluctuations, ratio control can be highly effective. A well tuned temperature control loop would however be expected to achieve better results.

Q8. Considering the blowing of the plant, What is the best for gauzes? Continuous blowing just after a planned stop, or shut down , prepare and start again the turbo-compressor and blowing by steps?

A8. Considering the gauzes in isolation it is best to minimise time in the rhodium oxide forming regime. Whilst gauze packs have little thermal inertia and, in isolation, can cool rapidly, this is not necessarily the case for equipment and catalysts (eg: N2O removal) in close proximity to the gauze which have greater thermal inertia and can conduct/convect heat to the gauze. A continuous flow is likely to preferable.

Q9. Do you have any advice on the type or design of filter that should be used in these systems?

A9. Impurities vary from site to site (eg: source of ammonia; local air quality in proximity to process air compressor intake). Our advice is to conduct a thorough assessment of impurities which are likely to be present in your own plant and to discuss the best method of removal with a reputable filter supplier.

Q10. Does cauliflowering weaken the integrity of the gauze?

A10. The formation of cauliflowers and general restructuring of the wire surface results in a change to the composition of the surface of the wire. The cauliflower itself is formed by the movement of metal oxides which are removed from and then settle on to the surface. The catalyst is more fragile to plant trips and manual handling following the restructuring, as the cauliflower structures are microscopic in scale and can be removed during a plant upset. While the restructured catalyst is weaker than the as-manufactured wires, the cauliflower structures create a significant increase in the surface area of the catalyst and the number of platinum sites available for catalysing the reaction. The restructured wire has sufficient strength such that it does not suffer from mechanical loss during normal operation. The metal loss associated with PGM catalysts is a result of the restructuring process itself and the loss is primarily in the form of platinum oxide.

Q11. Does JM offer CFD modelling of the burner if we think we have a problem with flow distribution?

A11. JM has extensive CFD modelling capability and offers this technique, as a paid service, to understand and improve flow distribution.

Q12. Does JM provide Top and Bottom suport, Khantal Screens, Gauze pack (180, 270, 360 day)?

A12. Johnson Matthey can supply Kanthal screens, and these are provided as standard as part of a catchment/getter system or to support a corrugated gauze catalyst. Specialised screens can also be provided on request, e.g. the support screen which sits below N2O abatement catalyst or Raschig rings. We can supply gauze packs that can run from 180 days up to 1 year for medium pressure and low loading plants. The optimal campaign length will depend on the operating conditions of the plants. Please contact Johnson Matthey with more information on the operating conditions of the plant in question and we will be able to propose a catalyst design that is suitable.

Q13. Does Moisture in the air impact on performance of gauze, given reaction produces water vapor?

A13. The various ammonia oxidation reactions proceed to completion, the water content inlet the converter is much smaller than the water content exit the converter and reaction stoichiometry is such that changes in water content have minimal theoretical effect on selectivity. As a result, gauze performance is not affected to any meaningful extent by the moisture content of atmospheric air drawn through the air intake. High humidity levels can however have an effect if this results in soluble substances being reintroduced into the process air from damp filter media.

Q14. Even all gauzes have same diameter, is it true that some gauzes are little stretchable due to slight change in composition? do you think it will lead to witness slightly bigger gauzes at top as compared to bottom one?

A14. All knitted gauzes, regardless of alloy, are slightly flexible and can be stretched due to the nature of the structure. The force required to stretch a gauze to the point of damaging it is much higher than the forces it experiences during manufacturing and installation. However, care should always be taken during installation to fully support the gauze when transferring it from its packaging to the burner, to prevent it stretching out under its own weight or catching and tearing. Woven catchment gauzes are less flexible than knitted gauzes; when installing the catalyst and catchment layers, the bottom gauzes will feel less stretchable than the top gauzes. This is due to the different structures rather than the different alloys.

Q15. How do you determine the difference in damage to the gauze structure from in service damage or mechanic damage from separating the layers for SEM?

