Solving problems in nitric acid plants

Troubleshooting and root cause analysis help to identify and solve problems in the operation of nitric acid plants and to prevent future reoccurrences. Johnson Matthey, Casale and Sabin Metal Corporation discuss their approach to solving problems in nitric acid plants to improve plant reliability and efficiency and to avoid unplanned shutdowns, costly replacement of equipment and loss of production.

JOHNSON MATTHEY

Root cause analysis of poor performance in nitric acid plants

J. Ashcroft, R. Lopez-Garcia and I. Hepplewhite

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 by-passing 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 conversion efficiencies of up to 5% and a threefold 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

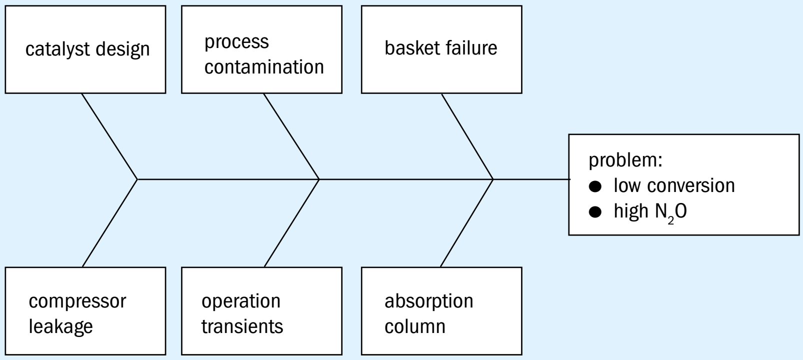
As the cause of the poor performance is often not immediately clear, the first stage in identifying the cause is to proceed with a detailed root cause analysis (RCA) to identify all possible causes of the problem, identify all probable causes and, when identified, prepare and implement the corrective 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?
  - 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

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



Source: Johnson Matthey

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 th e 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 performance 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.

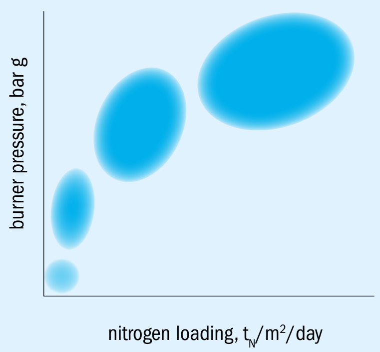
Plant temperatures are reviewed in the days leading up to and following the reduction in performance. Several cases have reported uneven temperature distribution across the gauze, with one thermocouple reading significantly higher or lower temperatures than other thermocouples. Higher temperatures can 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.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad \Delta H^o = -907.28 \text{ kJ}$$

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O \quad \Delta H^o = -1104.9 \text{ kJ}$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad \Delta H^o = -1269.0 \text{ kJ}$$

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



Source: Johnson Matthey

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 loading 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 oxidation 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 optimal recovery given the prevailing PGM market conditions at the time, and to minimise the pressure drop.

Modelling the reaction profile through the catalyst

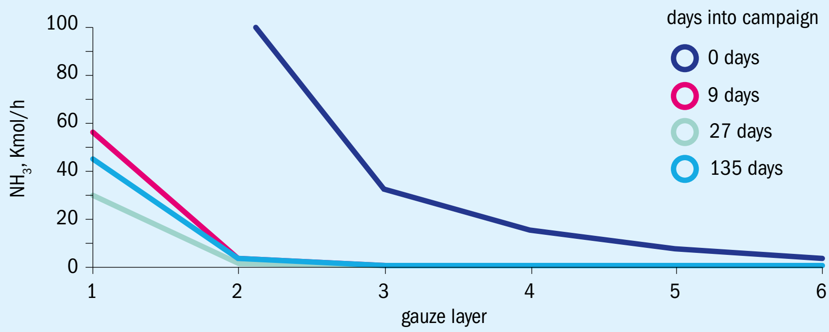
To ensure that the gauze design could not be a contributing factor to any sudden decrease in efficiency, a simulation of the catalyst pack is often run using the ammonia oxidation kinetic model to verify that the ammonia oxidation reaction is completed at the appropriate point within the pack. The case 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.

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.

Fig 3: **Reaction profile of the catalyst after various days of operation showing the bulk of the reaction is completed after the second gauze layer**



Source: Johnson Matthey

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.

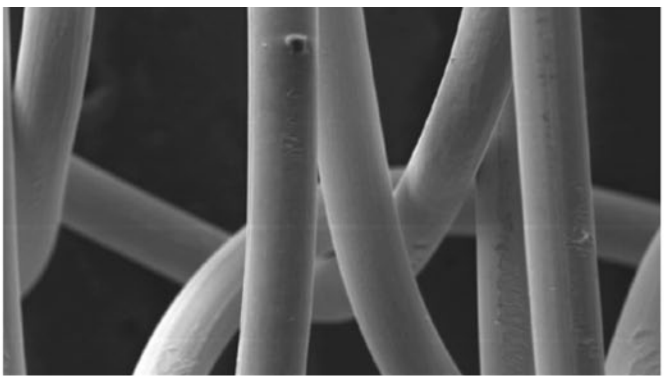
It is often not possible to further narrow down the root cause of the problem without a visual inspection of the gauzes and the basket containment system. The affected plant will often schedule a shutdown to carry out a full visual inspection of the basket. If contamination or physical damage to the 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 upstream gas filtration system.

Conclusion

The use of root cause analysis in this scenario 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.



