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Optimising metal content in PGM ammonia oxidation catalysts

A technical review of catalyst design methods

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Platinum based knitted gauzes are the most efficient catalysts for the production of nitric oxide (NO), as a precursor to the manufacture of nitric acid and caprolactam. Decades of research and optimisation have resulted in a greater understanding of ammonia oxidation kinetics and associated metal movement within these catalyst packs, along with the development of beneficial binary and ternary alloys. The design of a pack has evolved from the simple addition or removal of metal to modelling the optimal installed metal content and distribution. This review discusses the fundamental kinetics and in-situ metal loss for ammonia oxidation catalysts in nitric acid applications and outlines how they can, in conjunction with prevailing PGM market conditions and plant KPI's, influence the optimal catalyst design.

Introduction and history

The production of nitric acid, a key industrial process, requires the synthesis of nitric oxide as a precursor to the desired end product. Nitric acid, with a current annual production is 65.9 million metric tons, is primarily used in the production of ammonium nitrate for fertiliser applications, with the remainder (around 20%) used in industrial applications including the production of explosives (1).

Johnson Matthey has manufactured PGM ammonia oxidation catalysts for over 100 years, selling the first platinum gauze pack to the UK Munitions Invention department in October 1916. This pack contained woven wires manufactured from pure platinum and the required one kilogram of platinum to manufacture one tonne of nitric acid (2). In the century that followed, a number of advances in technology resulted in lighter and more efficient catalyst packs and reduced the installed metal content per tonne of nitric acid produced from kilograms to milligrams.

The first advancement in technology was the substitution of pure platinum with a 10% rhodium 90% platinum alloy, first patented by DuPont in 1929 (3). Rhodium increased

the mechanical strength of the alloy and reduced in-situ metal loss, allowing the catalyst to be operated at higher temperatures and benefit from the associated increase in selectivity to nitric oxide (4).

Despite the reduction in metal loss from the optimisation in alloy, the metal lost from the catalyst in-situ remained high and formed a significant part of the plant operating costs. To reduce the cost of the metal loss, gauzes comprising woven palladium-alloy wires were developed in 1968, using a gold-palladium alloy, with up to 20% gold (5). The catchment pack sacrificially collects platinum whilst losing palladium, reducing the cost of the total metal loss. Further research to reduce the cost of the catchment system resulted in the development of nickel-palladium and tungsten-palladium alloys (6, 7) with research showing that a low concentration of the base metal was required for high collection efficiency (8). As a result, alloys used in catchment systems today typically contain 95% palladium.

The 1990's saw a significant change in the design and manufacture of PGM catalysts, with Johnson Matthey introducing new technology that superseded woven gauzes with knitted. As well as introducing more flexibility to catalyst design, the new technology was observed to have a positive impact on the catalyst selectivity to nitric oxide (6). This technology is now the standard for ammonia oxidation catalysts and is offered by all major catalyst suppliers.

Gauze manufacturers make use of different technologies, warp and weft knitting, to manufacture the catalyst gauzes. Recent advances driven by knitting including the manufacture of very high-density gauzes to concentrate metal towards the top of the pack. There are different methods to achieve this: Johnson Matthey have achieved this by minimising the open area of a weft knitted gauze, using high density structures that increase the metal content per gauze by over 90% compared to the basic knit structure. Other manufacturers such as Umicore, limited to greater open areas, have developed 3- dimension knit structures to achieve a high-density gauze (9).

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The mid-2000's saw a fundamental change in ammonia oxidation catalyst design, with ternary Rh-Pt-Pd alloys, containing high concentrations of palladium, replacing traditional Rh-Pt alloys in the lower portion of the pack. Johnson Matthey developed **ECO-CAT™** gauzes using these principles, and this new technology saw a reduction in installed weight required to produce a set amount of nitric acid. The length of time the plant could run with a catalyst pack (known industrially as the "campaign") was increased. Lower density palladium-based alloys in the lower layers collect volatilised platinum from the top layers, with the captured platinum being used later in the campaign as the reaction progresses further into the pack. Variations on this technology are now the standard offering by most catalyst suppliers for medium pressure nitric acid plants.