A15. Care is always taken to minimise mechanical damage to the gauze layers when separating them for SEM and EDX analysis. The level of damage caused by this separation is linked to the condition of the returned catalyst. Our laboratory analysts will evaluate the integrity of the returned catalyst prior to separation. If the catalyst has low mechanical integrity the layers may be left intact, and analysis carried out only on the top gauze layer. However, sometimes a catalyst that appears to be stable will still lose some restructuring during the separation and manual handling. The key difference between this type of damage and in-service loss of restructuring is that manual handling damage tends to be more localised, with in-service damage or loss being widespread across the sample. Damage from manual handling in our lab is also obvious as dust will be generated when handling the sample. Most damage to the catalyst surface occurs during transport. Most larger gauzes (>2m diameter) are typically rolled up or folded when being returned to Johnson Matthey to be refined. To get a representative sample, it is critical to cut the sample from the gauze on site prior to preparing the gauzes for transport and to safely package the samples to minimise loss during transport. While we can take samples from a gauze that has been returned, the sample will have seen significant damage and is unlikely to be representative of the catalyst at the end of the campaign. The results from analysis of a sample of this nature are likely to be limited as the cause of the damage (handling, transport or in-service) is extremely difficult to determine. We can provide further guidance and advice on taking and transporting samples if required.

Q16. How if the operating condition is increase (pressure and production), should we do an improvement to catalyst? can you tell what the impact of this condition?

A16. Any major change in operating conditions (production rate, campaign length, operating pressure and temperature) should be reported to your catalyst supplier to ensure the catalyst design is updated to reflect the new operating conditions. Small changes in operating conditions (e.g. fluctuations in operating temperature and pressure) are unlikely to impact the catalyst design or performance, but it good practice to keep the operating conditions updated when ordering a new gauze pack. An increase in daily production rate can have a significant impact on the catalyst design. Our catalyst designs can withstand an increase of 5% in the design production rate, which allows for some flexibility during a campaign. However, if the increase in production rate is likely to be permanent, this should be communicated. The total metal loss from a catalyst will increase if the production rate increases, or if the campaign length is extended for a constant production rate. As a result, the catalyst design would likely require some additional PGM than your current catalyst design to ensure there is sufficient metal to sustain the reaction to the end of the campaign without any significant ammonia slip. If the burner operating pressure changes substantially due to an upgrade to the compressor, the catalyst design is likely to change. The intrinsic selectivity and primary metal loss of the catalyst are influenced by the operating pressure, and the catalyst design is tailored to the operating pressure. Increase the pressure will see an increase in metal loss and a reduction in selectivity to nitric oxide. For a decrease in pressure, the opposite is true.

Q17. How long we should use H2 during startup before we will put NH3 to reactor?
A17. Plant start up procedures need to take account of the manner in which each individual plant is designed. A time which is too long on one plant might be too short on another plant. JM is happy to discuss start up procedures on a case by case basis.

Q18. If a gauze is contaminated, is it possible to recover the performance of the gauze whilst continuing to operate?
A18. It is rarely possible to recover the activity of a contaminated gauze without shutting the plant down. If a short outage can be tolerated, some contaminents can be removed by vacuuming the gauze. Others can sometimes be removed by pickling. Adding an extra gauze is also a possibility as might be replacing one or more gauzes.

Q19. If reaction is on ratio control and temperature is not strictly controlled, do you think ammonia to production ratio will decrease?
A19. Depending on the stability of the plant and magnitude of diurnal fluctuations, ratio control can be highly effective. A well tuned temperature control loop would however be expected to achieve better results.

Q20. If you poison or contaminate the gauze, can the performance be recovered?
A20. It is rarely possible to recover the activity of a contaminated gauze without shutting the plant down. If a short outage can be tolerated, some contaminents can be removed by vacuuming the gauze. Others can sometimes be removed by pickling. Adding an extra gauze is also a possibility as might be replacing one or more gauzes.

