PIPEOTECH

The importance of sealing materials in safe and efficient integrated fertilizer production

DeltaV Seal ™

Introduction

The need to optimize fertilizer plant operations, driven by a range of external and internal influences, means that plant operators must be confident that all equipment is both reliable and high performing

A facility for production of nitrogen containing mineral fertilizers (>46%) often integrates plants for ammonia production, nitric acid production, fertilizer (NPK) plant for calcium and/or ammonium nitrate production and plants for production of urea.

These plants typically employ various corrosive, hazardous and abrasive fluids, and chemicals. The temperatures may stem from processing and handling of cryogenic liquids (for example at -186°C for auxiliary liquid argon) and at -33°C for liquid ammonia storage to over 1000°C in the reformers. The pressures are as high as 175-350 bar in ammonia converters and 150-250 bar in urea plant reactors.

The industrial production of ammonium nitrate entails the acid-base reaction of ammonia with nitric acid: $HNO_3 + NH_3 \rightarrow NH_4NO_3$. The ammonia required for this process is normally obtained by the Haber process from nitrogen and hydrogen. Ammonia produced by the Haber process can be oxidized to nitric acid by the Ostwald process. Downstream of the ammonia production, the ammonia and carbon dioxide are then reacted at high temperature and pressure to produce molten (liquid) urea which is cooled and manufactured into granules or prills for industrial use and as an agricultural fertilizer. The hot melt can also be used to prepare urea solutions.

The aim of this paper is to describe the challenges placed on gaskets and sealing materials in the different parts of typical fertilizer manufacturing plants and provides an analysis of available sealing technologies. The paper also includes examples of successful sealing solutions.

Selecting the right gasket material can minimise downtime, maintain safety and maximise the efficiency of plant operations as demonstrated by the provided case studies.

The paper addresses the current trends in the fertilizer industry which is looking at decarbonise its processes by adopting new 'green' technologies and where selection of high-performance sealing technology will be important.

Ammonia

This part of the paper puts particular focus on syngas production upstream of the ammonia synthesis.

The production of ammonia normally starts with synthesis gas (syngas), a gas mixture commonly produced through steam methane reforming, using a natural gas feedstock to convert to hydrogen (with CO_2 as a by-product). Hydrogen and nitrogen are then synthesized to create ammonia (Haber process) which is used across a range of applications and produced in volumes of over 180 million tonnes/year globally. Approximately 80% of the ammonia output is used in the production of fertilizers. Other uses include plastics, nylons, and dyes.

The need to balance yield, costs, and emissions, while maintaining stringent safety standards, has seen a range of solutions implemented on many plants to optimise their operations. These include increasing the reforming pressure and preheating the process air for the secondary reformer to a higher temperature. Sometimes underestimated within the context of broader improvement plans, gaskets are worthy of consideration, particularly in extreme service environments. These applications require materials resistant to challenging process conditions, making the decision on which gasket technology to choose a crucial component to help improve processes efficiencies.