Historically, catalyst packs were designed using rules of thumb and best estimates. An increased understanding of ammonia oxidation and primary metal losses within PGM catalysts has resulted in the creation of bespoke design tools, which allow Johnson Matthey to optimise the metal content and distribution required within a catalyst pack. Using these tools, catalyst designs can be tailored to plant operating conditions and KPI's. A tailored design can result in higher selectivity to nitric oxide, along with increased campaign lengths and reduced metal content in catalyst packs.

Improvements have also been observed in nitric acid plant designs over the last 100 years. The first industrial nitric acid plants operated at atmospheric pressure and were to low production rates. In the late 1920's, nitric acid plants were constructed that could operate under pressure, resulting in more compact plants that could achieve higher rates (10).

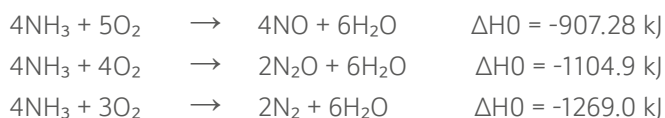
Today, new nitric acid plants are typically dual-pressure plants or ultra-high mono- pressure plants (10). Dual-pressure plants utilise a low operating pressure for the ammonia oxidation reactor to ensure high selectivity to nitric oxide (typically 3 – 6 barg) and increase the pressure in the downstream absorption column to improve the column efficiency. Ultra- high pressure plants operate at one pressure, typically 10 – 13 barg, benefiting from lower capital costs but achieving lower plant efficiencies.

2. Understanding ammonia oxidation

2.1. Reaction fundamentals

Ammonia reacts with oxygen to produce nitric oxide, nitrogen and nitrous oxide. The selectivity of ammonia to each reactant is dependent on process conditions and catalyst specification. Nitrogen is the favoured products at lower temperatures, whilst nitric oxide formation is favoured at higher temperatures and at lower pressures. At low temperatures, NO is formed but is bound strongly to the platinum surface. This allows the NO to react with ammonia to form N₂ which will then desorb. At high temperatures, the NO formed will desorb from the catalyst surface before this secondary reaction occurs, increasing the catalyst selectivity to NO (11).

In industrial production, the reaction is mass transfer limited due to the relatively slow diffusion of reactants to the wire surface compared to the almost instantaneous surface kinetics (12). In industrial operation, the catalyst operates between 850 - 930°C and plant operating pressures range from atmospheric to 13 bar g. Typical selectivity to nitric oxide ranges from 90 – 97%.



In addition to these primary reactions, ammonia can react with nitric oxide to produce nitrogen and nitrous oxide, which reduces the efficiency of the reaction.



As a result, an effective catalyst will be designed to convert 100% of ammonia in the

top few layers of the catalyst pack at the beginning of a campaign; although the reaction will progress further through the pack as platinum is lost and the top layers of the catalyst lose activity.

The surface chemistry and metallurgy of the catalyst used impacts the selectivity achieved. Several precious metals have been shown to catalyse the ammonia oxidation reaction, including platinum, rhodium, palladium (13), silver and iridium (14). Platinum has the greatest selectivity to nitric oxide, making it the most suitable catalyst for nitric acid plants. Rhodium-platinum alloys, containing 3-10% rhodium, are the most common alloys offered in ammonia oxidation catalysts today, although often in conjunction with a Rh-Pt-Pd alloy.

While rhodium containing alloys are primarily used to increase the alloy strength during manufacture and operation (15), rhodium-platinum alloys have been observed to have a higher selectivity to nitric oxide than pure platinum (4), and palladium-containing alloys have a reduced selectivity to nitrous oxide at all temperatures as demonstrated through ab initio modelling of the selectivity of ammonia oxidation to NO, NO₂, N₂ and N₂O on pure platinum and palladium-platinum alloys (Fig.1). The benefit of lower selectivity to N₂O is partially offset by an increase in selectivity to N₂: palladium-based alloys can help reduce N₂O emissions but at the cost of reduced selectivity to NO (16). The benefit of using palladium-based alloys has been demonstrated within the nitric acid industry, with catalyst packs using **ECO-CAT** technology or other catalyst manufacturers ternary-alloy technologies, shown to reduce N₂O emissions by up to 30% compared to standard Rh-Pt catalyst packs (17).