Q21. Is it recommended to add H2 to the stream with the idea to recover some of the activity?
A21. Any attempt to re-reduce in the manner described would require careful risk assessment and is unlikely to recover anything close to full activity. In addition, care would need to be taken not to melt the gauze pack.

Q22. Is there a recommended spec for the hold-down ring. The thicker the gauze, the heavier the hold down ring must be, correct?
A22. It is advisable to check with your basket manufacturer on what advice, if any, they provide for weight ring specifications. In general, the following criteria should be observed for a weight ring: 1. The weight ring should sit flat on the gauze support ring. This should be checked and monitored during shutdowns, as over time the gauze support ring will begin to creep. Visual monitoring along with the use of feeler gauges can be used to confirm if the weight ring is flush with the support ring. 2. The weight ring should sit around the inner diameter of the gauze support ring/contact diameter of the gauzes rather than sitting toward the outer diameter. This ensures that the weight ring will continue to hold the gauze pack in place as it moves outward during thermal expansion.

Q23. Is there a rough rule of thumb for what temperature is too high or too low?
A23. The optimum operating temperature varies with plant design. In general terms, the higher the operating pressure, the higher the optimum temperature.

Q24. Is there a specific alloy composition that you would recommend for to reduce rhodium oxide formation?
A24. First and foremost, our recommendation would be to try to operate the plant in a manner in which Rh2O3 formation is not favoured. When that is not practicable, we can also offer gauzes with low (3%) rhodium content.

Q25. Is there a theoretical minimum ammonia conversion efficiency at which ammonium nitrate begins to form in the absorption section?

A25. Ammonia conversion efficiency can vary for a number of reasons with differing effects and consequences. As an example the consequences of a tear in a gauze pack may be different from the consequences of poisoning. As a result it is not possible to specify a theoretical minimum conversion efficiency below which AN will form.

Q26. Is there an optimum operating temperatures for the gauze?
A26. The optimum operating temperature varies with plant design. In general terms, the higher the operating pressure, the higher the optimum temperature.

Q27. Is there any automated device for N2O concentration monitoring after gauzes? In our plant lab takes samples after ammonia burners at 300ºC, We would like to check N2O concentration in case any ammonia leakage due to ammonia by-pass caused by gauzes movements or damages, burner jacket holes, etc?
A27. The analysis of N2O in samples taken as you describe can be done using Gas Chromatography. A porous polymer column (such as Poropak Q) will separate the N2O and it is easily detected with and ECD.

Q28. Is there some alloys that can be used to reduce rhodium oxide formation?
A28. First and foremost, our recommendation would be to try to operate the plant in a manner in which Rh2O3 formation is not favoured. When that is not practicable, we can also offer gauzes with low (3%) rhodium content.

Q29. Natural day/night cycle causes flow to change through the gauze in a single day-does this cycle have impact on gauze efficiency due to cycling heat flux?
A29. Depending on the stability of the plant and magnitude of diurnal fluctuations, ratio control can be highly effective. A well tuned temperature control loop would however be expected to achieve better results.

Q30. Once we have seen severe deactivation, and we opened the reactor to change the gauses, we saw a big "orange stain", which after some analysis, we discovered that it was iron, sourced from corrosion on upstream piping.
A30. Upstream pipework can be a source of contamination and it is well worthwhile checking its condition whenever possible eg: during overhauls and gauze changes. Debris can collect in upstream pipework during a shutdown before being carried through onto the gauze surface if the pipework is not inspected prior to start-up. Appropriate selection of materials of construction also helps.

Q31. Thank you for the great idea of the webinar. We want more!
A31. Thank you for the compliment. We are planning to hold more webinars.

Q32. The Coils are dropping on the west and Eastern sides of the PGC beneath the catalyst basket . Any suggestion to level the basket?
A32. The most optimal solution will depend on the basket design, and further advice can be provided when this information has been shared. A general solution is to first suspend the honeycomb over the boiler tubes as level as possible and survey the distance between the tubes and the honeycomb. To level out the honeycomb above the coils, a quick solution would be to add metal shims below the honeycomb supports to add height to this section of the honeycomb. A more technical solution would be to fabricate a legs with a slot which the honeycomb would sit through. The foot of these legs would find their own level and then the honeycomb can be welded to the leg to fix it in place.