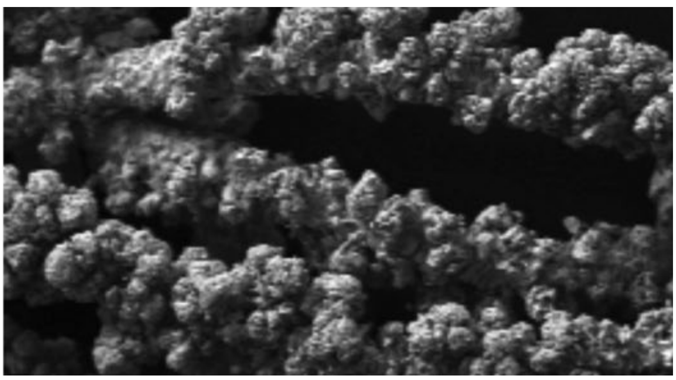


PHOTO: JOHNSON MATTHEY

Wire surface as manufactured (left) and after cauliflower formation (right). The significant increase in surface area can be observed.

CASALE SA

Solving operational and design problems in nitric acid plants

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Casale's nitric acid technology, includes process and mechanical knowhow as well as experience in operation and troubleshooting, strengthened by almost six decades of experience of GP in operating nitric acid plants. As a result, Casale's clients can take advantage not only of its strong engineering and technology capabilities but also its experience of plant operation which gives Casale a unique position in the fields related to the design, reliability, and troubleshooting of these plants.

Furthermore, the implementation of remote plant monitoring provides a new opportunity that enables Casale to further support customers to predict and solve plant issues, combining long-term troubleshooting experience with an accurate and constant analysis of the plant data.

Fundamentals of reliability

The reliability of a plant is linked to many factors such as the quality of the equipment, plant maintenance and the way the plant is operated.

The quality of the equipment is important but it is not always easy to make the proper choice between a very expensive item of equipment and a cheaper one with a shorter lifetime. For example, should a tantalum cooler condenser be installed instead of a stainless steel one, if the latter has a lifetime of more than ten years?

Maintenance is also crucial. Very often, a lot of pressure is put on the shoulders of the people in charge of maintenance to minimise the duration of any shutdowns. There are many examples showing that it is crucial for the future of the plant that these turnarounds should be prepared and performed in a professional way. The fact that the catalytic gauzes must be changed on a regular basis provides opportunities to carry out maintenance activities. Since the gauze changes are always planned, there is no excuse for not taking the opportunity to perform some maintenance at that time.

Reliability is also linked to operation. It is obvious that, in any plant, respecting the operating instructions is fundamental for the reliability of the plant and directly impacts its safety.

At the same time, the reliability of the plant is driven by the design choices originally made. Take, for example, the cooler condensers, where the process gas can be either on the shell side or the tube side of the equipment. The main issue with cooler condensers is corrosion by condensation and re-boiling of nitric acid. If the condensation happens when the process gas is in the tubes, it is quite easy to forecast and determine, but when it is on the shell side it is not so easy.

A bad approach to solve an issue

When a problem appears in a nitric acid plant or any other fertilizer plant, the first people to face it are the operational team and later the maintenance people. Leaving aside the fact that quite often operations blame maintenance and vice versa, the natural tendency is to modify the equipment to solve the issue. However, this approach is quite dangerous since it generally does not solve the root cause and could potentially generate additional issues.

Another response is to change some operating instructions to solve the problem, but again this is not the best way forward. The correct approach would be to carry out a deep analysis of the problem to clearly identify the issue. This implies involving people who have experience in both process and operation. Maintenance or equipment specialists are also useful at this stage to confirm the options considered by the team.

In this scenario, the operational analysis becomes a fundamental part of a more extensive analysis that not only supports the diagnostics of failures but also helps to understand the root causes during mechanical inspections.

Casale approach to troubleshooting

Casale's approach to troubleshooting includes the following steps:

- safety first;
- data collection;
- identify technical elements;
- recognise faulty measurements;
- adopt a simpler process analysis;
- multidisciplinary root cause analysis;
- digital opportunity.

Safety first: All HSE general aspects and specific safety constraints should be checked before acting. Rushing to implement a solution can expose to safety hazard.

Data collection: First, the team collects all available data which can contribute to solve the issue. To succeed on this, an open and frank communication between the different people involved is established. This prevents certain elements from being omitted or hidden.

Identify technical elements: In some cases, it could be possible to identify the problem by a quick analysis of the collected data. In particular, if the data is not in agreement with the normal and expected operation of the plant.

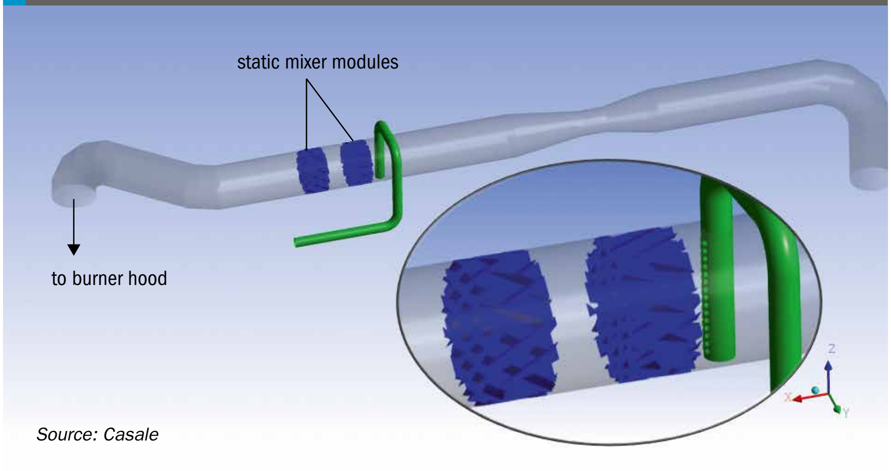
Recognise faulty measurements: Measurement errors and faulty instruments are often the root cause of operational problems.

For example, a few years ago, when lightning up the gauzes of a nitric acid plant, a red plume was emitted to the stack within a couple of minutes. Despite the different checks to the plant instruments, the problem was not solved. This led the operational team to elaborate a sophisticated explanation of the observed phenomena. However, when the process team arrived, they identified the lack of air as a root cause. After insisting that the air flow meter be rechecked, it was found that one flowmeter was inaccurate. After correction, the plant was restarted without any problems.

