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Number 357

January | February 2019

nitrogen 60 YEARS ANNIVERSARY ISSUE 1959-2019 + syngas

www.nitrogenandsyngas.com



1959-2019

Celebrating 60 years
of service to the world nitrogen industry.



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A diamond jubilee

NITROGEN+SYNGAS
ISSUE 357
JANUARY-FEBRUARY 2019

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Cover: Nitrogen+Syngas magazine celebrates its diamond anniversary. Image: coreDESIGN/Shutterstock.com



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JANUARY | FEBRUARY 2019

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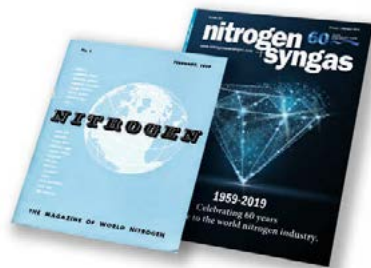
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Then and now



As you'll see from the cover, this edition marks the 60th anniversary of the first issue of *Nitrogen* magazine. It began life as a quarterly publication, but after two years moved to the bi-monthly frequency that it has maintained ever since – which is why this anniversary issue is the slightly odd number 357 and not the more satisfying round number of 360.

On pages 22-24 there is a more in depth look at the very first issue of the magazine, from February 1959, but in writing that piece it was striking to notice that, for all of the changes that have happened since then, the nitrogen industry of today was still easily recognisable. The 1950s were an era when cheap, 'stranded' natural gas and the scale-up of major processes was beginning to transform the industry from the previous coal-based business based around manufacturing centres in the industrial heartlands of Europe, the United States and Japan, and moving it to new, further flung locations around the world. And in Asia and Latin America, the first shoots of the 'Green Revolution' were taking hold, about to revolutionise agriculture in those regions and paving the way for a world today that is able to support 7 billion people, more than half of them kept alive by the nitrogen fixed in Haber-Bosch plants.

But as transformational as those developments would be, it might be argued that otherwise, an ammonia plant then was much the same as now – feed treatment, a reforming section, shift conversion, and an ammonia synthesis section; an iron catalyst and a method of heat recovery. In terms of overall flowsheet, aside from some wrinkles, the main difference is one of scale – today's plants of 3,000 t/d and more are a far cry from the 200 t/d units typical in 1959.

Yet 'under the hood', many aspects of the technology have changed. Catalyst technology has become far more advanced due to new methods of analysis and manipulation at the smallest scales. The increasing digitisation of the industry continues, and now the so-called 'Industry 4.0' revolution is bringing new interconnectedness, smart devices and data capture and analysis techniques to bear on old problems. Likewise feedstocks have become

more diverse, with biomass, municipal waste and hydrogen produced from renewable electricity all joining the traditional coal, coke, gas and naphtha. Looking back at old issues of the magazine it's possible to see a similar, parallel evolution in the publishing industry. In the 1960s the company had a TELEX address, by the 1980s a fax number, and by the 1990s an email address, while typesetting has moved from hot metal and physical page make up sheets (I can vividly remember when 'cut and paste' meant exactly that) to today's all-digital world where pdf proofs are emailed to printers who could be anywhere in the world.

Over the years the magazine has changed publishers, from the original British Sulphur Corporation, then, when that company was taken over by CRU in 1992, to newly founded subsidiary arm British Sulphur Publishing, which ultimately became CRU Publishing in 1997, before being spun off as a separate entity – BCInsight Ltd – in 2007. It has changed name – from *Nitrogen*, to *Nitrogen&Methanol* and finally *Nitrogen+Syngas*, as various syngas derivatives are increasingly seen as part of a portfolio that can all be made from a single complex. However, it has continued to publish the same mix of prices and market coverage, new plants and project announcements, and details of new technologies and processes, and I hope will continue to do so for many more years. It has been my privilege to be editor for the past 24 of those 60 years, and on behalf of all of us at BCInsight, I would like to thank you, the reader, for your continued support, without which none of this would have been possible. ■

Richard Hands, Editor



MELAMINE

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Price trends



MARKET INSIGHT

Alistair Wallace, Head of Fertilizer Research, Integer Research, assesses price trends and the market outlook for nitrogen.

The urea market weakened significantly in Q4 2018, as increased Chinese and Iranian availability exceeded expectations and surprised the market by featuring heavily in November's 1.8 million tonne MMT tender. Lacklustre Mediterranean demand also underperformed seasonal norms as currency and credit crises in Turkey curtailed import buying and an extended period of dry weather in Germany and central Europe limited Europe's pre-buy. Prices began falling in late October, and by December around \$70/t had been wiped off urea values at f.o.b. Middle East.

Of course, urea was not the only commodity or asset class to tumble in Q4 2018. Both energy and equity markets reversed strong performances to return losses for the year, and in doing so managed to heap further downwards pressure on the urea market. Indeed, falling gas prices in Europe will have contributed heavily to weaker nitrogen pricing sentiment. By the 31st of December gas prices in Europe were \$3.00/MMBtu below the \$10.00/MMBtu peak they reached in September 2018, and producer costs in Europe look to be around \$60-70/t lower as a result (assuming an average gas consumption of around 23-24MMBtu/t of urea).

Last year had looked to be very promising for urea prices as the expected curtail-

ments of Chinese operating rates initially played out as the market had expected in H1 2018. Environmental controls limited coal consumption in Chinese urea plants to the extent that China was barely able to cover its domestic urea requirement during its application season. At peak demand levels in April and May, Russian and Middle Eastern imports were needed to top up domestic urea supply. When the domestic season ended in mid-July, Chinese operating rates began falling fast, with lower production swiftly limiting export availability. As the fall demand season kicked off in the northern hemisphere, prices rallied to almost \$350/t f.o.b. Middle East. Calendar-year Chinese exports totalled just 2.2 million tonnes – more than 50% lower than the 4.6 million tonnes shipped from China in 2017.

However, a burgeoning triangular trade developed between Iran, China and India in H2 2018 to circumvent US trade sanctions on Iran. And despite the imposition of stringent US sanctions on Iran last year, Iranian urea producers still managed to export a record quantity of urea by moving their exports through Chinese ports and, in doing so, obscuring the urea's country of origin. We would estimate that between 800,000 and 1.0 million tonnes of Iranian urea was re-exported through China this year, lessening both the impact of China's domestic

supply curtailments and the US sanctions on Iran. As fourth-quarter demand proved much weaker than the market had hoped, the impact of this expanded Chinese and Iranian export availability was more pronounced and prices tumbled.

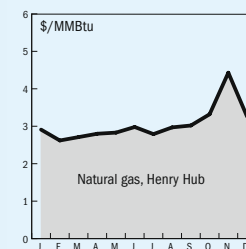
Despite all this fourth-quarter doom and gloom, conditions in the urea market were, overall, much improved in 2018. Year-average prices were up \$45/t f.o.b. Middle East, from \$232/t in 2017 to \$277/t in 2018, and after the downwards correction in Q4 2018, the market had, at the time of writing, rediscovered stability at \$280-290/t level. With more tender business expected from India in Q1 2019 and delayed European business expected to begin in earnest by February, we could even see a limited recovery in pricing over the next three months.

Conditions in the global ammonia market also improved in 2018, with average pricing for the year increasing by around \$25/t over 2017 levels. However, supply/demand fundamentals remain weak relative to those in the urea market, and a large part of this price recovery last year will have been driven by higher industry costs at the margin. Poor fourth-quarter pre-buying for the US direct application season has worsened the outlook for Q1 2019, and with energy prices falling across the oil and gas sector, summer 2019 could prove a tough period for the industry. One highlight, however, was the continued increase in Chinese import buying as the domestic ammonia industry grappled with tightening environmental standards. China now looks to have imported almost 1.0 million tonnes of ammonia in 2018, up from just 400,000 tonnes two years ago.

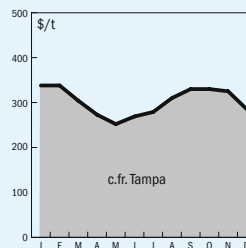
Looking into 2019, the most important event in the ammonia market will be the commissioning of Eurochem's Kingsepp standalone ammonia plant near St Petersburg. This plant's capacity of almost 900,000 t/a will focus on supplying the company's domestic ammonia requirements of around 350,000 t/a (for DAP/ MAP production). This should leave over 500,000 t/a of ammonia available for export supply to its nitrates and NPK facility at Antwerp in Belgium, and for sale into the international traded market. The sheer size of this plant is likely to oversupply the market this year, and that is before we consider that Navoiyazot will also begin production in Uzbekistan in Q4 2019, adding around 400,000 t/a of merchant ammonia capacity.

END OF MONTH SPOT PRICES

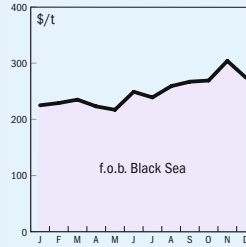
natural gas



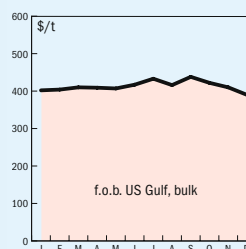
ammonia



urea



diammonium phosphate



MARKET INSIGHT

Mike Nash, Global Business Director, IHS Chemical, assesses the market for methanol.

METHANOL

Spot methanol prices fell in all regions in November, in line with softer sentiment in China due to falling commodity prices. The sustained high methanol prices in October had continued to put MTO producers under economic pressure, causing demand erosion and prices began to fall globally.

The official US posted reference-prices from major producers for December were \$1.41/gal for Methanex (down \$0.15/gal) and \$1.42/gal for Southern Chemical (down \$0.11/gal from November, equivalent to \$469/t and \$472/t, respectively). IHS Market Chemical's contract net transaction price for December is officially posted at \$1.415/gal (nominal \$470/t), down \$0.13/gal (\$44/t) from the previous month. Demand into winter applications rose during the second-half of November, with temperatures in parts of North America falling below freezing. Demand into construction applications and durable goods also picked up due to ongoing repairs in the US Gulf and North Carolina following storm damage, as homes are repaired and cars are replaced. On the supply side, there were some natural gas curtailments in Trinidad due to offshore platform maintenance. Methanex's Chilean unit is estimated to have run at a level of around 75% of nameplate capacity towards the end of November; as we are in the warmer months of the year for the southern hemisphere, operations have improved due to greater gas availability with the need for heating is reduced. Methanex started up its Chile IV (840,000 t/a) unit last month.

European spot prices (T2 f.o.b. Rotterdam) for November were down €31/t from their October level at €340/t. The 4Q 2018 West European Contract Price settled at up €9 at €428/t, f.o.b. Rotterdam T2. The ongoing suspension of duty on methanol arriving into the EU implemented by the European Commission is due to expire at the end of 2018 but it is likely that the duty-free allowance will now be extended. There was some increased supply into Europe; The one line at Sirte Oil in Libya that shut down following an explosion at the plant restarted early in December. Shchekinoazot in Russia had started production at its new unit in October and operated at healthy rates.

European formaldehyde demand was generally stable at healthy rates but declined slightly towards the end of the month due to issues with bringing feedstocks into mainland Europe via the Rhine. Demand into MMA was likewise reduced in November due to issues with obtaining feedstock methanol due to low water levels on the River Rhine.

In India, port prices averaged \$340/t in November, down \$47/t due to hesitancy in buying from Iran following the US withdrawal from the Joint Comprehensive Plan of Action. Demand remained stable at low levels. Inventories were high during the start of November at West Coast Indian ports. Saudi Arabian producers preferred to ship methanol to Southeast Asia, rather than India, as the netbacks there were higher.

Asian prices in November traded down \$55/t. China weekly average prices were down \$79/t in a range of \$275-400/t. Methanex's posted APCP for December was \$430/t, a decrease of \$80/t from its posted price for November. In China, coastal inventories increased significantly and started to put pressure on prices in November. Some large natural gas based units stopped or lowered their operating rates at the end of November for getting ready to the gas restriction during winter time. Coking gas-based methanol producers in North China ran at 43% utilisation in November and coal-based methanol plants in Northwest China at 61%. The natural gas-based operating rate in China in November averaged 43%, down 6% from October and likely to fall further due to the usual natural gas restrictions in winter.

Demand into MTO increased modestly at the end of the month. Fund Energy Ningbo and Nanjing Chengzhi increased production levels to full rates, driven by the improvement in economics, but overall MTO operating rates averaged 67% in November, down sharply from the previous month due to high methanol prices at the start of the month.

In Southeast Asia, supply recovered to a normal level and inventories were higher at the end of the month, with all units in the region running. End-user inventories were at manageable, mid-tank levels. Spot demand into the biodiesel sector weakened over November due to a fall in crude oil prices.

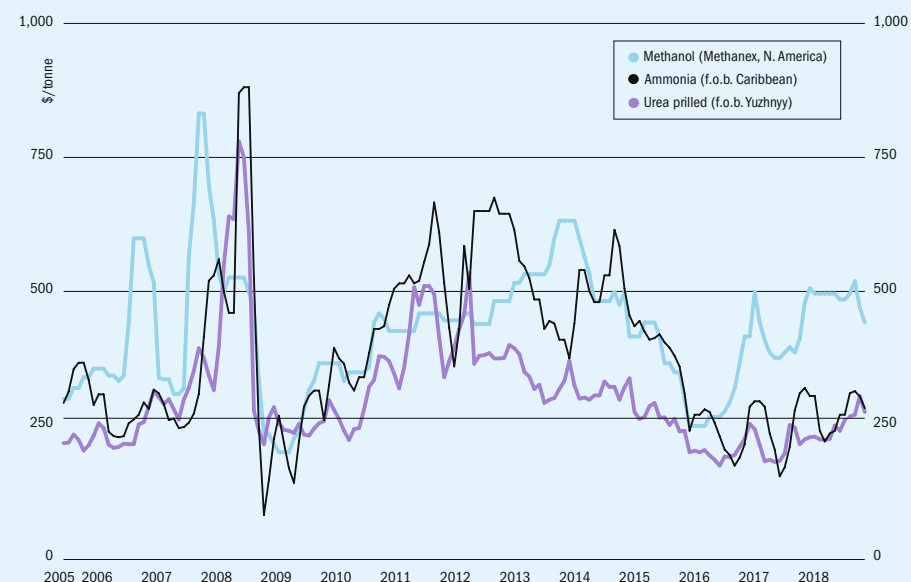
Table 1: Price indications

Cash equivalent	mid-Dec	mid-Oct	mid-July	mid-May
Ammonia (\$/t)				
f.o.b. Black Sea	270-290	335-360	244-250	280
f.o.b. Caribbean	280-290	305-316	270	220
f.o.b. Arab Gulf	280-305	340-365	260-280	263
c.fr N.W. Europe	330-355	380-387	300-310	280-305
Urea (\$/t)				
f.o.b. bulk Black Sea	270-280	280-300	245-260	215-220
f.o.b. bulk Arab Gulf*	280-290	320-340	270-280	215-223
f.o.b. NOLA barge (metric tonnes)	261	316	220-242	219-224
f.o.b. bagged China	275-290	320-338	270-290	257-262
DAP (\$/t)				
f.o.b. bulk US Gulf	425	458-461	427-430	408-410
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	268-274	253	n.a.	153-158

Notes: n.a. price not available at time of going to press
n.m. no market * high-end granular

Market outlook

Historical price trends \$/tonne



Source: BCInsight

AMMONIA

- A very poor direct application season in the US is weighing on import demand and c.f.r Tampa prices. If buying stays below seasonal norms, prices may continue to correct downwards.
- Long delays for vessel transits through the Turkish Straits is limiting the popularity of Black Sea export sales. Until this is resolved, Black Sea business is likely to be both limited and discounted.
- International gas prices are forecast lower this year, with both oil and the traded LNG markets expected to be in surplus. European hub prices should trade in the \$6.00-7.00/MMBtu range.
- Kingisepp commissioning pushed back to Q2 2019, but the project is expected to begin full operations by the summer and will likely tip the market into over-supply.
- Integer is expecting the start-up of Kingisepp to push ammonia prices below \$240/t f.o.b. Black Sea by early summer.
- However, we are currently predicting that the market will shift into deficit by

Q3 2019, which should trigger a pricing rally back above \$300/t.

UREA

- Early Indian tender business in January has tightened the market East of Suez. But with just 510,000 tonnes purchased, prices have only been stabilised.
- Strong spring demand is going to be needed to force prices to correct upwards.
- New production from Turkmenistan and Azerbaijan will begin to ship from the Black Sea in Q1 2019, however, ongoing logistics issues in the Turkish Straits will limit initial impact.
- Indian production will receive a boost when Chambal's Gadepan III is successfully commissioned and begins full production. The Indian government is also expecting Matix and Ramagundam to begin production of their 1.3 million t/a urea plants in H2 2019.
- Despite this new Indian output, we are still expecting a positive year for prices as Chinese output remains constrained and the Chinese state limits the re-export of Iranian material.

- Brazilian production is also forecast lower as Petrobras begins to limit output from two loss-making urea plants.

METHANOL

- OPEC production cuts should see oil prices rising in 2019, and with it methanol prices.
- European supply has been temporarily dented by the Tjelbergodden methanol plant's outage due to a fire at an electricity substation, but longer term the re-start of one train at BioMCN, and extra supply from Trinidad should see more than ample supply, provided that river levels rise again on the Rhine.
- Extra demand is expected in China with the start-up of new MTO plants in Q2 2019 at Jiutai Energy, Nanjing Wison and Baofeng Energy.
- Kaveh Methanol in Iran is due to add 2.4 million t/a of new capacity there, but ongoing US sanctions may mean that China is the only potential outlet for this methanol. Chinese imports of Iranian methanol are already up 70,000 tonnes per month.

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RUSSIA

Tecnimont awarded urea plant contract

Maire Tecnimont subsidiary Tecnimont SpA. has been awarded a €200 million contract for the development of a granulated urea plant on an EPC basis by Volgafert LLC. Volgafert is owned by Kuibyshevazot, a leading Russian producer of fertilizer and caprolactam. Volgafert will produce and sell high-quality urea both for domestic and export markets. Project finance, including a credit line of approximately €160 million provided by some international commercial banks and guaranteed by Italian export credit agency SACE (CDP Group) is currently being finalised.

The new urea unit will be located inside Kuibyshevazot industrial premises (in Tolyatti, located in the Samara region) and will be developed using Stamicarbon urea technology. The project's

scope of work includes the provision of engineering services, equipment and material supply and construction activities up to commissioning, start up and guarantee test run of a granulated urea plant with a capacity of 540,000 t/a. Final notice to proceed is expected by early 2019, while the completion of the project is expected in the fourth quarter of 2021.

Pierroberto Folgiero, Maire Tecnimont Group chief executive officer, commented: "We are eager to strategically cooperate with an industry leader such as Kuibyshevazot in one of our core business areas, fertilizers. With this new collaboration we confirm the reliability of our Group's value proposition covering the whole value chain, from project development, to licensing to complete EPC execution". ■

EuroChem starts up UAS plant at Novomoskovsk

Russian fertilizer producer EuroChem says that it has formally opened Russia's first urea ammonium sulphate (UAS) plant at the company's Novomoskovskiy Azot plant, 200 kilometres south of Moscow.

Stamicarbon designed the ammonium sulphate plant at Novomoskovsk with a capacity of 400 t/d urea and 600 t/d UAS, and supervised the start-up of granulation and UAS production, which went "very smoothly" according to EuroChem. Stamicarbon developed a process for the production of granulated urea containing ammonium sulphate (UAS) following an increased demand for granulated urea containing macro- and micro-nutrients. This technology can produce a wide range of ammonium sulphate concentrations (0-50 wt%) without modifying the granulation plant and the quality of UAS granules produced.

Urea ammonium sulphate helps farmers increase crop yields by incorporating sulphur nutrient, and EuroChem says that it will complement the company's current portfolio of sulphur-enriched fertilizers, which includes ammonium sulphate (AS) and ammonium sulphate-nitrate (ASN).

NIIK commissions new urea unit using its own technology

NIIK says that for the first time in the company's history it has commissioned a new urea production unit based on NIJK's own patented URECON[®] 2006 technology. The project was completed in November 2018 at the Acron Group site in Veliky Novgorod. URECON[®] 2006 is an improved liquid recycle technology, which has been successfully used for the revamping of low capacity

units. This process uses a single high pressure urea synthesis reactor with optimised hydrodynamics and highly efficient heat and mass transfer, according to NIJK. The company says that the main principle of the project is based on the use of existing equipment for items with the longest lead-time, such as the synthesis reactor and pneumatic pumps. The new urea unit uses a backup synthesis reactor from the existing production unit, which initially had a design capacity of 270 t/d. In order to scale up the process, NIJK equipped it with a unique internal configuration which increased capacity to 620 t/d.

Stamicarbon to license granulation technology for Acron

Maire Tecnimont subsidiary Stamicarbon has signed contracts with Russian fertilizer producer JSC Acron for the licensing of technology and the delivery of proprietary equipment for a grassroots urea granulation plant. The granulation plant will be built in Velikiy Novgorod, with a capacity of 2000 t/d, and will use Stamicarbon's latest granulation technology entailing both investment and operating costs savings and meeting environmental requirements. Stamicarbon's granulation technology uses film spraying nozzles, which the company says results in a better quality end-product because the granules are built up layer by layer. Before a new layer of liquid melt is applied on the seed particle, the layer on the particle is completely solidified.

"Acron has decided to expand its product portfolio by including granulated urea, which is popular among clients. Cooperation with Stamicarbon, the technology leader in the industry, ensures us advanced technologies for manufacturing

top-quality product", said Alexander Popov, chairman of Acron's board of directors.

Acron is also planning to expand nitric acid production at its Veliky Novgorod site. Two nitric acid plants with a combined capacity of 270,000 t/a are under development at the site, and are expected to be completed in 2019. The plants were designed by LLC Novgorod GIAP, part of the Acron Group.

UNITED STATES

Blasch licenses reformer tunnel system to BD Energy Systems

Blasch Precision Ceramics has signed an agreement with Houston-based BD Energy Systems granting them exclusive rights to market and sell the Blasch StaBlox[™] reformer flue gas tunnel system in ammonia and methanol synthesis gas production facilities worldwide. The two companies say that they will "collaborate on advancing their innovative technologies and strategically addressing global market opportunities". StaBlox, combined with BD Energy's patent-pending Tunnel Optimal Performance (TOP) flow controlling tunnel technology offers what they describe as a significantly improved and differentiating technology to the market, providing faster and simpler installation, and a more robust, mortar-free structural tunnel system.

"The signing of this agreement is a critically important and positive development in the early life-cycle of the StaBlox product line," commented Jack Parrish, president and CEO of Blasch Precision Ceramics. "Blasch and BD Energy Systems are very bullish on the power of our combined technologies, and our ability to grow our market share exponentially, especially based

on our very positive recent installation successes, and the early performance indicators of the StaBlox/TOP technology."

Simplot to lease terminal at Rivergate

JR Simplot Co has agreed to lease its Rivergate ammonia terminal to CF Industries. Rivergate, on the Willamette River near Portland, Oregon, has two 25,000 st ammonia tanks and is considered the largest deep-water ammonia terminal on the US west coast. Simplot uses the site to store anhydrous ammonia and transport it in pressurised liquid form via rail cars and trucks to markets throughout western North America. It also ships urea from the terminal. However, it has reduced its use of the site over the past 12 months since completing its own ammonia plant in Rock Springs, Wyoming. CF Industries says that it will transport ammonia to the terminal which it produces at its Medicine Hat, Alberta, nitrogen complex, and then ship it onwards to growing export markets in the Pacific Rim.

First application of SCS

Sabin Metal Corporation says that it has completed its first successful installation of its new line of SCS Catalyst System for the production of nitric acid and related chemicals. Nitric acid and its derivatives are the most commonly used fertilizers' intermediates in the world. The launch of SCS Catalyst System completes Sabin's portfolio of products and services for the nitric acid industry which already includes SRS platinum recovery systems, cleaning services and a wide range of metal recovery and refining services ranging from filters and sludges to metal refining from demolished plants.

AUSTRALIA

Contract awarded for Karratha urea project

Perdaman Chemicals and Fertilisers has signed a binding heads of agreement with SNC-Lavalin for the engineering, procurement and construction (EPC) work on its Karratha urea project in Western Australia. Perdaman will invest a total of A\$4.0 billion (US\$ 4.3 billion) to develop the 2.0 million t/a ammonia-urea plant, which will use local natural gas supplied by Woodside as a feed for fertilizer production aimed at the export market, using what Perdaman describes as "innovative and low emissions technologies".

The contract forms an exclusive three-phase agreement between SNC-Lavalin and Perdaman, who will jointly form an integrated project management team of dedicated personnel to manage various aspects of the overall project delivery. SNC-Lavalin has completed phase one, and has now begun phase two and will deliver an open book full-cost estimate and design for the delivery of the urea fertilizer plant and related facilities, including a water treatment plant, a power plant, as well as urea storage, loading and unloading facilities. Upon successful completion and approval of phase two, expected in Q1 2019, phase three would begin on the delivery of urea fertilizer plant, subject to a final investment decision.