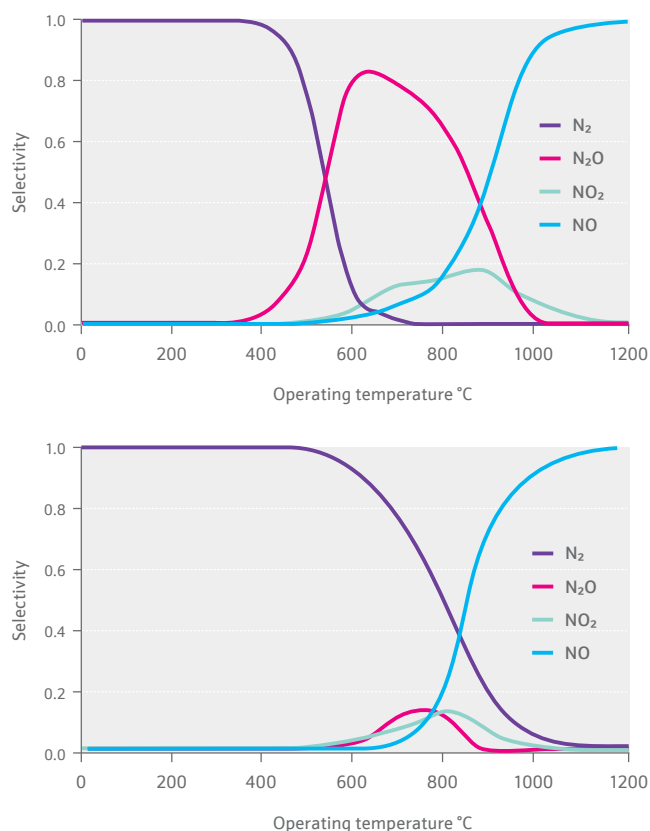


Figure 1. In-house modelling by Johnson Matthey using ab initio kinetics and density function theory (DFT) demonstrates the significant reduction in selectivity to N₂O for a palladium-doped platinum alloy across a range of temperatures (right) compared to a pure platinum alloy (left). An increase in selectivity to N₂ at higher temperatures is also demonstrated (16).

2.2. In-situ restructuring and metal loss

When exposed to the ammonia-air feed gas, the structure of the PGM wires begin to restructure, forming high surface area dendritic multiplanar crystal growths, known in the industry as “cauliflowers”. The formation of cauliflowers results in a significant increase in the specific surface area of the wire, with 10 to 20-fold increases in surface area observed after of industrial operation, with the initial period of restructuring taking several days (18, 19, 20). After initial restructuring, cauliflower formation is greatest in the top layer of the catalyst (Fig. 2), as this is exposed to the greatest concentration of ammonia, with layers further down the pack seeing little to no restructuring until later in the campaign.

The restructuring mechanism is poorly understood, with several mechanisms suggested for the production of cauliflower structures at the surface of platinum alloy wires. The prevailing theory is that the adsorption and subsequent reaction of NH_x species results in localised areas of high temperature which promotes the dissociation of surface PtO_x and RhO_x; the presence of gas phase platinum species during ammonia oxidation has been demonstrated by mass spectrometry (21). The hotspots occur close to surface defects, such as grain boundaries, and this is where the restructuring process is observed to begin (14). As these gaseous species contact regions of the gauze where the reaction is slower, condensation occurs due to reduced temperatures, which forms new crystallites (22). These colder regions can be found very close to the hotspots, which results in a localised temperature gradient that drives the chemical vapour transport of the metal oxides. Some of these metal oxides will condense on the wire surface in these colder regions; further ammonia oxidation then occurs at this deposition and this rapidly results in the growth of cauliflower structures observed in activated and spent gauzes (18).

Whilst this vapour phase mechanism results in capture of a proportion of the metal, some is lost downstream of the gauze pack. The addition of palladium and rhodium will reduce the overall metal lost from the pack, as these alloys see a reduction in platinum volatility compared to pure platinum (14). Catalyst packs will typically lose half of the installed PGM content at the end of a campaign.

The movement and loss of metal within the catalyst pack is a key constraint during the pack design phase, and it is critical to ensure sufficient metal is installed to maintain a high selectivity for the desired campaign length. As the campaign progresses, the catalyst begins to lose significant levels of platinum in the top gauze layers, with the wires becoming enriched with rhodium.