The ammonia production processes

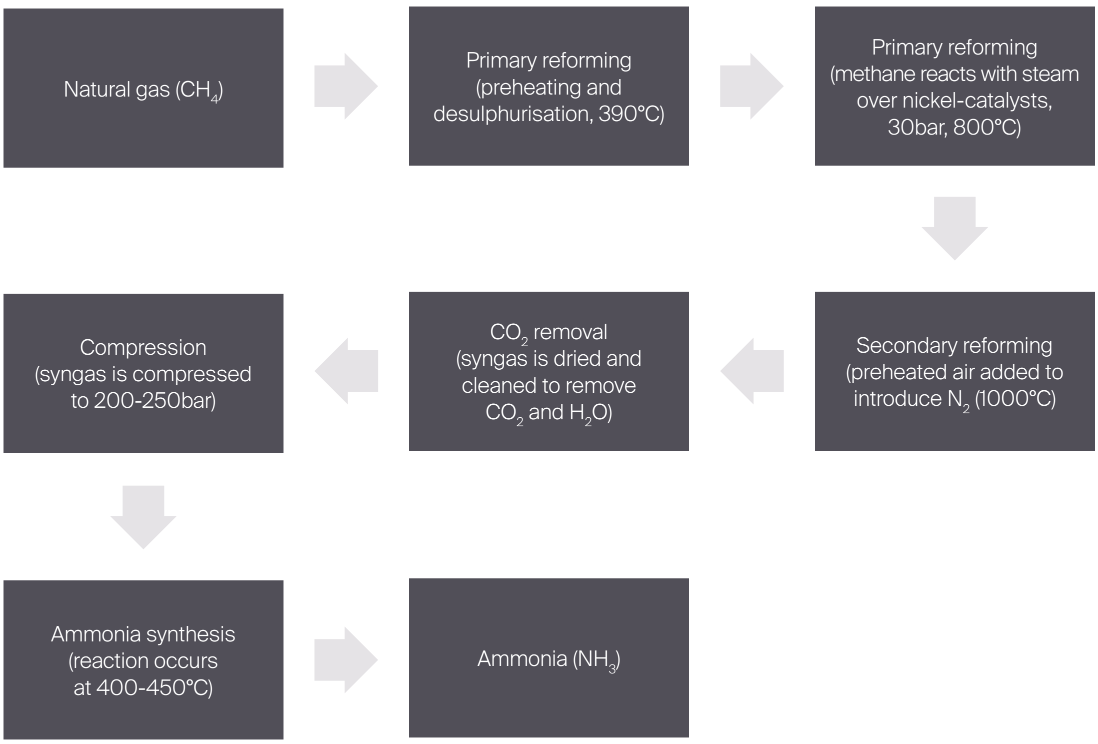
Within ammonia production there are several different processes used to generate syngas. These include gasification (coal), electrolysis (water), partial oxidation (heavy oil) and reforming (natural gas).

Steam methane reforming and alternative processes, including gasification and partial oxidation, present real challenges for gasket materials. For example, the very high temperatures present in the reforming and partial oxidation processes, in some cases more than 1200°C, places significant demands on sealing materials such as graphite. Such extremes in temperature can often lead to gasket failure or leakage and severely affect plant efficiency.

In addition to the energy required for the steam methane reforming process, ammonia synthesis requires high pressures, placing further strain on the components in this part of the process. The purification of syngas releases large amounts of carbon, placing increasing pressure on plants to efficiently manage emissions. With a growing pressure for all manufacturers to support global environmental directives, including the EU framework that aims to cut greenhouse gas emissions by 40% by 2035, there is now an increasing urgency for every plant to respond to these environmental imperatives whilst continuing to balance energy costs and production objectives. Ensuring that best available technology is selected is critical for any plant's efficiency and performance.

Ammonia process overview

The typical process steps for ammonia production from natural gas are provided in the following figure:



Nitric acid

Nitric acid is produced by two methods. The first method utilizes oxidation, condensation, and absorption to produce a weak nitric acid. Weak nitric acid can have concentrations ranging from 30% to 70% nitric acid. The second method combines dehydrating, bleaching, condensing, and absorption to produce a high-strength nitric acid from a weak nitric acid. High-strength nitric acid generally contains more than 90% nitric acid.

Weak nitric acid production

The high-temperature catalytic oxidation of ammonia typically consists of three steps:

- Catalytic ammonia oxidation at 750°C to 800°C
- Nitric oxide oxidation
- Absorption

Each step corresponds to a distinct chemical reaction.

The nitric oxide formed during the ammonia oxidation must be oxidized. The process stream is passed through a cooler/condenser and cooled to 38°C or less at pressures up to 8 bara. The nitric oxide reacts non-catalytically with residual oxygen to form nitrogen dioxide (NO_2) and its liquid dimer, nitrogen tetroxide.

High-strength nitric acid production

High-strength nitric acid (98% to 99% concentration) can be obtained by concentrating the weak nitric acid (30% to 70% concentration) using extractive distillation. The weak nitric acid cannot be concentrated by simple fractional distillation. The distillation must be carried out in the presence of a dehydrating agent. Concentrated sulfuric acid (typically 60% H_2SO_4) is most used for this purpose.

The nitric acid concentration process consists of feeding strong sulfuric acid and 55% to 65% nitric acid to the top of a packed dehydrating column at approximately atmospheric pressure. The acid mixture flows downward, counter current to ascending vapours. Concentrated nitric acid leaves the top of the column as 99% vapor, containing a small amount of nitrogen dioxide (NO_2) and oxygen (O_2) resulting from dissociation of nitric acid. The concentrated acid vapor leaves the column and goes to a bleacher and a counter current condenser system to affect the condensation of strong nitric acid and the separation of oxygen.

