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Root cause analysis of poor performance in nitric acid plants

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Johnson Matthey (JM) has assisted in root cause analysis for several customers in recent years, working in conjunction with the plant engineers to improve nitric acid plant performance. JM was supplying the primary platinum group metal (PGM) ammonia oxidation gauze for these plants, when they began to experience performance issues, typically seeing a reduction in both conversion efficiency and increase in N_2O emissions. In most of these cases, the initial conversion efficiency started high before rapidly dropping several percent during the campaign.

In all these cases, a combined team of engineers, from JM and the customer plant, proceeded with a detailed root cause analysis (RCA) to identify the possible causes of the problem and to prepare and implement the corrective actions to solve this issue. By following the RCA process, a fault tree analysis was developed from an identification exercise, which highlighted potential cause factors to the problem. A range of root causes have been identified in different plants over the last few years, including catalyst contamination from poor gas filtration and boiler leaks. The most common cause, typically resulting in the worst drop in performance, has been a structural problem with the basket within the burner, resulting in ammonia bypassing the catalyst.

Symptoms of poor performance

JM supplies ammonia oxidation catalyst in the form of knitted PGM gauzes to a range of nitric acid plants. These plants operate across a wide range of operating pressures and nitrogen loadings, and different design principles are applied to the catalyst design for each category of plant. Catalyst packs are also designed and manufactured to allow for ease of installation, which can reduce any potential downtime.

This optimised design approach results in JM catalysts achieving high performance, often increasing conversion efficiencies by over 1% compared to competitor product performance. End of campaign catalyst analysis and further optimisation of the design can result in greater increases in both performance and campaign lengths achieved.

However, there have been occasions where the plant performance has been reduced, with plants experiencing a sudden drop in conversion efficiency and a corresponding increase in N_2O emissions. The magnitude of the reduction in performance can vary depending of the plant pressure and loading, and the root cause of the poor performance. Reductions in conver- sion efficiencies of up to 5% and a three-fold increase in N_2O emissions have been observed, which raises concern about both the plant and catalyst performance.

Following notice from the customer on any poor performance, JM begins discussions both internally and with plant engineers to determine the cause of the reduction in performance.

Identification of potential causes

As the cause of the poor performance is often not immediately clear, the first stage in identifying the cause is to proceed with a detailed root cause analysis (RCA) to identify all possible causes of the problem, identify all probable causes and, when identified, prepare and implement the corrective actions required to solve the problem. Well-structured RCA processes can greatly reduce or eliminate costly problems and minimise the impact to the producer.

There are a number of methods available to carry out root cause analysis. A common method is to use the A3 problem solving method, along with additional tools including a fishbone cause and effect diagram. This allows for all potential root causes to be systematically identified, and the likelihood of each cause can then be assessed. The root causes deemed most probable are then investigated further by engineers from the customer plant and JM.

The root cause analysis consists of several steps:

- Identification and description of the problem, asking the following questions:
    - What deviation was observed?
    - Which object had the deviation?
    - When did the deviation occur?

