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NITROGEN+SYNGAS
ISSUE 379
SEPTEMBER-OCTOBER 2022

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Winter is coming

As we near the end of the third quarter of 2022, the attention of the nitrogen industry is focused on the coming northern hemisphere winter, and the prospects for higher natural gas prices as temperatures fall and power and heating demands rise. Vladimir Putin has been stoking these worries to try and force a climbdown from European countries over the sanctions that followed his invasion of Ukraine, with the flow of gas through the Nordstream 1 pipeline across the Baltic Sea gradually dwindling over the summer and finally stopping altogether at the end of August due to "technical issues" – an explanation somewhat undermined by the subsequent statement from spokesman Dmitry Peskov that gas would flow again once sanctions were eased. This is a familiar enough tactic; Russia has used gas stoppages to pressure Ukraine and Europe several times over the past two decades.

At time of writing, Europe was still receiving Russian gas via Ukraine, albeit at reduced rates, and the TurkStream pipeline across the Black Sea, where flows have actually increased to states more sympathetic to Russia like Turkey, Serbia and Hungary. However, the ongoing crisis is leading to forecasts of record gas prices as winter approaches, and with it likely continued shutdowns for ammonia producers across the continent. By the end of August, about half of European ammonia capacity and one third of nitrogen fertilizer production had been shut down by high gas prices, with CF Industries at Billingham in the UK, the last operating ammonia plant in the country, announcing a shutdown on August 24th. Yara was only operating 35% of its ammonia capacity across the continent.

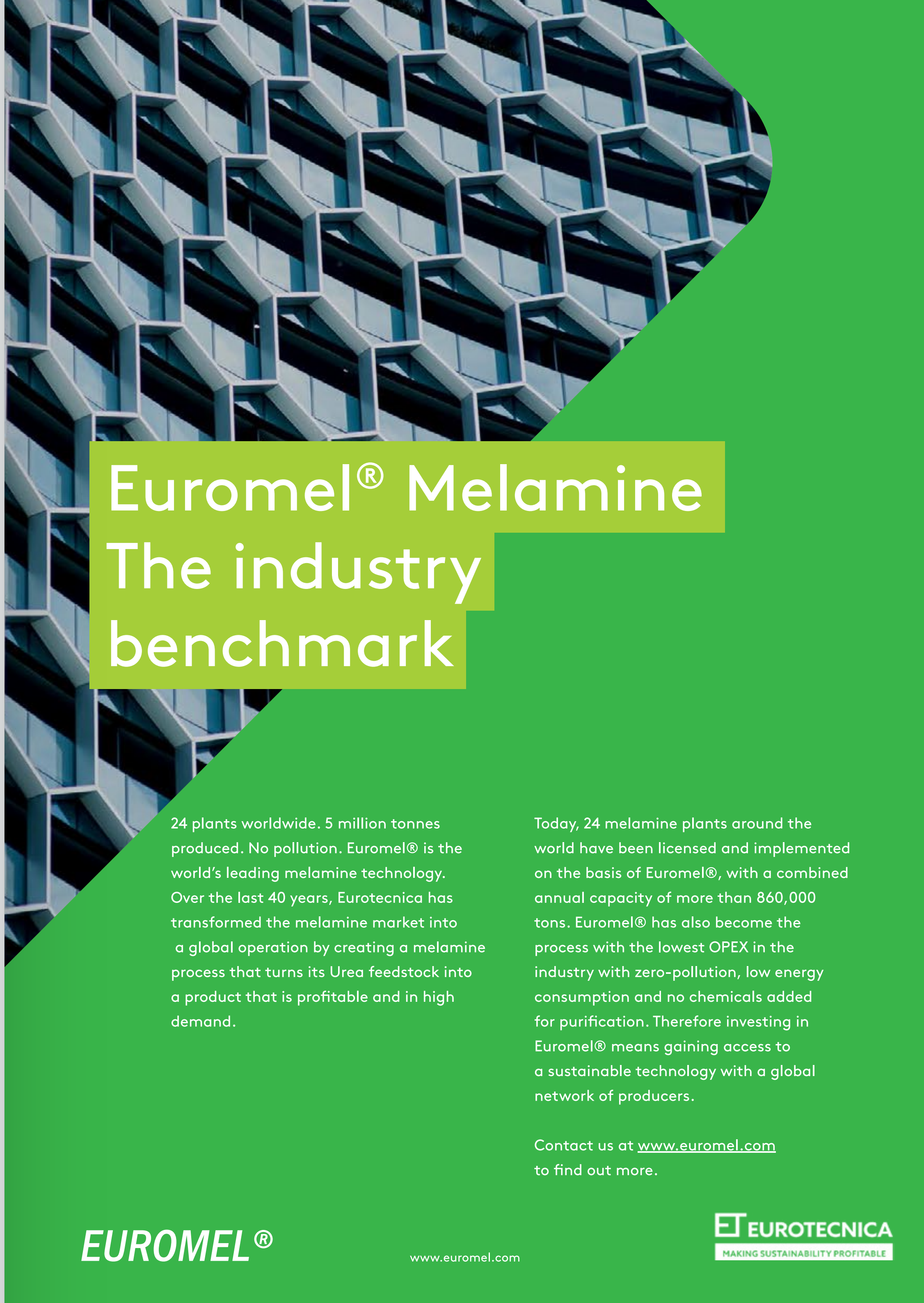
> **"It is looking likely that there will be some kind of cap on gas prices to end users"**