Adopt a simpler process analysis: The production of nitric acid is a well-known process. Hence all observed plant behaviour can be easily explained with standard concepts.

Plant operators should therefore avoid creating new theories or elaborate explanations to describe observed plant phenomena. This could be an indication of lack of training or understanding of these concepts. Casale with its strong operation and design background can quickly identify the root cause and propose a robust solution to the identified problem.

Fig. 1: **CFD Module mixer element**



Source: Casale

For instance, in a monopressure plant, there was a problem with a cooler condenser which had corrosion in the inlet tubesheet area. A new equipment design to solve the corrosion issue was initiated based on an elaborate theory about corrosion by NOx present in the gas. This made the equipment much more sophisticated and used more expensive materials. As this was unsuccessful, it was decided to reanalyse the problem from scratch. In turned out to be both an operation and process issue. In a monopressure plant, upstream of the tail gas NOx exchanger there is a steam heater on the tail gas line. In order to save some MP steam, this was operated almost without any steam. As a result, the temperature of the NOx gas was low at the outlet of the gas-gas exchanger resulting in a temperature lower than the dew point at the inlet of the cooler condenser. This was creating conditions favourable to condensation regarding boiling phenomena on the tubesheet and was the cause of the corrosion. After readjustment of the operating parameters, there is no longer a problem and the cooler condenser equipment is back to its original design.

Multidisciplinary root cause analysis: In some cases, the solution to a technical issue, requires the contribution of different engineering competences that are not normally available as part of the plant staff.

For instance, during the commissioning of a new nitric acid plant, a high temperature spread on the thermocouple located underneath the catalyst gauzes of the ammonia burner was reported. This temperature spread was leading to difficult operating control and poor efficiency. Furthermore, the temperature difference was exposing the catalyst to an uneven PMG loss over the catalyst surface and therefore to a potentially shorter campaign length.

After excluded other causes and validating through a pyrometer the presence of the temperature span over the gauzes, the issue was found in the air-ammonia mixer.

A more detailed check of the entire air-ammonia feeding line was then carried out to precisely identify the root cause with the purpose to minimise the intervention and reduce the plant shutdown time and the intervention cost.

This activity required a detailed analysis of plant data and vendor documentation together with a computational fluid dynamic analysis of the air ammonia mixer along with the entire burner and feeding gas geometry.

The mixing elements and the relevant ammonia sparger have been simulated through a CFD tool to evaluate the contribution of each single element to the ammonia distribution over the gauzes (Fig. 1).

As shown in Fig. 2, the CFD analysis resulted in a proper mixing capacity of the inline mixing elements but highlighted poor ammonia distribution by the ammonia sparger over the mixing element, causing a high distribution ammonia spread over the gauzes and higher temperature operating span.

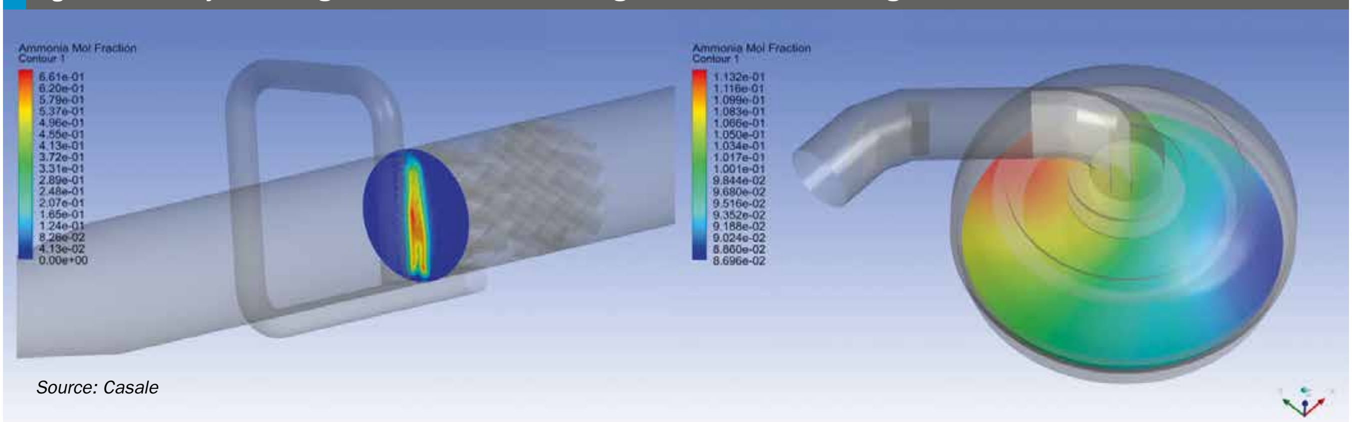
A new ammonia sparger design (Fig. 3) was developed to improve the ammonia distribution upstream of the existing mixing elements and to reduce the temperature spread over the gauzes.

Thanks to the proper identification of the root cause, with the replacement of the ammonia sparger, the temperature span over the gauzes has been solved. This was accomplished by replacing only a small element of the mixer device and without affecting the integrity of the overall mixer internals.

This in situ replacement had the added benefits of reducing plant downtime and cost savings by avoiding the expense of replacing the entire mixer.