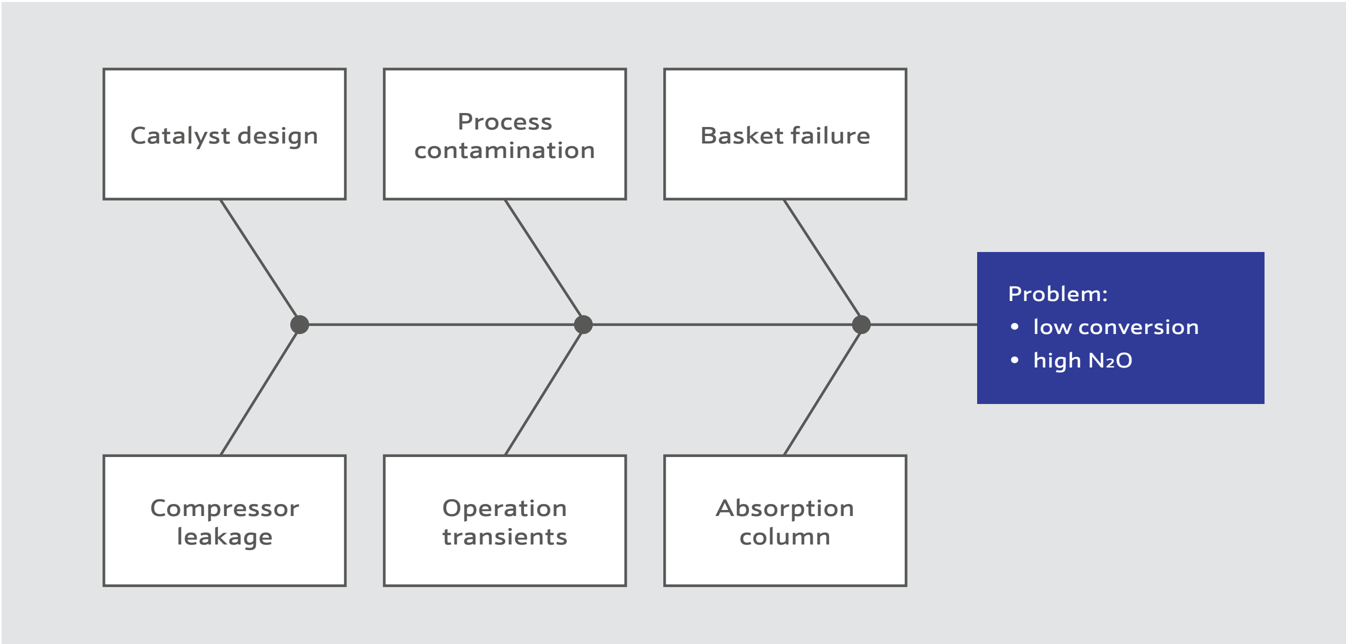

Fig. 1: The main factors considered during the root cause analysis

- Where did the deviation occur?
- How much of a consequence did it have?

- Selection of the team in charge of the RCA
- Identification of the potential hypotheses and reasons that have caused the problem
- Establish a workplan and strategy to rule out hypotheses
- Definition of steps to solve the problem with minimum impact

The A3 methodology followed an 8-stage process to identify and correct the root cause of the reduction in performance.

1. **Define the problem:** Clarify the problem using data and quantify the impact of the problem.
2. **Break down the problem:** Generate current process data to understand the entire process; collect information to visualise the current situation; break the problem into parts that can be solved separately; prioritise parts of the problem with the greatest impact.
3. **Define objectives:** Define the desired outcome based on the specific problem identified; decide what specific results are required; state the goals using SMART criteria (Simple, Measurable, Achievable, Relevant and Time).
4. **Identify potential direct causes:** Establish hypotheses of direct causes using fishbone diagram or brainstorming sessions; validate or discard the hypotheses using data, field observation and/ or expert judgement.
5. **Identify root cause:** Find the root causes of the direct causes validated in step 4.
6. **Define action plan:** Identify actions required to tackle the root causes identified; prioritise the actions according to their impact and feasibility.
7. **Follow up action plan:** Assign responsibility for executing actions and track progress; check the effectiveness of the actions.
8. **Standardise successful process:** Extend solutions to other processes if they encounter similar problems or common root causes.

The team that carried out the root cause analysis was a team of engineers from both the customer plant and JM. Initially, an exhaustive list of potential factors that could have an impact on plant efficiency were listed. This list was then reviewed by the team of engineers and several factors could be ruled out. The main factors considered for the majority of these case studies are summarised in Fig. 1. The team at the customer plant and at JM were then both given tasks to rule out certain hypotheses.

Process contamination

A potential root cause for reduction in per- formance was identified as high levels of contamination on the gauze surface resulting in lower selectivity to nitric oxide. There are many sources of contamination, with iron contamination the most damaging as it both blocks the platinum catalytic sites and oxidises ammonia with a greater selectivity to nitrogen and nitrous oxide.