Ammonium nitrate

Ammonium nitrate is produced by neutralizing nitric acid with ammonia. All ammonium nitrate plants produce an aqueous ammonium nitrate solution through the reaction of ammonia and nitric acid in a neutralizer. The process involves several unit process operations including:

- Solution formation and concentration
- Solids formation
- Finishing
- Screening and coating
- Product bagging and/or bulk shipping.

In some cases, solutions may be blended for marketing as liquid fertilizers. The number of operating steps employed depends on the specification of the product. For example, plants producing ammonium nitrate solutions alone use only the solution formation, solution blending and bulk shipping operations.

In terms of especially challenging conditions for gasket material selection, high temperature (160°C) pipework for transportation of liquid ammonium nitrate has proven to be an inherently problematic part of the production systems with associated leakages with serious HSE issues and costly repairs as the result. The leaking flanges have commonly been gasketed with soft sheet type gaskets made of PTFE with very poor performance.

Plants producing a solid ammonium nitrate product may employ all the operations. Approximately 15–20 volume-% of the ammonium nitrate prepared in this manner is used for explosives and the balance for fertilizer.

Additives such as magnesium nitrate or magnesium oxide may be introduced into the melt prior to solidification to raise the crystalline transition temperature, act as a desiccant (removing water) or lower the temperature of solidification. Products are sometimes coated with clays or diatomaceous earth to prevent agglomeration during storage and shipment, although additives may eliminate the need for coatings. The final solid products are screened, and sized, and off-size particles are dissolved and recycled through the process.

Selection of gasket materials

When it comes to choosing the best available gasket technology, how do you know which sealing material is most appropriate for your fertilizer plant? Gaskets made from unsuitable sealing materials will degrade prematurely, causing leaks that in many cases require unplanned shutdowns for costly and complex maintenance operations.

The key parameters that have a direct impact on the selection of suitable sealing technology in regards of service conditions and that need to be considered for optimization of fertilizer production processes are:

Temperature

With temperatures approaching 1200°C in the hottest areas of fertilizer plants and other equipment also operating up to 600°C, it is crucial that gaskets can deal with extreme heat without compromising on sealing performance.

Pressure

Combined with high temperature, significant pressure across the production process, up to 200 bar during ammonia synthesis, places additional requirements on piping components and sealing materials.

Thermal cycling

Typically caused by routine maintenance, unplanned shutdowns, or activities such as de-coking for the gasification processes, thermal cycling can adversely affect gasketed joints as components struggle to cope with repeated contraction and expansion. Mitigating avoidable sealing failures across the plant is crucially important to avoid further unplanned shutdowns or maintenance. This is especially critical when the gasket and the flange are selected in dissimilar materials with different thermal expansion properties.

Oxidation

Within most of the stated processes, the chemistry is highly oxidizing, providing an additional challenge for sealing materials, and for graphite, a service environment where failure is ultimately inevitable.

Consideration of the most suitable sealing materials from each of these perspectives can help to drive further improvements by improving safety, increasing time between failures, improved reliability, and reduced operations costs.

Acids and corrosion

The nitric acid systems represent a key application challenge: achieving reliable sealing with gaskets for strong acid service, including also other strong acids like sulphuric acid.

Strong acids, such as sulphuric/nitric acid, are extremely corrosive and, unless the gasket material is chosen wisely, the risk of gasket failure with resulting leakage can be high. This is especially applicable to gaskets containing stainless steels which may lose their passivity and therefore show high corrosion rates. An important factor to consider in any strong acid service application is the concentration of the acid being serviced, as well as the temperature of the media. For example, applications involving sulphuric acid at concentrations of 96% and above can be extremely challenging, and the challenge is exacerbated when hot acid is involved.

Similarly, it is extremely important to select the flange and gasket material such that the corrosion potential difference between the gasket and the flange is not causing galvanic corrosion of the gasket and thereby causing premature failure and leakage of the joint.

Review of conventional sealing materials for oxidizing conditions

Background

In chemistry, strong oxidizers are substances (like chromic acid) that can cause other substances (like seals and gaskets) to lose electrons. So, an oxidizer is a chemical species that undergoes a reaction that removes one or more electrons from another atom.

This causes a change in mass. Metals will turn into their respective heavier oxides, and the carbon in graphite will oxidize into carbon dioxide—which, although molecularly heavier, is a gas at room temperature.