Speaking at the signing ceremony, Perdaman chairman and managing director Vikas Rambal said that the award "marks a significant step forward for the Karratha urea project... We are now full steam ahead on this project, working with Western Australian government departments for the various approvals regarding this project, including the community consultation processes which will continue later this month".

The expected date for the start of construction will be either the end of 2019 or early 2020, pending environmental approval. Perdaman has selected Haldor Topsoe as ammonia licensor, using its new SynCOR[™] technology making the plant the first worldwide to use Topsoe's state-of-the-art technology for large-scale ammonia production. Stamicarbon's LAUNCH MELT[™] pool condenser design was chosen for the urea plant.

Perdaman's urea plant, called project Destiny, will be located within the Burrup Strategic Industrial Area on the Burrup Peninsula, approximately 10 km from Dampier and 20 km north-west of Karratha on the northwest coast of Western Australia.

Perdaman has previously signed a long-term gas supply agreement with Woodside Petroleum Ltd, back in April 2018 for the supply of 125 terajoules of gas per day over the next 20 years with an option to extend the supply for a further 5 years. Gas will be supplied from Woodside's overall Western Australian portfolio, but primarily sourced from the company's proposed development of the Scarborough gas field in deep water on the Exmouth Plateau. The gas will be processed through the Woodside-operated North West Shelf and Pluto facilities on the Burrup. Supply is expected to begin between 2023 and 2025 when

the urea plant and the Scarborough field are brought on stream.

The proposed facility will however face intense scrutiny over its environmental performance after a concern over the potential impact on native Australian rock art on the Burrup Peninsula.

Casale buys Orica's LDAN technology

Casale and Orica have agreed on a deal for the acquisition, by Casale, of Orica's complete process and know-how to produce Low Density Ammonium Nitrate (LDAN). Casale says that this acquisition is in line with the company's long-term growth strategy in the syngas-based chemical production sector, aimed at offering complete production chains, from feedstocks to final products. In particular, the move strengthens Casale's technical and commercial footprint in the solid nitrates field by complementing its well-proven high density/fertilizer grade ammonium nitrate (HDAN) technology, which it acquired from GPN.

The deal includes the right to use in all new and revamped plants based on LDAN prilling technology, from now on supplied exclusively by Casale, of Orica's proprietary, well-known additive Sapphyr, on commercial terms to be agreed. In addition, during the technology transfer phase, Orica will provide assistance to Casale and grant access to Orica's plants. Casale says that it endeavours to continue to work on creating value for their customers through synergic acquisitions, while growing in its markets.

CHINA

Second melamine unit commissioned

Eurotecnica is pleased to announce that a second Euromel melamine unit has been commissioned at Xinjiang Xinliian Energy Chemical Co., Ltd, making the site now the largest high-pressure melamine complex in the world, according to Eurotecnica. The 60,000 t/a melamine project was delivered in a record 18 months. Euromel technology can deliver such a relatively high melamine capacity in a single train, based on a proven architecture, as well as, according to Eurotecnica, delivering zero total pollution at high levels of energy efficiency and low capital cost. Eurotecnica is part of Proman Group, a global player in natural gas derived products with operations and assets all over the world, including Europe, the United States, Oman and Trinidad and Tobago.



PHOTO: IWS

One of the existing ammonia plants at Ma'aden.

SAUDI ARABIA

Ma'aden to use thyssenkrupp ammonia technology again

The Saudi Arabian Mining Company (Ma'aden) has chosen the thyssenkrupp Industrial Solutions dual-pressure ammonia process for the new 'Phosphate 3' ammonia plant at its fertilizer complex at Ras al Khair on the Arabian Gulf coast. thyssenkrupp Industrial Solutions is providing the process license and extensive engineering, supply and monitoring services for the 3,000 t/a plant as a subcontractor of South Korea's Daelim Industrial Co. Ltd. The plant is scheduled to be completed in early 2022.

The thyssenkrupp dual-pressure ammonia process is already being used in the first two ammonia plants at the Phosphate fertilizer complex. In total the three Ma'aden ammonia plants, which are part of one of the world's largest integrated fertilizer complexes, will have a capacity of around 3.5 million t/a.

"This third contract to build a new ammonia plant intensifies the already outstanding collaboration and great trust between Ma'aden and thyssenkrupp Industrial Solutions. It reflects our position as a technology leader for super-size ammonia plants and confirms thyssenkrupp's reputation in the industrial sector," said Ralf Richmann, CEO of the Fertilizer Technologies business unit at thyssenkrupp Industrial Solutions.

INDONESIA

KBR commissions first ammonia plant based on PurifierPlus technology

KBR says that it has fully commissioned its first PurifierPlus ammonia process based greenfield plant at PT Panca Amara Utama (PAU) in Sulawesi, Indonesia. The

700,000 t/a plant has been built in the Batui district of central Sulawesi. Indonesia is prioritising local manufacturing to convert the country's natural resources into industrial products, and support the development of the manufacturing sector in the east of the country. PAU will be the first ammonia plant in Sulawesi and the second privately-owned plant in Indonesia.

In addition to PurifierPlus technology, KBR is also providing its proprietary Ammonia InSite digitalisation technology, which maximises operational performance and profitability of ammonia plants with five applications focused on production management, energy efficiency, maintenance, reliability, and environmental compliance. The online real-time system includes performance diagnostics and analytics, benchmarking, predictability of outcomes, and prevention of unplanned downtime, along with support from KBR experts.

"I am pleased to announce that the first PurifierPlus based project has been successfully commissioned at PAU and is currently operating at 110% of design capacity," said John Derbyshire, KBR President, Technology. "Our PurifierPlus technology delivers our clients the lowest total installed cost for ammonia plant projects in the industry while at the same time providing state-of-the-art energy and environmental performance."

TRINIDAD & TOBAGO

New gas sales agreement

The National Gas Company of Trinidad and Tobago Limited (NGC) has signed a new gas sales agreement with Nitrogen 2000, allowing for the continued operation of N2000's world-scale anhydrous ammonia plant at the Point Lisas Industrial Estate. N2000's sister plant, the Caribbean Nitrogen Company Limited (CNC), signed an agreement with NGC in April 2018 after three months of downtime following the end of the previous contract with NGC in January 2018. NGC and N2000 began negotiations immediately following the conclusion of the CNC negotiations and the parties were able to agree upon and achieve the deadline for the conclusion of negotiations.

INDIA

Urea production begins at Gadepan

Chambal Fertilisers & Chemicals Ltd says that trial production began on November

30th 2018 at its Gadepan III urea plant. The new plant, at the existing site at Gadepan in Rajasthan, has a capacity of 1.34 million t/a.

EUROPEAN UNION

Fertilizers Europe criticises reduction of anti-dumping duty

The European Commission's move to reduce the anti-dumping duty on ammonium nitrate from €47/Mt to €32/Mt has been criticised by one industry body. Fertilizers Europe said it is concerned that despite recognising Russian ammonium nitrate industry as a considerable injurious threat for EU nitrogen industry, the Commission decided to reduce the anti-dumping duty on ammonium nitrate from €47/Mt to €32/Mt. While it welcomes the European Commission's central finding in the interim dumping review that there are no changed circumstances on the Russian gas market where state fixed pricing dominates gas price formation. It says that the European mineral fertilizer industry is very concerned that the Commission, having recognised this profound structural problem which results in 'structural dumping', does not apply a consistent logic that there is thereby persistent 'structural injury' in the interim injury review made by EU based farming organisations.

Jacob Hansen, Director General of Fertilizers Europe commented: "As an industry, we are very concerned with the Commission's decision to reduce by one third the anti-dumping duty on ammonium nitrate originating from Russia despite recognising structural dumping, as it sets a very dangerous precedent which puts at risk high-skilled jobs and competitiveness of European fertilizer industry as a whole."

The Russian ammonium nitrate industry still represents a considerable injurious threat as it maintains a spare export capability of over 1.2m tonnes per annum, he said. "Moreover, the Russian industry remains a powerful export industry with exports reaching over 3.5m tonnes per annum in 2017. In comparison, the EU ammonium nitrate market is estimated between 6.4-7.5m tonnes annually." No amount of EU industry re-structuring or improved efficiencies can compensate for the massive "gas gap" between Russia's typical state fixed price of \$2.50/MMBTu against the EU's wholesale gas price of nearly \$10.00/MMBTu, he said. ■



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www.bcinsightsearch.com



UNITED STATES

Contractor selected for Kalama methanol plant

Northwest Innovation Works has formally asked local contractor JH Kelly to build major parts of its proposed \$2 billion Kalama methanol plant. The Chinese developer has also committed to using local union construction labour, as part of its efforts to win around local opinion in the region in the teeth of determined opposition by environmentalists. The \$100 million plus construction contract and 1,000 local jobs are an important incentive, as is the company's commitment to have zero water discharges to the Columbia River and to use ultra-low emissions technology.

The draft supplemental environmental impact statement, released recently, found the project would displace coal-based

methanol plants in China which produce far greater volumes of carbon dioxide. The plant, therefore, would decrease annual carbon emissions by 12.7 million t/a worldwide, the equivalent emissions of 2.7 million cars. While the plant would release about 1.1 million t/a of carbon at the Kalama site, NWIW has said it would work to reduce or compensate those carbon releases as well through actions such as purchasing verified carbon credits or paying a comparable amount to a greenhouse gas mitigation fund. The future of the development, one of the largest methanol plants in the US, which had been a little shaky after environmental setbacks last year, is starting to look more secure. ■

Hydrogen plant for western US

Air Liquide will begin building a \$150m liquid hydrogen production plant in California early in 2019, according to the company. Air Liquide has signed a long-term agreement with FirstElement Fuel Inc (FEF), a leader in retail hydrogen infrastructure in the US, to supply hydrogen to FEF's retail liquid hydrogen fuelling stations in the state. It will be the first world-scale liquid hydrogen production unit dedicated to the hydrogen energy markets and have a capacity to produce nearly 30 t/d of hydrogen, fuel up to 35,000 fuel cell electric vehicles. There are 35 hydrogen fuelling stations operating in California, with 29 others to follow, according to the California Fuel Cell Partnership. Through the investment Air Liquide will enable the large-scale deployment of hydrogen powered vehicles on the west coast, providing a reliable supply solution to fuel the 40,000 FCEVs expected to be deployed in California by 2022. On top of the long-term supply agreement, Air Liquide and FEF have entered into an agreement outlining Air Liquide's intent to make an equity investment in FEF, following previous assistance to the company by Toyota and Honda.

Hydrogen plant for Delaware City refinery

PBF Energy and partner Linde have broken ground on a hydrogen plant at the Delaware City refinery. The plant will help the refinery convert more crude oil products into higher quality fuels. The plant, a methane steam reforming facility, will produce hydrogen from natural gas. The refinery will use that hydrogen to remove sulphur from the crude products left behind in other refining processes. The Linde Group will build, own and operate the plant, which is expected to become operational in 2020.

INDONESIA

Air Liquide to provide hydrogen plant for Pertamina

Air Liquide Engineering & Construction has been selected as a technology licensor by Pertamina, the state-owned oil & gas company of Indonesia. Air Liquide will provide a licence and basic engineering for a hydrogen production unit, steam methane reformer (SMR), with a production capacity of 120,000 Nm³/h to be installed at Pertamina's refinery site in Balikpapan, Borneo. The contract is part of a 'refinery development master plan' being undertaken by Pertamina which will increase the Balikpapan refinery's crude processing capacity as well as enable production of cleaner fuels conforming to Euro 5 standard.

Domenico D'Elia, Senior Vice President, Sales & Technology, Air Liquide Engineering & Construction commented: "We appreciate the confidence Pertamina has placed in Air Liquide Engineering & Construction. This new contract further enhances our position as the leading technology provider for large scale hydrogen solutions in the refinery sector."

AZERBAIJAN

Honeywell to modernise SOCAR hydrogen plant

Honeywell has announced that the State Oil Company of Azerbaijan Republic (SOCAR) will use Honeywell UOP's pressure swing adsorption (PSA) technology to supply high-quality hydrogen as part of the modernisation of the Heydar Aliyev oil refinery (HAOR) in Baku, Azerbaijan. The hydrogen is used to decontaminate oil and facilitate catalytic processes that produce clean-burning fuels, including those

that meet Euro V standards for vehicle emissions. The PSA technology will help Azerbaijan meet growing domestic demand for transportation fuels that meet the Euro V standards.

"Honeywell UOP's hydrogen technology is an important element of SOCAR's modernisation program for the Heydar Aliyev Oil Refinery," said Nigel Orchard, regional vice president – Europe, Africa and Central Asia, at Honeywell UOP. "The modernisation program will help SOCAR to remain among the most advanced refiners in the region, further improving environmental protection along with the quality of life in Azerbaijan."

When completed, the modernization will enable the refinery to process 7.5 million t/a of crude oil blended from local sources, including heavier Neft Dashlari and lighter Surakhani and Shirvan crude oils and efficiently produce Euro V gasoline and diesel, jet fuel and asphalt. The Heydar Aliyev Oil Refinery was originally established in 1953 by the Ministry of the Oil Industry of the former Soviet Union.

RUSSIA

Gazprom looking at hydrogen for Europe

Gazprom says that it is exploring ways to produce emissions-free hydrogen from its natural gas and create a €53 billion per year market by 2050. With Europe working to make dramatic reductions in greenhouse gas emissions, Russia – Europe's largest gas supplier – is looking for ways to make its gas green enough to remain part of the energy mix. Hydrogen is an option because it can be made from natural gas without generating additional emissions.

While several technologies to produce hydrogen are being developed, Gazprom is investigating one known as thermal meth-

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ane pyrolysis. This reaction takes place in a low-temperature, non-equilibrium plasma that's put under high pressure in a small reactor. The company is trialling the technology in the Siberian town of Tomsk. With no contact with oxygen, no CO₂ is emitted when hydrogen atoms are split off from natural gas. That process makes a stream of pure hydrogen, with carbon dropping out as a solid instead of escaping into the air as CO₂.

Gazprom's vision is to introduce an emissions free form of hydrogen into its business over the next few decades. The first stage in the Gazprom programme envisages switching power plants and vehicles to gas from coal and petrol respectively. The next stage would involve building up hydrogen in a mix with natural gas. The current blend limit of hydrogen into gas grids varies from zero in the UK to 12% in the Netherlands, but a mix with as much as 20% of hydrogen could be used in the majority of applications, without challenges or infrastructure changes, according to Gazprom. Higher ratios can lead to hydrogen embrittlement of pipelines and other infrastructure.

JAPAN

Renewable ammonia turbine development

A collaboration between JGC, the National Institute of Advanced Industrial Science and Technology (AIST), the National Institute of Technology, Numazu College, and JGC's subsidiary, JGC Catalysts & Chemicals Ltd., says that the group's joint study programme has successfully generated ammonia using hydrogen from water generated by renewable energy, and then used the resulting ammonia to generate electricity in a gas turbine. This is claimed to be the first time renewable hydrogen has been used to make ammonia that is subsequently used for CO₂-free power generation – effectively using ammonia as a 'hydrogen carrier' to overcome the difficulties in transporting hydrogen.

Last May, JGC announced the development of a new ruthenium catalyst supported by rare earth oxides, which is capable of efficiently synthesising ammonia at a low (300-400°C) temperature and low pressure (5-8 MPa), far milder than the 400-500°C and 14-30 MPa used for an iron-based Haber-Bosch process. The catalyst is said to have "excellent stability" compared to ruthenium catalysts that use carbon-based carriers. JGC began operating a demonstration plant at Fukushima Renewable Energy

Institute, AIST in Koriyama City that is capable of producing 20 kg/d of ammonia.

NEW ZEALAND

Low carbon urea project with a hefty price tag

Pouaki NZ, a wholly-owned subsidiary of US company 8 Rivers, says that it has approached the New Zealand government for NZ\$50 million for a feasibility study on what the company estimates could be a \$4 billion 'clean' hydrogen power plant at Taranaki. The proposal would use natural gas to create hydrogen and electricity, as well as urea fertiliser for domestic use and export, with capture and storage of the carbon dioxide generated by the process. The company argues that using gas to generate hydrogen is a 'bridging' technology towards a hydrogen economy. However, over and above the cost, questions have been asked about whether there is enough gas at Taranaki to support such a development.

Hydrogen plant for Auckland

Ports of Auckland will build a hydrogen production and refuelling facility at its Waitemata port in New Zealand, set to be operational by the end of 2019. Along with project partners Auckland Council, Auckland Transport and KiwiRail, Ports of Auckland will invest in hydrogen fuel cell vehicles including port equipment, buses and cars as part of the project.

"We have an ambitious target to be a zero-emission port by 2014. In order to meet that target we need a new renewable and resilient power source for heavy equipment like tugs and straddle carriers, which are difficult to power with batteries," said Tony Gibson, Ports of Auckland Chief Executive.

Ports of Auckland will fund the construction of a hydrogen electrolysis facility. Demonstration vehicles will be able to fill up with hydrogen at the facility. In addition to purchasing hydrogen fuel cell vehicles, project partners will provide technical support. Global hydrogen experts Arup are also helping support this project through the development, design and delivery phases.

SAUDI ARABIA

Sabic increases its stake in Ar-Razi

Saudi Basic Industries Corporation (Sabic), has increased its stake in the Ar-Razi Methanol Company after buying out part of Japan Saudi Arabia Methanol Company's (JSMC) 50% interest for \$150

million. Sabic and JSMC's holdings in the methanol company located in the eastern industrial city of Jubail will now be 75% and 25% respectively, Sabic said in a stock exchange filing. The deal comes after the two companies' joint venture agreement expired on 29 November, giving Sabic the right to purchase JSMC's 50% share in the company. Ar Razi produces 5 million t/a of methanol at the massive Al Jubail complex.

TRINIDAD & TOBAGO

CGCL methanol plant set for mid-2019 completion

According to owner and developer Caribbean Gas Chemical Limited (CGCL), the company's new 1 million t/a methanol and 20,000 t/a dimethyl ether (DME) plant at La Brea is 90% complete and should be up and running by June 2019, slightly later than the planned date of March because of construction delays. CGCL is a joint venture between three Mitsubishi firms (Mitsubishi Corp, Mitsubishi Gas Chemical, Mitsubishi Heavy Industries), the National Gas Company of Trinidad and Tobago (NGC) and Trinidad-based Massy Holdings.

MHTL gets gas supply boost

DeNovo Energy has announced its first commercial supply of gas from the Iguana field in Block 1a. Part of the Proman Group, DeNovo is now Trinidad & Tobago's fifth largest gas supplier. The Announcement of 80 million scf/d of gas is expected to be a boost for DeNovo's sister Proman Group company Methanol Holdings Trinidad Ltd (MHTL). The gas will be delivered to plants



MHTL's Point Lisas site.

operating on the Point Lisas industrial estate via the National Gas Company of Trinidad & Tobago (NGC).

Iguana was discovered as far back as 1982 but has remained undeveloped until DeNovo became the operator in 2016. The company fast tracked the gas field development to become the first west coast natural gas field development off Trinidad.

MALAYSIA

Sarawak Petchem signs methanol marketing agreement

Petronas Group marketing company Petronas Chemicals Marketing (Labuan) Ltd (PCML) has signed a sales and purchase agreement with Sarawak Petchem to market methanol from the Sarawak Methanol Plant in Bintulu for 20 years, with an option for further extension. Sarawak Petchem, owned by the state government of Sarawak, is building a 1.7 million t/a methanol plant which is expected to come onstream at Bintulu in 2022. Gas feedstock will come from Petronas. Petronas is the largest methanol producer in the Asia-Pacific region, and the fourth largest in the world, with an annual production capacity of 2.4 million t/a.

Sarawak Petchem chairman Tan Sri Datuk Amar Dr Abdul Aziz Husain said that the agreement marks a "very significant milestone and achievement for Sarawak in its journey to pursue the realisation for downstream petrochemicals in Bintulu. This historic event not signifies the beginning of the collaboration between Sarawak Petchem and Petronas Chemical Marketing (Labuan) Ltd but also to provide challenges for us to deliver world class methanol safely, timely and at optimum cost with the required quality," he said at the signing ceremony.

Executive Vice President of Petronas Downstream Business Datuk Mohamad Arif Mahmood said through the partnership, PCG is able to strengthen the supply of methanol to its customers. "It will enable us to fulfil the rising demand from Asia Pacific, especially in Southeast Asia, China, Korea, Taiwan, Japan and India, where the growing middle class is contributing to the high consumption of petrochemical products."

UZBEKISTAN

Finance in place for GTL plant

Uzbekistan has secured \$2.3 billion out of the estimated \$3.6 billion cost of financing a plant in the Kashkadarya region for the production of synthetic fuel using gas-to-liquids (GTL) technology. Project development company Uzbekistan GTL signed the loans with Uzbekneftegaz JSC and 11 international financial institutions, organisations and commercial banks from China, South Korea, Japan, Russia and Europe, including the China Development Bank (CDB), the Export-Import Bank of Korea, the Korea Trade Insurance Corporation K-Sure, Gazprombank, the Russian Agency for Export Credit and Investment Insurance, Credit Suisse, and Japanese banks MUFG, SMBC and Mizuho.

The plant will process 3.6 billion cubic meters per year of gas and produce 1.5 million t/a of fuel, including 311,000 t/a of jet fuel, 743,000 t/a of diesel fuel, 431,000 t/a of naphtha and 53,000 t/a of liquefied gas. Hyundai is the lead contractor, using technology from Sasol, Haldor Topsoe and Chevron. EPC work is said to be 65% complete and construction 23% complete. The plant is expected to be commissioned in 2020.



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People

The International Fertilizer Development Centre (IFDC) has announced the appointment of **Albin Hubscher** as its new president and CEO. Hubscher is scheduled to step into the role on February 18, 2019. Hubscher is joining IFDC from the International Livestock Research Institute (ILRI), where he served as the interim corporate service director. Prior to ILRI, Hubscher was the chief finance officer (CFO) – director of finance for the CGIAR System Organisation. He also served as deputy director general for the Centro Internacional de Agricultura Tropical (CIAT) for eight years. He has also held technical and executive marketing and sales roles with the Ciba-Geigy Corporation and Novartis in Colombia, Switzerland, and the United States. With Syngenta, Hubscher was the head of International Corn and Soybean Business before being entrusted with implementation of the company's business strategy in China.

Patrick Murphy, interim president and CEO of IFDC, said that he believes Hubscher's varied experience will be beneficial to IFDC's growth: "Albin has worked in a variety of roles throughout the public and private sector," Murphy said. "Having someone who understands the private industry, someone who understands the value of research, and someone who understands the work we do with small farmers and businesses will be an amazing asset for the organization."

Hubscher was preceded by **Dr. J. Scott Angle** who has been appointed to become the director of the National Institute of Food and Agriculture (NIFA), a research arm of the United States Department of Agriculture (USDA).

Acron Group has announced several changes in its managing board. **Dmitry Balandin** has been appointed as the Group's Vice President for Finance. **Alexander Lebedev** has been appointed as Vice President for Domestic Business. They replace Oscar Valters, who is leaving Acron Group, and Ivan Antonov, who remains with the Group as an advisor to the CEO, but who will no longer be on the Managing Board.

Dmitry Balandin graduated from Kurgan State University with degrees in finance, credit and law, and received a PhD degree in economics upon defending his doctoral thesis in the Higher School of Management at St. Petersburg State University. He has been with the Group since 2013 as Director for Corporate Finance. Previously, he held several management positions in Gazprom Neftekhim Salavat.

Mr Lebedev graduated from Vladimir State University with a degree in marketing. He has worked at Acron since 2011, serving as head of the organic and non-organic chemical product sales team, deputy head of the sales department and

head of the sales department. In November 2018, Mr Lebedev was appointed Vice President for Domestic Business.

"The new Managing Board is aligned with the Group's new strategy, which includes investments in developing our production capacity and our sales network in Russia and abroad", commented Alexander Popov, chairman of Acron's Board of Directors. "On behalf of our Group, I would like to express our deep gratitude to Mr Valters, who has been with Acron for over 20 years and decided to retire from his position as Senior Vice President. Mr Valters has made an invaluable contribution to the Group's business development, built an effective system of finance management and ensured sustainability of our production facilities".

Dmitry Konyaev, Uralchem's deputy chairman, was elected to the executive board of the International Fertilizer Association (IFA) in November, becoming one of only five board members. The decision was taken at a meeting of IFA's board of directors during last year's annual Strategic Forum, held in Beijing, China, in mid-November. The board also extended Dmitry's term as chairman of IFA's Communications & Public Affairs Committee until IFA's Annual Conference in Montreal in mid-June.