EU energy ministers met in Brussels at the start of September to try and ease the coming pain for consumers and industry alike. Although Europe has managed to fill the targeted 80% of its gas storage capacity (85% in Germany), a cold snap, particularly if combined with the kind of stationary high pressure area that generates still air and a lack of power from wind turbines, could still hit hard. It is looking likely that there will be some kind of cap on gas prices to end users, though the prospects of shortages and rationing or targeted shutdowns of high gas consuming sectors like fertilizer production cannot be ruled out. Across the continent, mothballed coal-fired power stations are being pressed back into service, and Germany has finally belatedly agreed not to shut down its last remaining nuclear power plants for now, keeping them in case they are required over the colder months.

Across the Atlantic, although the US is now a gas exporter, the price of LNG has helped drag up Henry Hub prices to $10.00/MMBtu; levels not seen since the 2008 financial crisis, when the US was still an importer, and double that of last winter, with the government unlikely to intervene as it has in Europe. The knock-on effect of high prices is also being felt in Brazil, which imports virtually all of its nitrogen needs. India, which had been aiming to increase LNG import capacity by 40% this year, has seen those project completion dates pushed back into 2023, with high LNG prices potentially problematic for the country's rapidly growing urea industry. At such a time, the news of the slowdown in the Chinese economy is almost a relief, as it may mean less pressure on commodity markets going forward.

The only good news for now is for producers in the Middle East or other places with low and fixed gas costs and no issues with availability. Egypt has been able to capitalise on its proximity to Europe to make some very lucrative urea sales. Longer term, it is also sure to be a spur to Europe's accelerating move towards renewable energy and its use in fertilizer production. But for now, we have to get through the coming winter.

Richard Hands, Editor



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Price Trends

Market Insight courtesy of Argus Media

NITROGEN

Ammonia prices have been bound within a range, with the market counterbalanced by increasing supply options globally, though this is set against the backdrop of the continuing gas crisis in Europe. Growing supply options for September are creating competition for sellers trying to place cargoes into Europe and putting slight downward pressure on spot prices.

In the spot market, OCP bought its first cargoes from Salalah – the 1,000 t/d Salalah ammonia plant in Oman loaded its first commercial export cargo in August and OCP bought 15,000 tonnes from Oman's OQ Trading, loading in late- August on Gas Walio to Jorf Lasfar. OCP has bought another 25,000 tonnes for September-loading on an f.o.b. basis. Ameropa also purchased a cargo from Ma'aden for delivery into northwest Europe, all at undisclosed prices.

European buyers are covering positions as far in advance as possible, and other large buy regions previously dependent on Black Sea exports appear to be covered with new supply contracts. In the east, there is a growing disconnect between Asian markets and the west, as buyers look to distance themselves from the inflated pricing in Europe. While supply is outstripping demand for now, baseline European production cost estimates are now over $2,500/t. Global supply optionality continues to provide cargoes at around half the price of this cost, but whether or not producers can continue with current production strategies into 4Q at this level remains uncertain. European gas costs continue to be high; the month-ahead Dutch TTF contract closed at a new high of over $70/MMBtu today. Further volatility is anticipated as a result of supply uncertainty regarding Norwegian outages and weak Russian deliveries into the region.

Urea prices fell for consecutive weeks in mid-August, across most markets around the world on thin demand and amid producer length in key regions. Middle East prices dropped sharply as producers cut prices to clear remaining August and early September cargoes – three were confirmed trading between $550-556/t f.o.b. Similar f.o.b. prices were seen in southeast Asia in mid-August, with deals between $540-557/t f.o.b. in Brunei and Indonesia. Some pockets of activity bucked the softening trend though. Prices for granular urea delivered to Myanmar rose by around $30/t, while Iran f.o.b. prices climbed by $20/t from last business in a series of deals at $500/t f.o.b.. But overall, with demand in Europe, Brazil, US and southeast Asia low the market remains soft.

Natural gas crisis – feedstock costs for Europe and LNG-dependent nitrogen plants pushed to new highs in mid-August and more plants in Europe are talking about shutting down. Though premium nitrogen prices would normally attract product, some ammonium sulphate and urea suppliers from non-traditional origins are struggling to comply with the EU's new quality and traceability regulations, blocking this trade flow. ■

