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Is your ammonia oxidation catalyst fit for purpose?

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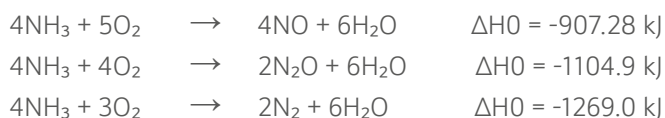
As a mature industry, there are a large range of nitric acid plant designs and operating conditions. From a catalyst design perspective, all nitric acid plants can be broadly grouped into four categories based on operating pressure and nitrogen loading. Basic design principles differ for each category, and these principles are applied to ensure the most optimal catalyst is installed in the plant. Further optimisation of a catalyst design will be driven by specific operational targets. This paper will review the fundamental constraints in designing PGM ammonia oxidation catalysts and discuss specific design developments by Johnson Matthey, both current and historical.

Introduction

Johnson Matthey has been designing and supplying PGM ammonia oxidation catalysts for over 100 years, since the first catalyst was supplied to UK Munitions Invention Department in October 1916. Continuous research and development have resulted in many developments in general catalyst design principles, as well as allowing catalysts to be tailored to meet the operating requirements of individual nitric acid plants. There are a wide range of plant designs and operating conditions within the nitric acid industry, and it is important to recognise that there is no "one size fits all" approach in catalyst design and optimisation. The optimal catalyst design for a nitric acid plant is guided by a number of external factors, including the fundamental kinetics of ammonia oxidation, intrinsic loss of PGM during operation and plant operating targets and strategy.

Selectivity

The catalyst performance is fundamentally constrained by the reaction kinetics of ammonia oxidation. When ammonia reacts with oxygen, three main products are formed: nitric oxide (NO), nitrogen (N₂) and nitrous oxide (N₂O).



The maximum achievable selectivity varies for different platinum alloys (Fig. 1), and an efficient catalyst can be designed by using a range of rhodium and palladium doped platinum alloys. The actual selectivity to each product is a function of operating temperature and pressure, with higher temperatures and lower pressures favouring nitric oxide production. Industrial operating conditions, with temperatures ranging from 850 - 930°C and pressures from atmospheric to 13 bar g, can achieve selectivity to nitric oxide in the range from 90 - 97%.

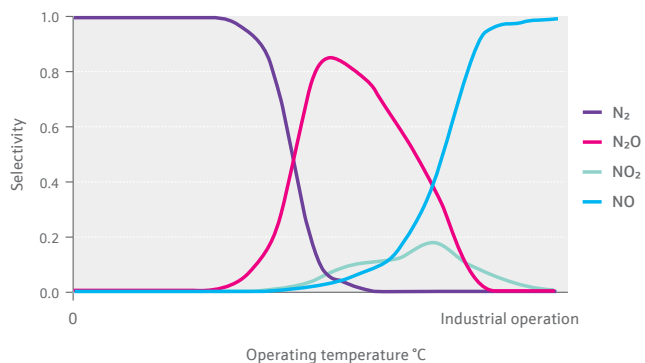
The physical characteristics of the catalyst (wire diameter, knit density and number of layers) will also influence the selectivity achieved. While the reaction completes over a relatively small path length, under certain conditions there is enough time for ammonia to react with nitric oxide, producing further nitrogen and nitrous oxide.



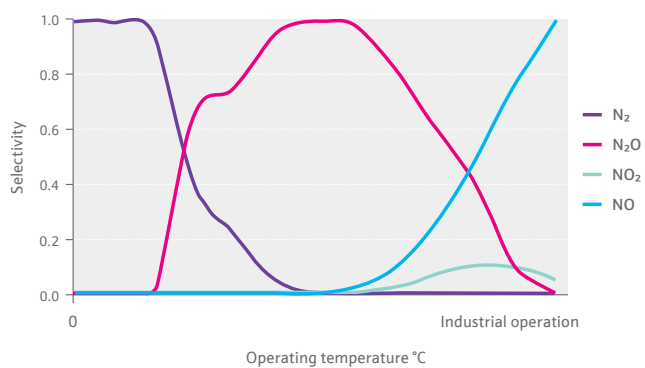
The extent of these reactions can be minimised by ensuring the reaction is completed within a minimum number of catalyst layers, by utilising higher density structures in the top portion of the pack.