This happens in pumps, valves, pipelines, or any other equipment that have seals and gaskets carrying a strong oxidizer. It will cause pitting or rust and, depending on your choice of seal material, may require shorter service intervals. Ultimately, you may have to look for a more suitable material that can handle strong oxidizers.

More importantly, an oxidizing agent can cause or contribute to the combustion of another material.

The U.S. Department of Transportation defines oxidizing agents specifically. DOT's Division 5.1(a)1 means that a material may enhance combustion or quickly raise pressure causing a rapid chemical reaction. A fire may start or, even worse, create or facilitate an explosion.

There have been instances of fires or explosions in mining, chemical process and even fertilizer factories where strong oxidizers were used.

A West Texas fertilizer company storage and distribution facility caught fire on April 17, 2013. As firefighters attempted to extinguish the blaze, the plant exploded with the force of 10 tons of TNT, killing 15 people and injuring 200. It destroyed 60 nearby homes and left a 93-foot-wide crater where the plant once stood.

All said, it is important to choose the right sealing material for strong oxidizers. There are multiple sealing products on the market for the chemical processing, oil and gas, mining, and aerospace industries.

Graphite is widely used in industrial sealing applications due to its acceptable sealing properties and ability to cope with moderate temperatures. However, its performance reduces significantly in high temperature applications and particularly in oxidizing environments where material degradation can be severe and rapid, leading to gasket failure and leakage.

Within the steam reforming process, both conditions are present, creating a serious problem for operators who need to ensure gaskets provide leakproof performance with a minimum impact on operations.

Graphite's short operational life in these more challenging environments is a known problem in the industry but often tolerated without considering better alternatives.

But what other options are there?

This paper is intending to answer this question by proposing to apply the new and unique DeltaV-Seal™ technology at these and other critical and challenging locations throughout fertilizer manufacturing plants. These proposals are underpinned by several case studies where this new technology has been successfully applied, see below.

Assessing the impact on gaskets

High temperature applications

In the steam reforming and nitric acid processes, the combination of high temperatures and oxidizing conditions make for a demanding environment which directly impact on gasket life and performance. In addition, thermal cycling exposes gasket and flange materials to different degrees of thermal expansion and contraction. Often occurring due to plant maintenance shutdowns or process upsets, thermal cycling frequently results in a critical drop in bolt stress, leading to a loss of gasket compression with a detrimental impact on sealing performance.

For those syngas plants using the partial oxidation processes, the higher temperature and more severely oxidizing environment, in comparison to the steam reforming process, will cause a faster and more severe degradation of sealing materials such as graphite.

Cryogenic applications

Ammonia synthesis uses syngas generated by steam reforming natural gas (as the feedstock). This reaction also produces several other gases that do not contribute directly to the ammonia reaction. These purge gases need to be continuously removed from the synthesis loop and are generally fed back to the reformer furnaces as fuel gas. A typical purge gas contains about 60% hydrogen, 20% nitrogen, 5% argon, 10% methane and 4% ammonia in varying concentrations, depending on the process in place at the ammonia plant. Instead of burning purge gases, it makes good financial sense to recover valuable gases such as ammonia, hydrogen, nitrogen, and argon, see below.

The recovery of these gases involves cryogenic processes ($T<-70°C$) which pose challenges to the gaskets and there are several reasons to choose a specialist seal over a standard seal in these types of low temperature operations.

These include:

- Protection of dangerous cryogenic fluids: Depending on the type being used, cryogenic liquids can burn, can cause asphyxiation and can be toxic. Some materials can be a risk of fire and explosion too, which makes suitable protection and containment an absolute necessity.
- Conventional o–rings may fail: In many cases, the working temperature of the application will be too low for standard o-rings to function properly. Very cold temperatures can lead to some elastomers reaching a glass transition state (T_g), which causes it to become less flexible and more brittle, risking failure.
- Contraction needs to be accounted for: Expansion and contraction which occurs naturally as temperatures change can cause o-rings to become unseated, risking cracking, leaks and failure occurring.
- Cold set must be avoided: In applications where, cryogenic operations work alongside higher temperature operations, the risk of stresses on o-rings being unable to relax at low temperatures is high when the wrong type of seal is used. Known as ‘cold set’, this will create an unviable seal, leading to leakage and failure.

In summary, for cryogenic operations, the right choice of seal is crucial.

