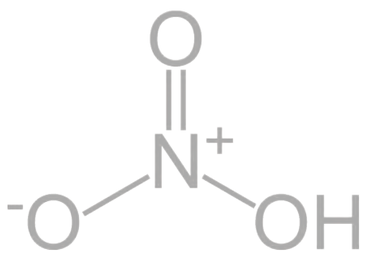
Flexitallic®

MAINTAINING SAFE AND EFFICIENT OPERATIONS THROUGH SEALING MATERIALS: Nitric Acid

CHEMICAL PROCESSING



Introduction

This document describes the demands placed on Nitric Acid production plants, exploring the broader operating environment of an industry which globally produces 55 million tonnes/year[1].

It details the role gaskets and sealing materials play in supporting safety and efficiency objectives and highlights key factors plant operators should consider in choosing the most suitable gasket materials for their plant.

Balancing the Nitric Acid equation

Nitric Acid production places a range of demands on plants striving to strike a balance between a diverse range of factors. Yield objectives must be synchronised with the variable cost of feedstocks, utilities and energy, all within a regulatory environment where plant emissions must meet stringent objectives set by the global community and where safety standards must be maintained at all costs.

Nitrogen oxides (NOx), specifically nitrous oxide (N_2O), produced as a by-product of the Nitric Acid process, has been identified as the third largest greenhouse gas contributor by the Intergovernmental Panel on Climate Change (IPCC) and cited as 298 times more impactful on the environment than CO_2 in terms of its heat trapping qualities in the atmosphere[2].

As such, in Europe, for example, targets set under the Industrial Emissions Directive 2010/75/EU have continued to ensure plants operate with yield and environmental factors in balance[3]. It's no surprise then that whilst safety is paramount, for many plant operators, NOx emissions and energy recovery, alongside the optimisation of capital and operating costs, are also of primary concern.

As a consequence of these demands, combined with local conditions, plants vary significantly in the way they are designed and operated, creating different stresses and tolerance requirements across each part of the process.

Each element in the chain can have a significant impact on how yield objectives are met and how emissions are managed, with plant performance heavily affected by combustion conditions including pressure and temperatures, catalyst composition and age, as well as overall burner and heat exchanger design.

For example, where some modern dual-pressure plants can drive lower emission levels due to higher pressure absorption systems, some single, lower pressure plants have installed extended abatement systems as part of their selective catalytic reduction (SCR) processes to effectively manage their emissions levels.

Therefore, depending on the plant design, differing demands are placed on the infrastructure and sealing materials.

For example, increased temperatures and pressures in the oxidation stage will drive lower N_2O yield. So, whilst emissions are reduced from the process, it can increase the temperature that the equipment, including gaskets, is expected to operate at.

1. Nitric Acid Market By Application (Fertilizers, Adipic Acid, Nitrobenzene, Toluene di-isocynate, Nitrochlorobenzene) Expected To Reach USD 14.00 Billion by 2022: Grand View Research, Inc., 2016.
2. https://www.epa.gov/ghgemissions/understanding-global-warming-potentials.
3. http://ec.europa.eu/environment/industry/stationary/ied/legislation.htm.

A catalyst for consideration

Regardless of demands specific to each plant's design, routine start-up and shut-down periods are essential on every plant due to the replacement of the reactor gauze material (typically around 95% platinum with up to 5% palladium, as well as rhodium in some cases).

On some plants, this gauze replacement can be as frequent as every 90 days[4] but with fine tuning of the process, proactive maintenance management and selection of best available sealing technology this can be extended to over six months, therefore having a significant impact on annual operational costs.

As a consequence of the shutdown, and besides the environmental considerations of this process as increased volumes of NOx gas clear the system while the plant stabilises, many parts will consequently go through abrupt thermal cycling, creating additional stresses on materials, equipment and piping systems.

With this in mind, gaskets that are made from unsuitable sealing materials will degrade prematurely, causing leaks that, in many cases, require unplanned plant shutdowns for costly and complex maintenance operations.

Following are a set of considerations which can be explored when thinking about optimising the Nitric Acid production line in relation to sealing materials and gaskets in order to maintain production efficiencies across the process without compromising on safety.

1. Temperature

With temperatures approaching 930°C (1706°F) in the hottest areas of the plant and other equipment operating in the range of 400°C -500°C (752°F - 932°F), it's crucial gaskets can deal with extreme heat without compromising on sealing performance.

2. Thermal Cycling & Thermal Transience

Caused by routinely planned gauze replacement, abrupt thermal cycling can impact sealing materials. Mitigating against any avoidable sealing failures across the plant is crucially important to avoid further unplanned shut-downs or maintenance outside of the planned gauze change.