Depending on the severity, surface contamination is often visible on the gauze surface in the form of dark patches. In these cases, JM recommends plant engineers observe the gauze surface for signs of obvious contamination, as well as any physical damage (e.g. tearing) to the gauze surface.

It is also recommended that plant engineers check the pressure drop over the mixed gas filter. If the filter material has been lost or damaged there will be a change in pressure drop over the filter. A review of the ammonia quality certificates can also be carried out to review if levels of iron contamination sourced from the ammonia feed have increased during the campaign.

Although these checks reduce the likelihood of contamination as a root cause, it is often not sufficient to completely rule it out, and contamination or damage to the catalyst often remain as an active hypothesis.

Basket failure

Basket failure is very difficult to rule out as a hypothesis. A visual inspection through the burner sight glass can be carried out, however often nothing unusual will be observed. This is because basket failure often occurs in the form of cracks along welds which would only be visible during a full inspection of the open basket during a shutdown. Basket failure often remains a probable hypothesis for the reduction in performance.

In the event of a basket failure resulting in significant by-pass of the catalyst, the ammonia oxidation reaction may begin to take place on the surface of the burner. This results in the burner material reaching high temperatures, and the resultant heating can often be observed through hot spots on the burner surface. In this case, basket failure would become a very probable root cause. Further heating of the burner can result in early aging, and plant engineers who observed this symptom would often choose to shut down the plant to carry out a full inspection of the basket and burner.

Compressor leakage

JM has worked with many plants historically to determine the root cause of performance problems and, depending on the plant configuration, it can be possible for a compressor leak to result in tails gas being introduced upstream of the gauzes, introducing nitric oxide which could react to form additional nitrogen and nitrous oxide. Plant engineers are advised to check the configuration of the compressor and expander and if the set up does not result in mixing of inlet and tail gas streams in the event of a leak, this hypothesis can be ruled out.

Operation transients

During a root cause analysis, detailed process data is requested from the customer and sent through and reviewed by JM. The outcome of this review is highly dependent on the data received, however several common themes have been observed in multiple plants, including the nature and magnitude of the increase in N_2O emissions. For example, when poor performance is linked to the PGM catalyst, the increase in emissions and corresponding drop in efficiency is gradual as the reaction moves too far into the catalyst pack too early in the campaign.

Often, plant data will show a sudden spike in N_2O emissions, rather than a gradual increase. Step changes in emissions can be linked to catalyst performance if they are following a compressor trip: often the force on the gauze results in a loss of the high surface area growth (cauliflowers), resulting in a temporary and sudden reduction in available catalytic sites for the oxidation reaction. The performance would be expected to improve as the gauze begins to restructure again, however if the damage is great enough then the previous levels of performance may not be reached again. In some cases, the sudden reduction in performance in the plant is not preceded by a plant trip. In these cases, ammonia by-pass becomes a probable root cause.

Plant temperatures are reviewed in the days leading up to and following the reduction in performance. Several cases have reported uneven temperature distribution across the gauze, with one thermocouple reading significantly higher or lower temperatures than other thermocouples. Higher temperatures can indicate uneven flow patterns and a higher loading in one section of the gauze. It could also indicate a higher selectivity to nitrogen and nitrous oxide in this area of the basket, as these reactions are more exothermic than the production of nitric oxide.