Post campaign analysis of catalysts have observed surface rhodium levels of over 40% in extreme cases that suffered mechanical loss of platinum, with further research observing 33% rhodium enrichment in non-damaged gauzes (14). As a result of the platinum deficiency, full conversion of ammonia is no longer achieved in these top layers and the reaction zone stretches further into the catalyst. Lower gauze layers will be exposed to the ammonia oxidation reaction and begin restructuring.



Figure 2. Layers 1, 3 and 5 of a catalyst pack composed of 5% rhodium 95% platinum alloy after 5 days operation at 4 bar g showing a high level of restructuring and cauliflower growth in the top layer and negligible restructuring on the bottom layer. Images are at 4000 times magnification (23).

The design of the lower half of the catalyst pack is key to maintaining a high selectivity to nitric oxide in the later stages of the campaign: installing too many catalyst gauzes or not correctly distributing the metal within the pack can result in residual ammonia reacting with nitric oxide. These reactions result in both the reduction in selectivity to nitric oxide and an increase in unwanted side products, N_2 and N_2O . These reactions are suppressed in the presence of excess oxygen (24), and as a result are more likely to occur in lower layers of the pack. Conversely, if too few layers are installed then 100% conversion of ammonia may not be achieved as the campaign progresses, resulting in ammonia slip downstream of the catalyst.

The use of ternary Rh-Pt-Pd alloys in the lower portion of the catalyst pack is a key feature of **ECO-CAT** packs. The concentration of palladium in the alloy can vary from low levels to constituting the majority of the alloy and allows the lower half of the pack to function as part catalyst, part catchment. During operation, volatilised platinum from the top Rh-Pt layers is captured on the lower layers, increasing the platinum content on the surface of the wire, while palladium is lost from the catalyst. A successful **ECO-CAT** catalyst will have a wire surface covered in platinum at the point the ammonia begins to break through and react on the layer, and selectively react to produce mostly nitric oxide.

The restructuring mechanism within **ECO-CAT** packs differs from Rh-Pt cauliflower formation. Surface growths are more block-like (Fig. 3), showing a resemblance to catchment restructuring (Fig. 4) and the lower layers will fuse together during operation; a similar mechanism has been observed with catchment gauzes which are always separated with steel layers to prevent this. As a result of this formation, the gauze open area is reduced, and the pressure drop over the system increases.

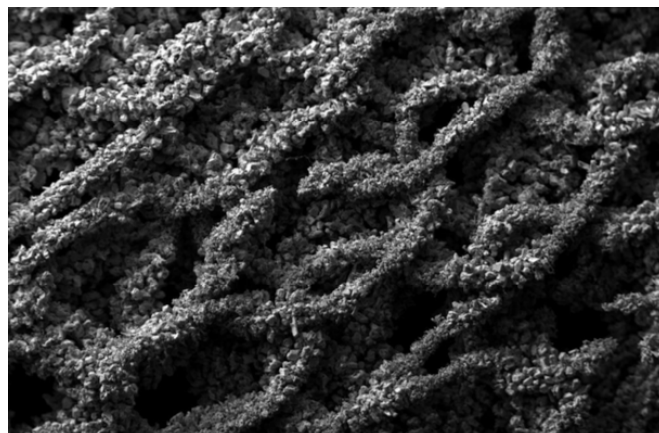


Figure 3: SEM at 250 times magnification showing the top layer of the fused structure at the bottom of an **ECO-CAT** pack which had been installed in a high-medium pressure plant.

Platinum capture is also possible through the use of palladium-based catchment gauzes and glass-wool platinum filters. Glass-wool filters see recovery rates of 10 – 20% (5), and catchment packs can recover from 25% to 95% of platinum lost in the catalyst gauzes depending on the weight and distribution of palladium is installed (6). 95% palladium alloys used in the catchment pack exhibit a different end of life morphology than the Rh-Pt and Rh-Pt-Pd catalyst gauzes, with the observed restructuring driven by the collection of platinum. However, palladium and palladium-based alloys can catalyse the ammonia oxidation reaction, and if exposed to the NH_3-O_2 containing gas, will restructure to produce cauliflower structures similar to those observed in Rh-Pt alloys (14).

Industrial ammonia oxidation is carried out at high temperatures (ranging from 850 – 930°C) and at pressures ranging from atmospheric to 14 bar g. Depending on the daily acid production, the flux of ammonia (known in industry as the nitrogen loading) can range from 3 to 100 tonnes of nitrogen per m^2 of cross sectional area of the ammonia oxidation burner per day (units are based on nitrogen from ammonia, excluding air).