Calendar 2019

FEBRUARY

12-14

AFA Annual Forum & Exhibition, CAIRO, Egypt
Contact: Arab Fertilizer Association, 9 Ramo Buildings, Al Nasr Road, Nasr City, Cairo, Egypt.
Tel: +20 2 23054464
Fax: +20 2 23054466
Email: afa@arabfertilizer.org

27-1 March

Argus Africa Fertilizer 2019, Marrakech, Morocco.
Contact: Argus Media, Ltd
Tel: +44 (0)20 7780 4340
Email: fertconferences@argusmedia.com

MARCH

4-7

Nitrogen+Syngas 2019, BERLIN, Germany
Contact: CRU Events, Chancery House, 53-64 Chancery Lane, London WC2A 1QS, UK.

Tel: +44 (0) 20 7903 2444
Fax: +44 (0) 20 7903 2172
Email: conferences@crugroup.com

6-7

IFA Production and International Trade Meeting, LONDON, UK
Contact: IFA Conference Service, 49 Avenue d'Iéna, 75116 Paris, France.
Tel: +33 1 53 93 05 00
Email: ifa@fertilizer.org

11-13

Syngas 2019, HOUSTON, Texas, USA
Contact: Betty Helm, Syngas Association, Baton Rouge, Louisiana.
Tel: +1 225 706 8403
Web: www.syngasassociation.com

APRIL

8-11

IFA Global Technical Symposium, NEW ORLEANS, Louisiana, USA
Contact: IFA Conference Service, 49 Avenue d'Iéna, 75116 Paris, France.
Tel: +33 1 53 93 05 00
Email: ifa@fertilizer.org

MAY

29-30

Syngas Nitrogen Russia and CIS, MOSCOW, Russia.
Contact: Milana Stavnya, Programme producer, Vostock Capital
Tel: +7 (499) 505 1 505
Email: MStavnaya@vostockcapital.com

JUNE

IFS 2019 Technical Conference, BRUSSELS, Belgium
Contact: International Fertiliser Society, PO Box 12220, Colchester, CO1 9PR, UK.
Tel: +44 (0)1206 851 819
Fax: +44 (0)1206 851 819
Email: secretary@fertiliser-society.org

11-13

IFA 87th Annual Conference, MONTREAL, Canada. Contact: IFA Conference Service
Tel: +33 1 53 93 05 00
Email: ifa@fertilizer.org

16-19

IMTOF 2019, LONDON, UK
Contact: Polly Murray, Johnson Matthey
Email: polly.murray@matthey.com



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A diamond jubilee

NITROGEN+SYNGAS
ISSUE 357
JANUARY-FEBRUARY 2019

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Plant Manager+

Problem No. 52 High nickel content in high pressure urea synthesis

The detection of active corrosion in a urea plant is difficult. Local corrosion can hardly be detected unless leak detection systems or conductivity measurements in steam/condensate systems are used. Overall corrosion however can be detected in the warehouse by checking for discoloration (reddish colour) of the product or via analyses of the urea final product.

In many plants, product analyses are used to verify the condition of the plant. An element that is often analysed is nickel because it is a reliable parameter to verify local active corrosion in a urea plant. Nickel is present in the stainless steel that protects the pressure vessels and as an alloying component in

the HP piping. Since there is ongoing corrosion in the synthesis section, there is always some nickel present in the final product.

How much nickel can be tolerated cannot be easily stated and varies from plant to plant. The type of alloy protection in HP synthesis sets the fingerprint of the amount of nickel that will be found. In order to have an indication about what is going on in your urea plant it is important to look at trends; in case of active corrosion one will observe a linear increase of the nickel content. Of course in case of increasing nickel in the product adequate actions are needed. That means shut down the plant, eliminate the source and re-passivate.

Krzysztof Czachór from Grupa Azoty Zakłady Chemiczne Police in Poland starts the round table discussion: I would like to ask what the standard nickel content measured in the high pressure (HP) urea synthesis section is? When should we be worried about corrosion? In which vessels do you check the nickel in your plants? We are worried because the nickel content in our HP scrubber outlet has increased compared to previous years and is higher than the standard level. What could the reason be for this?

Mark Brouwer of UreaKnowHow.com replies: Nickel is measured to check for active corrosion. In case of active corrosion it cannot become passive again unless the plant is shut down, drained and then re-passivated. Look for increasing trends, not peaks, then you should know what nickel levels are normal and if there is an increasing trend. It does not make a lot of sense to make comparisons with other plants as it depends on, for example, the materials applied. For example, 316L UG and 25-22-2 have completely different nickel contents.

Krzysztof replies: Thank you for quick reply. We decided to increase the amount of oxygen in the urea synthesis from 0.8 to 1.1 vol-% and noticed that passive corrosion started to decrease. Do you have any advice what could have happened?

Mark asks for further information: For which equipment did the passive corrosion decrease? How did you conclude that passive corrosion rates decreased when you increased the oxygen content? Are we talking about a Stamicarbon CO₂ stripping plant with falling film high pressure carbamate condenser (HPCC)?

Krzysztof replies: Yes, it's a Stamicarbon CO₂ stripping plant with falling film HPCC. We noticed that the nickel level started to decrease in the HP scrubber, but remained stable in other equipment. We started to measure the nickel level in the HP carbamate pump and noticed that it was high. Can this be the reason for a high Ni level in the HP scrubber? Do you measure the Ni level in the LP section as well?

Mark responds: The HP scrubber has one has relatively high partial oxygen levels in the gas phase, so one would not expect that going from 0.8 vol-% (which is already high) to a higher figure would give benefits in the HP scrubber. One should look at trends as the analysis

Fig. 1: HP reactor Ni content

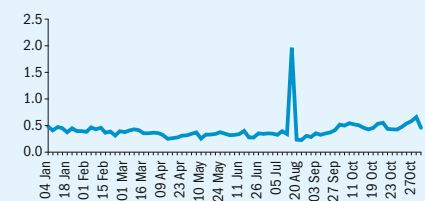


Fig. 2: Low pressure rectifier Ni content

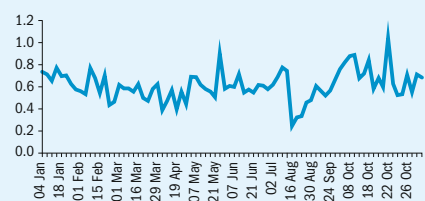


Fig. 3: HP stripper Ni content

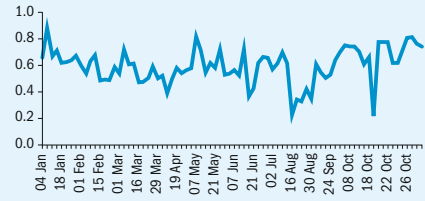
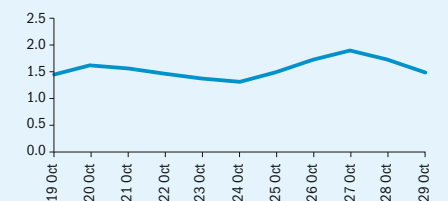


Fig. 4: HP scrubber Ni content



Fig. 5: HP carbamate pump Ni content



is not very accurate. For example, what change in nickel level did you observe over the HP scrubber at 0.8 and 1.1 vol-% oxygen? Did you look at this trend? Yes, one can also measure nickel in the LP section as the stainless steel there is also passivated by the oxygen dissolved in the liquid coming from the HP stripper.

Krzysztof provides some data: Please see the nickel content trends for the synthesis and HP carbamate pump in the figures. We increased the oxygen content on 19th October. Any conclusions?

Mark replies: Further discussions lead to the conclusion that the changes in nickel are likely related to turnaround activities (the T/A was from July 12 to August 16). After a turnaround it is very likely that nickel contents increase due to grinding and other work in the synthesis section. When cleaning is not perfect this material will dissolve in the ammonium carbamate and higher nickel levels will occur.

Krzysztof concludes: Thank you for your constructive discussion and for sharing the experience of you and your colleagues. It has helped us to understand what could have happened.

Related to this topic is another round table discussion below which asked the question: **Do You know why only nickel provides trustworthy information for active corrosion?**

Gholam Moazzez of Khorasan Petrochemical Company in Iran replies: The passive layer consists of chromium complexes; therefore if the passive layer fails for any reason, the chrome of the grain boundaries remains and contributes to the chromium complexes on the surface of the liner and nickel is soluble in product.

Ahmed Hegazy of MOPCO in Egypt gives his opinion: As urea-formaldehyde forms a violet-colored nickel salt of diphenylcarbazide and iron or chromium do not, this provides good evidence for nickel analysis from alloy in vessels of high pressure synthesis.

Norozipour of Khorasan Petrochemical Company in Iran adds: I think chromium and iron are insoluble in urea solution, but nickel is soluble in this solution which makes it a suitable indicator for active corrosion in urea plants. In this case iron and chromium precipitate in the exchangers and vessels and cause fouling of the equipment.

This series of discussions is compiled from a selection of round table topics discussed on the UreaKnowHow.com website. UreaKnowHow.com promotes the exchange of technical information to improve the performance and safety of urea plants. A wide range of round table discussions take place in the field of process design, operations, mechanical issues, maintenance, inspection, safety, environmental concerns, and product quality for urea, ammonia, nitric acid and other fertilizers.

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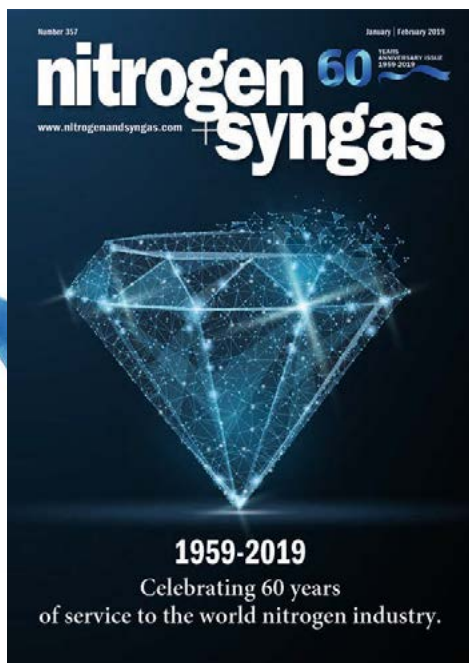
A diamond jubilee

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“It was the US where there was the greatest boom in new ammonia production.”



A diamond jubilee

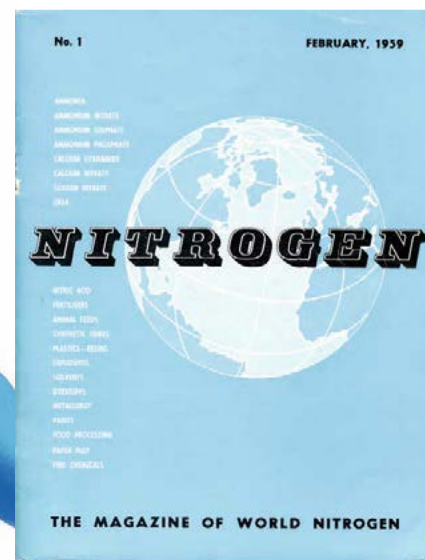
Nitrogen+Syngas magazine – beginning life as simply *Nitrogen* – is 60 years old this month. In this article we take a look back at the first issue, what has changed since 1959, and what has not.

In February 1959, following up on the launch of its initial publication, *Sulphur*, in 1953, the British Sulphur Corporation printed its first issue of *Nitrogen*. It would be followed in 1962 by *Phosphorus & Potassium*, completing the quartet of nutrients that were and are so vital to the world’s fertilizer industry.

The British Sulphur Corporation was founded as the Sulphur Exploration Syndicate in 1950 as part of an attempt to identify and help exploit new sources of mineable sulphur deposits – in those days the only significant source of industrial sulphur. Its director, John Lancaster, had anglicised his name after fleeing Nazi-occupied Czechoslovakia to the UK, and had served during the war as an intelligence officer tasked with locating necessary raw materials for the war effort, and once it finished, in the company of the wonderfully named Major-General Wildman-Lushington, he turned that expertise into a commercial proposition. From the sulphur and sulphuric acid industries, which our sister publication *Sulphur* still covers to this day, British Sulphur soon moved to the fertilizer industry, which then as now occupied most of the demand for sulphur, and the next key nutrient was of course nitrogen.

The first issue bore the blue cover that became for many years the magazine’s trademark, and a picture of a globe, to show the publication’s global ambitions. Along the left hand side are a list of industries to be covered, most of them based around synthetic ammonia production and its downstream derivatives.

It’s an unusual paper size – 246x189 mm, which used to be known as ‘Crown Quarto’ in the UK, and was a standard size for books. The magazine moved to a larger, non-standard format in 1964, and finally settled in 1967 for the A4 format that it has kept ever since. There is no masthead or list of staff, and of course no colour. A subscription cost £24 per year – the equivalent of about £550 per year today according to the Bank of England’s inflation calculator – yes, the magazine has actually become cheaper! Still, many of the contents of that first issue would be familiar now to readers of *Nitrogen+Syngas*; a review of world markets, news of the industry and new projects, articles on the development of ammonia and related markets, and technical articles detailing processes and advancements in technology.



World review

The issue begins with a review of the nitrogen fertilizer industry in 1959, and it begins with a preface that sets the scene for the piece:

“Only 50 years span its [ammonia’s] establishment amongst the heavy chemicals industries and its present day key position. Expansion of output and greater process diversification of manufacturing capacity, which has developed from the relatively rigid pattern of the pre-World War II period, have been outstanding features during the past two decades. Now the industry’s rate of growth is accelerating under the twin impact of nitrogen as a fertilizer and as a basic raw material in a rapidly increasing range of new products.”

Ammonia synthesis represented 81% of world nitrogen capacity in 1959. Calcium cyanamide supplied another 7.5% of nitrogenous fertilizer, and various by-products (presumably mostly ammonium sulphate from coke oven gas and nylon production) another 7.5%. Interestingly, 4% of world nitrogen fertilizer demand in 1959 was still being satisfied by natural deposits of sodium nitrate from Chile – it was of course the prospect of world demand for nitrogen fertilizer outstripping the capability of Chile to supply nitrates that led to William Crookes issuing in 1898 his famous call to action at the Royal Society in London, which in turn led to the research that culminated in Fritz Haber’s discovery of synthetic ammonia production in 1909, and Carl Bosch’s industrial scale-up of the process at Oppau in 1913.

Fifty years on from this discovery, the magazine reports that ammonia production in 1959 came from 350 plants around the world, which produced a total of 8.7 million tonnes N. As small as this may seem compared to 2017’s figure of 142 million tonnes N, it was nevertheless nearly three times the pre-war 1939 figure of 3.0 million tonnes N, and 45% higher than the 6.0 million tonnes N produced just five years earlier in 1954. The industry was then concentrated in Western Europe and North America, and was growing fastest in the USA, although Japan was also rapidly scaling up production.

Feedstocks were changing, and in a way this formed some of the raison d’être of the magazine. Prior to 1939, about 90% of ammonia production had come from coal and coke gasification. However, as Figure 1 shows, by 1959 capacity was much more diversified, with coal and coke now representing only 40% of capacity, refinery off-gases 9%, fuel oil gasification 15%, but natural gas 31%. Most of the new capacity built since the war was based on natural gas – France and Italy were noted as having made “extensive use” of gas-based production. However, it was the US where there was the greatest boom in new ammonia production, with two million t/a of new capacity – one quarter of the world’s total, being built in the US between 1951 and 1957, almost all of it based on natural gas.

Plant sizes in the era were small – a typical ammonia plant produced 200 t/d or 66,000 t/a. But this was soon to change. At the time the industry stood just on the cusp of the development by M.W. Kellogg of the larger scale plants of 1,000 t/d and up that gave the ammonia industry its boost during the 1960s that *Nitrogen* magazine was so well placed to report on.

Finally, and if you’ll forgive me a parochial note, the magazine also reports that “three quarters of Western Europe’s [ammonia] capacity is situated within the area of the European Common Market”. Britain of course, stood outside the common market in 1959, and may foolishly do so again very soon.

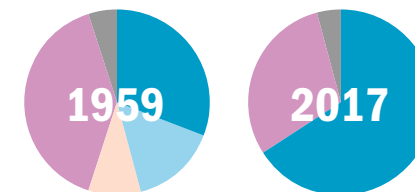


Fig. 1: Ammonia production by feedstock

1959: 8.7 million tonnes N		2017: 142 million tonnes N	
Natural gas	31%	Natural gas	66%
Fuel oil	15%	Coal and coke	30%
Refinery gases	9%	Other	4%
Coal and coke	40%		
Other	5%		

Source: *Nitrogen* magazine, IFA

Markets

Nitrogen markets were in surplus in 1959 as a result of over-building of capacity, and as a result prices were depressed – a familiar enough story in the nitrogen industry! International nitrogen fertilizer trade was dominated by the leading exporters – Western Europe, Japan and the US exporters, all of them trying to secure markets in Asia for their surplus production.

Ammonium nitrate could be bought for \$57 per short ton in the US and ammonium sulphate for \$35/st, while across the Atlantic in the UK it was £21 5/6. A 70,000 tonne urea cargo was sold out of Japan to South Korea at \$94.60/t and to India at \$107.30/t c.f.r – equivalent to \$816/t and \$926/t respectively today, and that in a depressed market! It’s worth remembering that improvements in technology and the economies of scale provided by larger plants have brought nitrogen prices down to just a fraction of what they were then in inflation-adjusted terms.

Market news was marked by a boycott of fertilizer imports by the People’s Republic of China which had hurt Japanese exporters.

This was the time of Mao's 'Great Leap Forward', which had begun in 1958, and which radically overturned existing practise in Chinese industry and agriculture. The fertilizer import ban was no doubt to try and help encourage the development of domestic fertilizer production. What was not known at that time was that the ban on fertilizer imports, along with poor weather and drought which began in 1959, and the disruptions and dislocations of the Great Leap Forward would help to cause the Great Chinese Famine, which killed anything between 15 and 45 million people between 1959 and 1962. Mao's goal of creating a Chinese domestic nitrogen fertilizer industry, based on hundreds of small, coal-based ammonia plants which were then used to produce ammonium bicarbonate, came to become a reality, but at a terrible cost.

New plants

Nitrogen #1 also reports on new plant construction, and the global nature of these reports is a reminder of how the industry was changing in 1959. An ammonium nitrate plant was being commissioned by Fisons Ltd at Stanford le Hope in the Thames Estuary east of London; the 140,000 tonne plant – built at a cost of £4 million (!) took its ammonia feedstock from a neighbouring Shell plant. Fisons of course is no longer with us – it survived as an agribusiness and pharmaceutical company into the 1990s but was bought by Rhone Poulenc and disappeared into the Aventis merger with Hoechst, and finally Sanofi. But Europe was no longer the focus for new developments. A new urea plant, this with only a 20,000 t/a capacity, was also starting up in California, for the Hercules Powder Company, while another, this with 73,000 t/a of production, was to be built at Claymont, Delaware for SunOlin, using MW Kellogg technology. But construction was spreading wider afield. In South Africa, Sasol was raising ammonia capacity to 145,000 t/a at its Modderfontein site to achieve self sufficiency, and in Pakistan, the Pakistan Industrial Development Corporation was building two new urea plants, at Fenchuganj and Multan, with capacities of

1959



The Modderfontein ammonia complex, South Africa.

www.nitrogenandsyngas.com



2019

PHOTO: TECNIMONT

THEN & NOW

February 1959 can feel like a long time ago. Che Guevara and Fidel Castro captured Havana, the Space Race was hotting up with the launch of monkeys into space and probes to the moon, and Buddy Holly and Ritchie Valens were killed in the infamous 'Day the Music Died' air crash. Europe and the world were divided by ideology into what the magazine somewhat quaintly describes as the "Free World" and the "Communist Bloc". But the concerns of the nitrogen industry were much the same then as now – producing good quality product in the most efficient way possible and achieving a good price for it.

Although the world, and the industry, have seen many twists and turns since then, *Nitrogen* magazine has been a constant companion to the industry throughout, reporting each new development as it occurred, and gradually broadening its outlook to cover first methanol and then all syngas derivatives as it did so. What chemical production may look like in 60 years' time is anyone's guess, but it is a safe bet that ammonia will continue to be as important then as it is now, and presumably there will still be a publication of some kind, in whatever format, to share information about it. ■

The Kingisepp ammonia plant under construction, Russia.

105,000 t/a and 59,000 t/a respectively, the first was to be constructed by Japan's Kobe Steel Company, the other by Grande Paroisse. And at Aswan in Egypt, a 400,000 t/a fertilizer plant was being built to produce calcium ammonium nitrate from ammonia made using hydrogen generated from water electrolysis using hydroelectric power from the Aswan dam – something that these days would be widely touted as 'large-scale renewable ammonia'.

Processes

Nitrogen has always had a very significant technical content, and the first issue set out its stall with close looks at two of the dominant industrial processes. The first, the Fauser-Montecatini urea process, was a total liquid recycle urea process developed by Montecatini and in 1959 licensed through M.W. Kellogg. Its low capital and operating costs, high purity urea, low corrosion rates and low biuret content made it extremely popular, and it became the basis for hundreds of urea plants over the succeeding decades – both the Stamicarbon and Toyo Engineering urea processes began as refinements of the Montecatini process.

On the ammonia side, the magazine describes what it calls the 'Texaco-Casale' ammonia process; in fact a Casale ammonia synthesis section fed by a Texaco partial oxidation reactor. The ammonia synthesis occurs at low temperature (100F/38C) but very high pressure (620-820 bar). The magazine notes that Foster Wheeler were the sole licensor of a process described as "flexible and economic" as well as "widely used" – ten plants had been constructed to date.

As well as these, *Nitrogen* casts its net wider than just ammonia processes, with a look at the commercial production of nitrogen gas, as well as industrial nitrocellulose manufacture – used as a binding agent in paints, inks and lacquers, and for cellulose films used for wrapping food, coating leather. ■

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Natural gas: prices and policy

PHOTO: PORT OF PORT ARTHUR



Loading LNG at Sabine Pass terminal, Louisiana.

A look at the prospects for the market for natural gas, still the most widely used feedstock for syngas production and a key determinant of profitability.

Outside of China, where coal and coke remain the mainstays, the predominance of natural gas as a feedstock for syngas-based industries continues. This is primarily due to its relatively low cost and ease of handling – gas-based plants do not require expensive feedstock treatment and gasification front-ends, and hence require less capital investment, and gas has generally been a relatively abundant and fairly cheap source of energy. However, the worldwide marketplace for gas continues to evolve, with the spread of LNG use beginning to tie together a truly global gas market, while in places such as North America and Europe the spread of hub-based pricing has started to erode the market's previous reliance on oil-indexed pricing.

Gas is used for a variety of uses, but its consumption rests on three 'pillars' –

power generation, domestic heating, and industrial uses (including as a feedstock for hydrogen, methanol and ammonia production). Demand for all of these uses continues to increase. Global natural gas demand grew by 3.3% in 2017, its highest increase since 2010. Significantly, nearly one third of this increase was represented by China alone, where natural gas demand grew by 15%. According to its most recent annual gas market report, the International Energy Authority (IEA) believes that global natural gas consumption will grow at an average rate of 1.6% year on year to 2023, with demand passing the 4 trillion cubic metres (tcm) mark by 2022 and reaching 4.1 tcm in 2023, and with China and emerging Asian markets accounting for more than half of the growth in global natural gas consumption to 2023. Continuing industrialisation and urbanisation

are driving long term gas demand growth, as well as its status as a relatively clean fossil fuel, compared to coal, which is facing increasing pressure on environmental grounds (although as a result coal has become cheaper because of lower demand for power production).

China

China is becoming one of the dominant forces in the natural gas market as it makes a determined policy effort to improve air quality in its major cities and improve its environmental credentials by converting coal-fired boilers to gas-firing in the residential and industrial sectors. Chinese gas consumption is rising the fastest of any major nation. From 2007-2017, Chinese gas consumption more than tripled, from 70 bcm to 240 bcm, and although

current 5%. One way that this is being achieved is through encouraging domestic gas consumption and supply by liberalising its domestic gas market, moving from government set prices and quotas to 'cost plus pricing'. There has also been convergence between residential and non-residential benchmark rates to give markets greater flexibility to determine prices. Previously, domestic prices were insufficient to cover import or production costs. The government is also said to be considering spinning off the pipeline assets of the three state oil and gas giants into a separate national operator, allowing for fairer access and price competition among companies.

Supply is growing, but not as fast as demand. Although China has made large strides in tapping into unconventional gas reserves, including tight gas, coalbed methane, shale gas and sour gas, there are limits to how quickly these can be exploited. In particular, water availability for fracking operations remains an issue. Chinese shale gas production is set to roughly double to around 17 bcm per year over the coming five years, but this is well below the initial target of 30 bcm that the government had been looking to achieve.