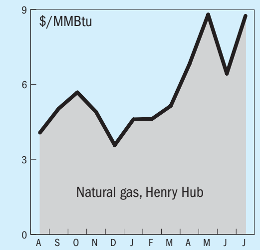
Table 1: **Price indications**

Cash equivalent	mid-Aug	mid-Jun	mid-Apr	mid-Feb
Ammonia ($/t)				
f.o.b. Black Sea	n.m.	n.m.	n.m.	1,115-1,140
f.o.b. Caribbean	1,050-1,095	925-950	1,350-1,550	1,020-1,075
f.o.b. Arab Gulf	915-1,030	880-970	975-1,150	860-985
c.fr N.W. Europe	1,165-1,250	1,000-1,085	1,400-1,490	1,150-1,180
Urea ($/t)				
f.o.b. bulk Black Sea	n.m.	n.m.	n.m.	518-620
f.o.b. bulk Arab Gulf*	570-680	535-650	700-850	750-825
f.o.b. NOLA barge (metric tonnes)	465-585	570-595	935-970	570-580
f.o.b. bagged China	475-530	525-625	690-820	560-700
DAP ($/t)				
f.o.b. bulk US Gulf	803-836	822-888	1,001-1,066	785-849
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	605-609	583	837-859	680-740

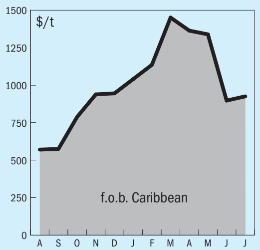
*Notes: n.a. price not available at time of going to press. n.m. no market. * high-end granular.*

END OF MONTH SPOT PRICES

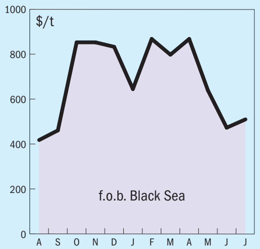
natural gas



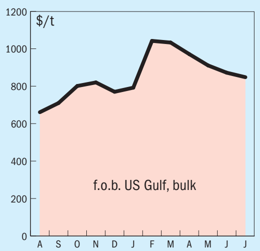
ammonia



urea

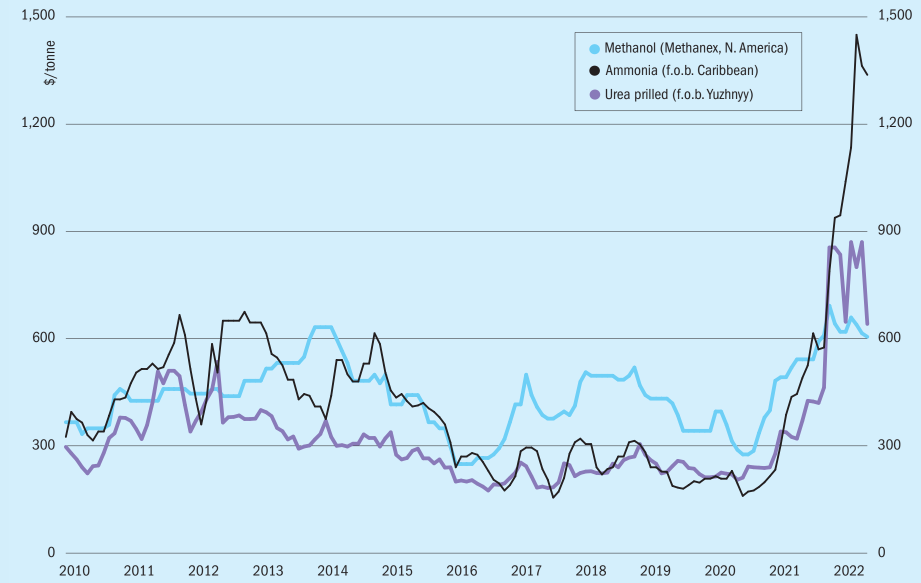


diammonium phosphate



Market Outlook

Historical price trends $/tonne



Source: BCInsight

AMMONIA

- Overall the market finds itself in a period of illiquidity, and is exposed to further uncertainty in 4Q because of the European energy crisis. Spiralling natural gas costs in Europe, with Dutch TTF gas prices trading around €200/MWh, are forcing European fertilizer producers to close ammonia capacity and buy in from overseas.
- Outside of Europe, however, there is something of a price disconnect, with the market relatively bearish due to weak demand from major chemicals producers in northeast Asia and DAP producers in India and the US, freeing up cargoes for Europe. Fertiglobe in Spain bought a cargo from as far away as Indonesia for August delivery.
- With Russia continuing to pressure Europe over Ukraine via lower gas deliveries, and winter approaching, there is no sign at present of gas prices settling down in Europe, and ammonia prices are likely to stay high.

UREA

- The current period of market weakness is demand driven, but supply-side fundamentals remain extremely supportive. It is likely that there will be another rally within the next few weeks and months as importers in most markets are behind on purchases, waiting for the market to stabilise before firming up commitments.
- CF Industries said in its quarterly earnings call that it expects the global nitrogen balance to remain tight for some time. Agricultural-led demand for nitrogen has been robust, with a need to replenish global grain stocks, and the USDA projects that US corn plantings will be lower than previously projected this season due to poor weather. Meanwhile the gas supply situation in Europe and to a lesser extent in Asia means greater competition for LNG cargoes and high production costs, leading to continued uncertainty about global production and export supply availability.
- India is expected to tender on a regular basis into 2023 as increased domestic urea production is still unlikely to fully meet demand. Brazilian urea consumption is also forecast to remain strong in 2022, supported by high crop prices and higher plantings.