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Pure platinum



Rhodium doped platinum



Palladium doped platinum

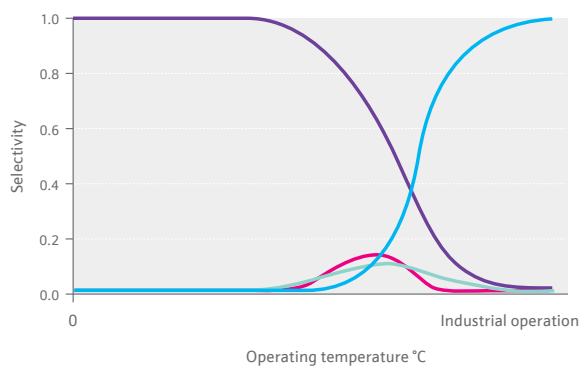


Figure 2. Selectivity trends for ammonia oxidation on pure platinum (top), rhodium doped platinum (middle) and palladium doped platinum (bottom) generated by ab-initio kinetic modelling at 1 bara

Metal loss

Another key design consideration, and fundamental constraint, is the PGM loss of a catalyst during its operating lifetime. During normal operation the PGM wire surface restructures to form high surface area growths or “cauliflowers”. While the formation of these structures is key to achieving a high selectivity to nitric oxide, the process results in PGM, primarily platinum in oxide form, being lost to the gas stream. The rate of metal loss increases with pressure and nitrogen loading (Figure 2) and can also be negatively impacted by process transients.

Metal loss places an upper constraint on campaign length, with plant efficiency dropping when over 50% of the PGM is lost. This is most significant for ultra-high pressure plants, due to the high rate of primary metal loss observed at these conditions, and as a result maximum campaign lengths of around 90 – 110 days are achieved before the catalyst must be replaced.

In addition to the fundamental constraint of metal loss and the associated drop in conversion efficiency, the operating strategy of individual nitric acid plants must also be considered when calculating the optimal installed PGM content. Two extremes are observed in industry for determining campaign length: plants where this is determined by shutdown schedule and plants that aim to extend campaign as long as is feasible. The acceptable cut-off point, or definition of “feasible” will vary between plants. Where ammonia costs are low, the plant can accept running to a lower plant efficiency than plants operating in areas where feedstock prices are significantly higher. These different approaches can be summarised as maximum production rate vs minimum ammonia consumption.

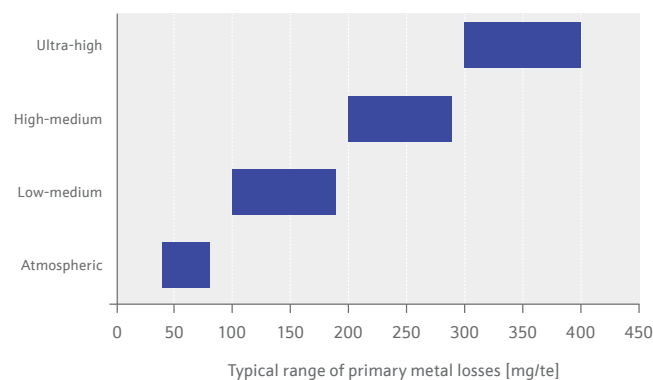


Figure 2: Typical range of primary metal losses observed by plant category.

Developments in catalyst design

While the fundamentals of catalyst design have not changed significantly in 100 years – install sufficient metal to produce the desired tonnes of acid – decades of technical development allow for the design options to be tailored to a plant's requirement. Depending on plant operating strategy, this can be extending the campaign length, improving the average efficiency, optimising the installed PGM weights or reducing primary N₂O emissions from the catalyst.