The upshot is that China is forecast to become the world's largest gas importer in 2019, overtaking Japan, and the import share of Chinese gas demand will rise 39% to 45% over the next five years, a total of 170 bcm of imports, with most of this arriving as LNG.

Other Asia

Other emerging Asian economies are also increasing their natural gas consumption. India is likely to be one major factor, where the economy is still growing at more than 7% per year, and energy consumption at 4.2% per year, according to BP projections. By the late 2020s, India could overtake China as the world's largest energy market. Again the extra gas demand, as with China, is likely to come mainly from LNG imports. The IEA also forecasts strong growth in gas use in other parts of Asia, including in South and Southeast Asia, driven by strong economic growth and efforts to improve air quality. As well as power generation, there is forecast to be increased gas demand for industry, including fertilizers and petrochemicals.

This is part of a significant trend in natural gas consumption. Previously,

power generation has driven most of the increase in natural gas consumption over the past few decades, including switching from coal, oil and in Japan's case even nuclear power in mature markets. Gas demand for power production will continue to increase in the US and Middle East, according to industry forecasts, but with India and China, as well as some other Asian countries like Vietnam still heavily reliant on coal, gas may not make as many inroads into the power sector in Asia as it has done in the past. However, increasing production of chemicals and fertilizers from natural gas as well as gas's use for heating in the chemical and petrochemical sectors will mean that industry is projected to account for 40% of the increase in global gas demand to 2023 according to the IEA, with much of that increase coming in Asia and the Middle East.

Europe and Russia

Europe is a net gas importer, and while demand is mature and relatively static, falling domestic production from the North Sea and onshore areas is expected to lead to increased imports of natural gas into Europe. European gas supply may fall by 45 bcm per year by 2023, which will need to be met by additional import volumes. Some of this will come from existing pipeline suppliers Algeria and Russia, but LNG is also increasingly beginning to catch on as a supply source in Europe. Current LNG import capacity is 225 bcm, and projects in Greece, Belgium, Germany and Poland amongst others will take this to 250 bcm in the next few years. However, current utilisation rates at LNG import terminals are only around 25%, so even without this new construction there is plenty more capacity for Europe to take extra LNG if the price is right.

That price depends on the relationship between global LNG prices and Asia's ability to outbid Europe for cargoes, as well as the pipeline gas price charged to Europe by Russia. Europe remains umbilically linked to Russia via gas pipelines. There has been a trend for Gazprom's gas output to stagnate, as it fought to overhaul an ageing and underinvested gas production and transmission system. However, new investment is now beginning to bear fruit, and Russian gas production increased by 50 bcm in 2017. Russia continues to build pipeline capacity, with a new 55 bcm Nordstream line completed in 2020, and a

similar 30 bcm project to Turkey the same year. The Yamal LNG project started up in 2017 and by the end of 2019 aims to be exporting 18 bcm of natural gas into Asian LNG markets, and the 38 bcm 'Power of Siberia' pipeline to China is expected to be complete by 2024, giving Gazprom options to send gas to China as well as Europe.

North America

North America remains the largest factor on the supply side of the gas equation. The huge increase in gas production from unconventional sources, especially fracking of shales, has turned the US from a net gas importer to an exporter. Tight gas and coalbed methane supply about 15% of US natural gas, but shale gas and associated gas from tight oil production now produce around two thirds of US gas, and that it still forecast to increase. IHS Markit projects that US natural gas production will grow by another 60% over the next 20 years. Natural gas production in the United States has already risen by more than 40% between 2007 and 2017, pushing natural gas prices down by more than two thirds during the same period. Since 2008, US gas prices have fallen from \$9-12.00/MMBtu to a stable level of around just \$3-4.00/MMBtu.

While the US has been exporting gas by pipeline to Mexico, it became an LNG exporter in 2016, and now the next step is for those exports to grow dramatically over the next few years. The Sabine Pass gas terminal in Louisiana has ramped up to four trains over the 2016-17 period, and in Q1 2018 it was joined by the Cove Point

LNG terminal in Maryland. Now there are a flurry of new projects that will more than double US LNG export capacity by 2021, including more expansions at Sabine Pass and more capacity on the US Gulf Coast at Cameron in Louisiana, and Freeport and Corpus Christi in Texas, as well as Elba Island further north in Georgia. These will take US gas liquefaction capacity to 10 bcf/day or just over 100 bcm per year, and turn the US into the second largest LNG exporter in the world, almost on a par with Qatar and potentially ahead of Australia.

LNG

It is the continuing growth of the global LNG market which has transformed and is continuing to transform the way that the world uses natural gas. Production and consumption of liquefied natural gas reached 395 bcm in 2017, representing about 11% of the global gas market, and 35% of internationally traded gas. Both liquefaction and regasification capacity continue to grow, with the latter reaching 1,147 bcm during 2018 – regasification capacity has grown faster than liquefaction, which is helping to make the LNG market more liquid (if you'll excuse the pun). And both are forecast to continue this growth. The current wave of LNG export projects will increase liquefaction capacity by 30% by 2023. This will be led by an increase in output from the United States, as noted above, which accounts for nearly three-quarters of the growth in total global LNG exports in the period, followed by Australia and Russia.

This in turn is leading to LNG taking a progressively larger share of global gas trade,

especially in Asia. LNG trade as a share of total gas trade is forecast by the IEA to rise to almost 40% in 2023, with emerging Asian markets accounting for about half of global LNG imports by 2023. Russia's Novatek, which operates the Yamal LNG project, has estimated that the global LNG market will reach 700 million t/a by 2030 (775 bcm/year), almost double its current size, and Asia represents 85% of the projected growth in LNG demand.

On the supply side, as well as the new projects in the US, there is the potential for some additional capacity from Australia, which has come in just a few years to be the world's second largest exporter. However, its bid to overtake Qatar, the world's largest producer, has run into problems. Australia's nameplate LNG capacity is 88 million t/a (97 million bcm/year), but it consistently runs about 15% below capacity. One issue is that the coalbed methane that some of the Queensland projects were based on has not proved to be as easy to recover as predicted, and the gas must also supply domestic markets, where demand from the power sector has also been higher than expected. In theory there is another 30 bcm of extra production scheduled over the next few years, but it is no longer certain how much of this will be produced, and how much of what is produced will be shipped. Qatar has some additional capacity coming to reach 110-120 bcm per year by 2023-4, and Russia is building another 15 bcm. Longer term there is the huge LNG Canada project in British Columbia, which could export up to 30 bcm per year. However, the period 2021-23 actually looks a little thin in terms of new LNG supply in comparison to the expected increase in demand in Asia, and there have been warnings of supply tightness if no new projects emerge in that time frame. While the market has been oversupplied for some years, bringing prices down, China's huge increase in LNG imports in 2018 took prices to \$12.00/MMBtu in late 2018, and prices have only dropped back to \$9.00/MMBtu at the start of 2019 because of the unusually mild winter in the northern hemisphere.

Gas pricing

One thing that the flood of new US LNG capacity may change, however, is the way that LNG supply contracts are drawn up. In the early days of LNG, supply contracts were often long-term, fixed price

or indexed to oil prices. Gas pricing has changed in Europe and North America as markets have liberalised and moved to hub prices and gas-on-gas competition, but the LNG market has stubbornly stuck to oil-indexed prices, even though there is much more spot trading in LNG cargoes today and fewer long-term contracts. But the emergence of large scale US exports with flexible destination and gas-indexed pricing presents a different model from historical fixed-delivery, oil-indexed supply agreements and could accelerate a major transformation of the LNG market.

Other factors influencing this include the diversification of supply and demand in the LNG market as it grows. There are many more producers now, and many more consumers. The barriers to entry have fallen, leading more countries to import LNG. However, while gas is being traded more widely than ever, and the LNG market has grown at 8-12% per year over the past two years and is forecast to grow at 6% per year in the medium term, compared to the 1.7% per year of the overall gas market, only 30% of all gas is traded across an international border, and only a few percent at spot rates. Gas pricing currently still remains heavily regional and often dependent on state intervention in the form of fixed prices or subsidies. This too is evolving. Over the past decade the percentage of gas sold at market rates has increased from 30% to over 45%, while for internationally traded gas, oil indexation has fallen from 60% to 50% – much of the shift has been in Europe, where gas prices have progressively decoupled from oil. But it is a slow process. While Europe and North America both now have mature gas trading hubs, there is still no real equivalent in Asia. As 90% of traded gas in Asia is shipped as LNG, the most logical hub would be one that could see both import and re-export of significant LNG volumes. But the preponderance of LNG demand in east Asia as opposed to other regions still distorts the LNG market and prevents it from becoming a truly global market; there are still significant regional variations in delivered LNG prices. Could the spread of gas-based LNG pricing out of the US help accelerate this process?

The future for gas prices

So where does this leave gas prices over the next few years. US gas prices look set to continue their run of low prices, although as more and more new gas supply is exported, whether global LNG prices drag US prices upwards, as has happened in Australia, remains to be seen. In the medium term, the slew of new US LNG capacity may depress global LNG prices for a couple more years. However, as Asian, and especially Chinese demand continues to increase, and with that hiatus of new LNG projects on the horizon between 2021 and 2024, there are some who anticipate that global LNG markets could become quite tight in that period. LNG projects take 4-5 years to develop and build, so if no-one has started them by now, then there is little hope of new supply before 2023.

Europe remains in a tug of war between Chinese demand and Russian supply. In 2018, Chinese LNG demand pulled supply away from Europe and helped increased prices there. This linkage between the Dutch TTF hub price and Asian LNG prices seems set to continue, according to Timera Energy, as both markets are often vying for the same spot LNG cargoes. Timera projects that the most likely outcome for Europe is that Russia expands pipeline

GECF

And what of the Gas Exporting Countries Forum (GECF)? When this was founded in 2001 there were concerns that it could become a cartel in the same way that OPEC has for oil markets. The 11 members of the GECF – Russia, Qatar, Iran, Algeria and Nigeria are the most important in terms of reserves and production – hold about 62% of the world's natural gas reserves, control about 38% of production, and supply 43% of exports. A few years ago they also controlled 85% of all LNG trade, but the rapid rise of Australia and the US is changing this significantly. Furthermore, the GECF has not imposed production quotas on member states, and its charter does not have any provisions that would give it the authority to do so. While individual members have considerable power in certain markets – such as Russia's and Algeria's influence over European gas prices, for example – there has so far been no attempt to maintain any collective market discipline, and the comparisons with OPEC seem overblown for now.

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supply at a price sufficient to undercut LNG cargoes, and is forecasting a long term average of \$7.50/MMBtu for European gas prices. Asian LNG prices will most likely run at their usual \$1.00-2.00MMBtu premium to European prices, but a tightening market after 2021 might see this rise further.

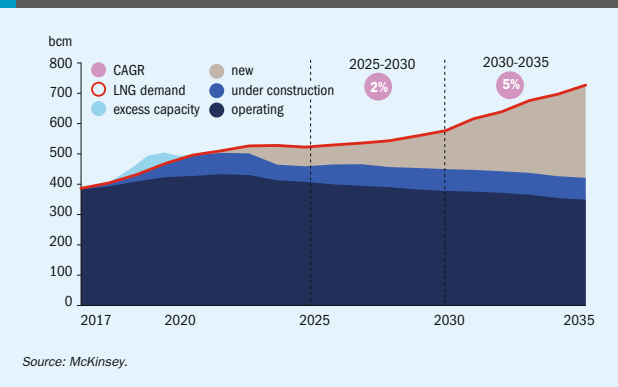
Downstream producers

The main effect of global gas market prices on syngas production will continue to be felt in Europe and North America, as it is there that producers must pay market rates for natural gas. The continuing increase in North American supply should see US and Canadian producers continue to be advantaged in that regard, while European producers may struggle. Chinese natural gas-based producers will continue to pay premiums as more gas is used in power production and heating, which has kept operating rates low for Chinese gas-based capacity. Russian and Central Asian capacity likewise continues to be advantaged as gas remains in surplus, and the strong dollar also helps feedstock prices low relative to product prices.

Outside of these regions, most producers are still paying fixed, subsidised or other controlled prices for gas. However, in India, much of the new ammonia-urea capacity that is expected over the next few years will need to use LNG as feedstock, and the government will need to find a way of keeping this operating when LNG prices are high and demand from power production has privileged access to gas. Governments in the Middle East, likewise, have been left with a legacy of very low gas prices to industrial users, but are finding that bringing incremental new gas capacity on-stream requires expensive investment in, for example, sour gas production, and the continued willingness of governments to subsidise domestic producers is an open question.

Overall, the global gas market continues to liberalise and become increasingly interconnected as more pipeline and LNG capacity is built. Countries such as Malaysia are now beginning to see more gas on gas competition. So-called 'stranded' gas, which led to much of the investment in ammonia and methanol capacity in the 1980s and 90s, is now rare, and limited to a few parts of Africa such as Mozambique and Angola, eroding the rationale for building export-oriented plants in far-flung locations.

Fig. 1: Global LNG supply and demand to 2035





Grain harvesting in Russia.

Cheap, stranded natural gas and favourable exchange rates have combined with increasing domestic demand to produce a boom for nitrogen production in Russia and parts of Central Asia.

Nitrogen in Russia and Central Asia

Russia and Central Asia continue to be one of the bright spots in the nitrogen industry for new construction, representing the largest tonnage of new capacity likely to come on-stream over the next few years outside of India. Several factors have combined to bring this about, including abundant natural gas, rising domestic demand for fertilizer, and favourable exchange rates.

Natural gas

Natural gas production in the region saw a record high of 815 bcm in 2017 after several years of stagnation. Most of this increase came from Russia, where a programme of investment by Gazprom and the growing importance of other, smaller suppliers is seeing the overturning of years

of production stagnation. Russian gas production increased by 46 bcm in 2017 to 635 bcm, and was forecast to have reached nearly 700 bcm in 2018. Exports of gas from Russia increased to a record 194 bcm in 2017, and Gazprom says that it expects this to have increased to 200 bcm in 2018, with more incremental volumes going to Europe as the latter's gas production continues to decline.

Other countries in the region have not seen as much of an increase, except in Kazakhstan, where production grew by 18% in 2017. Kazakhstan is the third largest holder of gas reserves in the region, but most of it is associated with oil production from the Tengiz and Karachaganak fields. Production has been boosted by the Kashagan oil project finally coming on stream after delays due to corrosion in pipelines.

In some cases this is not necessarily due to lack of gas availability, however, but lack of opportunities to bring this to market. For example, Turkmenistan, which has the fourth largest gas reserves in the world, found itself locked out of supplying gas to/ via Russia in January 2016. There was good news on this front recently, as Gazprom now says that it plans to resume imports of gas from Turkmenistan in 2019. In the meantime, Turkmenistan has tried to forge alternative destinations for its gas, including a 30 bcm per year pipeline to China, but outside of this, most of the country's gas went to either Russia (around 10-11 bcm per year) or Iran (6-8 bcm/year), and with the Russian market closed and a falling out with Iran over payment for previous deliveries, Turkmenistan found itself unable to export excess production in 2017 and

Fig. 1: Nitrogen capacity in Russia and the CIS



Russia

1. EuroChem (Nevnyomyssk)
2. EuroChem (Novomoskovsk)
3. UralChem (Berezniki)
4. UralChem (Perm)
5. UralChem (Kirovo-Chepetsk)
6. Sibur (Kemerovo)
7. TogliattiAzot (Togliatti)
8. KuibyshevAzot (Samara)
9. JSC Acron (Novgorod)
10. JSC Acron (Dorogobuzh)
11. Minudobreniya Rossosh (Rossosh)

Ukraine

12. PhosAgro (Cherepovets)
13. AO Salavat (Salavat)
14. JSC Angarsk (Angarsk)
15. Odessa Port Plant (Odessa)
16. Concern Stirol (Gorlovka)
17. DniiproAzot (Dniprodzerzhinsk)
18. RovnoAzot (Rovno)
19. Severodonetsk Azot (Severodonetsk)
20. OJSC Azot (Cherkassy)

Kazakhstan

21. KazAzot (Aktau)

Turkmenistan

22. Turkmenchimiya State Concern (Tedzhen)
23. MaryAzot (Mary)

Uzbekistan

24. UzKimyoSanoat (Navoi)
25. UzKimyoSanoat (Ferghana)
26. Maxam-Chirchik (Chirchik)

Belarus

27. GrodnAzot (Grodno)

Tajikistan

28. TajikAzot (Sarband)

New plants

29. EuroChem (Kingisepp)
30. SOCAR (Sumgait)
31. JSC Acron (Novgovod)
32. Metafrax (Gubhaka)
33. Turkmenchimiya (Garabogaz)
34. UzKimyoSanoat (Navoi)
35. Kuibyshev Azot (Togliatti)

production was cut back to 62 bcm. A pipeline via the Caspian Sea to Turkey and on to Europe looked to be a possible solution, and some cynics have suggested that it is the threat of this pipeline which has persuaded Gazprom to start taking Turkmen gas again. Uzbekistan, meanwhile, has similar sized gas reserves to Kazakhstan and is the third largest regional producer after Russia and Turkmenistan, but in spite of an export pipeline to China has not been able to fully monetise them. However, this lack of market opportunities for the abundant gas of the region has itself been the driver for some of the fertilizer projects that have been developed; it is much easier to export urea than natural gas.

Ukraine, too, has seen gas become a front in the ongoing struggle with Russia that has seen it lose the Crime and part

of the east of the country to Russia or Russian-backed separatists. The existing delivery contract between Gazprom and Naftogaz Ukrainy expires on 31 December 2019. Gazprom has already substantially reduced the volumes of gas it transits across Ukraine, and plans to reduce this further by completing pipelines which allow alternative routes to Europe such as Nord Stream and Turkish Stream. Lack of gas availability and higher prices have severely cramped Ukraine's nitrogen industry.

Gas pricing in the region still remains generally state controlled but this too may change, as in Russia, the dominant regional producer, there is also a switch towards market-based pricing mechanisms. At the end of 2017, president Putin approved the National Competition Development Plan, which calls for a transition

to market based prices for natural gas by 2020, and the transition to market prices in the wholesale market is due to happen by July 2019. The domestic gas market is still dominated by Gazprom, although Gazprom's share continues to fall. Novatek and Rosneft now also have major shares, although there are still wrangles over third party access and pricing for gas.

Domestic demand

Another driver for new fertilizer capacity has been increasing regional demand for nitrogen fertilizers. IFA forecasts that Russia and the CIS will see an increase in demand of 1.1 million tonnes N over the next five years, with overall fertilizer use rising by 20% once phosphorus and potassium demand increases are taken into

Table 1: Ammonia production, consumption and exports, Russia and Central Asia, 2017 ('000 t N/a)

Country	Production	Consumption	Imports	Exports
Belarus	883	901	44	26
Russia	13,954	11,178	0	2,783
Kazakhstan	162	194	32	0
Turkmenistan	525	540	15	0
Uzbekistan	1,155	1,132	0	23
Ukraine	981	1,039	176	117

Source: IFA

Table 2: New nitrogen capacity in Russia and Central Asia

Company	Location	Product	Capacity	Start-up
StchekinoAzot	Stchekino, Russia	Ammonia	140,000 t/a	2018
Turkmenkhimija	Garabogaz, Turkmenistan	Ammonia	660,000 t/a	2018
		Urea	1,155,000 t/a	2018
EuroChem	Kingisepp, Russia	Ammonia	955,000 t/a	2019
		Ammonia	400,000 t/a	2019
SOCAR	Sumgait, Azerbaijan	Urea	660,000 t/a	2019
		Ammonia	to 690,000 t/a	2019
TogliattiAzot	Togliatti, Russia	Urea	730,000 t/a	2020
NavoijAzot	Navoij, Uzbekistan	Ammonia	660,000 t/a	2020
		Urea	580,000 t/a	2020
Metafrax	Gubhaka, Russia	Ammonia	300,000 t/a	2021
		Urea	575,000 t/a	2021
KuibyshevAzot	Togliatti, Russia	Urea	540,000 t/a	2021

Source: BCInsight

account. Russia and Ukraine in particular are projected to see significant growth in demand, as they increase their grain output, with Russia alone providing 0.5 million tonnes N of the increase. Grains account for three quarters of Russian agricultural production, with wheat representing close to half of the total harvested area. Russia harvested 27.3 million hectares of wheat in 2017 – its largest ever crop – although this dropped slightly to 25.5 million ha in 2018 following a prolonged drought, and its exports were more than 40 million tonnes in 2017, compared with only 5 million tonnes in 2010. Russia's main grain producing region is in the south in the Rostov and Volga regions towards the Caucasus mountains and the Ukrainian border, and CRU reported recently that fertilizer application rates in the Rostov region had increased by 50% in 2017 compared to 2014, and forecast that fertilizer consumption overall in

Russia would increase by 4% year on year to 2023. Domestic nitrogen fertilizer consumption is mainly as ammonium nitrate and some UAN, while urea, UAN and surplus ammonia tend to be exported.

Exchange rates

Finally, there has been a boost to Russian fertilizer production caused by the weakness of the rouble, which in turn has been further weakened by international sanctions on Russia. Figure 1 shows how the rouble has fallen against the euro over the past decade. The weakness of the rouble, especially since 2014-15, has boosted the competitiveness of Russian grain production, increasing demand for nitrogen fertilizer, at the same time that it has increased the competitiveness of Russian fertilizer production – the weak rouble makes gas prices much lower compared

to product prices, which are sold in dollars on the international market. Russia exports 75-80% of its fertilizer production, as Table 1 shows.

New production

This favourable combination of circumstances means that capacity has been steadily increasing and is forecast to continue to do so. Table 2 shows current and planned expansions in capacity in Russia and Central Asia, totalling 3.8 million t/a of ammonia and 4.2 million t/a of urea.

Russia

Russia has the largest slice of new production, with an increase in ammonia capacity of 1.6 million t/a and urea capacity of 1.8 million t/a. This is on top of the 500,000 t/a urea plant completed at Cherepovets in 2017 and the 700,000 t/a unit that started up at Ammonii's Mendeleevsk plant in 2015. JSC Acron subsidiary JSC Dorogobuzh is revamping its ammonia plant at the Dorogobuzh site near Smolensk, with technical assistance from KBR. Ammonia production is being increased to 2,100 t/d using the KBR Reforming Exchanger System (KRES™). Acron is also conducting works at its Veliky Novgorod site. Two nitric acid plants with a combined capacity of 270,000 t/a are under development at the site, and are expected to be completed in 2019, designed by Acron subsidiary GIAP. Stamicarbon is also licensing its granulation technology for a new 2,000 t/d urea granulation facility to expand the company's product offering from the site. One of the urea plants at Veliky Novgorod was also revamped by NIIC using its own liquid recycle technology to increase capacity from 270 t/d to 620 t/d.

Metafrax says that construction work began in March 2018 on the company's new AUM (ammonia-urea-melamine) plant at its Gubhaka site. Completion is expected in 2021. Once operational, the plant will produce 300,000 t/a of ammonia, 575,000 t/a of urea and 41,000 t/a of melamine. Casale is the main project licensor and contractor.

Tecnimont has been awarded the EPC contract to build a new 540,000 t/a urea plant for Kuibyshevazot at the company's Volgafert subsidiary in Togliatti. The plant will use Stamicarbon technology. Final

notice to proceed is expected by early 2019, while the completion of the project is expected in the fourth quarter of 2021.

There have also been revamps with production expansions at EuroChem's Novomoskovsk urea plant and Nevinnomyssk ammonia plant. Some other project proposals, such as the ICT Baltic Ust Luga project and a proposal to build two ammonia-urea plants on Russia's Pacific coast at Nakhodka, have not managed to find financing, however.

As well as ammonia and urea, other nitrogen fertilizers are seeing expansions. As noted in our news this issue, EuroChem completed Russia's first urea ammonium sulphate (UAS) plant at the company's Novomoskovskiy Azot plant, 200 kilometres south of Moscow in late 2018. Stamicarbon designed the ammonium sulphate plant at Novomoskovsk with a capacity of 400 t/d urea and 600 t/d UAS.

Kazakhstan

One of the features of the Central Asian economies over the past few years has been the increasing presence of China and Chinese investment. This move has been given a boost by China's 'Belt and Road' initiative, which looks to develop Chinese economic ties and sources of raw materials across Asia and Africa. One fruit of this is that Chinese money is becoming available for large infrastructure projects, and that includes large scale fertilizer complexes. Last year Kazakhstan's KazAzot JSC announced that it was partnering with China's Inner Mongolia Berun Holding Group Co. Ltd to build a \$2.8 billion gas-based chemical complex in Kazakhstan's Aktau city. In its first stage, the plan envisages the construction of 400-600,000 t/a of ammonia/urea and methanol capacity, as well as a gas-fired power plant with a capacity of 300MW. Further stages will take total capacity to a planned 1.2 million t/a of urea and 600,000 t/a of methanol.