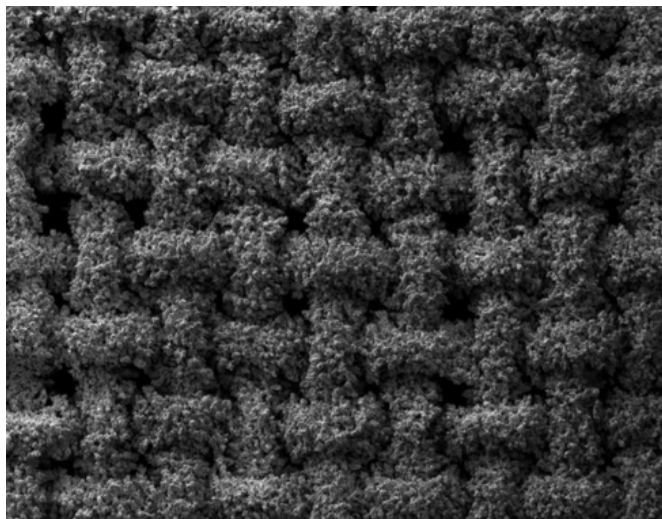


Figure 4: SEM at 250 times magnification showing the top layer of a catchment pack in a high-medium pressure plant. The observed low open area results in a high pressure drop as the gas passes through this gauze layer.

At industrial operating conditions, the selectivity to nitric oxide can range from 90 – 97%, with the large range due primarily to the reduction in efficiency caused when operating at higher pressures. In addition to reduced selectivity, higher pressure plants also see an increase rate of metal loss from the catalyst in-situ.

Nitric acid plants in industry have a wide range of operating conditions; however, they can broadly be defined in four categories. These categories are derived from plotting ammonia oxidation pressure against nitrogen loading (Fig. 5).

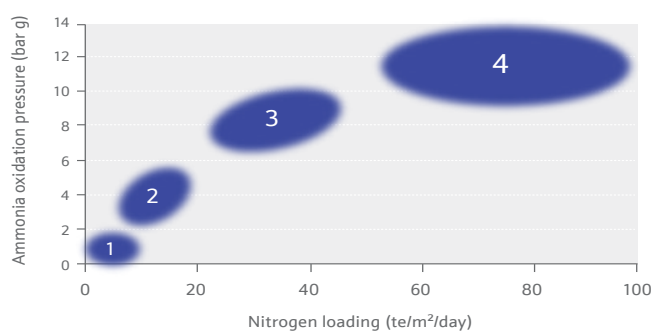


Figure 5. Plotting individual nitric acid plant operating pressure against nitrogen loading gives rise to four distinct categories of plants. The majority of nitric acid plants will have operating conditions that lie within one of the four operating ranges illustrated here.

1. **Atmospheric plants**, with nitrogen loadings of <10 teN/m²/day and pressures of < 1 bar g, were the first type of nitric acid plants to be built industrially, and benefit from high selectivity to nitric oxide. However, due to the low nitrogen loading, the acid production rates are low.
2. **Low-medium pressure plants**, which include most dual-pressure plants. These plants continue to benefit from relatively high selectivity to nitric oxide, with efficiencies of up to 96.5% observed. Operating at higher pressure allows for a significant increase in daily acid production and, due to relatively low metal losses, campaign lengths of up to 1 year can be achieved.
3. **High-medium pressure plants** have a wide range of operating conditions. Some of these plants will benefit from similar design principles to low-medium pressure plants, whilst others from those for ultra-high-pressure plants.
4. **Ultra-high pressure plants** operate at high pressures (10 - 13 bar g) and high temperatures (920 - 930°C). The selectivity to nitric oxide of around 90% is significantly lower than other plant types. The intrinsic rate of metal loss is substantially higher, limiting campaigns to around 100 days. As a result of the metal loss, the catalyst designs for these plants have the highest level of installed PGM weight per tonne of acid.