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad \Delta H0 = -907.28\ kJ$

$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O \quad \Delta H0 = -1104.9\ kJ$

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad \Delta H0 = -1269.0\ kJ$

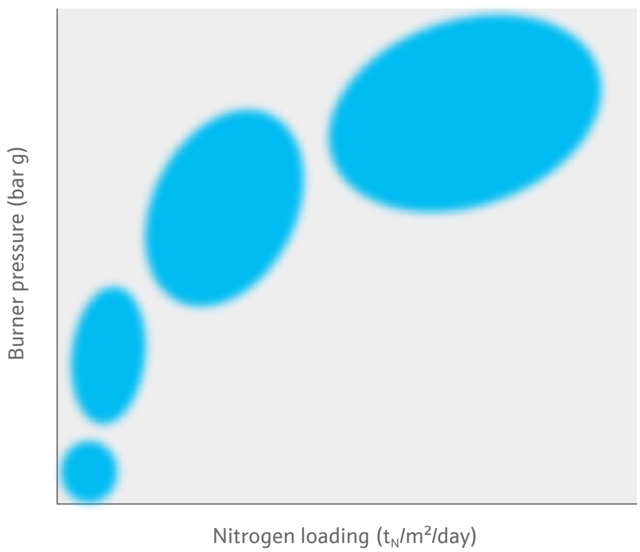

Fig. 2: Four plant operating ranges demonstrated in terms of nitrogen loading and burner pressure

Absorption column

Poor performance in the absorption column can result in reduced plant efficiency. To rule out this hypothesis, the NOx emissions in the tail gas are plotted against time and if they show a decreasing trend as the nitrogen loading is decreased this would suggest normal operation within the column.

Poor performance in the column would have no effect on N_2O emissions, which are only generated or abated within the ammonia oxidation burner and tertiary tail gas systems. If the reduction in conversion efficiency is accompanied by a corresponding increase in nitrous oxide emissions, this suggests the absorption column is not a probable root cause.

Impact of catalyst design

While plant engineers investigate process conditions and unit operations that have been identified as potential root causes, JM reviews the catalyst design using proprietary kinetic models to simulate the performance of the catalyst at the appropriate point in the campaign to determine the reaction profile within the catalyst packs.

In some cases, the reduction in performance has coincided with a new catalyst design being installed. The new design will typically have changed the alloys and knit structure used within the pack and will have been optimised for the plant operating conditions. However, due to the design being new, customers are often understandably concerned that the catalyst pack could be the root cause of the poor performance.

Catalyst design principles

When designing catalyst packs, JM considers the plant operating conditions and campaign requirements to design a pack with a competitive PGM weight that will deliver high performance throughout the campaign. The design rules applicable vary depending on the plant type, with four plant categories covering almost all operating conditions (see Fig. 2).

For medium pressure plants, operating around 2-6 bar g and with a nitrogen load- ing of less than 20 tonne $N/m^2/day$, JM designs the catalyst pack using proprietary design tools to generate a highly efficient design whilst minimising the installed metal content. This design utilises high surface area gauze structures in the top layers of the pack, providing sufficient platinum sites to complete the majority of the reaction at the beginning of the campaign in the top two layers of the pack.

The kinetics relating to ammonia oxida- tion have favourable selectivity to nitric oxide when the reaction path length is short. If the path length increases, and more gauze layers are used before the ammonia is all converted, the likelihood of nitric oxide reacting with ammonia increases, and reduces the overall efficiency of the pack.

$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$

$2NH_3 + 8NO \rightarrow 5N_2O + 3H_2O$

In addition to minimising the reaction path length with high density knit structures, the design rationale for medium pressure plants will often utilise high palladium alloys in the bottom part of the pack. The system gives greater average conversion efficiency and lower N_2O emissions for medium pressure plants than standard technology. A catchment system is often installed below the catalyst gauzes and will be designed for opti- mal recovery given the prevailing PGM market conditions at the time, and to minimise the pressure drop.

Modelling the reaction profile through the catalyst

To ensure that the gauze design could not be a contributing factor to any sudden decrease in efficiency, a simulation of the catalyst pack is often run using the ammonia oxidation kinetic model to verify that the ammonia oxidation reaction is completed at the appropriate point within the pack. The case study below was carried out to illustrate the expected reaction profile of a medium pressure plant gauze design at various points within the campaign. The reaction profile modelling carried out during a root cause analysis will vary depending on the category of nitric acid plant and the issues faced by the customer.