Turkmenistan

The Garabogazkarbamid urea plant was officially opened on September 17th by Turkmenistan's president Gurbanguly Berdimuhamedov. The plant, sited at Garabogaz on Turkmenistan's Caspian Sea coast, consists of a 2,000 t/d ammonia unit designed by Haldor Topsoe and 3,500 t/d urea plant designed by Saipem, with an Uhde Fertilizer Technology granulation section for product finishing.

Azerbaijan

After some delays, the State Oil Company of Azerbaijan Republic (SOCAR) started production at its new ammonia-urea plant on January 16th 2019. The new facility has a capacity of 1,200 t/d of ammonia and 2,000 t/d of urea. Around 25% of this will be sold domestically, with the remainder exported to Turkey, Georgia and into the Black Sea and Mediterranean markets. Samsung Engineering has been the lead EPC contractor, with ammonia licenses supplied by Haldor Topsoe and urea license from Stamicarbon.

Uzbekistan

NavoijAzot, the chemical production arm of state-owned Uzkimyo sanoat, has awarded the EPC contract for its new gas-based ammonia-urea fertilizer plant at Navoij to Mitsubishi Heavy Industries and Mitsubishi Corporation. Once it is up and running, the plant will produce 2,000 t/d of ammonia and 1,750 t/d of granulated urea. Timing has slipped on the project, which is now scheduled for 2020. Casale is also building a 1,500 t/d nitric acid plant, at the site.



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PHOTO: CASALE

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	OPZ signs new gas tolling arrangement	Nov/Dec	11
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UK	Atlas Copco acquires Walker Filtration Ltd	Mar/Apr	12
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NITROGEN+SYNGAS
ISSUE 357
JANUARY-FEBRUARY 2019

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Nitrogen+Syngas

CRU's Nitrogen+Syngas Conference and Exhibition returns to Berlin this year and will be held at the Estrel Berlin, Germany, 4-7 March 2019.

PHOTO: FRETSCHE / SHUTTERSTOCK.COM

The four-day agenda incorporates practical workshops, industry insights from CRU's nitrogen analysts and other industry experts, and a comprehensive dual-streamed agenda featuring over 45 technical papers focused on the latest technology, process and equipment innovations and operational best practice. The conference runs alongside an exhibition of world-class process, materials, equipment and technology solution providers. Opportunities for networking is scheduled throughout the agenda.

Above: A detail of the Berlin Cathedral with the TV Tower in the background.

Day one of the conference will feature a full day **Amine Experts training course** hosted by **Amine Experts**. Amine plants are frequently used to remove CO₂ gas streams prior to ammonia synthesis. This training course provides a thorough grounding in amine operational theory and field troubleshooting of amine systems in terms of corrosion, foaming and meeting treated product specification. The amine treating course has been presented more than 300 times worldwide with more than 8000 engineers and operators benefitting from attendance. A condensed version of the course, normally lasting a full week, will be presented.

In addition on **Day one** there will be two other morning events running in parallel:

This year the **UreaKnowHow.com Clinic**, hosted by **UreaKnowHow.com** will focus on leaks in urea plants, and will cover different types of leaks, consequences, safety risks, as well as prevention and mitigation measures. The clinic will also discuss several historical cases. Approximately 75% of the major safety hazards in a urea plant can result in a leak, whereby corrosive ammonium carbonate and toxic ammonia will be released. This has already led to at least 36 casualties and 198 people injured. In nearly 90% of these incidents, the leak occurred suddenly, without any pre-warning.

KPI will be hosting a **training workshop for ammonia and methanol operations**. This workshop will provide practical insights and realistic strategies for better decision making when striving to maximise the profitability and reliability of plants without compromising on safety. The workshop covers ammonia/methanol process technology advances, key considerations in the operation of critical equipment, options for maximising reforming capacity and synchronising the front end and synloop to maximise production.

In the afternoon there will be a **technical showcase agenda** – short presentations from technology providers and producers covering a wide range of topics relevant to the nitrogen and syngas industries.

Day two of the conference features: outlooks for gas and nitrogen, challenges and opportunities for the European chemical market, the role of ammonia in the new energy economy, technical innovation to enhance production economics and commissioning case studies.

Day three sees the start of the dual-streamed technical programme over 1½ days, with this year's main topics being: new process technology and developments to increase the production of ammonia, methanol and syngas, improving the production economics of urea plants, new innovations in methanol production, increasing the production and profitability of nitric acid and ammonium nitrate plants, effective emissions management and CO₂ removal, new developments in urea production, ammonia operations, fertilizer granulation and finishing developments, materials of construction, effective reformer management strategies for increased reliability and productivity, operational case studies, incident analysis and safety.

Technical programme highlights

A selection of presentations from the technical programme are highlighted below.

Ammonia based on renewable energy

Safety considerations, new CO₂-free energy sources and increasing regulation are just some of the trends that have influenced an increased demand for smaller ammonia plants. thyssenkrupp Industrial Solutions will present a study for alkaline water electrolysis-based (AWE) 50 t/d and 300 t/d ammonia plants using minimal and simple equipment to reduce investment cost. The ability to use AWE-based hydrogen to substitute natural gas in a conventional ammonia plant will also be discussed.

Improved water gas shift process

The water gas shift process is a key process in most ammonia plants. Johnson Matthey will review a new shift product which extends life allowing ammonia and hydrogen plants to increase their process reliability and production efficiency. The presentation will cover the new product development and its application in large ammonia plants.

Online urea process control and analysis

In the majority of urea plants, the composition of the process stream in the high-pressure synthesis is determined through laboratory analysis in terms of % NH₃, % CO₂ and % urea. However, there are a number of drawbacks in current sampling techniques. Casale and Kaiser Optical Systems will describe the features of a new online analyser based on Raman spectroscopy that is designed to measure the full composition and the most important key performance indicators of the synthesis.

New route to methanol

Haldor Topsøe will describe a new route to methanol production, the Sincor Methanol™ process. The new process eliminates the need for a steam reformer, contains no tubes and operates with a single burner in the top of the reactor. The process offers both economic and operational benefits, improved ease of operation and faster turnaround resulting in high on-stream performance, thereby improving plant profitability.

Innovations in granulation design

Stamicarbon will chart the evolution of its fluid bed granulation technology and its benefits including increased capacity, and reduced capex, opex and footprint. Special focus will be given to the latest innovations of this technology: a multi-functional granulation design that is able to produce specialty products such as UAS in addition to urea. The new technology can be applied to both new and existing plants.

Benchmark safety standards

Axo Welding and GPIC will share the benchmark safety standards and high on-stream figures that have been developed through a risk-based maintenance system. Risk assessment, mitigation measures and turnaround activities will be detailed.

Co-production of methanol and ammonia

The concept of co-producing methanol and ammonia via integrated process designs has a long history and there are many ways of producing both products in a single production asset. Co-production schemes can suffer from a degree of compromise because the incorporation of both products into a single flowsheet can mean that the process conditions for both are suboptimal. Johnson Matthey will present a range of ammonia-methanol co-production technologies, which are both efficient and can accommodate any product mix.

In addition, thyssenkrupp Industrial Solutions will present a new technology – AdwinCombined™ – a highly integrated process plant concept for the production of methanol and ammonia. This new plant configuration leads to substantial reductions for both consumption figures as well as investment cost compared to two individual stand-alone plants. The process concept features the simultaneous operation of both product plants at nameplate capacity but also provides freedom of operation at partial loads. Single operation modes are also possible.

New high-efficiency scrubbing technology

Worldwide, fine particulate emission regulations are becoming increasingly strict. Stamicarbon will discuss the application of a new high-efficiency scrubbing technology designed to remove submicron dust and ammonia gas at extremely high efficiencies, and capable of meeting the most stringent emission levels. The MicroMist™ Venturi Scrubber technology has been deployed at the Koch Enid facility. The project realisation and results will be discussed.

Pan granulation – lessons learned over 35 years

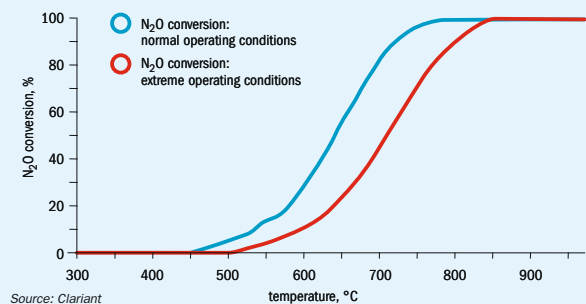
New Karvali Fertilizers will share their experiences and lessons learned over 35 years from the operation of a high-temperature pan granulator (HTPG) in an AN/CAN fertilizer production plant. The AN/CAN plant was installed in 1982 with a capacity of 600 t/d of AN grade or 800 t/d of CAN grade fertilizer. The production plant is fed by AN solution 99.5%. The initial installed HTPG and the additional related equipment were extensively modified from the first installation. The speaker will explore the advantages and disadvantages of pan granulator vs drum granulators.

Enhanced efficiency fertilizers

While urea is a popular nitrogen source, as much as 50% of the nitrogen applied can be lost to the environment. One way for growers to protect against N loss is to utilise an enhanced efficiency fertilizer (EEF). These products can include treating urea with a urease inhibitor or using a nitrification inhibitor designed to protect nitrogen from loss and be readily available for plant uptake. Using case studies, Koch Agronomic Services will provide key details of EEF and the associated environmental and economic benefits.

Meeting stricter N₂O limits

Fig. 1: N₂O conversion with EnviCat N₂O-S at different temperatures



Above left: EnviCat N₂O catalyst, iron on zeolites; Above right: EnviCat N₂O catalyst, cobalt/manganese on alumina.

Nitric acid is an important chemical feedstock. It is used primarily in fertilizer and nylon production, the photographic industry, precious metal separation and explosives manufacture. About seven kilograms of nitrous oxide (N₂O) are generated as a by-product per tonne of nitric acid produced. An estimated 400,000 tonnes of nitrous oxide are therefore emitted every year by nitric acid plants worldwide. Since nitrous oxide is about 300 times more harmful than CO₂, as a climate gas, this has the same atmospheric pollution impact as 120 million metric tons of carbon dioxide – equivalent to the emissions from about 50 million cars, the total number at present on the road in Germany and the Netherlands. For several years, legislators have therefore been imposing ever-stricter limits on nitrous gas emissions. Exhaust gas must now contain no more than 400 ppm of N₂O.

Zeolite catalysts to remove nitrous oxide

To ensure compliance with these limits, Clariant with its 40 years of global expertise in catalytic air and gas purification has developed the catalyst EnviCat N₂O. It removes more than 99% of nitrous oxide from the tail gas of nitric acid plants. Moreover, it also renders innocuous other nitrogen oxides (NOx).

The nitrous oxide can be converted in two stages: in the first stage, the nitrous oxide is decomposed to oxygen and nitrogen with the aid of the catalyst EnviCat N₂O. In the second stage, the nitrogen oxides are mixed with ammonia to produce harmless nitrogen and water. Any ammonia slip is prevented by EnviCat N₂O – an iron zeolite catalyst – as it is also able to oxidise ammonia to nitrogen and water.

“The highly active catalyst EnviCat N₂O consists of porous, crystalline zeolites”,

explains Dr Roderik Althoff, Head of Sales and Product Management Zeolite Powders at Clariant. Zeolites are a group of minerals containing mainly aluminum, silicon and oxygen. “In EnviCat N₂O, we have dispersed iron into the crystal lattice of the zeolites by means of an ion exchange process.” Like all catalysts, EnviCat N₂O takes part in the chemical reaction without itself being used up. In the reactor, the nitrous oxide passes through the catalyst bed at temperatures between 300 to 500°C, depending on the application. The nitrous oxide molecules attach to the iron cations and temporarily bind firmly to them because of the strong chemical bonds (chemisorption). The nature of the catalyst determines the degree of this chemisorption. On the one hand, it must be strong enough for oxygen and nitrogen atoms to separate and form new bonds with further oxygen atoms, but on the other hand it must not be so strong as to prevent the new molecules leaving the catalyst and block further reactions. In this way, harmless nitrogen and water are formed.

New drop-in catalyst solution

To date, EnviCat N₂O catalysts have been installed in more than 25 nitric acid production plants globally. Combined, the installations reduce annual N₂O emissions equivalent to approximately 15 million tonnes of CO₂. In 2016, Clariant added a new drop-in solution to its EnviCat N₂O series with additional benefits for customers and the environment. The new EnviCat N₂O-S catalyst can be easily installed in existing nitric acid plants without revamping the facility, and converts the majority of N₂O generated as undesired by-product from primary catalyst or high N₂O gas streams, such as in adipic acid production. At the same time, it reduces ammonia requirements for the same amount of nitric acid yield, thus substantially lowering operating costs.

Fig. 1 shows a graph of N₂O conversion with EnviCat N₂O-S at different temperatures, based on Clariant laboratory data and customer plant data.

The EnviCat N₂O catalyst needs to reach a temperature of about 350-420°C in order to provide the requested N₂O and NOx removal performance. For start-up conditions, therefore, it is recommended to heat up the catalyst by hot air before introducing N₂O/NOx-containing tail gas.

EnviCat N₂O-S converts up to 100% of N₂O in the secondary stage of chemical production. ■



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Reducing ammonia plant emissions

With global concerns over air quality and its impact on the environment, ammonia plant emissions are subject to tightening environmental standards. Several different strategies are available to reduce ammonia plant emissions. In this article we discuss environmental compliance strategies for new and existing ammonia plants around the world.

During recent years, restrictions in the formation of ozone (O₃) in the troposphere (i.e. near ground) by air pollutants have gained significance in the desire to reduce smog. The presence of precursors such as volatile organic compounds (VOCs), nitrogen oxides (NOx) and sunlight enhances the formation of ozone; the main emission sources of ozone precursors being traffic and industry.

The presence of NOx and VOC emissions originate from combustion processes from any kind of heater, cracker, FCCU, gas turbine and boiler. The negative effects of both NOx and VOCs are well known and include breathing problems and acidification of ecosystems. Easily observed effects include reduced visibility and a 'brown haze' over larger cities or industrial areas. For these reasons, many countries and territories have limits for the quantities of NOx and VOCs that may be emitted from combustion sources.

The main emissions from ammonia production plants are NOx, methanol, CO and

CO₂. Although ammonia plants are by no means the largest industrial source of NOx and VOC emissions, they are subject to tightening standards. As a consequence, ammonia production plants are being built with technology to reduce emissions of NOx from reformers and VOCs from CO₂ stacks.

Regulations impacting ammonia plant emissions focus primarily on the primary reformer furnace due to its large heat liberation rate and quantity of combustion products.

Limits and guidance to industry with respect to emissions of pollutants such as NOx are described in the American National Emission Standards for Hazardous Air Pollutants (NESHAPs) and the European Industrial Emissions Directive (IED). Both NESHAPs and the IED use a permitting mechanism to monitor and control.

Under the IED, operators of industrial installations must obtain a permit from the authorities that takes into account the overall environmental performance

of the plant, including emissions, waste generation, raw material usage and many other aspects. The permit conditions the best available techniques (BAT) which are state-of-the-art techniques that can be used to achieve a high level of environmental protection capable of being implemented in the relevant sector under economically and technically viable conditions.

In the US, the federal and state regulations address air emissions on a local area level directly for NOx and secondarily for ozone control depending on attainment of national ambient air quality standards. Site specific or regional air quality concerns from air pollution lead to categorising areas as attainment areas, where national air quality standards are met, and non-attainment areas where national standards have not been achieved. BAT determinations are made in attainment areas and lowest achievable emission rate (LAER) and emissions offsetting are applied in non-attainment areas.

Similar to the EU BAT, the US BAT is the most effective technique to achieve a high level of environmental protection, taking into account the costs and benefits.

Associated emission limits (AEL) have been compiled and are published as BAT-AELs. Chapter III (with Annex V) of the IED sets out special provisions for certain pollutant emissions from combustion plants with a total rated thermal input equal to or greater than 50 MW, irrespective of the type of fuel used.

Emission concentration levels for ammonia plant primary reformer furnaces for new and existing facilities in the USA and the EU are presented in Table 1.



Fig. 1: New process condensate stripper

NOx sources in an ammonia plant

Fuel-bound nitrogen

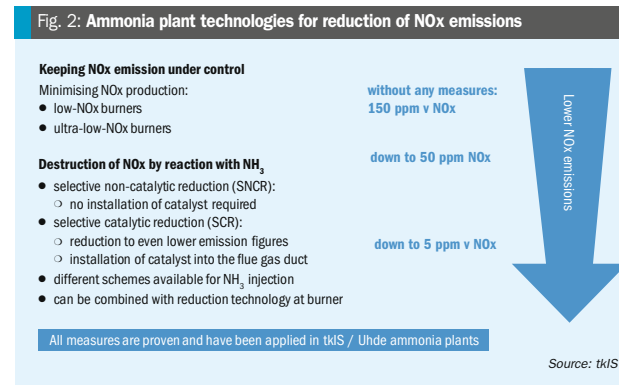
Although NOx is emitted from the primary reformer burners the major precursors to NOx formation are from chemically-bound nitrogen compounds, such as ammonia and MDEA. Conversion of nitrogen fuel components to NOx is significant in high temperature furnaces and burner technology is generally ineffective at reducing NOx from fuel-bound sources. The logical first step in NOx reduction is therefore to eliminate all fuel-bound nitrogen from the fuel system.

With all fuel-bound nitrogen sources eliminated, burner emissions can typically be controlled to 60 to 70 ppm and significantly lower upon introduction of a clean waste gas fuel which, as a diluent, reduces the flame temperature and consequently NOx. Use of waste gas (also referred to as purge gas) in the burners requires experience and expertise on the part of the process licensor and burner supplier.

Case study 1

Older ammonia plants which are not equipped with purge gas or flash gas recovery will generate additional NOx from the combustion of ammonia-containing flash gas or purge gas that is mixed with the fuel.

A study has been carried out by thyssenkrupp Industrial Solutions (tkIS) to reduce the NOx emissions from such an existing ammonia plant. The installation of a scrubbing system was proposed which removes ammonia from the purge and flash gas. The benefits are twofold: Firstly, the production is slightly increased by the



recovered ammonia, and secondly the NOx emission is lowered.

Case study 2

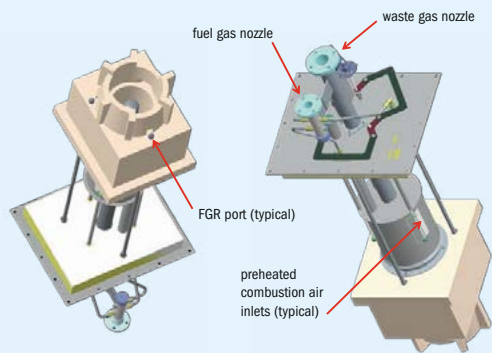
In a recent ammonia plant revamping project, Casale reduced the emissions from an ammonia plant using the following measures:

- process condensate stripping improvement;
- ammonia recovery from synthesis loop LP flash gases.

The original process condensate stripper where LP steam was required for providing reboiler heat and 3 t/h steam was vented to the atmosphere. This system has been replaced with a new medium pressure process condensate stripper (Fig. 1) along with new feed pumps, feed/effluent exchangers and associated system. In this scheme, the steam used for stripping is mixed with process steam going to the primary reformer i.e. there are zero emissions to the atmosphere because the stripped steam is recycled into the process.

The low-pressure flash gas from the ammonia let-down drum and refrigeration off-gas from the flash gas chiller were being used as fuel gas in the primary reformer. In order to recover ammonia from these gases and reduce NOx emissions from the reformer stack (ammonia at flame temperature produces mainly NOx), an ammonia recovery unit has been installed. A new LP flash column, pumps and associated system has been installed to recover ammonia from LP purge gas and recovered ammonia-water is being treated in the existing ammonia recovery unit (ARU) to recover ammonia (approx. 2 t/h).

Fig. 3: Modern low NOx raw gas burner using multiple tips, staged fuel and flue gas recirculation



of combustion technology, it is still higher than the emission levels of 5-10 ppm that are required in certain countries. If regulations required lower NOx levels than burners can achieve SNCR or SCR technologies are available. New methanol and ammonia plants are increasingly being built with an SCR to reduce NOx emissions.

SNCR uses the heat and residence time available in the furnace convection section to reduce NOx using a reductant such as ammonia or proprietary urea solutions. This technology has been tested extensively in boilers but it presents two major obstacles to adoption in primary reformers; 1) it requires a residence time of several seconds at a temperature of approximately 1,000°C and 2) the ammonia slip (unreacted reductant) is higher than with the competing technology using a catalyst (SCR).

SCR technology is commonly acknowledged as the best available control technology (BACT) since it is possible to achieve more than 95% NOx reduction, whereas SNCR technology is only suitable for achieving around 50% NOx reduction. Since ammonia is used for both technologies, the excess amount of ammonia (the amount of unreacted ammonia passing through the system, referred to as ammonia slip) should also be considered. The SCR system can control the ammonia slip to less than 1 ppm, whereas the SNCR system will likely have values between 15 and 20 ppm. In the US, for example, SNCR has not been adopted since the typical ammonia slip permit level for SCR systems is 10 ppmv.

SCR is significantly less expensive when applied to a grass roots project because the costs for increased fan power and increased height of the convection section are available at an incremental cost on a new facility. Application of SCR to an existing facility for all practical purposes requires replacement of the ID fan and a significant increase in height of the convection section; however, many convection sections are completely replaced as part of a capacity increase revamp so these could be incremental costs depending on the scope of the project. SCR catalyst cost has been approximately constant at \$10,000/m³ for many years.

Fig. 4 shows the ambient air mixing skid used with SCR systems in KBR ammonia plants. The skid mixes heated ambient air with ammonia vapour in a ratio of approximately 33:1 to lower the percentage of NH₃ in air to approximately 25% of the lower flammable limit (LFL). The high air ratio mixture provides volume to distribute the



Fig. 4: Ammonia-air mixing skid during construction for a 2,300 t/d ammonia plant.

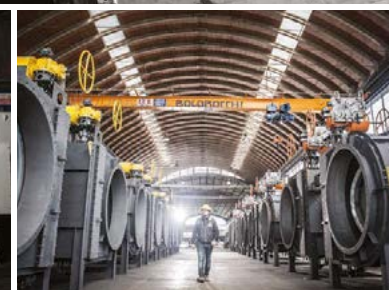
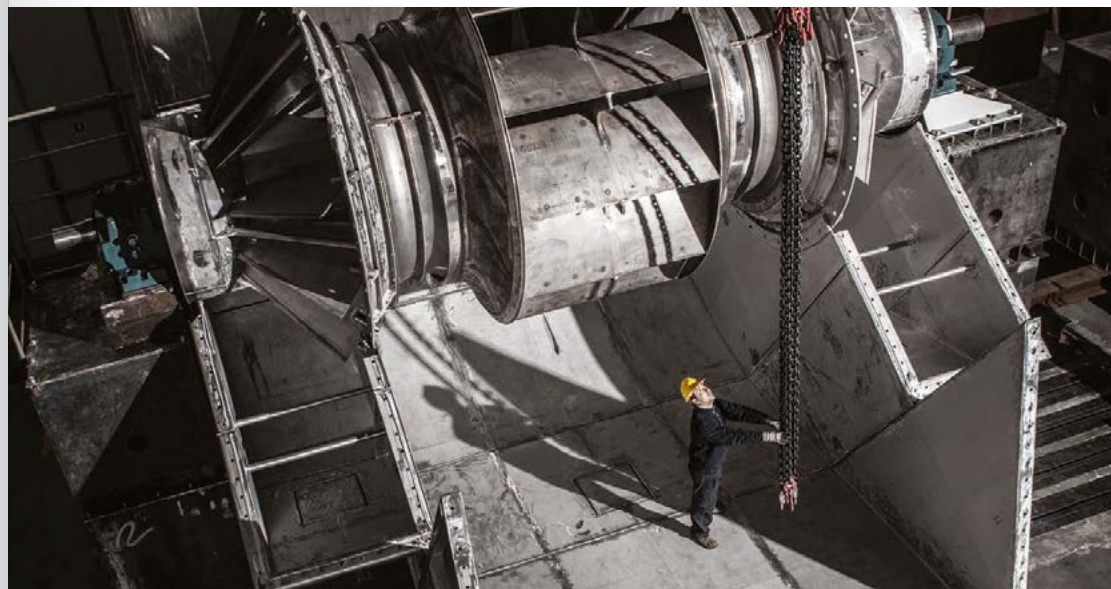
at which the fuel and oxygen mix and combust. This is often achieved by either staged combustion (air staging or fuel staging), in which combustion air or fuel is added in two stages, or by designing the burner so that there is internal flue gas recirculation (IFGR), whereby there is mixing of the fuel gas with flue gas prior to combustion (Fig. 3).