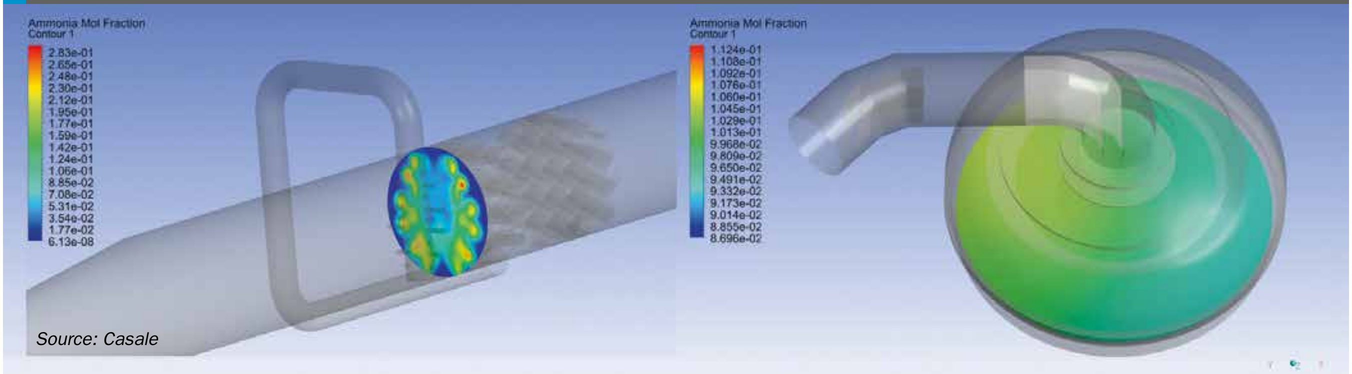
Digital opportunity: While the classical approach to troubleshooting will remain a valid solution in the years to come, modern technologies and digitalisation efforts, already being used in different industries,

Fig. 2: **CFD study of existing mixer element and resulting uneven distribution over gauze surface**



Source: Casale

Fig. 3: **CFD study of new mixer element and resulting even distribution over gauze surface**



Source: Casale

are gaining popularity due to their cost saving advantages and short execution times.

In this changing scenario, the operational data becomes fundamental for the development of maintenance programs aimed at improving reliability.

Casale's view is that, thanks to modern technologies, troubleshooting needs should be anticipated and likely avoided. In fact, most of the time the solution to a problem is found through analysis of historical data, meaning that it could be prevented through predictive analysis of data.

Casale has developed and is continuing to work on systems that provide greater insight and a more detailed analysis of DCS plant data through customised software tools and remote monitoring.

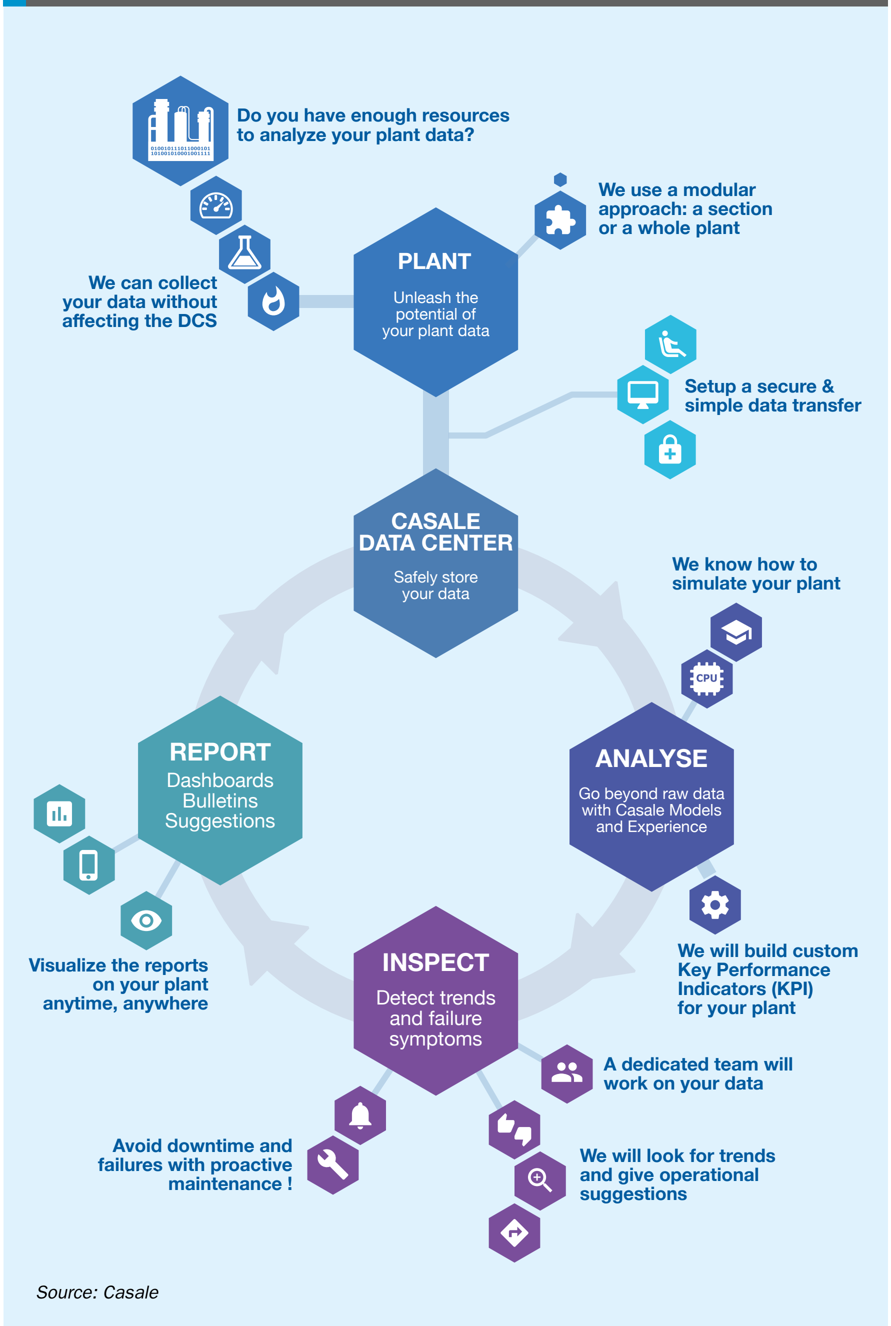
Plants generate a huge amount of data on a daily basis, but data is mostly used for DCS visualisation and archival purposes, and for helping field operations and control. Unfortunately, due to the lack of resources and time, prominent trends and data correlations are seldom analysed thoroughly, leading to suboptimal operation.