METHANOL

- Chinese methanol sales were high in July, as domestic prices reached an 18 month low, but prices rebounded towards the end of the month due to unplanned outages at Iranian suppliers.
- Although it is traditionally a slack demand season for methanol, US methanol prices rose by around 12% to around $1.14/gallon ($372/t) in July due to both planned and unplanned domestic production outages, and prices were looking to be towards $1.20/gal for August. Some producers were reported to have curtailed production due to oversupply. European prices rose in tandem with US rates, to around €380/t f.o.b. Rotterdam. Supply is expected to be higher in the second half of 2022, and demand stable leading to bearish market conditions. ■

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Nitrogen Industry News

AFRICA

Stamicarbon to license urea for African project

Maire Tecnimont's innovation and licensing company Stamicarbon has been selected as the licensor for a urea project in sub-Saharan Africa, its first license in the region. Stamicarbon will deliver the process design package for the front-end engineering and design for a 4,000 t/d urea melt and granulation plant. The urea melt plant with a pool reactor will use Stamicarbon's MP Flash design, a melt concept with improved energy efficiency, entailing a significant reduction of steam consumption. The minimal equipment items result in a significant reduction of the footprint and the overall capital cost of the plant. Less equipment also allows for a reduction in maintenance costs and OPEX savings.

Alessandro Bernini, Maire Tecnimont CEO, said "We are proud to be part of this remarkable project. It is a genuinely solid project with an innovative concept that is bound to add value to the community and the region at large. Thanks to this project, our Group has increased its footprint in Sub-Saharan Africa and positioned itself as the world leader in cutting-edge technology and solutions to contribute to reduce the carbon footprint of the fertilizer industry". ■

IFDC announces update to Africa Fertilizer Watch

The International Fertilizer Development Center (IFDC) has announced an update to its Africa Fertilizer Watch. Covering 16-plus countries across sub-Saharan Africa, added indicators track the impact of the Russa-Ukraine crisis on the delivery and use of fertilizers to identify changes in productivity and food security across the continent. The IFDC says that the Africa Fertilizer Watch supports efficient and effective responses to the evolving food and fertilizer crises and ensures that sufficient quantities of appropriate fertilizers reach farmers.

Currently, the region has the lowest fertilizer usage in the world – insufficient to replace the soil nutrients lost every year to crop production. In addition, huge demographic shifts could have a major impact on food security. Understanding where and how barriers to fertilizer access and availability are affecting farmers is crucial for agricultural productivity.

The Africa Fertilizer Watch was developed through a partnership between IFDC's AFO initiative and Development Gateway. It is jointly funded by the US Agency for International Development (USAID) Bureau for Resilience and Food Security, through the Feed the Future Soil Fertility Technology Adoption, Policy Reform, and Knowledge Management under the Sustainable Opportunities for Improving Livelihoods with Soils (SOILS) Consortium, and the Bill & Melinda Gates Foundation, through the Visualizing Insights on Fertilizer for African Agriculture (VIFAA) program. Other technical partners include the African Fertilizer and Agribusiness Partnership (AFAP) and AFRIQOM.

AUSTRALIA

Scientists achieve sustainable ammonia breakthrough

Scientists at Melbourne's Monash University say that they have achieved a breakthrough in their quest to develop a more sustainable ammonia production process. Reporting in *Nature*, lead researcher Dr Hoang-Long Du and team leaders Dr Alexandr Simonov and Professor Doug MacFarlane say that they can achieve almost complete selectivity for the conversion of nitrogen from air and renewable electricity into ammonia at an unprecedented rate. The researchers have developed a unique electrolyte that produces a high-performance layer on the operating electrode to support the reaction that converts nitrogen into ammonia.

Dr Simonov said a process for the carbon-free production of fertilizers using renewable energy had been known for some time but it was not very selective. "Typically, a significant portion, sometimes as large as half of the electricity was used in making other unwanted compounds, making the process impractical," Dr Simonov said. "Our new discovery shows how ammonia can be made with complete selectivity."

Dr Du said another important feature of the new electrolyte was the high stability it provided to the process. "Since the electricity is exclusively used for the nitrogen to ammonia reaction, no degradation processes can occur and the process can operate stably on a long timescale," Dr Du said. Monash has spun off a company, Jupiter Ionics, which is scaling up the process discovered by the research team.

Jupiter Ionics recently initiated a scale up project supported by funding from the Federal Government CRC Program along with partners Fortescue Future Industries, WesCEF and SJDC Produce Ltd.

Jupiter Ionics hopes to have its first prototype devices on a farm in regional Victoria next year, according to the company's CEO Dr Charlie Day. "This new research is opening up a novel pathway to ammonia production, over a century after Haber and Bosch first developed their eponymous process," Dr Day said. "Importantly, it will enable production at a range of scales and in a range of settings, all powered by increasingly abundant and cheap renewable energy."

It is anticipated that the technology could be installed on farms or in regional centres producing fertilizers locally using on-site renewable energy supplies.

Contract awarded for low carbon ammonia project

US contractor McDermott International has won a pre-front end engineering and design contract for Woodside Energy's proposed H2Perth project for the production of renewable and lower-carbon hydrogen and ammonia in the Kwinana/Rockingham area of Western Australia. McDermott says its scope encompasses pre-FEED services for a proposed export-scale production facility. Woodside plans to invest $1 billion in green hydrogen and ammonia in Australia.