Many older plants, without air preheat systems, were originally supplied with pre-mix burners which typically have higher NOx emissions than the alternative raw gas burner type. The pre-mix burner is a good match for the characteristics of top fired furnaces providing a stiff flame to minimise flame impingement on the tubes.

In KBR's experience, significant improve-

ment in NOx performance is available with modern versions of pre-mix burners but they have not reached the low levels available from the more common raw gas type low NOx burner. As an example, on a recent capacity expansion project new pre-mix burners replaced the original generation pre-mix to allow more air flow and firing. The NOx level achieved was approximately 140 mg/Nm³, whereas new projects with air preheat systems using raw gas burners with fuel staging, flue gas recirculation and waste fuel addition have been able to achieve lower than 60 mg/Nm³.

Although well designed low NOx burners are able to achieve much lower NOx emission levels than earlier generations



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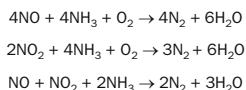
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ammonia throughout the width and length of the convection section cold leg. The skid contains primary and spare blowers, electric heaters and the ammonia metering components. Prior to exiting the skid the ammonia and air goes through a static mixer to achieve a homogeneous composition.

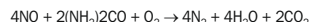
How SCR works

SCR is a relatively simple acid base reaction in which ammonia reduces acidic NOx on the surface of a catalyst. Although this often occurs at temperatures in the range 250°C-450°C, operation as low as 200°C is possible. Fig. 5 shows a simplified depiction of SCR.

Efficiencies of above 90-95% are typical. NOx reduction occurs as the exhaust gas/ammonia mixture passes over a monolithic catalyst. The chemical equations for the reaction with anhydrous or aqueous ammonia are:



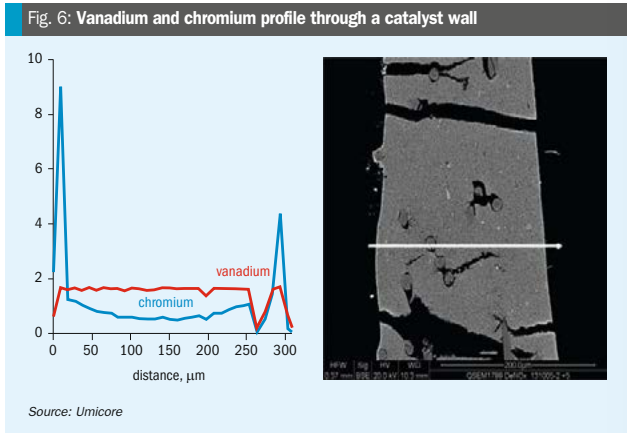
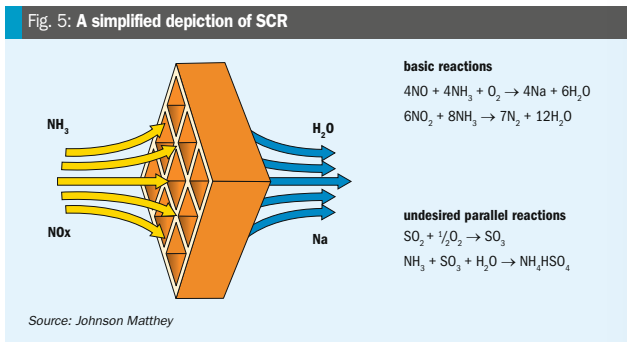
When urea is used as a reductant, the reaction is:



Over the last decades, more and more SCR DeNOx systems have been applied in refinery and chemical plants. For the SCR catalyst, the type of unit has some importance, but when comparing the SCR catalyst service from a typical hydrogen plant to a methanol plant to an ammonia plant, the SCR catalyst service is fairly similar. Combined for all fired heaters, the SCR catalyst will be sandwiched in between tube bundles in the convection section on the downstream side with temperatures preferably in the range from about 250-400°C.

SCR can be easily installed in a new build plant but can be more difficult to install as a retrofit. Since the actual catalyst depth may only be 0.5-1.0 m, there is often space available somewhere within the right temperature window. The main challenge is to fit scaffolding and provide safe work conditions for the crew when working in a confined space since exit strategies should be considered. Also, if the space between tube bundles is too narrow, there may not be enough room for an additional man hole. In new units, space is often reserved and the location of manholes well defined.

SCR catalyst installations in the chemical industry deviate slightly from other



industries since the catalyst life at a minimum should follow the plant turnaround schedule and that once the plant is in operation, it should not shut down before the next turnaround. It also means that there is no chance to correct the path and one chance to do it right; no one wants to shut down an ammonia plant because emissions are too high. One of the technical challenges when operating SCR catalyst in reformers is chrome poisoning of the catalyst. The alloy tubes in the firebox will release chromium oxides to the flue gas, which later will condense in the SCR catalyst downstream due to the high surface area and cooler temperature at the catalyst location. It is therefore required to estimate the SCR catalyst deactivation rate to predict the end-of-run activity so the catalyst potential is high enough to last until the next turnaround. The turnaround cycle is therefore very important for the catalyst

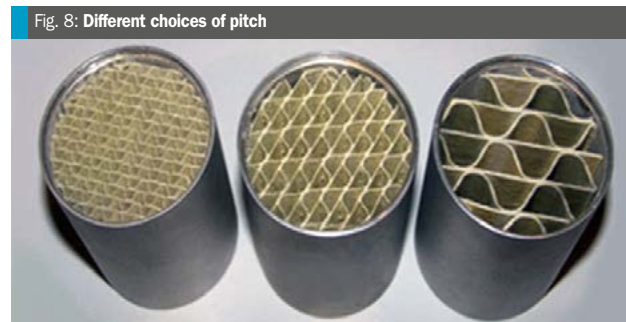
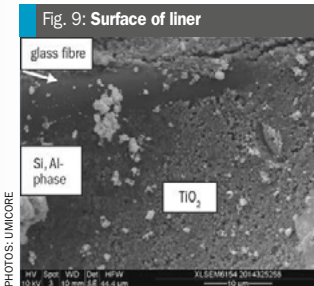
design since more chrome is expected to be released over a five year run vs. a three year run. The catalyst volume (and size) should be adjusted proportionally. A vanadium-based catalyst type is recommended where the active ingredients are homogeneously applied across the entire catalyst wall. Fig. 6 shows the chemical profiles of vanadium and chrome across a catalyst wall. More chrome accumulates on the catalyst surface. If the catalyst supplier has been involved early in the feasibility study or plant design, they can define a catalyst replacement strategy where the catalyst consumption is reduced over the life of the plant considering the accumulation profile of chrome.

Another technical challenge is the possibility for catalyst fouling from particulates. It is often observed that refractory or insulation material comes off the walls upstream of the SCR catalyst and travels



down through the waste heat recovery section until it reaches the catalyst (Fig. 7). It is known to increase back pressure over time and if the resistance is too high, the unit may have to come down for a catalyst cleaning. For the same reason, proper selection of the catalyst channel size should be carried out since larger voids will allow more particulates to pass through the catalyst (Fig. 8). However, a larger void will also decrease the surface area proportionally and hence increase the overall catalyst volume, so a close dialogue with the SCR catalyst vendor is recommended to define the optimal solution.

Apart from the visible effect of plugging, the upstream material is also expected to reduce the catalyst activity by masking the catalyst surface on a smaller scale. Referring to Fig. 9, large areas of a Si, Al-phase is observed in the left part of the image where the upper part of the image contains a glass fibre (from production). The origin of the silica and alumina is expected to come from the refractory or insulation material upstream of the catalyst. A close up of an interface between the Si,Al-phase and TiO₂ (carrier used from production) is shown in Fig. 10. This shows that the porosity normally observed in TiO₂ is significantly

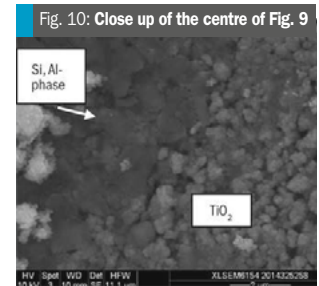


reduced in the part of the sample where the Si,Al-phase is observed. It also means that to maintain a high performance over time, an extremely porous SCR catalyst should be used since it is evident that the catalyst will lose porosity over time, which will influence activity.

DNX catalyst for reformers

Umicore's DNX® catalyst is specifically designed for high DeNOx performance in reformer applications, with extensive experience from close to 100 references. A high level of experience is essential for designing catalyst systems that can tolerate deactivation from chrome poisoning.

For example, Umicore supplied SCR catalyst to an ammonia plant in the USA in 2015. The NOx reduction performance has been excellent along with a low ammonia slip since the catalyst was put in service. One issue for the client has been a slow rise in back pressure over the last few years. This is likely due to loose refractory or insulation that has come free over time and deposited on the face of the catalyst. A vacuum cleaning could alleviate this issue, but this is only necessary if the back pressure is inhibiting performance. As this catalyst bed has also experienced



normal exposure to catalyst poisons such as chrome and is approaching its recommended lifetime, it is better in this case simply to replace with fresh catalyst at the next outage. A catalyst design with a larger channel size has been recommended to combat future issues with back pressure. Continued dialogue with the catalyst vendor will allow for optimisation of the catalyst design, as it is replaced periodically over the life of the unit.

Due to variability in operation, reformers may have SCR catalyst that deactivates at different rates. Pulling samples for laboratory testing is informative in determining remaining catalyst life and can be performed when the unit is offline or also on spent catalyst which has been removed for disposal. This will allow for optimal utilisation of the catalyst potential and possibly a reduction in catalyst requirements. The drawback with this approach is that it requires access to the actual catalyst and unless the unit has an unplanned shutdown no access is available before the planned turnaround. If the catalyst performance has been high during operation – but it is unclear if it is high enough to last another full turnaround cycle, users are often recommended not to dispose of the catalyst before a catalyst analysis is conducted. Based on the chrome accumulation pattern and actual end of run activity, the catalyst may be kept in storage and re-used at another occasion in the future. It may even be possible to utilise a catalyst replacement strategy to minimise the overall catalyst consumption, or simply reuse the catalyst for another run in the future.

SINOx SCR systems

Johnson Matthey (JM) has manufactured extruded SINOx® SCR catalysts since 1987 to control air pollution from

Fig. 11: SINOx SCR catalyst

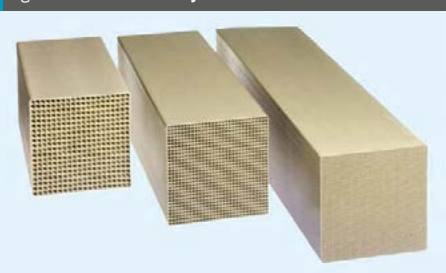


PHOTO: JOHNSON MATTHEY

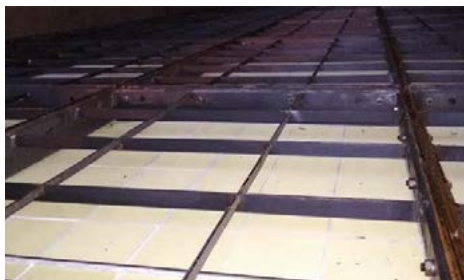


PHOTO: JOHNSON MATTHEY

Fig. 12: SINOx catalyst installed in flue gas duct.

industries and combustion sources worldwide. JM's homogeneous extruded honeycomb SCR catalysts consist entirely of catalytically active materials such as oxides of titanium, vanadium and tungsten, making them more active than coated SCR catalysts.

Extruded SINOx honeycomb SCR catalyst (Fig. 11) can be produced in a wide variety of cell densities to accommodate a range of operating conditions and achieve the desired NOx reduction at the lowest possible pressure drop.

SINOx honeycomb SCR catalyst is supplied pre-installed in element frames or modules for durability and easy handling. The SCR catalyst elements are installed into a SCR system housing and are sealed together to eliminate bypassing and maximize NOx reduction.

In an ammonia plant, SINOx is normally installed in the flue gas duct (see Fig. 12) upstream of the feed pre-heat coils and/or air-preheater and can achieve NOx emission levels in the range 5 to 10ppm.

VOC emissions - methanol

Methanol is the main VOC emitted from ammonia production plants. It is formed as a by-product across the high temperature shift (HTS) and low temperature shift (LTS) catalysts. In a conventional ammonia plant it is separated from the synthesis gas by the CO₂ removal unit and is vented to the atmosphere (or sent to a CO₂ consumer like a urea plant) together with the CO₂ stream (for further information see *Nitrogen+Syngas* no. 332 pp.36-45).

There are four options for reducing methanol emissions:

- reducing the methanol formation across the shift catalyst, e.g. by using low-methanol LT shift catalyst;

- removal or decomposition within the ammonia plant;
- removal or decomposition of methanol directly at the emission point;
- a combination of the above schemes.

Reducing methanol formation across the shift catalyst

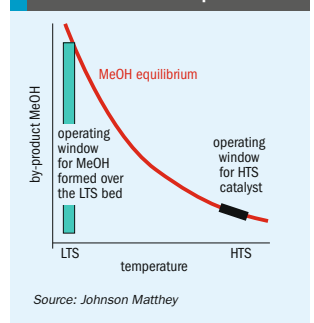
The chemistry and operating conditions of the HTS catalyst is such that methanol formation is normally limited by equilibrium with little flexibility for reduction.

The chemistry and operating conditions of the LTS catalyst is such that methanol formation is kinetically limited. The activity of the LTS catalyst with regard to methanol formation declines over time and hence the amount of methanol formed across the LTS decreases with time.

A selective LTS catalyst is specially formulated to reduce the methanol formation. JM's selective LTS, KATALCO™ 83-3X can, for example, reduce methanol formation by about 90% compared to conventional LTS catalysts.

Fig. 13 shows by-product methanol production as a function of temperature.

Fig. 13: By-product methanol as a function of temperature



Source: Johnson Matthey

Removal or decomposition within the ammonia plant

Several possibilities exist for removal or decomposition within an ammonia plant

Reducing the temperature of the process gas separator allows more methanol to leave with the process condensate, hence less is emitted to atmosphere in the CO₂ stack. The condensate is sent to a process condensate stripper in which the vast majority of the methanol is recovered as ammonia plant feedstock.

A water scrubber located upstream of the CO₂ removal unit can also be used to reduce methanol emissions to atmosphere, with the condensate again treated as described above.

Removal or decomposition of methanol at point of emission

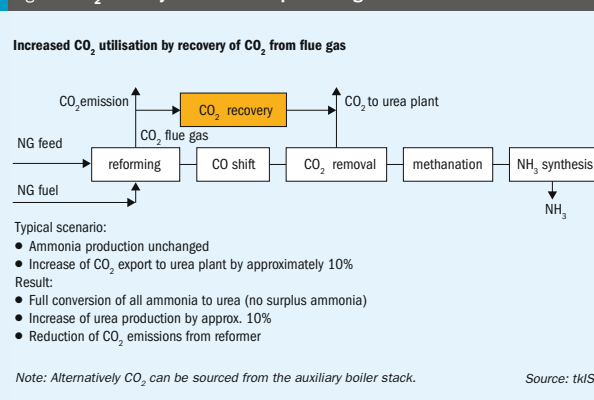
Even lower VOC emissions are possible if methanol is removed from the vent stream by catalytic or thermal oxidation.

When the stream to be vented is at low pressure, monolithic catalyst coated with a thin layer of Pt or Pd are used to minimize pressure drop. When the CO₂ is at pressure, catalyst pellets are more economic.

Full conversion by thermal oxidation takes place at higher temperatures than required for catalytic oxidation. Heat can be provided externally or by internal combustion (e.g. in a recuperative system).

Depending on site circumstances, a combination of schemes may be appropriate. However, in all cases, the use of KATALCO 83-3X provides a robust and reliable bedrock for minimising methanol emissions without incurring unnecessary losses of energy due to high and increasing pressure drop and by unplanned catalyst replacement.

Fig. 14: CO₂ recovery from ammonia plant flue gas



Reduction of CO emissions

The primary reformer is also a source of CO emission. CO is formed when the air to fuel mass ratio deviates from the normal range; about 18 for natural gas. When the ratio approaches stoichiometric, CO is formed from lack of oxidant (due to incomplete combustion), but when the ratio is high, CO is also formed from quenching which prevents reaching the proper temperature for complete oxidation. If the air to fuel ratio is correct for the fuel, and CO is exiting the radiant section of the primary reformer then typically a burner issue exists. CO is most frequently encountered in supplemental burner systems, located downstream of the radiant section, where it is more difficult to know the local air to fuel ratio due to more complicated geometry and stream mixing. Measurement and control of the air stream flows to supplemental burner systems is necessary to ensure a proper air to fuel ratio. Verification of mixing and determination of local air to fuel ratios throughout the mixing zone can be evaluated using CFD modelling.

Modern burners and proper fuel gas/air ratio control can easily limit the CO emission to stay within the statutory limits (Note 1). For example, CO emission figures down to 40 ppmv have been guaranteed by tkIS for new plants.

Reduction of CO₂ emissions

The primary reformer is also a source of CO₂ emission. It depends on the particular case whether there are more CO₂ emission sources linked to the ammonia plant

operation. Basically all carbon in the natural gas which enters the plant as feed gas leaves the process via the CO₂ removal unit (downstream of the reforming unit). If the ammonia plant has an associated urea plant the CO₂ stream is directed to the urea plant. In other cases, it is usually vented and represents a major source of CO₂ release.

Generally, all measures which aim at improving the energy efficiency of the plants in the end also lead to savings in CO₂ emission, either by savings in fuel or by savings in feed gas.

Also the electric power used by the ammonia process (even if rather small in the conventional process in comparison to gas) can also be laden with a CO₂ emission burden from its production.

Measures for lowering the CO₂ emissions of ammonia plants include:

- ammonia production from renewable sources;
- recovery of CO₂ for use as feedstock for other processes.

Ammonia production from renewable sources

Production of ammonia without any emissions of CO₂ is possible. Both ingredients, hydrogen and nitrogen, can be produced without any carbon input. To do so, hydrogen must be produced by the electrolysis of water instead of steam reforming of natural gas (for further information see *Nitrogen+Syngas* no. 354 pp.44-53). Of course such a process is only CO₂ free if the electricity employed is also generated without CO₂ emissions, which is only possible if renewable sources (e.g. wind, solar, hydro)

are used. Also all machines in the process (e.g. synthesis gas compressor) have to be driven by electric motors. The economics of this process are strongly dependent on the price of the electric power used. Currently the price for renewable power fluctuates widely, but sometimes there is more power available than consumed in which case it is available at a very low price.

It is also possible to combine hydrogen from water electrolysis with hydrogen from steam reforming and thus achieve a partial reduction of CO₂ emissions. Combining the two feed streams can provide a useful solution to balance and minimise the impact on ammonia production of what is often a fluctuating supply of renewable power.

Recovery of CO₂ for use as feedstock for other processes

A positive feature of the conventional gas-based ammonia process is the fact that it can generate a highly pure CO₂ stream which can be used for other processes. This is widely done for urea production from ammonia and CO₂, but the CO₂ stream can also be used for other purposes, or it can be sequestered. In contrast to the case of CO₂ occurring in a flue gas (e.g. from fossil power stations), this CO₂ stream is already pure and does not require any further separation steps prior to sequestration.

Another option for reducing the CO₂ emissions of an ammonia/urea complex is to extract the CO₂ from reformer or boiler flue gas and use it to increase the urea production as illustrated in Fig. 14).

Commercial processes are available for the separation of CO₂ from flue gas. They operate in a similar way to the process for CO₂ removal from synthesis gas but the solvents are designed to withstand the presence of NOx, SOx and O₂ in the flue gas.

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NAMAX – optimised turbomachinery for greater efficiency

MAN Energy Solutions has introduced a new, comprehensively optimised, turbomachinery concept named NAMAX that provides a new level of flexibility and efficiency for nitric acid production. **Dr Stefan Ubben** discusses the benefits of this technological leap which provides significant improvements to fertilizer production.



PHOTO: MAN ENERGY SOLUTIONS

NAMAX: optimised modular turbomachinery for nitric acid production.

In today's fertilizer industry, production processes have been well balanced over the years in terms of efficiency, reliability and output. With substantial power consumption, it is above all the efficiency of such processes and machinery trains that is an economic requirement of producers. Significant improvements have become quite rare here. As with all well-established technology, the maximum efficiency of associated production processes has been achieved in most cases.

Against this background, a newly established compression technology from MAN Energy Solutions now allows a rearrangement of machinery trains for the production of nitric acid (HNO₃). Redefining standards within the dual pressure process, this technological leap has led to potential energy savings of several percent for the production of this very basic feedstock for the fertilizer industry. Due to a modular design

with a basic configuration and additional engineered options, the individually tailored solutions are available to owners and operators quicker and at lower cost.

Nitric acid production

Nitric acid is a basic commodity, mostly used in fertilizers and pharmaceuticals, as well as explosives. As the world's population is growing and with the increasing prosperity in the newly industrialised countries, the demand for nitric acid is continuously rising.

Today, nitric acid is manufactured in a multi-step procedure where ammonia is converted to nitric acid (see Fig. 1). In the first step in this reaction, gaseous ammonia (NH₃) and compressed air are mixed; the ammonia-air mixture is fed into the reactor with a platinum-rhodium metal gauze which serves as a catalyst. The ammonia and air react to form nitrogen

monoxide (NO) gas – a strongly exothermic reaction generating a useful heat source which increases the gas temperature to approximately 800 to 900°C.

In the next step, the hot nitrogen oxide gas is passed through a heat exchanger, followed by another oxidising tower, where it is oxidised to produce nitrogen dioxide (NO₂) at approximately 50°C.

In the third step, the nitrogen dioxide is passed through an absorption tower where it is combined with water to obtain nitric acid.

Modern nitric acid plants are designed to carry out these three process steps via a mono pressure process (constant operating pressure of 4-6 bar abs. or 8-12 bar abs., respectively) or a dual pressure process where the ammonia is combusted at 4-6 bar abs., while 10-12 bar abs. is typical for nitric acid absorption.

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A diamond jubilee

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is the core of these nitric acid plants and a major factor in plant profitability. MAN Energy Solutions offers in-line and gear-type solutions for both mono pressure and dual pressure processes. Starting with the first nitric acid turbomachinery train, made by its predecessor "Gutehoffnungshütte" (GHH) in 1963, MAN Energy Solutions has gained more than 50 years of experience in engineering and constructing turbomachinery for nitric acid production. Today, the company is the leading and largest supplier of machinery trains for the nitric acid dual pressure process. More than 500 turbomachinery casings are used in approximately 180 nitric acid plants worldwide, including the world's largest plant in Porsgrunn, Norway, with a daily output of 2,000 tonnes of nitric acid.

Current compressor train design

The dual pressure process combines the advantages of low pressure at the ammonia converter stage and high pressure at the absorption section, enabling higher plant capacities, with benefits in terms of opex and capex. The turbomachinery train design for dual pressure nitric acid plants above 600 t/d – approximately 80% of all new plants are created based on this design – is an in-line machine concept, consisting of:

- A steam turbine as driver; the exothermal process generates heat which will be converted into steam, driving the steam turbine.
- A centrifugal nitrous oxide gas compressor, for compressing the NO gas from ammonia combustion from 4-6 bar abs. to 10-12 bar abs.
- An axial air compressor, which compresses atmospheric air to 4-6 bar abs.
- An axial tail gas expander, powered by reactor waste gas, which is increasingly becoming the main compressor drive unit in modern nitric acid production processes.
- A motor/generator can be added to the machinery train in case the steam turbine and the expander generate more energy than the compressors need.