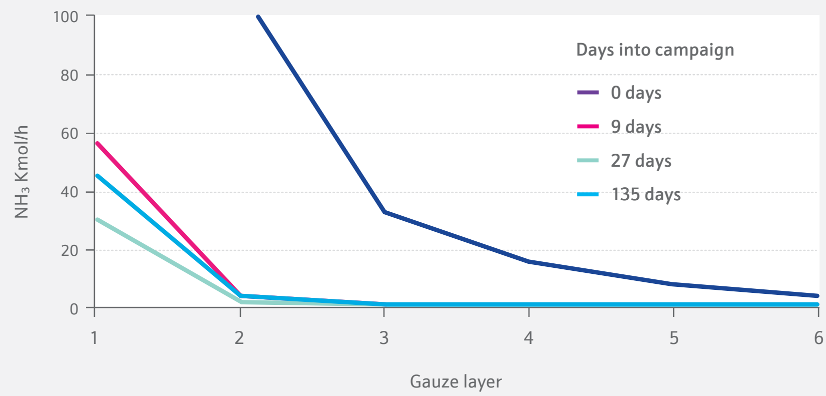

Figure 6. Kinetic model output for a gauze design for a low-medium press

During start-up, the gauze wires are flat and have limited surface area, and the reaction is completed within the 6-layer pack. Immediately following a successful light off, the wire surface begins to restructure to form high surface area growth, termed 'cauliflowers', and the bulk of the reaction is expected to complete within the top two layers for a plant with this pressure and nitrogen loading.

The results showed that within one week of operating, over 99% of ammonia had been converted after the second layer of the gauze design. Towards the end of the campaign the top layers would be expected to deactivate as they lose platinum throughout the campaign and the reaction profile would be expected to move further through the pack. By this stage that palladium-based alloys lower in the pack will have collected sufficient platinum to provide catalytic sites to continue providing a high level of performance.

If the kinetic modelling of the catalyst does not support the theory that the PGM catalyst design was not fit for purpose, then this result, along with the process data analysis, will allow the hypothesis of catalyst design causing poor performance to be ruled out.

Outcome of root cause analysis and mitigating actions

Following the elimination of many potential root causes for the reduction in plant performance, the three potential root causes most often found are:

- high levels of contamination on the surface of the catalyst;
- physical damage (e.g. tearing) to the gauze surface;
- damage to the basket resulting in ammonia by-passing the ammonia oxidation catalyst.

It is often not possible to further narrow down the root cause of the problem without a visual inspection of the gauzes and the basket containment system. The affected plant will often schedule a shutdown to carry out a full visual inspection of the basket. If contamination or physical damage to the gauze have remained as probable root causes, JM will often manufacture an additional gauze layer(s) that can be installed over the existing gauzes if required, often manufacturing with a reduced lead time due to the significant negative impact that low performance can have on a plant.

Common root causes that have been found in recent years include:

- cracks in baskets formed from weld failure and thermal cycling, resulting in ammonia by-pass;
- cracks in baskets formed due to using an abatement catalyst with an extremely high pressure drop, resulting in either ammonia by-pass of the oxidation catalyst, nitrous oxide by-pass of the abatement catalyst, or both;
- severe contamination on the gauze surface resulting from a boiler leak;
- severe contamination on the gauze surface resulting from damage to the up-stream gas filtration system.

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Conclusion

The use of root cause analysis in this sce- nario results in an in-depth and prompt review of potential causes of the reduction in performance. Through working together and using established problem-solving methodologies, customer plant engineers and JM engineers can reduce the large number of potential causes to a small number of probable root causes. This knowledge allows plant engineers to prepare and arrange for potential basket repairs in the case of basket failure, and to make the informed decision to order any additional gauze layers in the case that the gauze system is contaminated or damaged. As a result, the time spent shut down is often minimised and the impact from further production losses is reduced.

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