Q33. What are indications that ammonium nitrate is being formed in the reaction
A33. Ammonium nitrate is not formed across the gauzes but can be formed downstream. Periodic analysis of cooler condenser rundown can be used to provide an indication that ammonium nitrate is being formed, although this is not advisable is there is any suspicion that ammonia slip is abnormally high, conversion efficiency is abnormally low or when gauze temps are abnormally low due to the potential for ammonium nitrite formation.

Q34. What instrumentation would you recommend to check for ammonia carry over?

A34. Procedures and instrumentation need to take account of the manner in which each individual plant is designed. That said, common themes often include

- measurement and control
- Good instrumentation
- Pressure & temperature correction
- Maintaining steady operating temperature & pressure
- Preventing overshoot when adding ammonia eg:
- Slow start up valve
- Making slow and careful changes
- Preventing liquid droplet carryover
- Vaporiser on automatic level control with high alarm
- Low temp alarm & trip exit ammonia superheater
- Tracing/insulation of the ammonia gas pipework
- Ammonia system pressure control when the plant is shut down
- Consider low points in which liquid ammonia might collect
- Allowing the system time to reach the correct temperature before feeding ammonia to the gauzes
- Typical Trip Systems
- Gauze temperature – safeguards against relatively slow changes in ammonia concentration
- Ammonia concentration - safeguards against rapid changes in ammonia concentration
- High Vaporiser level (carryover)
- Low ammonia temperature (carryover)
- Proof testing – trip and alarm systems are only as good as the instrumentation and the maintenance regime

Q35. What is the longest campaign length observed for highly loaded high pressure plants?

A35. The longest acceptable campaign length will vary at different plants, as the lowest acceptable efficiency is not constant throughout the industry. In areas where raw material prices are lower, and ammonia cost is low as a result, plants will continue to operate the plant until conversion efficiencies are well below 90%. An additional constraint on the campaign length for high pressure and highly loaded plants is the pressure drop over the catalyst and catchment/getter pack. As a campaign progresses, the catchment collects a greater level of platinum and the open area of the catchment gauzes is significantly reduced. The pressure drop over the pack increases as a result and the plant begins to run at reduced rates to offset the impact on the compressor. For high pressure and highly loaded plants that run without catchment packs, campaign lengths of 120 days have been achieved. For those with getters and higher minimum conversion target, campaign lengths of 100 days have been achieved, although 90 days is more typical.

Q36. What recommendations do you have for the filtration for these systems, is there an industry standard?

A36. Impurities vary from site to site (eg: source of ammonia; local air quality in proximity to process air compressor intake). Our advice is to conduct a thorough assessment of impurities which are likely to be present in your own plant and to discuss the best method of removal with a reputable filter supplier.

Q37. You mentioned that startup is important for the performance, please could you explain again what are the most important steps and the main issues in the startup procedure?

A37. As mentioned above, start-up procedures need to take account of the vagaries of individual plant designs. Generalised recommendations are as follows..

- Start Up:
  - Raise gauze temps through the range 730-840°C (1350-1550°F) as quickly as possible

  - Increase ammonia quickly, but not so quickly (30s?) as to lead to overshoot or carryover.
  - Confirm light off (eg: x mins to reach yyy °C)
- Shut down:
  - attempt to get the gauzes below 725oC (1340°F) as quickly as possible
- Consistency:
  - Start-up and Shutdown procedures.
  - Maintain steady operating conditions throughout the campaign
- Checks:
  - Measured gauze temperature consistent with ammonia concentration?
  - Visual gauze check after light-up with defined criteria
  - Eg: Black patches > xx" for > yy mins, shut down

Further Information

Please contact your local Johnson Matthey representative for further information or send your enquiry to polly.murray@matthey.com