Fig. 2 shows a typical turbomachinery train with in-line machine concept for dual pressure nitric acid plants and Fig. 3 shows a turbomachinery train for a 900 t/d nitric acid plant

The four turbomachines of the in-line train are typically arranged on two separate

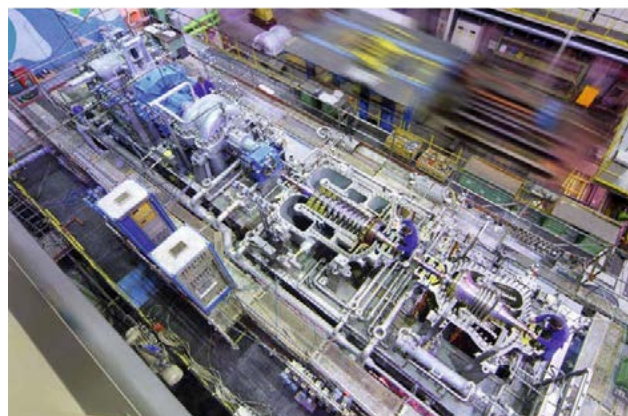
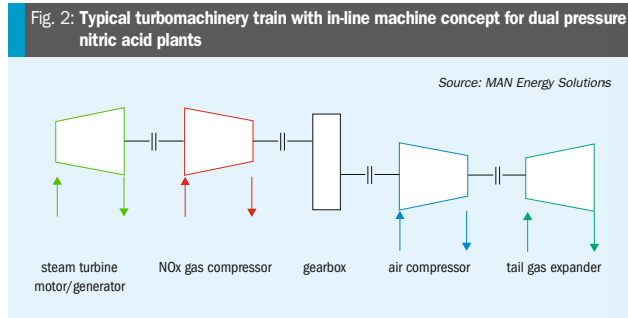
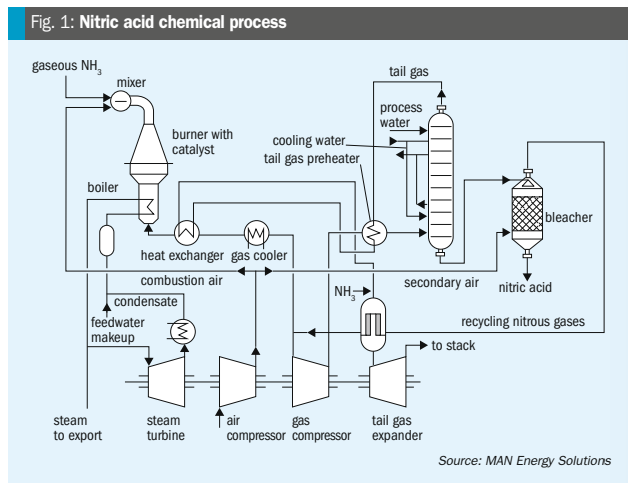


Fig. 3: Turbomachinery train for a 900 t/d nitric acid plant

Source: MAN Energy Solutions

Source: MAN Energy Solutions

PHOTO: MAN ENERGY SOLUTIONS

base frames: The steam turbine and the NO gas compressor are arranged on one frame, while the second frame incorporates the axial flow compressor and tail gas expander. Both train elements have different rotational speeds and are therefore connected by an intermediate gear. The reason for this is that efficient operation of the radial compressor at a low volume flow of the NO gas and a pressure ratio of around 3 is only possible at high speed, while the maximum possible speed of the axial compressor, which compresses a significantly larger volume of air, is significantly lower here.

Due to the requirement for a quick-running and slow-running train part, it has not yet been possible to develop alternative train concepts. This is why the continued technological development of the turbomachinery train primarily aims to optimise the individual core machines; however, the scope for their optimisation is relatively small.

Efforts on the part of turbomachinery manufacturers to standardise machinery trains as a whole have previously failed due to the complexity of customer-specific requirements which always necessitates custom train configurations.

NAMAX – the new modular nitric acid train package

With the development of the new modular nitric acid train package NAMAX, MAN Energy Solutions has taken a major step forward in terms of development. The result combines the constant efforts to reduce the use of natural resources during the manufacture, set-up and operation

of nitric acid compressor trains, with the aim of being able to offer customers at the same time plant components optimally tailored to the individual production process.

NAMAX is a modular system for turbomachinery and package elements from which all configurations of a nitric acid compressor train can be derived for sometimes very different customer requirements. As a result, nitric acid trains with improved performance can be assembled in less time and at lower cost.

Proven turbomachinery – optimised for higher train speed

A modular and flexible train concept is only possible when all turbomachinery in the train can be operated efficiently at the same speed. Especially with regards to an optimised axial flow compressor, this meant the requirement for a speed increase of at least 30%. MAN Energy Solutions has therefore developed a new axial blading generation in collaboration with MTU Aero Engines (Munich). The project name MAX1 stands for a concept which is the only one of its kind – a hybrid axial flow compressor combining the advantages of conventional industrial compressors, such as operating range, efficiency and robustness, with the benefits of gas turbine compressors, a higher power density, thus higher stage pressure ratios.

By increasing the speed by a third, it was possible to significantly reduce the total weight (minus 25%) and total length of the axial compressor (minus 30%). The machine is extremely resistant to

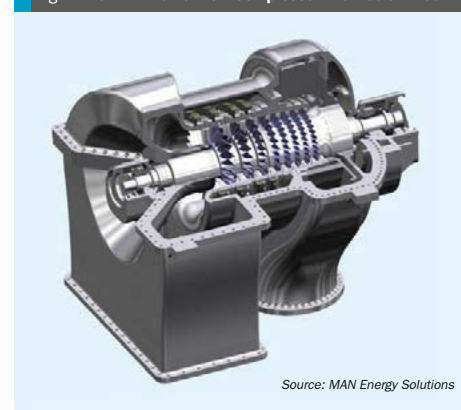
any blade vibration and is being called by specialists even surge robust. Additionally, MAX1 features an improved operating range and increased efficiency. This new axial blading generation is already being used in 19 MAX1 axial-radial compressors in the field, continuously operating in the air separation industry. MAX1 technology (see Fig. 4) has also been launched successfully in air compressors for styrene monomer plants, in wind tunnel blowers and in some projects in the iron and steel industry, where it will serve as blast furnace axial flow compressors.

The use of MAX1 technology in the NAMAX train now enables a fundamentally important change to be made – equalising the speeds of the train parts. This increase in train speed also benefits the axial expander (Fig. 5), which can now be manufactured up to two sizes smaller. The speed increase additionally benefits aerodynamics, with the result that the expander, which is increasingly becoming the main drive for the train in modern processes, makes a significant higher contribution to increasing efficiency.

The state-of-the-art design of the steam turbine fits perfectly with the modern NAMAX train approach. An inlet module with single control valves ensures reduced steam consumption when the nitric acid production process is initiated. The layout with integrated bearing housings and pendulum supports enable the turbine to have an extremely compact design which is up to 25% shorter than previous machines.

As for the axial expander, a standard casing concept has also been developed for the

Fig. 4: AG-MAX1 axial flow compressor with radial inlet



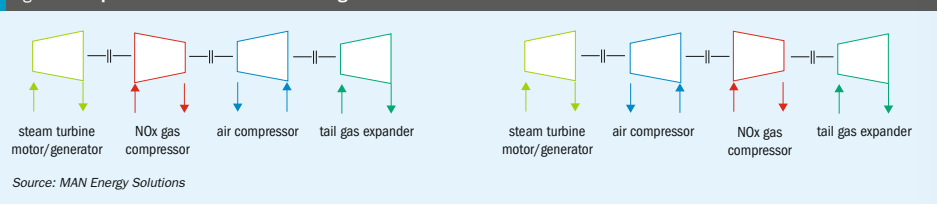
Source: MAN Energy Solutions

Fig. 5: Axial expander, optimised for higher train speed



Source: MAN Energy Solutions

Fig. 6: Example of flexible NAMAX train configurations



NO gas compressor, which makes it possible to fully modularise the compressor package. In addition, the design for NO gas cut-off was further optimised. Inside the machine, by contrast, MAN Energy Solutions employs technology which has been successfully used in more than 180 former orders.

Flexible train configuration with no intermediate gear

The higher speed of the axial flow compressor now offers a wide range of design options for arranging the turbomachines in the train (Fig. 6). Since all machines can be operated at the same speed, the intermediate gear, the related capex, frictional losses and also maintenance costs can all be omitted. With the exception of the tail gas expander, which can be decoupled from the process at times and therefore needs to be placed at one end of the train; all other units can be fitted in any position in the train. Depending on customer requirements, the compressors in the centre of the train can switch positions if the steam turbine is positioned at the second end of the train. With regard to commissioning, the train configuration according to Fig. 6 (right) offers the greatest savings.

Modularised units with smaller footprint

Each core machine has a separate base frame in the basic configuration. The core machines, including the supply lines and cabling, are assembled on this individual base frame as stand-alone units, are mechanically and/or thermodynamically tested, are transported to the installation site and are finally placed on a steel or concrete foundation on-site. As a result, separate transport frames are unnecessary. Compared to configurations with two or more machines on one base frame, handling of the train elements, which have been made smaller, is now much simpler during

Fig. 7: Comparison of conventional train configuration (bottom) with NAMAX (top)

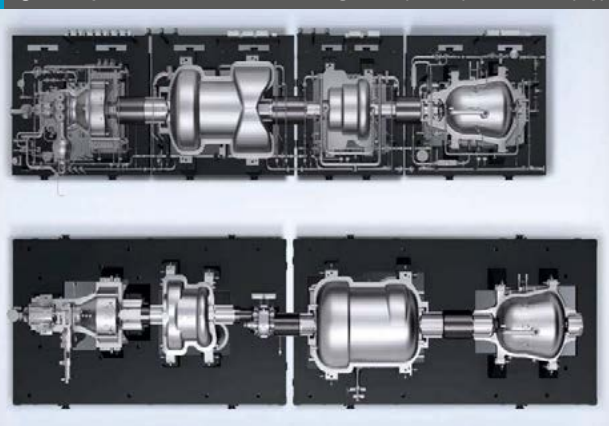


Fig. 8: NAMAX train package



transport and installation. This reduces the required crane capacity, among other aspects. The footprint of a NAMAX train is now significantly smaller thanks to the omission of an intermediate gear, the reduced size of axial flow compressor, axial expander and steam turbine, and the optimised arrangement of the package elements. All in all, trains are up to 15% shorter and 30% narrower – a valuable reduction in building

volume (Fig. 7). This makes the NAMAX concept also suitable as a replacement for existing trains for revamps.

The modularity of the train concept also makes it possible for a motor/generator to be added to the train and for the tail gas expander to be designed as a hot gas expander. In addition, the individual basic frames can also be combined to form a 2x2 frame.

Basic configuration and engineered options

In addition to the core machines, the package (Fig. 8) as a whole has also been subject to the modular assembly approach. This starts with a pre-assembled basic configuration for a nitric acid train. Furthermore, there are predefined “engineered options” which the clients can select according to their specifications, e.g. additional instrumentation, air filter, integrated oil system, etc.

Faster set up – faster commissioning

Such a modular design is also beneficial as regards lead-time. The machines can be set up regardless of the position in the train and do not have to wait on each other, as is the case with clustered base frames.

Commissioning can be significantly accelerated. The steam turbine can be operated in solo run as soon as it is set up; after the axial flow compressor is positioned, its surge limit can be recorded straight away. With the NO gas compressor positioned,

the surge limit of the centrifugal compressor can be directly determined without additional temporary piping. In parallel to these commissioning tasks, the machines which are not yet in operation can be set up on the base. This means that operators save several weeks of set-up time.

Conclusion

Although most production steps in the fertilizer industry have almost reached their theoretical limits, optimised concepts such as NAMAX still enable significant step changes to be made in terms of efficiency. A modular approach, together with the next generation of machinery, combines to result in significant gains in efficiency and flexibility that are quite rare in today’s industry.

For nitric acid production from 400 t/d to more than 3,000 t/d, the NAMAX concept provides additional advantages:

- Flexible train arrangement without intermediate gear in a basic configuration or with engineered options
- Improved robustness in terms of the availability of crucial machinery

- A reduced footprint, which makes it possible to save space during production, but also to facilitate transportation
- Accelerated set-up and commissioning procedure, saving time and money during installation

The first NAMAX train is currently under construction for thyssenkrupp Industrial Solutions (tkIS) for a new nitric acid plant in Poland. thyssenkrupp Industrial Solutions is an innovative world lead for planning, construction and services in the field of industrial plants and systems with many years’ experience in the design and construction of nitric acid plants. The delivery of this NAMAX will be in April 2019. This project marks the successful market entry of the enhanced concept and proves that NAMAX is far beyond the development or testing phase.

Probably one of the most impressive improvements in terms of fertilizer production efficiency, the NAMAX concept marks a long-awaited improvement in the production of one of the world’s most important feedstocks.

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- Grant Roberts, *Chief Agronomist, Asia, Yara Asia*
- Thadde Hein, *Group CEO, Myanmar Awba Group*
- Sukanto, *Senior Vice President, Corporate Research, PT Pupuk Indonesia (Persero)*
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Better nitric acid plant start-ups

While the problem of visible NOx emissions has been solved for almost all nitric plants in steady state, normal operation, the situation for the majority of plants when they are starting up is very different. thyssenkrupp Industrial Solutions, Hindustan Platinum and Espindesa focus on what can be done to achieve better colourless start-ups.

It is the bane of the nitric acid producer that nitrogen dioxide (NO₂) is not a colourless gas. In the past a nitric acid plant in operation could easily be identified by the reddish-brown plume of tail gas emerging from its stack with its burden of NOx (NO and NO₂). Technological improvements and increasingly stringent legislation driven by concerns about the adverse effects of NOx on human health and the environment have ensured a steady reduction in NOx emissions over the years. Most nitric acid plants nowadays are equipped with a NOx abatement system which reduces the NOx concentration in the tail gas to below the limit of stack plume visibility of 20 ppmv to 60 ppmv NO₂, the concentration depending on the diameter of the stack and the weather conditions. The most widely used technology is selective catalyst reduction with ammonia. A NOx plant stack concentration of 20 ppmv is no longer a technological challenge for such systems. Using the latest technology, NOx can be reduced to as low as 1 ppmv and almost all of the nitrous oxide (N₂O) can also be reduced¹.

The problem of visible NOx emissions has thus been solved for almost all nitric plants in steady state, normal operation. However, the situation for the overwhelming majority of plants when they are starting up is very different. The NOx abatement equipment often cannot be put into operation before the first NOx appears in the tail gas, and stack NOx concentrations can rise up to several thousand ppm, making the stack plume highly visible. Irrespective of the benefits conferred on society by the industrial production of nitric acid there is little public acceptance for facilities which advertise their presence in such an obvi-

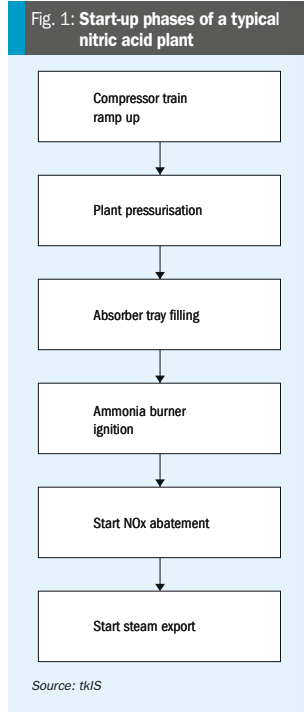
ous way. Also, regulators have increasingly been turning their attention to non-steady state operation. In 2012 the US Environmental Protection Agency (EPA) introduced a NOx emission limit for new plants of 0.5 lb NOx as NO₂/t nitric acid produced (~40 ppmv NOx) as a moving average over the previous 30 days of operation. A novelty is that the limit applies at all times, including periods of start-up or shutdown, and periods of malfunction². Compared with the previous limit of 3 lb NOx as NO₂/t nitric acid (~230 ppmv) for normal operation only, this is a strict limit indeed. Depending on the duration of a normal start-up and the peak levels of NOx emissions that occur, the inventory of NOx emitted during this period can correspond to several hours or a few days' worth of normal operation at the EPA 0.5 lb NOx/t of nitric acid limit. To compensate, the NOx abatement system must be designed to perform far below the required mean value, and operational flexibility is restricted since the plant operator cannot tolerate too many start-ups within a short space of time without running the risk of exceeding the moving average limit. There is thus a great need to improve plant emissions during start-up.

To address this need it is necessary to have a detailed understanding of what goes on during a normal start-up.

thyssenkrupp Industrial Solutions' EnviNOx® system

A normal start-up

The following discussion applies to a dual pressure plant although the procedure is essentially the same for a mono-pressure plant. The start-up can be divided into a number of phases as shown in Fig. 1. To



aid understanding the reader is referred to the simplified dual pressure plant flowsheet in Fig. 2.

Starting with the plant at atmospheric pressure the compressor train is started up and the process piping and equipment pressurised with air from the atmosphere. Typically the pressure at the ammonia

Fig. 2: Typical dual pressure nitric acid plant flowsheet (simplified)

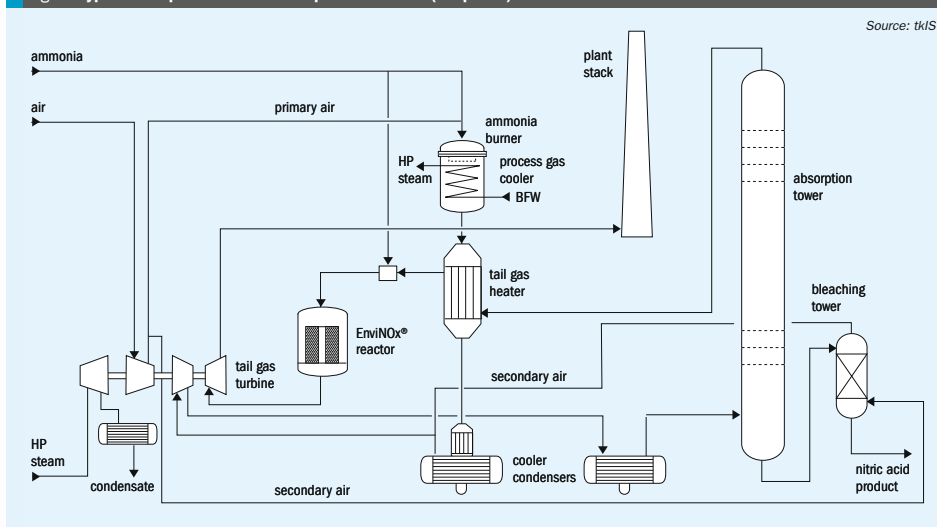
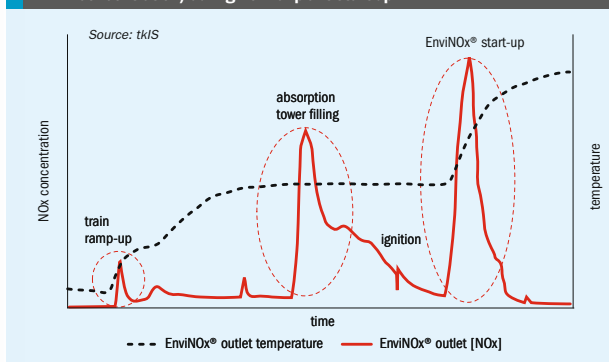


Fig. 3: Temperature and NOx concentration at EnviNOx® reactor outlet (= stack concentration) during normal plant start-up



burner will be raised to about 2-2.5 barg while the pressure at the inlet of the absorption tower is 8-8.5 barg. This latter pressure is a compromise. A high pressure is required for good absorption performance, but the higher the pressure the smaller the volume flow, and the closer the trays of the absorption tower are to the conditions which allow weeping. A further limit to increasing the pressure is typically the small margin between the operating point of the air compressor and its surge protection line. The maximum available air

flow during plant pressurisation is usually limited by the capacity of the steam turbine or electric motor driver, the tail gas turbine delivering little power as the air flowing to it is much cooler than the tail gas during normal operation.

The next step is to fill the trays of the absorption tower with process water and nitric acid from the previous period of operation. This process can take one to two hours. On completion, the ammonia burner is ignited and the production of nitric acid commences. It should be noted that at this

stage the tail gas NOx abatement system (an EnviNOx® reactor), is not yet in operation. Typically there are two interlocks which may prevent the NOx abatement unit from being supplied with ammonia: the temperature of the NOx abatement unit must exceed a certain temperature, typically 180-200°C, and the temperature of the gas in the plant stack must exceed typically 80°C. Both interlocks are aimed at eliminating the conditions which could permit the formation of solid ammonium nitrate from the NOx and water vapour in the tail gas and the ammonia supplied to the NOx abatement system. Often the first interlock does not pose a problem: provided the pressure of the start-up steam supplied to the process gas cooler is sufficiently high, the air heated up in its passage through the process gas cooler will transfer sufficient heat in the final tail gas heater to the air entering the EnviNOx® reactor that the interlock criterion is met. However, the temperature in the plant stack is, as a rule, too low (20-40°C) to meet the second interlock criterion.

The temperature of the tail gas in the stack only rises above the interlock setting of 80°C about thirty minutes to two hours after ignition of the ammonia burner, leading to significant NOx emissions.

How significant these NOx emissions can be is illustrated in Fig. 3. This shows

Fig. 4: Normal and emission optimised absorption tower filling patterns

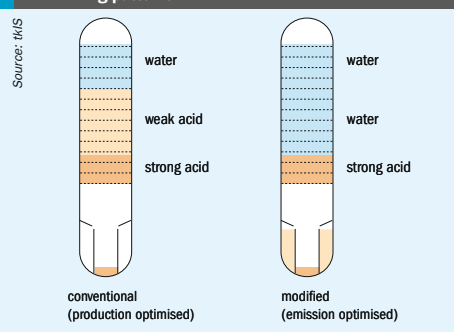
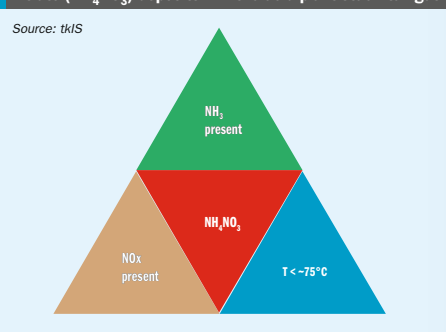


Fig. 5: Conditions for the formation of solid ammonium nitrate (NH_4NO_3) deposits in nitric acid plant stack tail gas



actual plant data taken from a recently commissioned thyssenkrupp Industrial Solutions dual pressure nitric acid plant, but is typical of most nitric acid plants with a non-optimised start-up procedure.

The first NOx emission peak occurs when the compressor train is started up and the plant is purged with air, driving out any NOx-containing gases left over from the end of the previous operation period. The next major NOx emission is caused by the filling of the lower trays of the absorption tower with unbleached nitric acid from the sump of the tower. In effect, the absorption tower becomes a very large bleaching tower, stripping out the $\text{NO}_2/\text{N}_2\text{O}_4$ dissolved in the nitric acid. Finally, the ignition of the ammonia burner massively increases the concentration of NOx in the plant resulting in the largest NOx peak and the brownest stack plume of all. The sharp rise in NOx emissions is ended mainly by the start-up of the EnviNOx® reactor after the tail gas temperature in the plant stack has passed the interlock value of 80°C sometime after the ammonia burner has been ignited. Improved absorption tower performance as the plant pressure rises plays a secondary role.

Improvements for reduced start-up NOx emissions

Absorption

The sump of the absorption tower in a thyssenkrupp Industrial Solutions nitric acid plant has two compartments which segregate the acid dumped from the trays at plant shutdown into two concentration zones. At the next start-up of the acid with the higher concentration is pumped onto the lower trays, while the more dilute acid

is pumped onto trays higher up in the tower. The uppermost trays are filled with water. The intention is to approximate the normal concentration profile of the absorption tower in order to reach stable operating conditions in the tower as soon as possible after ignition.

A reduction in start-up NOx emissions due to stripping of dissolved $\text{NO}_2/\text{N}_2\text{O}_4$ from the unbleached acid pumped to the lowest trays can be obtained if the more dilute acid is left in its compartment and the corresponding trays are filled with water instead. The small price to pay is the longer time than needed to establish the normal operating concentration profile in the absorption tower after ammonia burner ignition. Fig. 4 illustrates the two filling possibilities.

It is not recommended to fill the absorption tower entirely with water, although this would lead to further reductions in start-up emissions, because of the risk of formation of ammonium nitrite in solution during the initial stages of ammonia burner ignition. In the nitric acid industry, explosions, including at least one which has led to loss of containment, are known to have occurred during start-up due to the rapid decomposition of ammonium nitrite, which is stable only in alkaline solution. For this reason all thyssenkrupp Industrial Solutions nitric acid plants are designed to be started up without the risk of alkaline conditions arising.