"This award follows the successful completion of the concept study on H2Perth and decades of experience executing both onshore and offshore projects for Woodside Energy," said Tareq Kawash, Senior Vice President for Onshore at McDermott. "We are pleased to continue supporting Woodside's energy transition opportunities and are mutually aligned on the importance of driving lower-carbon energy to advance Australia's vision as a global leader in clean, innovative, safe, and competitive hydrogen production," he added.

The project is planned as a phased development, initially targeting 300 t/d of hydrogen production, which can be converted into 600,000 t/a of ammonia or 110,000 t/a of liquid hydrogen. Electrolysis technologies and natural gas reforming would both be used to produce hydrogen, with 100% of carbon emissions abated or offset. The initial capacity of the electrolysis component is 250 MW while the initial phase of the steam methane reformer will consume 40 terajoules per day of natural gas. The initial phase of the project has an estimated capital cost of approximately A$700 million.

Subject to necessary commercial and regulatory approvals and a positive final investment decision, construction on the initial phase of the project could commence in 2024.

Wood wins engineering oversight contract for Strike urea plant

Global consulting and engineering company Wood has been awarded the technical and engineering oversight services contract for Strike Energy's Project Haber lower carbon ammonia-urea plant in Western Australia. The project will use hydrogen from a 10MW on-site electrolyser using large scale wind and solar generation in addition to Strike's Perth Basin gas resources, lowering the carbon emission of production. The renewable share of production is aimed to eventually reach 170 MW, and the site will include carbon offsets including tree planting, as well as carbon capture and storage. Wood will monitor and assess work in progress, ensuring the engineering, procurement and construction contractor delivers work consistent with the project's requirements.

Stuart Nicholls, Managing Director and CEO, Strike Energy added: "Wood is recognised as an industry leader in energy and decarbonisation, and we are delighted to have them play such a key role in the successful execution of this project. Their expertise will be invaluable as we deliver on our strategy to help supply low-cost, low-carbon energy to Western Australia, and support the competitiveness of Australia's agricultural industry by building sovereign capability in the manufacturing of globally competitive low carbon nitrogen fertiliser."

The Strike fertilizer plant has signed up Koch Industries as its primary offtaker and will look to meet the local demand of the Western Australia wheat belt and, as it is located near the Geraldton port, will be strategically positioned to meet export demands for product throughout the 20-to-30-year life cycle of the plant. Project Haber will use a Topsoe ammonia plant and Saipem urea plant using thyssenkrupp granulation technology to produce 1.4 million t/a of urea. First production is currently scheduled for 2026.

Urea plant still in the balance

Australia's environment minister Tanya Plibersek is considering objections by indigenous peoples to Perdaman Chemicals planned 2 million t/a urea plant on the Burrup Peninsula in Western Australia. The A$4.5 billion (US$3.1 billion) development has been approved by the state government of Western Australia, but remains stalled at a Federal level over the potential threat from plant emissions to native petroglyph rock art in the region, some over 40,000 years old, which have been nominated for a UNESCO World Heritage listing. The WA government's approval was subject to removal of the rock art to an area further from the plant, but local indigenous groups oppose disturbing the site. The Burrup Peninsula is already home to an ammonia plant and an LNG facility.

UNITED ARAB EMIRATES

Fertiglobe reports 1H dividend of $750 million

Fertiglobe, a partnership between ADNOC and OCI, and the world's largest seaborne exporter of urea and ammonia, as well as the largest nitrogen fertilizer producer in the Middle East and North Africa region, has reported that its Q2 2022 revenues increased by 105% to $1.47 billion, while adjusted EBITDA grew 155% to $770 million compared to Q2 2021. Free cash flow increased to $789 million in Q2 2022 from $328 million in Q2 2021, supporting a first half dividend of $750 million, above previous guidance of at least $700 million.

Ahmed El-Hoshy, CEO of Fertiglobe commented: "Q2 2022's performance… [has been] driven by a favourable price backdrop supported by strong in-season demand, tight market balances and elevated gas prices in Europe, as well as higher sales volumes due to a phasing of some shipments from Q1 2022 to this quarter… The outlook for the fundamentals of our nitrogen end markets continues to underpinned by tight supply, healthy farm economics and low grain stocks globally that incentivise the use of nitrogen fertilizers. Forward curves imply that natural gas prices in Europe will remain at elevated levels through 2023 and beyond, setting breakeven pricing well above historical average global prices for ammonia and urea."

New shiploader for Ruwais terminal

Bedeschi has been contracted by Fertil to supply shiploader for the company's Ruwais terminal in Abu Dhabi for fertilizer and granulated urea to replace the existing one. The design capacity of the shiploader is 1,200 t/h and it will be delivered fully erected to site. The machine will run on rails, with a towed tripper to divert the product from a wharf gallery conveyor onto a transfer belt, then to a loading boom belt.

Feasibility study for green hydrogen and ammonia plant

Brooge Energy has engaged Ernst & Young to provide consulting services for its planned green hydrogen and ammonia plant. The study will provide a market assessment with expected future prices and an overview of the competitive landscape expected. The study scope covers the project's technical and cost assessment in addition to a financial and feasibility study report, expected to be delivered during 4Q 2022. The company is developing a 300,000 t/a ammonia plant and has signed a preliminary land lease agreement for a 150,000 square meter plot that will accommodate the project.