To help plant operations, support maintenance and improve mechanical reliability, Casale has created a portfolio of digital products that takes full advantage of existing plant data infrastructure and allows the remote analysis of plant conditions to help clients to improve the reliability of their nitric acid plants.

Casale Remote Engineering Service (CARES)

Casale's remote plant monitor service (CARES), has been designed to directly connect Casale's experts (ranging from process to mechanical engineers) with plant operators and managers to support daily operations and assist troubleshooting following a multidisciplinary approach,

Fig. 4: **CARES analysis cycle**



Source: Casale

as described. The service is like having a team of experts looking after the plant to anticipate operational problems. Fig. 4 shows the CARES analysis cycle.

At the core of remote engineering services, Casale uses an automatic data reconciliation algorithm to convert measured data from the plant into physically consistent values that respect global and local mass and energy conservation around units of operation, sections of the plant or the whole plant.

The data reconciliation is much more than a process simulation, it is a tailor-made process model built up to reveal the real-time performance of the plant, including full information of the critical process streams, which cannot be directly measured in the field. Thus, calculated key performance indicators (KPIs) based on reconciled data offer great value to clients, providing an effective way to identify critical aspects of the plant operation and their temporal behaviour.

Data reconciliation also allows the identification of faulty readings and anomalies in the field instrumentation used to guide the process operation. Thanks to the power of the data reconciliation, abnormal deviations among reconciled quantities and field measurements are promptly detected and thus used to alert critical conditions into the plant. Essentially the identification of erratic readings of the instrumentation may suggest the underperformance of a plant section or the drift of parameters towards critical operating conditions and constraints.

How does CARES help clients?

Using a combination of advanced analytics and expert advice provided by the customer care team, plant behaviour is analysed, focusing on the aspects that are most relevant to the client:

- Boost plant productivity: CARES provides continuous support to utilise the plant capabilities at its best and to achieve maximum production and efficiency.
- Troubleshooting: CARES offers support in identifying the root cause of plant upsets and unexpected shutdowns, providing solutions to improve reliability and increase the on-stream factor.
- Improve understanding and confidence in plant operation: Take the right action at the right moment. Feel confident and conscious of the plant behaviour. This is not an easy task. CARES provides valuable advice which allows improved knowledge and confidence of the plant operation and production process.
- Identify plant limitations: Identify equipment bottlenecks and operating procedures that are hindering plant performance.
- Supporting pro-active maintenance and inspection programs.

Expert advice is communicated to clients via a web dashboard available anywhere, anytime via a secure web page. The aim of the web dashboard is to provide a clear view of the plant and equipment performance using simple visual indicators (widgets) for the key performance indicators.

The dashboard service is completely customised according to customer needs. It is provided with a chat interface to maintain a direct link with the Casale customer care team and is complemented by periodic conference calls and written reports. The customer care team is also ready to support clients when problems occur.

Adopting the latest digital technologies has opened the door to new ways to merge Casale's operational and plant competences to provide more predictive and customised plant troubleshooting ■

SABIN METAL CORPORATION

A three-pronged approach to solving problems with ammonia oxidation catalyst

B. Cook and Dr Jürgen Neumann

There are a wide variety of problems encountered when it comes to ammonia oxidation catalysts within nitric acid plants. The spectrum extends from the ignition of the reaction on the catalyst to the way is ages, and from possible contaminations to mechanical damage to the catalyst package itself. It is not always easy to distinguish between cause and effect, which is why "band-aid" measures are so often applied; ones that cover and somewhat mitigate the undesired effect, but do not actually solve the causal problem.

There are essentially three tools available to the catalyst manufacturer to support the nitric acid producer in his process optimisation efforts: process modelling and simulation, CFD flow simulation and the analysis of the spent catalyst pack using scanning electron microscopy.

What all three tools have in common is that they create a visualisation of the problem(s) and can thus make a clear statement about cause and effect. Understanding the root cause(s) provides the possibility of defining clear measures to optimise the process or, in the event of deviations, to return the process to the normal state.

In this article Sabin presents three methods on the basis of two distinct problems: 1) the ignition of ammonia oxidation on a new catalyst, and 2) the influence of the flow characteristic on the performance of the catalyst. Customer-provided case studies are used to illustrate these two commonly confronted problems in nitric acid plant efficiency.

Impact of first ignition

The first ignition of a new catalyst has a dramatic effect on the development of its lifetime activity and the extent of its precious metal losses, and thus ultimately for its overall service life and achievable HNO_3 product yield. The problem lies in the fact that at the first start-up, ammonia oxidation must be ignited. The brand new, and almost completely inactive catalyst, is therefore introduced at temperatures that are far below the ignition temperature of ammonia.

In order to ignite the initial reaction, hydrogen combustion is used to create an ignitable region on the catalyst surface. The more intensely and homogeneously the hydrogen flame can be applied to the catalyst package, the easier this is to accomplish. The ignition of the reaction is initially

Fig. 1: **Chain-like arrangement of rhodium oxide agglomerates (coloured yellow) on the catalyst surface**

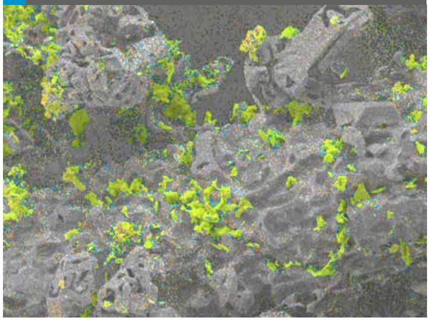


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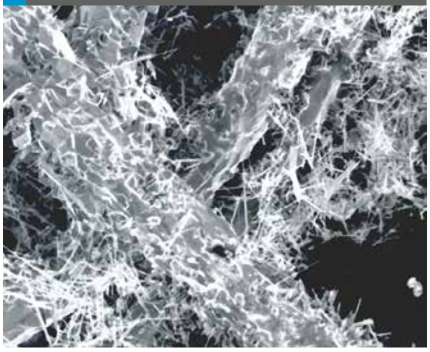
Fig. 2: **Needle-shaped crystallites between the catalyst gauze layers**



perceived visually as a glowing section of the catalyst package and instrumentally as an increase in the catalyst temperature.