In addition to the catalyst selectivity and metal loss, the pressure drop over the catalyst and catchment pack can also have an effect on industrial operation. This is most pronounced for ultra-high pressure plants: a high system pressure drop will put strain on the compressor and the plant will not be able to operate at maximum production rates. The pressure drop over binary Rh-Pt catalysts is relatively low, with higher pressure drops observed when operating **ECO-CAT** catalysts due to the high palladium layers fusing together and reducing the system open area. The catchment system will create the greatest pressure drop as the physical collection of platinum can reduce the gauze open area. Post campaign analysis by Johnson Matthey has observed the open area of used catchment gauzes to be as low as 2%.

3. Designing the optimal pack

The reaction fundamentals, restructuring and loss of metal and constraints in industrial operation must all be considered when designing a catalyst pack for ammonia oxidation in a nitric acid plant. The variables available to a catalyst designer and manufacturer include optimising the

metal content and metal placement within the pack and selecting the most appropriate alloys and optimising their placement in the pack.

3.1. Metal content

The optimal metal content installed in a catalyst pack is determined by the expected levels of metal loss during the campaign, which is modelled as a function of the burner operating pressure and nitrogen loading. For standard packs, the pack will be designed such that around 50% of the installed metal content remains after the completion of the campaign. For optimised packs utilising high palladium alloys, the remaining metal content can be as low as 30% of the installed weight.

A catalyst pack with an insufficient mass of PGM installed can lead to ammonia slip, where the reaction fails to complete within the catalyst pack. The introduction of ammonia downstream can result in the formation of ammonium nitrite and ammonium nitrate, which can pose an explosion hazard. Ammonium nitrite can form when NO_2 , NO and NH_3 are present; significant levels of NO_2 form downstream of the gauzes as NO undergoes oxidation, so avoiding ammonia slip downstream of gauze is crucial. Ammonium nitrite is highly unstable and can undergo explosive decomposition, which can result in the detonation of any ammonium nitrate present (25).

Defining the required mass of PGM required for the catalyst pack is critical, however thought must also be given to the distribution of metal within the pack to achieve high selectivity to nitric oxide. The underlying kinetics of the reaction require the ammonia oxidation is completed within as few gauze layers as possible to minimise the side reactions between ammonia and nitric oxide.

Modifying the metal concentration within the pack is achieved by varying the densities of the gauzes. Johnson Matthey manufacture multiple knit structures of varying density which are combined with a range in wire diameters ranging from 60 to 120 μm , as well as a range of different binary and ternary alloys. There are hundreds of configurations possible for each layer within the catalyst pack, and possible densities ranging from 300 to over 1200 grams per m^2 .

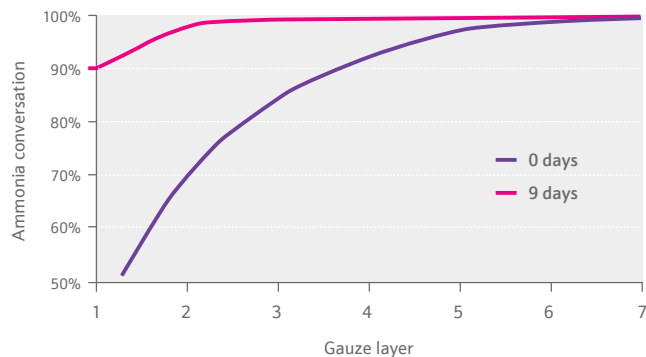


Figure 6. Kinetic model output for a gauze design for a low-medium pressure plant showing achieved ammonia conversion throughout the gauze pack at the start of the campaign and 9 days into the campaign. This shows sufficient metal has been installed to prevent significant levels of ammonia slip on start-up (0 days) and to carry out the majority of the reaction in the top two gauze layers after 9 days online.

To ensure the installed metal content is correct, Johnson Matthey uses theoretical and empirical models to estimate the primary loss expected from a catalyst at the required operating pressure and nitrogen loading. Distribution of the metal within the catalyst is also dependent on the plant category, and can be evaluated using an ammonia oxidation kinetic model, in conjunction with the expected primary losses, to determine where the majority of the reaction is carried out at different stages in the campaign (Fig 6.) and ensure sufficient metal is installed to prevent ammonia slip later in the campaign.

3.2. Alloy selection

The selection and placement of different alloys within the catalyst pack is critical to achieving high performance, with some alloys suited to the top part of the pack (the catalytic "engine") and others providing benefits when installed at the bottom of the pack.