Nicolaas Paardenkooper, CEO of Brooge Energy, said; "We are excited to begin the process of bringing this highly anticipated project to reality through engaging with the appropriate partners to see the project to completion. We strive to be in the forefront of the clean energy movement and our goal is to be one of the first private sector companies to successfully implement a green hydrogen/ ammonia project in UAE and demonstrate its economic and environmental benefits on a local and global scale."

MIDDLE EAST

Tecnimont to build low carbon ammonia synthesis loop

Tecnimont, in cooperation with its sister company Nextchem, has been awarded a lump sum turn-key EPC contract for a low-carbon ammonia synloop to be built at an undisclosed location in the Gulf Cooperation Council region. The contract value is approximately $300 million and its scope of work includes engineering activities, supply of all materials and equipment as well as construction activities. Tecnimont has been instructed to immediately start with engineering work in relation to the project; the commencement of the procurement and construction works will be confirmed later this year when a final investment decision will be made. The project entails a 3,000 t/d approximately (1 million t/a) low-carbon ammonia plant and completion of the project is expected by the second half of 2025.

Alessandro Bernini, Maire Tecnimont Group CEO, commented: "This strategic pro-

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ject is extremely important since it will provide a significant contribution to the energy transition of the GCC region by reducing the carbon footprint of the fertilizer value chain. It will also contribute to the steady expansion of our green energy business."

MOROCCO

Green ammonia pilot plant for Jorf Lasfar

Morocco's Mohammed VI Polytechnic University and Dutch company Proton Ventures BV have signed an agreement for the construction of a green ammonia pilot plant at OCP's chemical complex at Jorf Lasfar. The agreement covers the turnkey construction of a 4 t/d green ammonia unit using two PEM and alkaline electrolysers with a capacity of 2 MW each. This unit will also be equipped with an emulator that can simulate different electrical load profiles, in particular the hybridisation of photovoltaic and wind energy, in different geographical sites in Morocco and around the world. The plant is preparatory for plans for larger industrial projects, using knowledge and know-how generated during the exploitation phase, which will start in the first quarter of 2024.

CHINA

Eurotecnica wins contract for world's largest melamine plant

Proman subsidiary Eurotecnica, has been awarded a contract by Xinji Energy Chemical Co. Ltd. for the implementation of the world's largest high pressure melamine plant with a capacity of 120,000 t/a. Eurotecnica will use its 5th generation proprietary *Euromel*® technology for the design of this project, featuring low energy consumption, no catalyst, no added chemicals, and no effluents to be treated. It brings the company's total licensed nameplate capacity to more than 1 million t/a in 26 plants worldwide. Xinjiang Xuefeng, the group Xinji belongs to, is the largest melamine producer in the world.

SAUDI ARABIA

Aramco and Sabic certified for blue hydrogen and ammonia production

Saudi Aramco and state fertilizer producer Sabic Agri-Nutrients have received the world's first independent certificate of accreditation for producing blue hydrogen and ammonia products, according to the companies. TUV Rheinland, an independent testing, inspection and certification agency based in Germany, awarded certificates to the two companies. Sabic was recognised for producing 37,800 tonnes of blue ammonia, while Sasref, a wholly owned refinery of Saudi Aramco, received the certificate for producing 8,075 tonnes of blue hydrogen.

"Sabic recognises that hydrogen will play an essential role in decarbonisation and it is part of Sabic's overall road map toward carbon neutrality by 2050, with a 20% reduction target in carbon emissions by 2030," said Fahad Al Sherehy, Sabic's vice president of energy efficiency and carbon management. The new initiatives will also support Saudi Arabia's goal to become carbon neutral by 2060, he said.

Aramco recently announced it targets to produce up to 11 million tonnes per annum of blue ammonia by 2030 and is currently developing carbon capture and hydrogen capabilities. Blue hydrogen production is expected to contribute to its target to become carbon neutral by 2050.

Ma'aden 3 begins commercial ammonia production

The Saudi Arabian Mining Company (Ma'aden) has announced the end of trial operations and the beginning of commercial production at its third ammonia plant. The 1.1 million t/a plant, at the eastern port of Ras al-Khair, has been built by Daelim at a cost of $900 million. Construction was completed in February and the plan has been in trial operation since then.

LIBYA

Restart for Lifeco urea plant

The Libyan Fertiliser Company (Lifeco) has restarted operations at its second ammonia/urea train. The Libyan National Oil Corporation (NOC) said the daily production of urea was about 1,400 t/d, and that of ammonia was about 800 t/d, around 80% of nameplate capacity for each plant. The restart of operations comes after a two-month stop caused by the oil production/export embargo. The company said that operations at the first ammonia plant would also restart over next few days.