However, this perception only describes the process of kinetic self-acceleration of the exothermic reaction, not the ignition itself. The actual ignition takes place at an earlier point in time, but the released heat of reaction is withdrawn from the self-acceleration of the reaction and instead heats the catalyst and the immediate internals of the reactor, so that the ignition process is hardly noticeable.

Another problem is that the thermocouples are typically arranged below the catalyst and hence a significant delay occurs in the measured temperature signal. This effect results in the signal showing a considerably higher temperature increase than actually occurs. As a result of this apparent extreme rise in temperature, due to the self-acceleration of the reaction, the ammonia ratio in the mixed gas is often increased very slowly. The catalyst thus remains in this phase over a longer period of time in a temperature range which causes an accumulation of rhodium oxide on its surface and thus it is irreversible damaged.

Such an accumulation of rhodium oxide in the starting phase of the catalyst can be demonstrated by means of scanning electron microscopic analysis of samples of the used catalyst. The degree of damage ranges from agglomerates arranged in chains on the catalyst surface (Fig. 1) to the extreme case of needle-shaped crystallites between the catalyst gauze layers (Fig. 2).

Ultimately, the effects can be seen in the fact that the HNO_3 yield increase is delayed and the maximum yield is never reached. The aging of the catalyst starts earlier in the campaign and the increase in ammonia consumption develops faster. The cause, however, is the incorrect start-up procedure.

Process simulation is the only way to find this specific cause and optimise the start-up process. To simulate the start-up process, the heat capacities of the catalyst and the immediate reactor built-in components are required. These heat capacities can be determined from the cooling curves after the ammonia supply is interrupted. Taking into account the kinetic parameters of the reaction as well as the process parameters of the plant and its thermodynamic principles, a simulation model is developed based on the current start-up procedure, which is then applied in the process simulation for optimisation.

By means of such a process simulation, the necessary information about the temporal course of ignition and self-acceleration of the reaction is obtained. Calculations in the context of a case study show that when the reaction ignites, the amount of heat released is almost completely withdrawn from the self-acceleration of the reaction to heat the catalyst and the immediate reactor built-in components. With the rise in temperature of the catalyst and the immediate reactor built-in components, their heat capacity progressively decreases, so that an ever greater temperature increase is achieved with the corresponding amount of heat. The self-acceleration of the reaction starts from the first minimum of the heat capacity curve and only from that point onwards can the temperature measurement show that the reaction has ignited.

Fig. 3 and Fig. 4 show the corresponding calculations. Fig. 3 shows the course of the heat capacities over temperature. The graph shows the extreme gradient between the temperature at which the NH3 admixture begins (blue point) and the temperature at which the self-acceleration of the reaction starts (green point). Fig. 4 shows the corresponding heat flow rates. Initially, almost all of the reaction heat released (gray curve) flows into the heating of the catalyst and built-in components (blue curve). With decreasing heat capacity, this heat flow passes through a maximum, whereupon more heat is available for the self-acceleration of the reaction. With the onset of the increased self-acceleration of the reaction, the heat of reaction is increasingly discharged with the process gas (red

Fig. 3: **Course of the heat capacities of the catalyst and the immediate reactor built-in components over temperature**

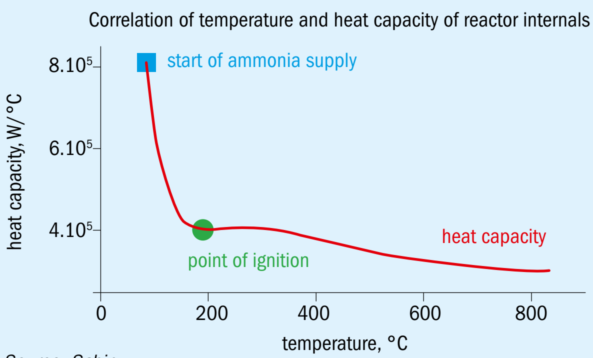


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Fig. 4: **Simulation of the progress of the start-up process by means of the occurring heat flows**

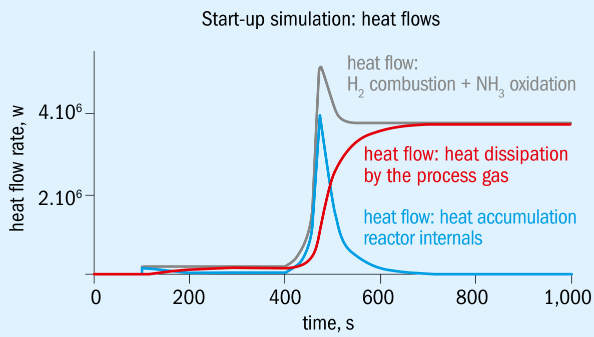

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Fig. 5: **Temperature profiles (red) and development of the ammonia ratio (blue) of the original procedure; example from a case study**

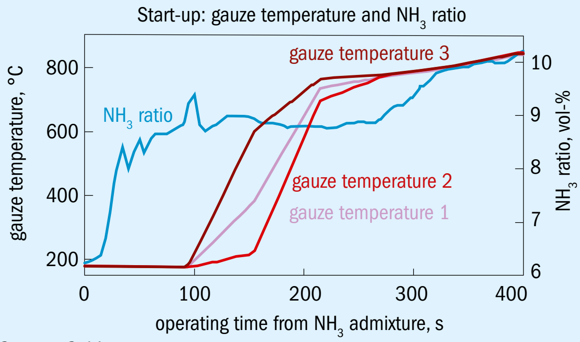

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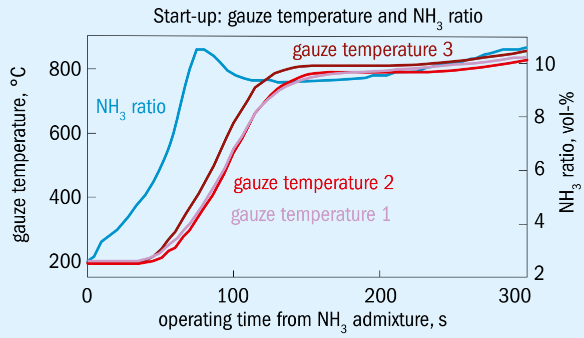
Fig. 6: **Temperature profiles (red) and development of the ammonia ratio (blue) of the optimised procedure; example from a case study**



Source: Sabin

curve). When the steady state is reached, the heat output by the process gas is equal to the heat input by the reaction.