Having a high platinum content in the top layer reduces the temperature at which the reaction begins to progress, in turn reducing the time between start-up and reaching peak efficiency. This can be achieved through a combination of alloy choice, selecting a binary alloy with <5% rhodium, and increasing the metal concentration at the top of the pack by using high density knit structures. Experimental data has demonstrated a reduction in the light-off temperature of around 100°C, and Johnson Matthey have developed specific products for plants that struggle with light off.

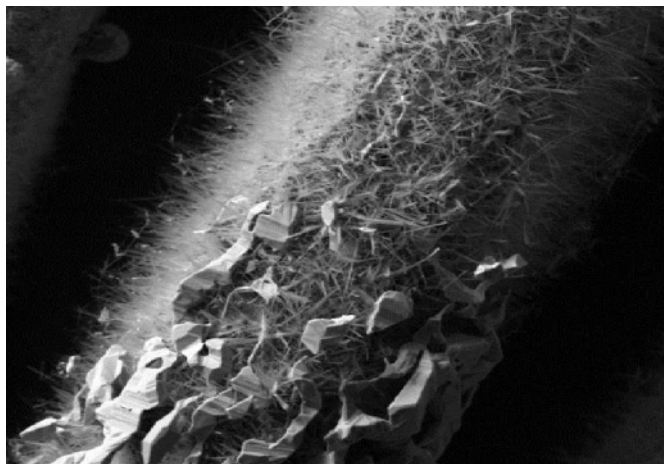


Fig. 7. SEM image of a gauze wire at 4,000x magnification, showing the formation of characteristic rhodium oxide needles. Optimising rhodium content and placement within the gauze pack can reduce the likelihood of formation.

A range of rhodium concentrations are available in binary Rh-Pt alloys. Lower levels of rhodium are advised when plants suffer from rhodium oxide (Rh_2O_3) formation (Fig 7), which is significantly less selective to nitric oxide (26), to minimise or prevent such formation. Plants operating at low temperatures ($<850^\circ\text{C}$) are at higher risk of rhodium oxide formation, and the risk increases for catalysts with significant levels of iron contamination. Interest in low-rhodium alloys has increased following the substantial increase in rhodium price, peaking at almost \$12,000 per troy oz in early 2020 (27).

Palladium proves a beneficial addition in the lower part of the catalyst pack, and the introduction of ternary alloys within the pack of Johnson Matthey's **ECO-CAT** catalyst results in a significant reduction in the primary N_2O generated by the catalyst pack (17). The catalyst pack achieves a higher efficiency towards the end of the expected campaign length due to the capture and recycling of volatilised platinum, allowing for campaign lengths to be extended, where maintenance schedules permit, whilst maintaining or even reducing the installed metal content. As a result of this technology, campaigns of up to one year are now commonplace in low-medium pressure plants.

There are a range of ternary alloys used in **ECO-CAT** catalysts. Initial developments of **ECO-CAT** used only one high-palladium alloy, but further work has shown that the average campaign efficiency can be improved through use of a gradient of palladium in the pack. This has been demonstrated, with an increase in the average efficiency of up to 1% reported by nitric acid plants, along with a reduction in N_2O emissions.

The optimal level of palladium is influenced by both plant performance and the relative price difference between platinum and palladium, balancing the cost of the installed metal, the net metal loss and any financial implications resulting from a change in N_2O emissions.

3.3. Catchment system

In addition to the catalyst gauze pack, a palladium-alloy catchment (or getter) system will often be installed below the catalyst to minimise the metal loss from the catalyst through platinum capture and palladium loss.

Recent changes to the PGM market have reduced the profitability of catchment systems. Palladium prices have continued to rise steadily since 2017, whilst platinum remained relatively flat. For 2020, the platinum market is expected to move into surplus and the palladium market to fall further into deficit (27), which has further implications for the optimal catchment pack design. The optimal catchment design is a function of the price differential and acceptable pressure drop.

4. Case Study

Optimisation of metal content is applicable for all categories of nitric acid plants and Johnson Matthey continually reviews existing catalyst designs to ensure they are the most optimal for plant operation and prevailing PGM market conditions. In recent years, significant steps have been taken to optimise metal content for ultra-high pressure plants, with design options tailored to the key drivers of each plant, e.g. maximising daily production rates or maximising plant efficiency from a set level of ammonia feed.