UNITED STATES

Paper on costs of green ammonia

Scientists at the US Department of Energy's Argonne National Laboratory have published the results of its modelling on the costs of environmentally friendly methods that emit less carbon to produce ammonia. Argonne senior scientist Amgad Elgowainy and his colleagues used Argonne's Greenhouse gases, Regulated Emissions, and Energy use in Technologies (*GREET*®) model to estimate the environmental impact of ammonia production from various energy sources. Then, they used a technoeconomic model to look at the cost of two different ways that ammonia could be produced more sustainably.

Their conclusion was that carbon capture can be implemented at relatively low cost, as the total cost to produce the ammonia increases by only about 20%. Fully 'green' ammonia, using water electrolysis to produce hydrogen, meanwhile, still has significant room for cost reduction of the electrolysis technology that could eventually make the water electrolysis pathway more cost competitive. "Research in this area could end up changing the market significantly, but it will take investment in developing and scaling up the production of the electrolysis technologies," said Elgowainy. "With the cost reduction and efficiency improvements to meet DOE's target of $1/kg of clean hydrogen, the electrolysis pathway could enable a close-to-carbon-free and affordable way of producing ammonia."

Heraeus adds smelter to its recycling capabilities

Heraeus Precious Metals is expanding its precious metal recycling capabilities by building a smelter in the US at Wartburg, Tennessee, where the company already operates a recycling facility. With its expanded capabilities, the company says that it will be able to treat new recycling materials and further strengthen its position in the recycling market. The smelter is planned to be operational within the next two years.

In line with Heraeus Precious Metals' sustainability goal to become carbon neutral by 2025, the smelter will be powered exclu-

PHOTO: HERAEUS PRECIOUS METALS

Computer rendering of the new Heraeus smelter at Wartburg, Tennessee.

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sively by renewable energy. It will mainly be used for the treatment of internal recycling material streams. Over the past years, Heraeus has seen strong growth at its eight recycling locations worldwide. This has resulted in a substantial increase in the quantity of internal streams suitable for smelter processing. Having the ability to treat these materials will increase the efficiency of the company's processes and reduce overall handling complexity. Heraeus says that this allows it to reduce its exposure to increasingly unreliable supply chains and become more robust within the value chain.

"We are convinced that the precious metals recycling market will continue to grow as a result of more regional supply chains and an increasing demand for both secondary recycled materials and circular solutions," said Uve Kupka, president of Heraeus Precious Metals Americas. "The investment in our site in Wartburg will be in the mid double-digit million dollar range and is part of a larger expansion program executed at our locations worldwide."

Logan delivers new methanator for fertilizer plant

Logan Industries International has completed the design, manufacture and delivery of a new methantor pressure vessel to produce synthetic methane for a fertilizer plant in the mid-western United States. The company says that the new vessel is fabricated from chromium and molybdenum and complies with the American Petroleum Institute's (API) recommended practice 934C, placing Logan in the top 10% of pressure vessel manufacturers in the US.

Dean Carey, technical director, Logan, said, "Logan is extremely pleased to participate in this effort and deliver the equipment on time to our customer. This was our first foray into API 934C specifications and we managed complex timelines, acquiring materials from both domestic and international resources and successfully mitigated a range of HSE concerns as our team completed their work within an extremely hot and challenging environment."

BRAZIL

Unigel installs industrial-scale green hydrogen production

Unigel, one of the largest chemical companies in Latin America and the largest manufacturer of nitrogen fertilizers in Brazil, has installed the first industrial-scale green hydrogen production in Brazil


PHOTO: THYSSENKRUPP NUCERA

Assembly of the thyssenkrupp Nucera electrolysers at Camacari.

at the Camacari industrial complex, for a total investment cost of $120 million. In the first phase of the project, Unigel installed three 20 MW electrolysers from thyssenKrupp Nucera, for a total capacity of 60 MW, which can produce 10,000 t/a of green hydrogen, equivalent to 60,000 t/a of green ammonia. The company says that it plans to quadruple its production of green hydrogen over the next few years by expanding the plant to a multi-hundred MW facility, which will produce approximately 40,000 t/a of green hydrogen.

Henri Slezynger, chairman and founder of Unigel, says: "Throughout our nearly 60-year history, we have always been attentive to technological innovations and have invested to meet industrial and agribusiness demands. With this project, Unigel takes the first step towards the decarbonization of several sectors, contributing substantially to combating climate change on the planet."

Dr. Werner Ponikwar, CEO of thyssenKrupp Nucera, said: "This project is the first of its kind in Brazil and reinforces the pioneering spirit of Unigel to produce green molecules on an industrial scale. As Brazil is one of the world-leading countries in terms of installed renewable energy, we are pleased to enter this partnership to make green hydrogen an affordable energy vector already today. Only through large-scale production with robust, reliable and cost-effective technologies at competitive renewable power prices green hydrogen will become market-ready with widespread use."

GERMANY

More ammonia shutdowns due to high gas prices

BASF has cut additional ammonia production due to high natural gas prices. In a media call following the release of the company's quarterly results, CEO Martin Brudermüller said that the company would purchase some ammonia from external suppliers to fill gaps but warned that farmers would face rising fertilizer costs next year. BASF has already cut ammonia output at its Ludwigshafen and Antwerp plants in September.