Traditional design optimisation

The introduction of knitted catalysts, superseding woven PGM wires, allowed for significant tailoring of each catalyst layer. A key advantage of this tailoring is the ability to increase the concentration of PGM, and as a result the number of catalytic sites, in the top portion of the pack, while keeping the pack weight constant by removing lower layers. This results in the reaction completing (defined as 100% ammonia conversion to all products) at a higher position in the pack, minimising the time available for the secondary ammonia and nitric oxide reactions to occur. There are many options available to increase the number of catalytic sites in the top portion of the packs, including the use of thicker PGM wire or use of higher density knit structures.

Wire diameter optimisation

The use of multiple wire diameters, and the placement within the catalyst pack, is a design option that has been in use by Johnson Matthey for decades. As a low-risk design change, this option is usually considered as a first step in optimising a catalyst pack. For some nitric acid plants, it remains the best option for design optimisation due to the relatively low change in pressure drop over the pack. As a result, it is a typical design option considered for ultra-high pressure nitric acid plants.

Denser knit structures

Another approach is to alter the density of the knit structure itself. This allows for a significant concentration of metal within the top 2-3 layers of the catalyst pack and is typically offered to medium pressure plants.

PGM content optimisation

For these traditional design optimisation methods, the key to a successful design change is understanding the metal utilisation and movement within the pack. As a minimum, this requires accurate estimates of the primary metal

loss expected for an individual plant and can be further enhanced by analysis of the spent catalyst after operation. Johnson Matthey can perform post campaign analysis on a spent catalyst gauze, using scanning electron-microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) to characterise metal movement and utilisation in the pack. This can be used to remove any redundant metal by looking at the extent of any restructuring in the lower layers of the pack.

Modern design optimisation

Johnson Matthey works to continually review and optimise catalyst packs, as previously successful designs can become sub-optimal with changes in plant operating strategy and changes to the PGM market. Many design developments are plant specific and the result of a clear dialogue between the plant operator and Johnson Matthey on the catalyst requirements. Some more general developments, that have been applied to designs for multiple plants, are discussed here.

ECO-CAT application in ultra-high pressure plants

The application of **ECO-CAT™** technology – the use of tertiary Rh-Pt-Pd alloys – is well established within medium pressure plants, and now forms the standard catalyst offering. More recent design innovations have resulted in this technology becoming applicable to ultra-high pressure plants. These plants typically operate in regions of higher feedstock costs and are driven by an aim to increase efficiency rather than campaign length. Initial design optimisation work for one plant applied high density knit structures in the top portion of the pack, along with high palladium alloys in the lower portion of the pack. The average conversion efficiency of the campaign increased, due to a lower drop in efficiency towards the end of the campaign. Further design changes, including the reduction and optimised placement of palladium content, resulted in a reduction in N₂O emissions from the gauze system.

Figure 3 shows the **NITRO-LOK™** and **PRO-LOK™** structure, with the latter seeing an increase in density of over 50%. There is an increase in pressure drop associated with higher density knit structures, and the plant tolerance to pressure drop is taken into consideration when evaluating whether to offer a design using this approach rather than using thicker wires. This approach can offer benefits when used in ultra-pressure plants where pressure drop is less of a concern.