3. Oxidation

Due to the nature of the Nitric Acid production process, a highly oxidising environment exists across the entire operation. This environment requires sealing materials which have high tolerance in oxidising conditions and as such, often causes issues with graphite sealing options which are susceptible to oxidation.

4. Pressure

Whilst the overall pressure across any Nitric Acid producing plant would be considered low compared to other industries in absolute terms (up to 15 bar corresponds to a low industrial pressure category[5]), any pressure variance across different sections of the production process can place additional demands on sealing materials, particularly when high temperatures are factored into the equation.

In addition, any inefficiencies caused by air pollution, contamination, poor ammonia/air mixing and poor gas distribution across the catalyst has been noted to reduce NO yield by up to 10%[6].

Overall, with such significant safety and efficiency impact potential on the plant, consideration of the most suitable sealing materials from each of these perspectives can help to drive further improvements by increasing time between failures and making savings on operational outgoings.

Oxidation and graphite

- Graphite is a form of carbon and so by its nature is susceptible to oxidation.
- The speed of oxidation depends on time, temperature and the media – the longer the exposure, the higher the temperature and the more oxidising the chemistry the faster graphite will oxidise.
- As the graphite in a gasket oxidises it loses mass. This mass loss translates into stress loss in the bolted connection and leads to leakage.

Gasket Inspection

You can learn a lot by looking at the gaskets removed from service and inspecting them for signs of oxidation:

- Physical gaps in the filler material.
- Metal cores visible that were previously covered with graphite.
- Leakage.

Call us to learn more about graphite oxidation

Insight

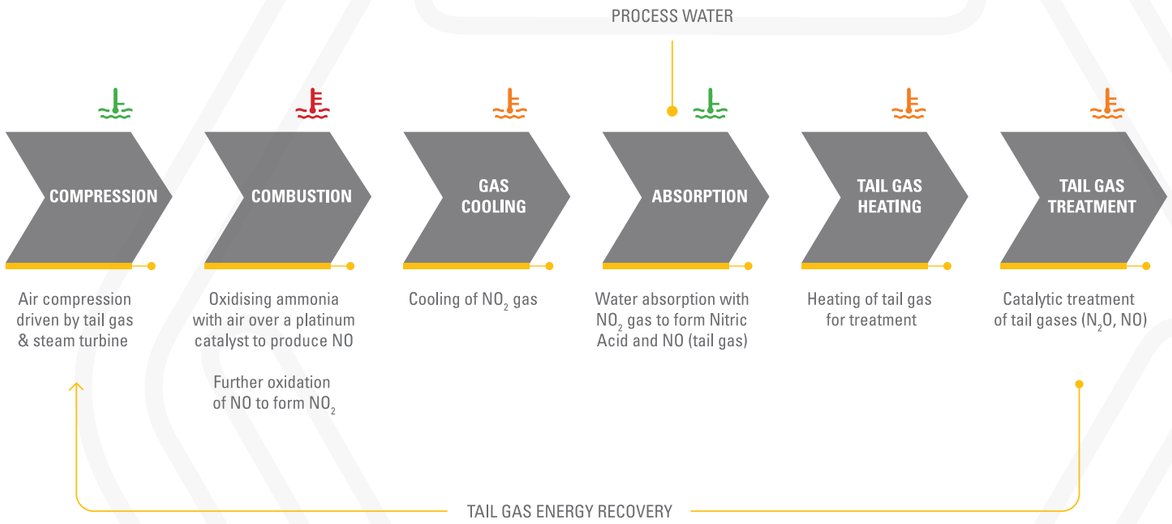
Gauze changes are an ideal opportunity to implement alternative sealing solutions on the plant. This prevents the need for any additional plant downtime outside of the gauze change and gives you the opportunity to evaluate new gaskets and sealing options with minimised impact and risk to ongoing operations.

Insight

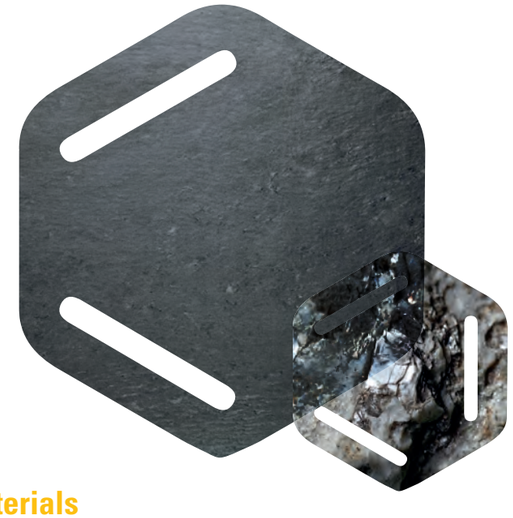
To assess the suitability of a new solution for corroded flange faces, new products were installed at the coolest end of the heat exchanger train during a routine gauze change. This meant a minimal impact on ongoing operations and allowed the plant to effectively validate the gaskets' performance potential across the system.