Typical challenging locations for gaskets in ammonia manufacturing plants

In ammonia production plants including support systems there is a range of known locations where gaskets are facing challenging conditions:

- Hydrocarbon (gas) feedlines and pre-heater exchangers
- The pre, primary and secondary reformers
- Pigtails and syngas piping
- Shell & tube heat exchangers
- Downstream syngas cooling
- Waste heat recovery and steam generation
- Superheated steam lines
- Purge gas recovery

Pipeotech DeltaV-Seal™ technology

Pipeotech is developing a wide portfolio of gasket products specifically designed for the complex environments present in current and future fertilizer production. Core products are:

- DeltaV-Seal S235
- DeltaV-Seal 316L
- DeltaV-Seal 800HT

The performance of DeltaV-Seal technology under different in-service conditions typical of fertilizer manufacturing plants is demonstrated by the following case study examples:

CASE STUDY 1 (ammonium nitrate)

A global fertilizer producer experienced several unplanned outages a year on insulated ammonium nitrate 304L pipework. The pipework flanges operating at 16 bar and 160°C were gasketed with Gylon microcellular PTFE sheet gaskets and constantly leaking causing expensive shutdowns and serious HSE implications.

Working with the customer for a long-term solution, Pipeotech proposed the DeltaV-Seal 316L. The austenitic stainless steel material match ensures corrosion resistance and galvanic compatibility, and the extensive product testing and certification creates confidence that a long lasting and non-leaking seal can be achieved.

> *"We are very pleased with both the service from Pipeotech but also the DeltaV-Seal of course."*
> (Client rep.)

> *"DeltaV-Seal was selected due to historic performance issues with previous incumbent gasket technologies, leakage, retorquing, shutdowns, CUI (especially within the ammonium nitrate piping trains) and meeting our company's overall operational excellence and corporate responsibility for zero leaks and zero fugitive emissions."*
> (Client rep.)

CASE STUDY 2 (steam)

In the gas processing systems typical of the methane steam reforming steps, high pressure steam, various chemical components and severe temperature fluctuations put continuous strain on the flanges and gasket seals of condensed steam lines, causing leakage and costly maintenance.

The customer plays a key role in processing and transporting gas and condensate/light oil from major sites on the Norwegian continental shelf. In the insulated 316L steam carrying pipework operating at 150°C and 20 barg pressure, traditional seals were causing leakage, resulting in costly downtimes for maintenance and repair.

Pipeotech suggested that the inherent fit, durability and all-metal design of the DeltaV-Seal 316L gasket would ensure a snug connection, one that can withstand temperature fluctuations, and would resolve the leakage issues.

The customer reported that there has been no leakage since switching to the DeltaV-Seal 316L during 2016. As the seal retains its fit without any intervention, no re-torquing or periodical replacement needed, the cost of maintenance is dramatically reduced. Not only is the solution cost effective but ensuring pipeline and process integrity also lends to a safer and more efficient work environment.

CASE STUDY 3 (cryogenic)

Following a highly successful test period, the client has announced that the DeltaV-Seal 316L has been named as their exclusive seal of choice for all current and future liquefied natural gas (LNG) operations. As a provider of services such as: LNG & LPG facility construction, control systems, and operation monitoring, the client understands the tremendous importance of utilizing the DeltaV-Seal unique sealing strengths. Its reliance on components capable of tolerating temperatures fluctuating from ambient, down to -160°C is integral in their operations.

> *"A service call to a location such as the Hammerfest facility would take us between two or three days. These kinds of operations can easily cost 100,000NOK (approx. $12,000), so DeltaV-Seal 316L gives us big savings. Previously, we used other sealing solutions that did not follow the movements of the piping in the same way. We began testing DeltaV-Seal 316L a little over two years ago and we now have switched to using this solution exclusively at all LNG plants."*
> (Client rep.)

> *"Since metals contract and expand with changes in temperature, producing the gasket out of comparable metal enables the seal and piping to expand or contract in unison, this way we obtain solid pipe connections without leaks."*
> (Client rep.)

CASE STUDY 4 (nitric acid)

A global manufacturer of agricultural fertilizer products with several large facilities in Europe and North America was experiencing constant flange leakage on their 60%/80°C/14 bar nitric acid pipework due to the use of traditional spiral-wound gaskets, leading to regular expensive shutdowns and HSE implications. The customer wanted to eliminate nitrous oxide emissions from the lines to increase safety and reduce environmental effects.