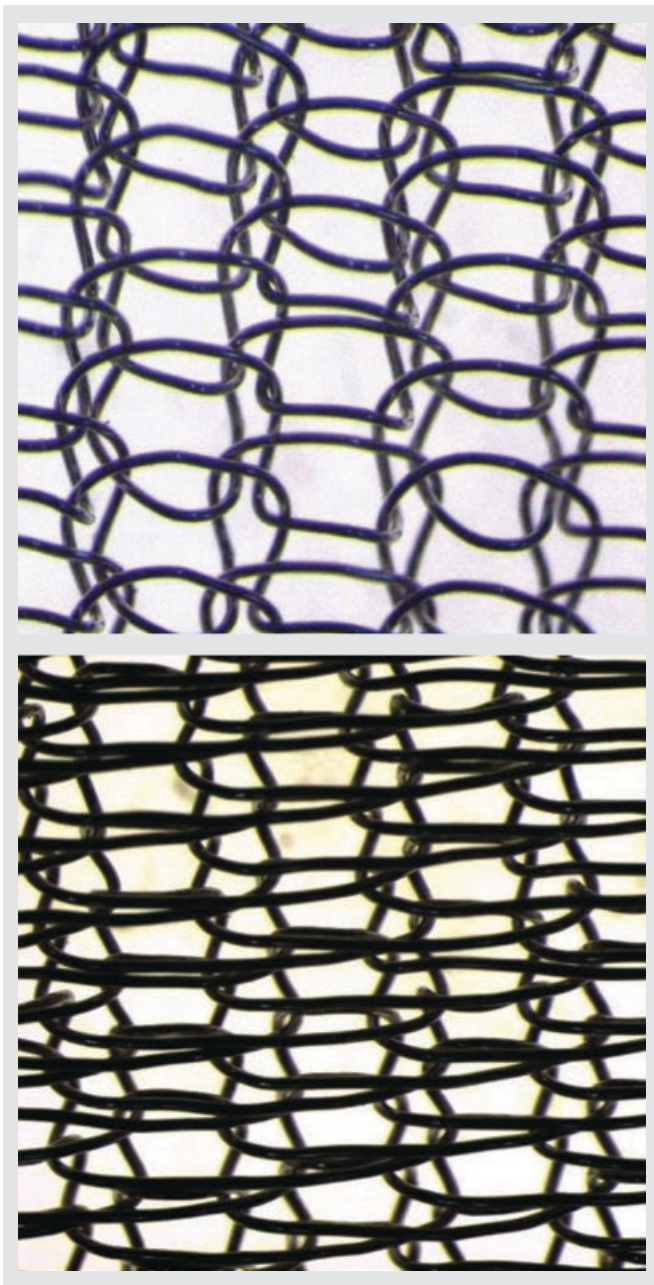


Figure 3: NITRO-LOK (left) and PRO-LOK (right) knit structures which are two possible knit structures that can be used in catalyst designs

Optimisation of rhodium and platinum concentration

Rhodium, originally added to platinum to create an alloy with lower metal loss, has seen a significant increase in price over the last few years. A range of alloys with varying rhodium concentration can be used in a catalyst design, and a small reduction in rhodium concentration can significantly reduce the cost of metal within the pack.

Rhodium doped alloys show an increased selectivity to N_2O at lower temperatures (Fig 1), so the optimisation of rhodium in the top layers of the pack, which see the low temperature mixed gas front, can have selectivity benefits. Lower levels of rhodium are also used when plants suffer from rhodium oxide (Rh_2O_3) formation, which is significantly less selective to nitric oxide, to minimise or prevent formation.

A consequence of lowering the rhodium concentration is increasing the platinum concentration. 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. Experimental data has demonstrated a reduction in the light-off temperature of around $100^\circ C$ using products that have been developed for plants that struggle to light off.

Conclusion

The optimal ammonia oxidation catalyst design is influenced by a myriad of factors, from fundamental reaction kinetics to specific plant operating strategy. Johnson Matthey considers multiple options available to optimise the catalyst design for each plant. Some options that have been utilised by Johnson Matthey for decades are still effective, including the use of higher diameter PGM wire in the top portion of the pack to enhance efficiency. However, recent optimisation options will consider the effect of alloy placement within the pack, looking to optimise the concentration and placement of rhodium and palladium used in a catalyst pack.

Having a deep technical understanding of ammonia oxidation catalyst design, in conjunction with over 100 years of experience, Johnson Matthey is well placed to ensure that the catalyst pack design matches the requirements of each individual nitric acid plant. Design optimisation is a dynamic process, and a continual review of plant operating targets, best achieved through open dialogue between the plant and catalyst supplier, and consideration of the impact of prevailing PGM market conditions are key to ensuring that the catalyst pack is fit for purpose.

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