At the end of such a study there is an optimised start-up procedure calculated from the simulation, which is then implemented accordingly by the operators. It specifies in detail the preheating by means of hydrogen combustion as well as the point in time for the addition of ammonia and the temporal increase in its ratio in the mixed gas. Fig. 5 and Fig. 6 show the time course of the temperatures at the three thermocouples (red) of the reactor as well as the temporal increase in the ammonia ratio in the mixed gas (blue), with Fig. 5 showing the original and Fig. 6 the procedure optimised by means of process simulation.

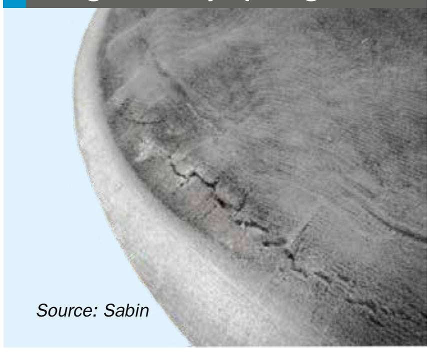
In addition to the start-up simulation, all conceivable operating states can generally be represented by means of modelling and process simulation and examined with regard to a wide variety of issues.

Impact of gas flow characteristic

An uneven gas flow characteristic in the reactor can have very different effects. Such an inhomogeneous characteristic is made visually recognisable by shadows that move in a recurring sequence over the catalyst surface or, in extreme cases, by regions that appear permanently darker on the catalyst package than the rest of the surface.

A different coloration of the catalyst surface ultimately testifies to a different surface temperature, which results from different loads caused by the flow and in particular a different ratio of axial to radial flow components. A high axial proportion allows the reaction to penetrate deeper into the catalyst package; the reaction is distributed over a larger number of catalyst gauze layers, which means that such a characteristic causes a lower temperature on the surface of the catalyst package. When the plant is shut down, such regions will cool down more quickly than the rest of the catalyst package, so that longitudinal stresses occur which can lead to cracks in the catalyst pack, especially in the edge area. Fig. 7 shows an extreme expansion of a crack through the entire catalyst package, which can be attributed to such a flow condition.

Fig. 7: **The most common sign of inhomogeneous gas flow: a crack through the catalyst package**



Source: Sabin

At the other extreme are flow characteristics with a high radial flow component. The reaction in this case does not penetrate far into the catalyst package and almost the entire amount of ammonia is converted at just a few of the uppermost gauze layers of the catalyst package. The consequence is an early onset of the aging of the catalyst due to high platinum losses in these regions.

The most common causes for the occurrence of such inhomogeneous flow characteristics are the elbow flow characteristic and the separation of the flow from the reactor wall at the transition from the elbow to the reactor. Other upstream units can also create a twist that propagates to the catalyst level.

The only way to visualise the flow characteristics is to simulate those using computational fluid dynamics (CFD). At the beginning of every project there is the transfer of the technical drawings into a three-dimensional computer graphic. Fig. 8 shows such an implementation using the example of a Weatherly high pressure reactor. The interface of the elbow, reactor, its built-in components and the catalyst package are provided with a structured surface grid which form the boundary surfaces of the calculation. The solution area is divided into a finite number of control volumes by construction lines. On the surfaces formed by the construction lines the grid is generated, which constitutes a three-dimensional framework for the final volume lattice (see Fig. 9).

By means of the CFD flow simulation, the influence of all aggregates and internals of the flow characteristics can now be determined and the flow in the reactor can be visualised using flow threads (Fig. 10). Furthermore, the direction of flow of the individual flow threads into the catalyst packet and thus their radial portion can be determined by means of the vector representation (Fig 11). The implementation of the reaction finally enables the linkage of flow and reaction, whereby the flow influence on the reaction behaviour in the catalyst package can be examined separately (Fig. 12).

Using the findings of the flow simulation of the current state, combined with the problem of the catalyst damage, solutions can now be developed that bring about more uniformity of the flow and thus a more homogeneous load on the catalyst pack.