Identifying the hotspots in the system

Fig 1: Across each phase of the Nitric Acid production process below, all hotspots have been highlighted to show the operational conditions which affect gasket selection during each phase of the process:



4. Fertilizer Manual, UN Industrial Development Organization, Int'l Fertilizer Development Center, Kulwer Academic Publishers, 1998.
5. http://www.wermac.org/flanges/flanges_pressure-temperature-ratings_astm_asme.html.
6. Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry, Production of Nitric Acid (Booklet No.2 of 8), Fertilizers Europe, 2000.



Reviewing conventional gasket sealing materials

In Nitric Acid production, extreme temperatures and highly oxidising chemicals among other factors, make for a very complex environment for gaskets to withstand. Different sections of the plant pose different challenges on sealing gaskets and choosing the right type of gasket and sealing material is critical to maintaining the plant's sealing standards, reliability, safety and environmental impact.

Conventional gaskets commonly used in the industry have intrinsic pitfalls that can impact plant safety and performance. In the case of graphite for example, pressure and moderate temperature tolerance are usually satisfactory, but when combined with a highly oxidising environment at temperatures over 350ºC - 450°C (480°F -750°F) graphite undergoes rapid oxidation, resulting in the need for frequent changes and consequently causing high levels of downtime and increased costs.

Graphite's compressibility and its excellent stress retention characteristics made it the go-to gasket material in the fertiliser industry, but its short life span hasn't gone unnoticed.

In some ammonia burner applications for example, leaks are observed before the end of the gauze campaign, particularly problematic when plants would prefer to replace gaskets at every catalyst recharge as part of a single maintenance operation.

As an alternative, mica has good resistance to chemicals and thermal oxidation, but its poor sealing properties make it an unviable alternative.

The chemical resistance of PTFE products has brought them into the fertiliser industry as a good solution in environments with highly aggressive chemicals. However, their poor resistance to high temperatures (max 250°C / 480°F) limits its usability in Nitric Acid production, except in sections such as absorption towers and cooler condensers. The tendency of PTFE sheet to creep can result in loss of stress and leakage.

Assessing the impact on gaskets

Nitric Acid is typically produced from ammonia oxidised by combustion with air in the presence of a noble metal catalyst (mainly platinum with up to 5% palladium as well as 5-10% rhodium in some cases). The reaction is highly exothermic generating temperatures of up to 930°C (1706°F). The presence of strong oxidising agents like nitrogen oxides, pressure and high temperatures can dramatically shorten asset life and in the case of gaskets, cause leaks that directly impact plant efficiency and safety.

In Nitric Acid production, most gasket leaks are attributable to thermal expansion and oxidation. From a technical perspective, due to the complexity of this type of plant, it wouldn't be realistic to attribute them to a single factor, instead, the demands placed on gaskets is the result of the conditions created by chemical compatibility, temperature and pressure specific to each section of the process.

Thermal cycling exposes gasket and flange materials to different degrees of thermal expansion and tightening, which may result in a critical drop in bolt stress and gasket deformation with a direct impact on sealing performance.

Beyond the underlying gasket material, an accurate analysis of the style of gasket to use is extremely important to maximise the ability to cope with thermal cycling.

Further, in Nitric Acid production, particularly those with extended heat exchanger trains, thermal transience between sections where changes in temperature are present, particularly due to gas cooling, can also place significant demands on gaskets and ultimately lead to joint failure.

Sections of the plant related to combustion and catalytic treatment in high temperatures are more subject to reduced service life caused by oxidation. Leakage caused by degradation of graphite are commonly experienced in ammonia burners, heat train exchangers, tail gas combustors and emergency stop valves.

TYPICAL LOCATIONS FOR GASKET LEAKS INCLUDE:

- **Burner head gasket due to oxidation and warped profiles**
- **Pressure burner due to degradation of compressed sheets**
- **Close coupled components on heat train due to oxidation and thermal mismatch**
- **Superheater due to thermal cycling and reduced bolt stress**
- **Emergency stop valves due to oxidised graphite packing/bonnet seals**
- **Absorption tower due to relaxation of sheet sealing material**

A US-based plant experienced several unplanned outages, mostly due to power failure issues. After the catalyst gauze change, thermal cycling caused leaks to the heat exchanger at every restart.