All valves and fittings in the nitric acid pipework were stainless steel 316L with the associated piping in 304L. Pipeotech put forward the DeltaV-Seal 316L as a long-term sealing solution. The material match ensures corrosion resistance and galvanic compatibility, and the extensive product testing and certification provides the customer confidence that a long lasting and tight seal can be achieved.

DeltaV-Seal 316L was installed and monitored with no leakage reported since the initial bolt-up. Installation of DeltaV-Seal provides a tight and maintenance-free sealing solution. In this example, gasket selection has played an important role in creating a safer, more profitable, and environmentally sustainable facility.

When developing new gasket products, Pipeotech adopts a suite of advanced techniques, methods, and software. These include finite element analysis (FEA) and bolted flange joint (BFJ) and piping/pipeline system mechanical strength calculations to ASME/EN pressure vessel design codes. Full galvanic compatibility between the fully metallic DeltaV-Seal product and the surrounding flange materials is ensured by corrosion modelling based on electrochemical polarization curves.

Proof of DeltaV-Seal gasketed BFJ mechanical integrity is also ensured through extensive international collaborative laboratory testing programs which include testing under simulated BFJ mechanical conditions as well as testing of actual gasketed BFJ at e.g., -196°C.

The DeltaV-Seal performance under cyclic conditions is ensured by vibration testing, pressure pulsation testing and temperature cycling testing.

The foundation for DeltaV-Seal product development for specific in-service conditions is the inherent and uniquely low leakage rates (<1e-8 mg/m/s) obtained during standardized gasket testing in accordance with e.g., EN13555.

Conclusions

The need to optimize fertilizer plant operations, driven by a range of external and internal influences, means that plant operators must be confident that all equipment is both reliable and high performing. High temperatures in a difficult environment where oxidation, corrosion and non-static process conditions occur is likely can lead to a variety of sealing complications. Ensuring that the best possible sealing materials are specified can help to prevent leaks, in turn increasing efficiencies across the board – with a significant reduction in unplanned shutdowns.

This will be even more important in the future for the fertilizer producers as they are seeking to cash in on the green energy transition by decarbonisation and reconfiguring their ammonia plants to produce clean energy to power ships. The consumption of oil for transportation is one of the top contributors to global greenhouse gas emissions that cause climate change, and fertilizer producers are currently joining a growing list of companies adjusting their business models to profit from a future lower-carbon economy.

This paper describes how fertilizer plants separate hydrogen from natural gas and combine it with nitrogen taken from the air to make ammonia, which farmers inject into soil to maximize crop growth. These processes generate carbon emissions that these companies say can be avoided by altering the production process for ammonia normally used for the fertilizers to instead look at produce hydrogen with a lower CO_2 footprint. The current options under discussion are by extracting hydrogen from water charged with electricity (green), hydrogen produced from natural gas with carbon capture and storage (blue) and hydrogen from biomass gasification.

It can then combine that hydrogen with nitrogen to make green ammonia, which the marine industry is testing as fuel. Adopting green ammonia or green hydrogen to replace crude oil-based fuel would help the International Maritime Organization (IMO) meet the target to reduce emissions and is suited to both short- and long-haul vessels. Methanol and liquefied natural gas (LNG) are other clean alternatives and fuel cells are another potential marine use for ammonia and hydrogen.

Notwithstanding these environmentally friendly initiatives, there are challenges that need to be addressed. Ammonia remains toxic and corrosive, requiring special handling on ships and combusting ammonia may produce nitrous oxide, a greenhouse gas, that ships would need to neutralize to prevent emissions.

Fundamental to addressing these challenges is to have the best sealing technology available and implemented.

Pipeotech is in the right spot to support these reduced emissions initiatives with the DeltaV-Seal technology to assure that piping/pipeline systems and equipment do not leak. The industry's traditional project development approach to seals and emissions needs to change to be much more front-end heavy (FEED) on these aspects. Successful outcome is depending on an early implementation of best available seal technology in project specifications and design.

This paper demonstrates how Pipeotech's range of products are designed with these operators' current and future needs in mind, never compromising on performance in even the most challenging environments present in current and future fertilizer manufacturing plants.

Contact Pipeotech for further information and adoption of DeltaV-Seal technology and gasket parameters to your current and future fertilizer manufacturing facilities.