In the associated case study, there was a preferential flow caused by the elbow

Fig. 8: **3D computational graphic of a Weatherly high pressure reactor**

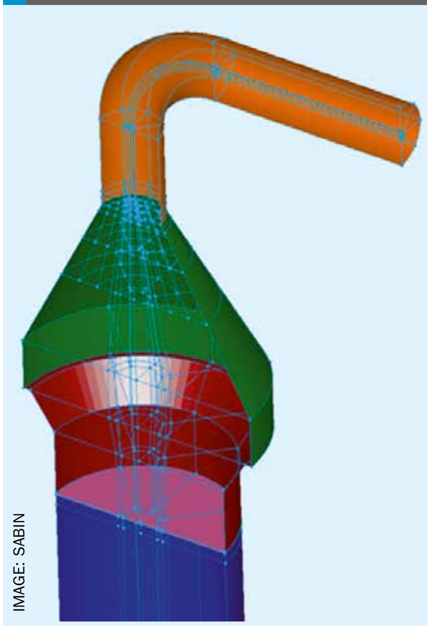


Fig. 9: **3D orthogonality of the volumetric calculation mesh**

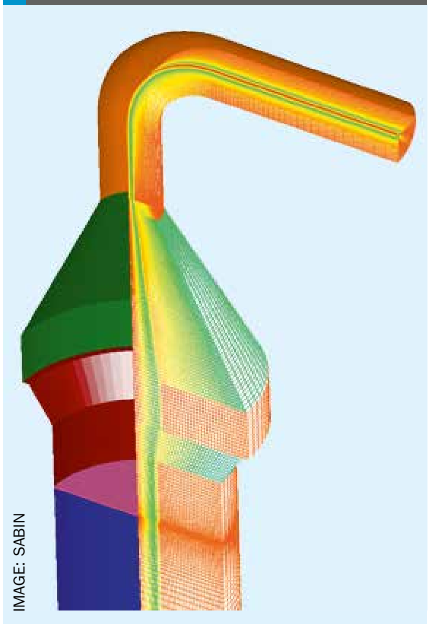


Fig. 10: **Visualisation of the flow characteristic**

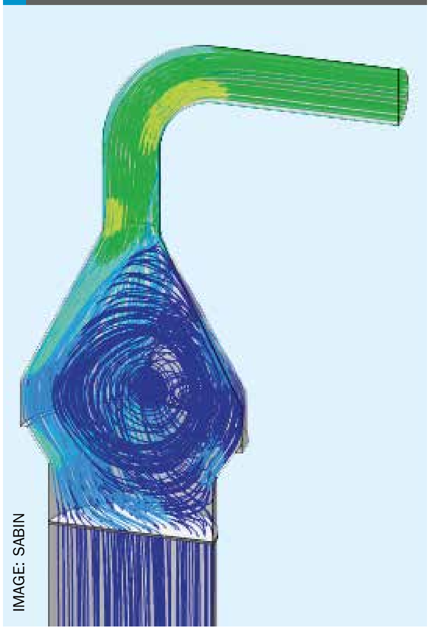


Fig. 11: **Vector representation of the flow into the catalyst**

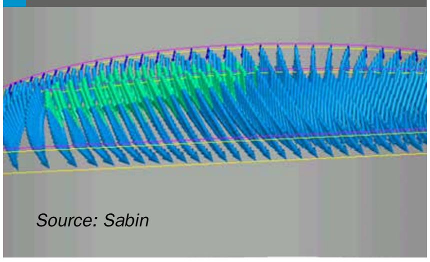


Fig. 12: **Linking flow characteristic and reaction; temperature profile in the catalyst package**

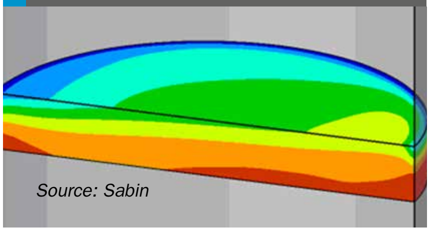


Fig. 13: **CFD simulation with additional distribution plate**

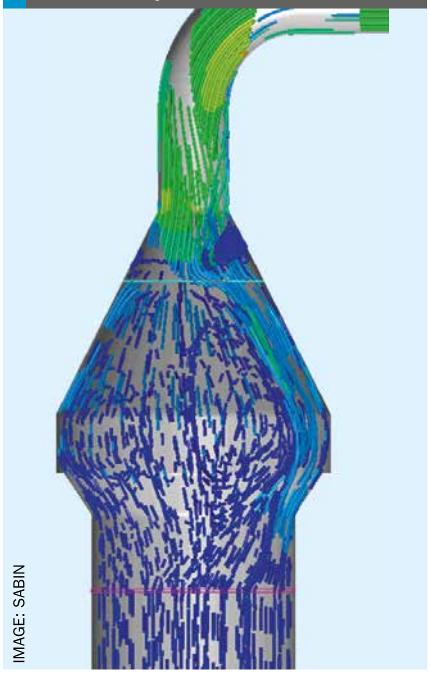
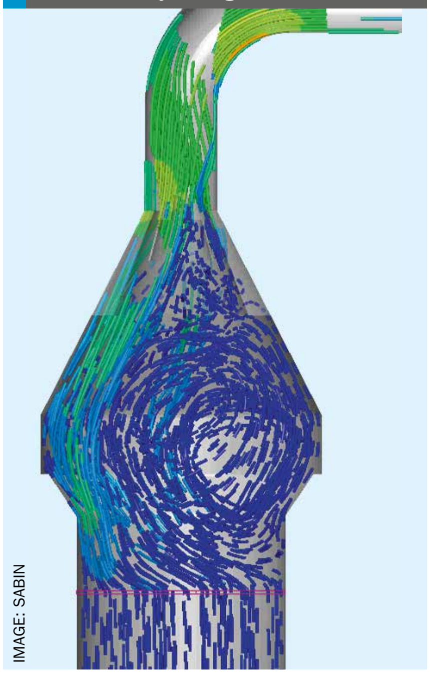


Fig. 14: **CFD simulation with additional concentrically arranged truncated cones**



which led to a flow separation on the right-hand side at the inlet into the reactor. As a result, this flow caused a radial proportion of the flow increasing to the left when it entered the catalyst package and thus a corresponding temperature gradient over the entire catalyst pack. The crack in the catalyst package occurred exactly in the region of the calculated highest temperature. This finding meant that the damage was not due to thermal stress but to material fatigue.

There were two possible solutions. One related to an additional installation of a distributor plate, which by generating an additional pressure drop, could bring about flow equalisation (Fig. 13); the other would be the installation of concentrically arranged truncated cones, which would generate a reduction in the inlet angle and thus prevent flow separation (Fig. 14).

The comparison of both flow patterns made it clear that only the distributor plate produced significant improvement in the flow characteristics. Using concentrically arranged truncated cones, the flow conditions were shown to be insufficient to prevent the flow from separating at the transition from the elbow to the reactor.

This case study shows that the CFD simulation is a powerful tool for studying the influence of flow characteristics on the performance of the process of catalytic ammonia oxidation. Another area of application of CFD simulation is the investigation of the feeding of ammonia and the quality of its mixing with the air flow in adjacent mixers. ■