Solution: Thermiculite®

In a Weatherly Burner Train, SWG graphite gaskets suffered from oxidation and needed replacing at every catalyst renewal. Frequent gasket changes lead to alignment issues, which, combined with the thermal mismatch and oxidation exerted on the gasket, required additional maintenance time.

Solution: Change™

Thermiculite® and Change™ gaskets

Fig 3: Material comparison table:

MATERIAL	SEALABILITY	RESISTANCE TO PRESSURE	RESISTANCE TO TEMPERATURE	RESISTANCE TO OXIDATION
Thermiculite®	▯	HIGH ▯	HIGH ▯	HIGH ▯
Thermiculite® + Change™	▯	HIGH ▯	HIGH ▯	HIGH ▯

▯ HIGH suitability to all potential environments in Nitric Acid production

Thermiculite®

Our tested and proven gasket material is comprised of chemically and thermally exfoliated vermiculite, a similar structure to exfoliated graphite, with one notable exception – it maintains integrity through a wide range of high temperatures.

All **Thermiculite®** products are designed and engineered for high temperature processes in services up to 1000°C (1832°F) working in highly oxidised environments such as is found in Nitric Acid production. **Thermiculite®** is intrinsically resistant to oxidation.

In comparison, conventional graphite gaskets are susceptible to high temperature and to attack by oxidising agents. The rate at which graphite oxidises depends on the application temperature and the concentration of oxygen present. But when it does happen in this environment, it happens quickly, with the end result being seal failure.

The unique composition of **Thermiculite®** gasket material ensures that seals maintain their integrity at maximum service temperatures far exceeding that of graphite.

Key features

- **Total freedom from oxidation**
- **Wide chemical compatibility**
- **Can be used in temperatures up to 1000°C (1832°F)**
- **TA Luft compliant**
- **Fire safe**
- **Proven track record**
- **Wide range of formats to suit all applications**

Change™ Gasket

Change™ is manufactured with proprietary equipment and a unique laser welding process which enables it to perform longer than any other heat exchanger gasket, CGI spiral wound, double jacketed, CMG or kammoprofile.

In environments where leaks are often caused by a sealing material's inability to cope with thermal cycling, **Change™** plus **Thermiculite®** could be the ideal solution.

Flange Rescue Gasket

Flexitallic's exclusive patented **Flange Rescue Gasket** (FRG) can be used for remedial repairs on corroded or damaged flange faces as well as a preventative solution for new equipment to help to prolong its life. As a result, all FRG gaskets can have a significant impact on operating costs and avoid costly plant shutdowns.

As the world's only **Flange Rescue Gasket**, each gasket enables bolted joints to be easily and effectively sealed to prevent internal corrosion. The soft **SIGMA®** inner ring of the FRGs conform seamlessly to the flange face, helping you to get the plant back up and running in a single day and prevent the need to replace flanges or complete welding or machining.

With oxidation of gaskets a key factor in the Nitric Acid production process, a simple, quick solution like Flexitallic's **Flange Rescue Gasket** can prolong asset life and allow plants to wait until the next gauze change is required for more significant maintenance operations or replacements.

Conclusion

While there are a variety of plant designs used to produce Nitric Acid, each plant shares the common challenges of making sure safety standards are met and production volumes maintained. Both objectives must be achieved within challenging environments, where parts are subject to high temperatures, thermal cycling and transience and where oxidation is likely.

By reviewing sealing materials used in gaskets and assessing their suitability against the tolerances required by the Nitric Acid process, further efficiencies can be made on the plant which can help to prevent leaks and work to streamline more significant maintenance operations around gauze replacements.

Flexitallic's range of products are designed to work in the operating environments of nitric acid plants with no compromise on performance. Using our **Thermiculite®**, **Change™** and **Flange Rescue Gasket** portfolio of products can bring a range of important benefits to your plant:

Key benefits

- **Increase plant efficiency**
- **Eliminate unplanned maintenance**
- **Maintain safety standards**
- **Reduce operational costs**

Look out for our syngas & ammonia production technical booklet, part of our chemical processing series. Each contains a full assessment of each process, the problems which can arise due to inefficient sealing materials and how to choose the most suitable materials for each part of the process.

For more information about **Thermiculite®** gasket materials and **Change™** gaskets get in touch.

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About The Flexitallic Group

The Flexitallic Group is a global leader in specialised sealing solutions and products serving the oil and gas, power generation, chemical and petrochemical industries in emerging and developed markets. Focused on the upstream, downstream and power generation sectors, it has operations in France, the United States, Canada, Mexico, the United Kingdom, Germany, United Arab Emirates, Kazakhstan and China plus a network of worldwide licensing partners and distributors.

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