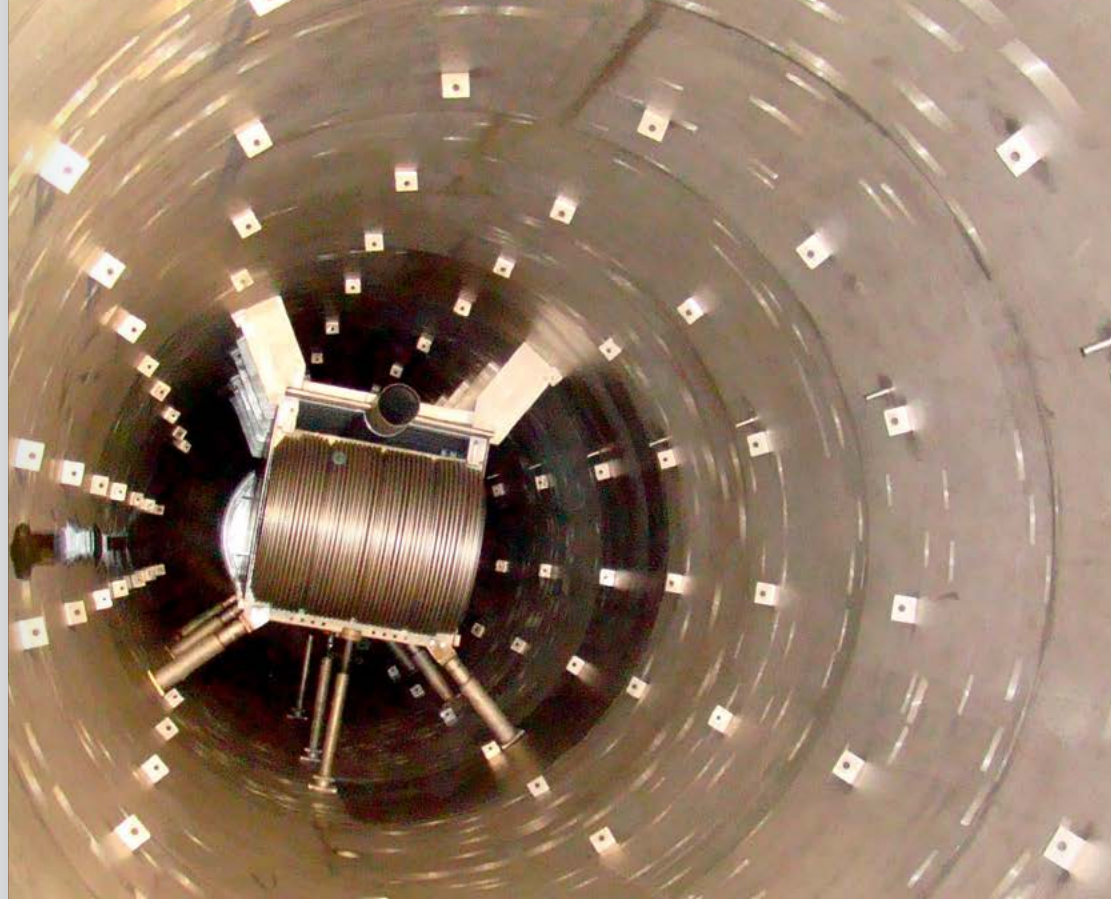
Tail gas NOx abatement

If ammonia could be supplied to the EnviNOx® reactor before the ammonia burner has been ignited, a substantial reduction of start-up NOx emissions could be achieved.

While the EnviNOx® reactor temperature usually rises to the required minimum operating temperature soon enough, the tail gas in the plant stack remains in the temperature range at which ammonium nitrate formation is possible, until after ignition of the ammonia burner. For ammonium nitrate to form, three conditions must be met at the same time, as illustrated in Fig. 5. All three conditions in the outer triangles must be met for NH_4NO_3 to form. This is valid for concentrations of NH_3 up to 5 ppmv and NOx up to 400 ppmv. Higher concentrations increase the temperature limit.

Customarily it is assumed that both NOx and ammonia are always present, and the temperature of the tail gas in the stack is used to decide whether it is permissible to supply ammonia to the tail gas NOx abatement system. Thanks in part to their high adsorption capacity, the catalysts employed in thyssenkrupp Industrial Solutions' EnviNOx® NOx and N_2O abatement systems have the special property that ammonia slip occurs only at very high excess ammonia rates. Thus with careful operation of the EnviNOx® reactor no ammonia appears in the stack gas and ammonium nitrate formation is impossible. Ammonia can therefore be supplied to the EnviNOx® reactor during start-up without regard for the tail gas temperature in the stack. The resulting improved start-up sequence is as in Fig. 6, with the EnviNOx® system being started up before the absorption tower is filled instead of after the ignition of the ammonia burner.

The plant which supplied the emissions data for the conventional start-up shown in Fig. 3 was started up according to the improved sequence of Fig. 6. The resulting



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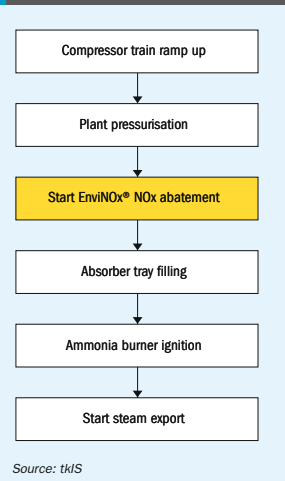
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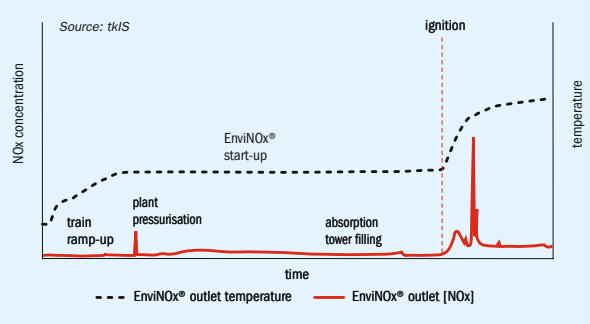
Fig. 6: Start-up phases of a nitric acid plant start-up with EnviNOx® system and low start-up emissions



emissions profile is shown in Fig. 7. The NOx concentration peak after ignition was caused by a brief interruption of the supply of ammonia to the EnviNOx® reactor. Neglecting this one-off spike, the stack NOx concentration averaged less than 10 ppmv, the stack plume was invisible at all times and the total mass of NOx emitted during the improved start-up was only about 10% of the quantity emitted during the normal start-up of Fig. 3. A sensitive analyser was used to monitor ammonia downstream of the EnviNOx® reactor continuously; none was detected.

As these results show, the start-up NOx emissions of nitric acid plants equipped with an EnviNOx® NOx and N₂O abatement system can be greatly reduced compared with those seen in conventional start-ups. This is made possible primarily by the special characteristics of thyssenkrupp Industrial Solutions' EnviNOx® systems which tolerate high ammonia inputs without allowing ammonia slip. Thus the NOx abatement can be brought into operation at an early stage of plant start-up. The technology finds application both in meeting regulatory NOx emission limits which are being extended to cover non-steady state operation, and in satisfying the need of plant operators to visibly demonstrate their concern for the environment to their local communities.

Fig. 7: Temperature and NOx concentration at EnviNOx® reactor outlet (= stack concentration) during improved low emissions start-up with EnviNOx®



A catalyst perspective by Hindustan Platinum

Although the start-up operation in a nitric acid plant is one of the most important stages, from the viewpoint of process performance, catalyst ageing and platinum loss in the entire campaign, the start-up procedure of the catalyst is still widely unknown and subject to high uncertainty. The problem is to ignite the reaction at low temperature at a virtually inactive catalyst³. In order to ignite the ammonia air mixture on the catalyst, ignitable points on the catalyst must be created, and the ammonia ratio in the mixed gas must reach the corresponding ignition limit.

Once the reaction has started, the reactor internals in the immediate vicinity of the catalyst withdraw heat from the reaction, which it requires for its further self-acceleration. The rise of the ammonia ratio in the mixed gas causes a marked increase in its heat capacity, whereby further heat is withdrawn from the reaction

In this phase it is often unclear whether the reaction has really started. Only an extreme increase in catalyst temperature combined with lighting up of the gauzes shows the successful ignition of the ammonia oxidation. The extreme temperature rise causes concern for the catalyst and the reactor so a further increase in the ammonia ratio is often avoided in this phase of the start-up process, or the ratio may even be reduced in order to dampen the temperature rise.

All of these interventions in the start-up procedure have a very different effect on the development of the catalyst activity and thus affect its performance over the entire campaign.

The catalytic surface

In addition to its composition, the activity of the catalyst is mainly associated with the presence of defects which are energetically favourable adsorption sites for ammonia and oxygen. In new condition, however, the catalyst shows an almost perfectly smooth surface – the gauze catalyst is therefore virtually inactive. The only disturbances are the grain boundaries (Figs. 8 and 9) at which crystal lattices of different spatial orientation collide.

The reaction therefore starts primarily at the grain boundaries. The extreme increase in temperature at the ignition of the reaction results in an excessive thermal stress and a breakup of the catalyst surface along the grain boundaries (Fig. 10).

While the actual wire surface has a homogeneous and unstructured texture, the cracks exhibit a large number of active imperfections such as dislocations and depression, where the reaction takes place preferentially in the starting phase of the reaction.

Oxygen-driven rhodium segregation

The heat release of the reaction causes an extreme rise in temperature, which triggers different processes in the various temperature ranges that the catalyst passes through.

Initially this affects the rhodium (Rh) atoms in particular which increasingly migrate in the crystal lattice with the tendency to cluster on the catalyst surface (Fig. 11).

Additional Rh atoms are drawn up from the underlying layer, forming Rh\O bonds. This minimises the overall free energy of the plane, and drives the enrichment.

Especially in the cracks along the grain boundaries, the Rh atoms are exposed at

the surface and react with the process oxygen to form non-volatile rhodium oxide, Rh₂O₃ (Figs. 12 and 13).

As these are the most favourable locations for nucleation, rhodium shows a tendency to form chains on the catalyst surface and less compact aggregates.

Low temperatures in the starting phase of the reaction therefore primarily cause an enrichment of rhodium on the catalyst surface, which is driven by the formation of non-volatile Rh₂O₃. Here, nuclei are formed, which are the starting point for further agglomeration of rhodium on the catalyst surface during the campaign.

Thermal etching

Diffusion of platinum (Pt) occurs only at significantly higher temperatures. Unlike the enrichment of Rh, which is driven by the exothermic formation of rhodium oxide, the diffusion of Pt is a purely kinetic process, in which platinum atoms dissolve from the metal lattice and migrate across the surface to agglomerate at colder or energetically exposed sites. This process is described in the literature as thermal etching (Figs. 14 and 15).

Thermal etching is the actual process which causes the increase in the activity of the catalyst and thus determines its yield and selectivity.

Preheating and ignition

To start the process, ignitable sites on the catalyst and an ignitable ratio of ammonia in the mixed gas are required.

If the reaction ignites, this occurs primarily at the grain boundaries and not on the initially inactive smooth surface of the catalyst. Therefore, only a small amount of heat is generated by the reaction at relatively low ammonia conversion.

At the same time, a relatively large amount of heat is required to heat up the reactor internals as well as the process gas, the heat capacity of which increases markedly with its ammonia content. Both the reactor installations and the process gas withdraw heat from the reaction, which requires the reaction for further self-acceleration.

Usually, therefore, the catalyst is first preheated by means of hydrogen combustion. At the same time, ignitable sites are generated on the catalyst. The more intensively the catalyst is preheated, the less heat is withdrawn from the reaction after ignition, thereby allowing the reaction and thus also the activity of the catalyst to develop significantly faster.

Fig. 8: Schematic representation of a grain boundary

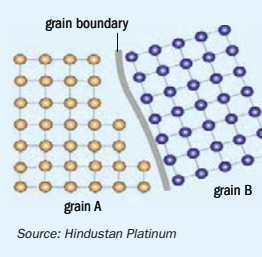


Fig. 9: Wire surface in new condition with grain boundaries



Fig. 10: Crack along a grain boundary in the initial phase of the start-up

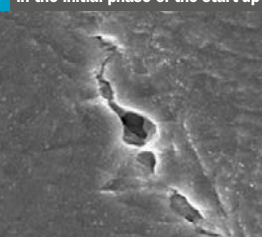


Fig. 11: STM image of Pt/Rh surface after annealing to a temperature of 700°C (Pt/Rh = dark/bright dots)

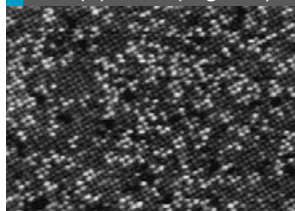


Fig. 12: SEM: Rh enrichment along the grain boundaries

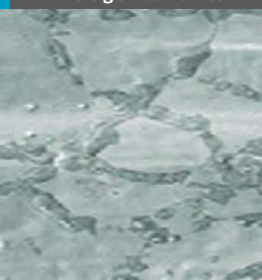


Fig. 13: SEM/EDX: Rh enrichment along the grain boundaries

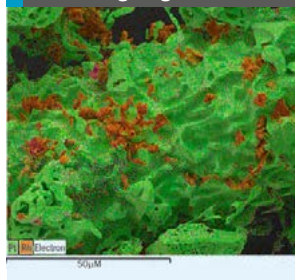


Fig. 14: Restructuring of the surface by thermal etching schematic



Fig. 15: Restructuring of the surface by thermal etching

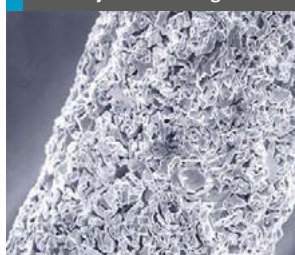
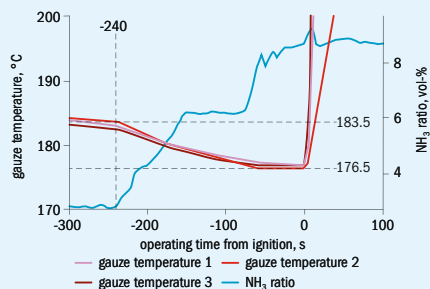
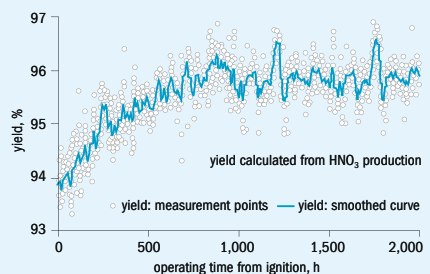


Fig. 16: Example of industrial start-up procedure



Source: Hindustan Platinum

Fig. 18: Example of industrial start-up procedure: development of yield



Source: Hindustan Platinum

Fig. 16 illustrates a typical example of such a described start-up procedure showing the course of the temperatures and the ammonia ratio in the mixed gas.

The catalyst is first heated to a temperature of about 183°C by means of hydrogen combustion. In the next step, the ammonia ratio in the mixed gas is increased to a value slightly above 6%. Simultaneously with the ammonia feed, the hydrogen combustion is stopped.

As a result, the reaction does not ignite on the catalyst and the temperature of the catalyst drops to the mixed gas temperature of 176°C.

The ammonia ratio is then further increased to almost 9%. The peaks in the curve indicate the attempt to ignite the reaction by a short-term strong increase in the ammonia ratio, which ultimately succeeds with a short-term exceedance of a 9 vol-%.

The result is shown by the inhomogeneity of the temperature curves at the three thermocouples, which indicate that the reaction has started at different times in the various regions of the catalyst (Fig. 17).

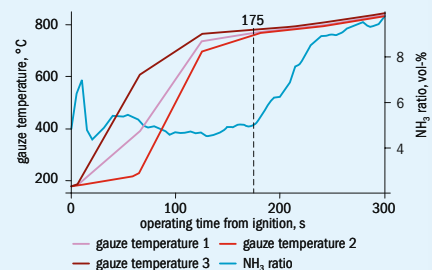
The unsatisfactory course of the start-up results from insufficient preheating of the catalyst, an early cut-off of the hydrogen combustion and too slow a rise of the ammonia ratio in the mixed gas.

As a result, the catalyst is operated at least at a low temperature, resulting in the formation of Rh/Rh₂O₃ nuclei on the surface which significantly retards the development of the catalyst activity.

Fig. 18 illustrates the time-delayed development of catalyst activity in the yield increase over a period of nearly 1,000 hours until the maximum yield is reached.

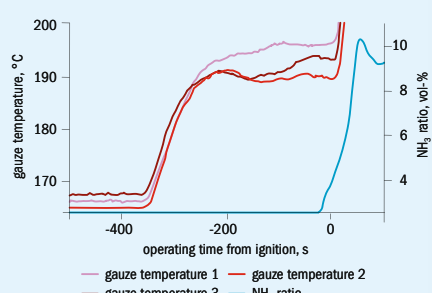
Fig. 19 shows the result of an optimised start-up procedure with a much more efficient preheating of the catalyst

Fig. 17: Industrial start-up procedure with inhomogeneity in the course of temperature



Source: Hindustan Platinum

Fig. 19: Example of optimised industrial start-up procedure



Source: Hindustan Platinum

and a faster increase in the NH₃ ratio in the mixed gas.

From Fig. 19 it becomes obvious that, due to the more intensive preheating and continuance of the hydrogen combustion during the increase of the ammonia ratio, the catalyst ignites without problems even at an ammonia ratio of about 4%.

Fig. 20 shows that such an optimised start-up procedure results in a nearly parallel, homogenous temperature increase at all three thermocouples. The temperature range of 550-700°C which is critical for the segregation of rhodium is crossed in the shortest possible time so that the formation of Rh₂O₃ nuclei is limited to a minimum.

Fig. 21 shows that the improved start-up procedure significantly increases the initial yield and its maximum is reached after a quarter of the time previously required.

Starting a plant and igniting the catalyst gauzes is a difficult craft and each



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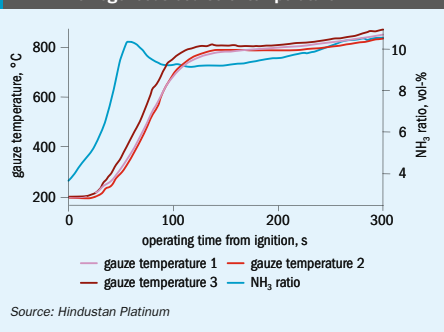
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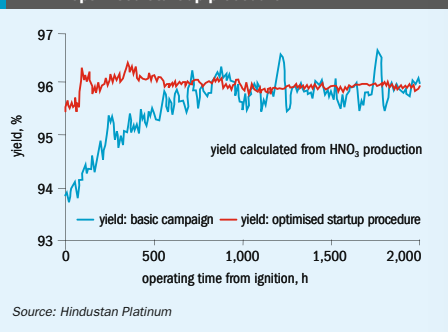
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Fig. 20: Optimised industrial start-up procedure with homogeneous course of temperature



Source: Hindustan Platinum

Fig. 21: Yield development: comparison of basic and optimised start-up procedure



Source: Hindustan Platinum

Fig. 22: Homogeneous ignition over the entire catalyst surface



SOURCE: HINDUSTAN PLATINUM

plant is different and subject to other conditions that limit the possibilities of an optimal start-up process. However, it is always possible to optimise the start-up process in order to achieve homogeneous and fast ignition of the reaction on the catalyst. This ensures that the catalyst achieves its optimum performance in a short time, limits aging and minimises the losses of precious metals.

Simulation helps to optimally adapt the strategy of the start-up procedure to the individual boundary conditions of a plant. Hindustan Platinum have used simulation to optimise the start-up procedure for numerous clients.

Fig. 22 shows the result of such project work to achieve homogeneous ignition over the entire catalyst surface despite challenging conditions.

Espindesa operating procedures and design alternatives

Several options regarding operating procedures and design alternatives are used by Espindesa to improve the start-up and shutdown of nitric acid units⁵.

Undesirable NOx emissions during the start-up of nitric acid units are formed due to several factors, the most relevant being the lack of pressure in the absorption tower that leads to a lower absorption efficiency. Other significant factors include: chiller water that is too warm and ammonium nitrate deposition.

Most nitric acid units use chilled water for higher efficiency of the absorber in normal operation; this chiller water is obtained by ammonia vaporisation (Fig. 23). During shutdown, but mainly during start-up, the temperature of the chilled water can be too high, especially in warmer climates as the temperature of the weather and solar radiation over chilled water pipes increases the temperature of the chilled water, bearing in mind that during these periods the ammonia vaporiser is not in use and will not be cooling the water. The situation is not so critical in colder climates where chilled water temperatures can be maintained.

The risk of ammonium nitrate deposition over expander blades is another factor. Most modern nitric acid units are provided with a NOx abatement system before the expander, however, to avoid ammonium nitrate and ammonium nitrite deposition on the expander blades a minimum temperature at the expander outlet is needed, this minimum temperature depends on the NOx and NH₃ content in the gas and ranges between 60-90°C. During plant start-up or shutdown if the required temperature at the expander outlet cannot be achieved to operate the NOx abatement system in operation, deposition of nitrates takes place.

To minimise these effects during start-up and shutdowns several developments

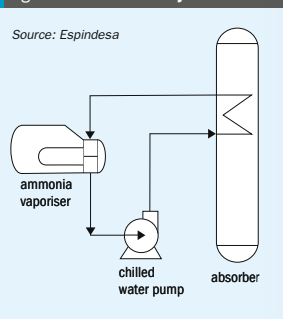
have been made, a brief description of some common practices are mentioned below. In general, there are 20-30 critical minutes immediately after ammonia ignition until absorption sets stable and expander outlet temperatures are achieved.

The actions suggested to improve the start-up and shutdown can be categorised into operational procedures and design issues.

Issues related to operating procedures:

- Ammonia-air ratio control: During start-up the ammonia-air ratio increases from 0%, when there is no ammonia in the reaction, to the required 9-12% as required by the process, depending on the ammonia oxidation pressure. The ratio should be increased fast enough to avoid damage to the platinum gauzes due to rhodium oxidation, and to pass the limit for high rhodium oxidation as fast as possible, but not so fast

Fig. 23: Chilled water system



Source: Espindesa

Fig. 24: Nitric acid absorption tower



SOURCE: ESPINDESA

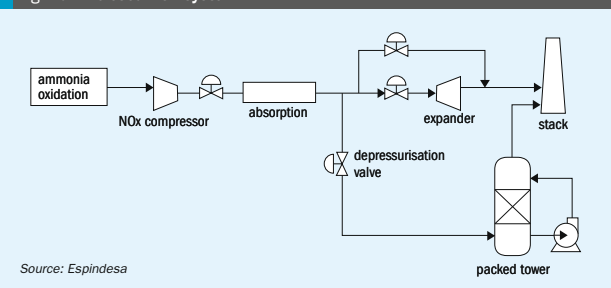
that the expander does not reach the required temperature for NOx abatement. When possible it is good practice to increase the ratio quite quickly until the temperature of the gauzes reaches about 810°C (to minimise rhodium oxide) and then continue at a lower rate until the reaction temperature achieves the nominal value in order to stabilise absorption and provide sufficient time for the tail gas to the expander to achieve the required temperature. The typical residence time from reaction to expander to warm the full unit is in the range from 15-30 minutes.

- Water flow to the absorber: The absorber is, in fact, a buffer for start-up and shutdown. It is therefore possible to maintain higher water flow during start-up and shutdown to maximise the buffer effect, the secondary effect on the unit being that it will handle a little more off-spec acid (more diluted) than can be reprocessed in normal operation.
- NOx abatement buffer effect: It is known that the NOx abatement catalyst retains ammonia during operation that will be useful for abatement at start-up. However, this effect is not suitable for longer shutdown periods⁵ as the adsorbed ammonia over the catalyst will be released.

Design issues:

- Extended absorption: The absorption tower can be designed to obtain higher NOx content after absorption during normal operation (about 500 ppmv NOx)

Fig. 25: Enclosed NOx system



Source: Espindesa

which will lead to very high emissions during start-up and shutdown. Alternatively, absorption towers (Fig. 24) can be designed for lower emission during normal operation (about 180 ppmv), which can also control the visual effect of NOx emissions during start-up and shutdown by maintaining the water flow to the absorber. The difference between the two concepts are about 10 m of absorption tower length.

- Increasing tail gas temperature: It is possible to increase the tail gas temperature during start-up and shutdown period by using in-line burners with natural gas to achieve the required temperatures of the NOx abatement system and expander in order to allow the NOx abatement system to be started at any time
- Hydrogen peroxide dosing: the benefits of using hydrogen peroxide (H₂O₂) for NOx abatement have been known since the 1970s⁶ and in the past Espindesa has designed NOx absorption system for nitro compounds in Spain and France for cases where NOx fluctuations widely (making it difficult to control with a SCR system). This system can also be effectively used for absorption towers during start-up to increase the buffer effect. Peroxide dosing is optimised and only used during start-up periods to minimise costs. This system has to take into account the ratio between hydrogen peroxide and nitric acid concentration to avoid the risk of explosion⁷ when the acid concentration is higher than 55%. However, the dilution of H₂O₂ is usually high enough to avoid any concern.
- Enclosing NOx: During the 1970-1980s, one of Espindesa's designs involved enclosing the NOx in the unit by shutdown valves (Fig. 25). To avoid further

corrosion by the enclosed NOx, this system requires an additional absorber (packed tower) with ammonia, dolomite solution dolomite or caustic to abate the NOx to low levels, and nowadays, expanders with higher speed would also require a source of plant air to avoid overheating during shutdown.

- NOx abatement after the expander: Some units use a NOx abatement system after the expander, but due to the low tail gas pressure a heating system as well as a higher volume of NOx abatement catalyst is needed.

Espindesa typically optimises the operating procedures, together with extended absorption, to achieve high reliability of the unit and provides the possibility to implement H₂O₂ abatement in the future. ■

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ISSN: 1750-6891

Design and production:
JOHN CREEK, DANI HART



Printed in England by:
Buxton Press Ltd
Palace Road, Buxton, Derbyshire,
SK17 6AE

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Published by: BCInsight Ltd

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