For a significant proportion of nitric acid producers operating ultra-high-pressure plants, the key driver is to produce the maximum amount of nitric acid from a gauze pack. In these cases, the introduction of palladium alloys is not recommended due to the increased pressure drop. The catalyst pack is instead optimised by increasing the platinum weight at the top of the pack by using larger wire diameters in the top layers. To maintain a constant pack weight, the total number of layers within the pack is reduced. As a result, ammonia oxidation is completed higher in the pack and the N_2 and N_2O producing side reactions are reduced. In addition to selectivity benefits, increasing the wire diameter in the top layers provides sufficient metal for further cauliflower formation in the event of mechanical metal loss following a plant trip.

For other ultra-high-pressure producers, typically operating in locations with higher raw material costs, the key driver is to maximise the efficiency of the gauze pack over a set campaign length. As a slight increase in pressure drop is tolerable for these plants, pack optimisation includes the use of **ECO-CAT** design principles. Initial design optimisation work for a plant in this category combined the use of high density knit structures in the top portion of the pack with high palladium alloys in the lower portion of the pack. The changes resulted in improving the conversion efficiency towards the end of the campaign, and as a result increasing the average campaign efficiency. Further design changes, including the reduction of palladium content whilst increasing the concentration of palladium higher in the pack, resulted in a reduction in N₂O emissions from the gauze system.

5. Conclusion

The catalysis of ammonia oxidation using PGM gauzes has been used industrially for over 100 years. Step changes in performance have been achieved throughout the decades, reducing the required PGM metal content required in a catalyst pack and introducing a range of alloys and knitted structures to construct a catalyst pack from. Research into ammonia oxidation has continued to support the development of catalysts with higher selectivity to NO and reduced N₂O emissions, giving rise to the current binary and ternary alloys used in catalysts today.

The underlying reaction kinetics and metal movement provide a basis for designing the optimal ammonia oxidation catalyst and have been used within Johnson Matthey to develop plant category specific design rules. Achieving a high selectivity to nitric oxide can be achieved by promoting near 100% ammonia conversion in the top layers, and the use of ternary alloys in the lower catalyst layers promotes recycling of platinum to maintain a high efficiency towards the end of the campaign. A wide range of knit structures, wire diameters and alloys are available to tailor the catalyst to the plant operating conditions and to distribute the metal within the pack in a way that promotes the highest selectivity to NO throughout the campaign. The concentration of rhodium and palladium in the top catalyst layers can be optimised to address plant specific issues, including the formation of rhodium oxide and helping the catalyst to light-off at a lower temperature.

Other factors must influence the optimal design, with the acceptable pressure drop over the catalyst pack being key. Despite having significant benefits, including reduced N₂O emissions, **ECO-CAT** and catchment technologies are not always suitable for ultra-high pressure plants due to the increased pressure drop.

Optimisation of metal content within the catalyst pack is now the expected standard for all medium pressure plants, with the development of high density knit structures and **ECO-CAT** technology resulting in improvements to conversion efficiency, reduction in installed metal content and the extension of campaign lengths. In recent years, further progress has been made in optimising catalyst packs for ultra-high pressure nitric acid plants operating at >10 bar and with nitrogen loading values in excess of 60 teN/m²/day, designing the pack to minimise unwanted side reactions. While the high intrinsic metal loss continues to constrain the maximum campaign length for these plants, the optimisation of PGM content within the pack has resulted in an improvement in plant efficiency and, where targeted, a reduction in N₂O emissions.

Despite being a mature and conservative industry, the operational targets for nitric acid plants continue to increase to support the global demand for fertiliser. Many plants will seek to operate in excess of the nameplate capacity and carry out de-bottlenecking studies to support this. Changing operational targets should always be communicated to the catalyst supplier, as a change in plant loading, temperature or pressure is likely to require an updated catalyst design. The dynamic PGM market also influences the optimal pack design; catchment packs see a reduction in profitability when the price of palladium exceeds that of platinum. Additionally, rhodium is currently seeing extremely high prices which are forming a significant portion of the pack cost and increasing interest in low-rhodium alloys.

The optimisation of a catalyst pack is never a complete process, and continual monitoring of catalyst performance and an open dialogue between plant operator and catalyst supplier are critical in creating and maintaining an optimal pack design.

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