Yara, which runs Germany's third-largest ammonia plant at Brunsbuettel, says that its output across Europe is currently 27% below capacity due to the surge in gas prices, mainly due to production cutbacks in Italy and France, while SKW Piesteritz is in the process of resuming production after a scheduled maintenance shutdown. SKW also reduced ammonia production by 20% in September 2021. Germany faces ongoing shortages of natural gas due to restricted supply from Russia. Gazprom resumed pumping gas via its main pipeline to Europe, NordStream 1, on July 21st after a 10-day maintenance outage, but has cut supplies to Germany to just 20% of capacity.

CANADA

Terrestrial Energy signs MoU with Invest Alberta

Canada's Terrestrial Energy and Invest Alberta (the Government of Alberta's crown corporation promoting high-value investments) have signed a memorandum of understanding to support commercialisation of Terrestrial Energy's Integral Molten Salt Reactor (IMSR) Generation IV small modular reactor (SMR) plant in Western Canada.

Terrestrial Energy says the IMSR plant is designed for industrial cogeneration as well as high-efficiency, grid-based power generation and is ideally suited for natural resource extraction, low-carbon hydrogen and ammonia production.

Sonya Savage, the Government of Alberta's Minister of Energy, said: "There is great potential for SMRs to provide zero-emission energy for industrial operations in remote areas and further reduce emissions from Alberta's oil sands." Simon Irish, CEO of Terrestrial Energy, said the IMSR cogeneration plant "provides a clear pathway for Alberta industry to achieve net zero, and develop production capabilities for industrial leadership in a net-zero energy economy of the future."

JAPAN

Agreement on ammonia floating regasification unit

NYK Line, Nihon Shipyard, ClassNK, and IHI Corporation have signed a joint research and development agreement for the commercialisation of the world's first ammonia floating storage and regasification barge (A-FSRB). Japan is aiming to make large scale use of ammonia as a low carbon fuel in mixed fuel combustion power generation at coal-fired power plants in order to reduce CO_2 emissions. However, when using ammonia in existing thermal power plants, there are issues such as the problem of securing land for new onshore facilities including storage tanks and regasification facilities, and the large initial investment cost. The companies' solution is an offshore floating facility that can receive and store ammonia that has been transported via ship as a liquid, and then warm and regasify ammonia according to demand, and then send it to a pipeline onshore. This offers the advantages of shorter construction time and lower costs in comparison to construction of onshore storage tanks and regasification plants.

QATAR

Uhde to build world-scale blue ammonia plant in Qatar

thyssenkrupp Uhde says it has won a new contract from its long-standing customer the Qatar Fertiliser Company (QAFCO), for the engineering, procurement, construction and commissioning of a world-scale ammonia plant, capable of producing its full output as blue ammonia. The contract was signed on August 31, 2022, and the plant is planned to be completed by the first quarter of 2026. The project will be realised via a consortium with the Consolidated Contractors Company (CCC). Thanks to the *uhde*® ammonia technology, the single-train plant will have a record capacity of 3,500 t/d.

Martina Merz, CEO thyssenkrupp AG, said: "thyssenkrupp has a long-standing business relationship with Qatar, and we are delighted to sign this contract today. With our proven technology and innovation expertise we are laying the foundation towards sustainable solutions jointly with our customers." Dr. Cord Landsmann, CEO thyssenkrupp Uhde added: "the ongoing trust of our esteemed customer clearly shows that we can deliver solutions for the rising demand in clean ammonia, be it blue or green, as fertilizer or as a transport medium for hydrogen. With our proven dual pressure technology, clean ammonia can be produced in large quantities and we are very proud to be QatarEnergy's and QAFCO's partner in this lighthouse project. We are ready for the green transformation."

UNITED KINGDOM

CF Fertilisers to temporarily halt ammonia production at Billingham

CF Fertilisers UK has temporarily halted ammonia production at its Billingham complex "due to market conditions". The company says that it intends to use the site's capability to import ammonia to enable it to continue to run its ammonium nitrate and nitric acid plants, and it expects to fulfil all ammonia and nitric acid contracts and all orders of AN contracted for delivery over the coming months.

CF says that, at current natural gas and carbon prices, its ammonia production is uneconomical, with marginal costs above £2,000/t, as compared to global ammonia prices at about half that level. The current cost of natural gas at the UK National Balance Point is more than twice as high as it was one year ago, with the NBP forward strip suggesting that this price will continue to rise in the months ahead.

The Company has notified customers who purchase carbon dioxide on a contract basis from the complex about the impending temporary halt of ammonia production. Once the ammonia plant is safely shut down, CO_2 production, a byproduct of the ammonia process, will stop until the plant is restarted. ■

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Syngas News

ITALY

Contract awarded for waste to methanol plant

Maire Tecnimont subsidiary MyRechemical has been awarded a basic engineering contract for a waste to methanol and hydrogen plant to be located in Empoli, Tuscany. The scope of work includes the basic engineering design of the plant and the provision of necessary documentation to start the plant's public authorisation process with the Tuscany region. The basic engineering phase is expected to be completed by the end of 2022. Once completed, the plant will process 256,000 t/a of non-recyclable waste and will produce 125,000 t/a of methanol and 1,400 t/a of hydrogen. The plant will use MyRechemical's chemical conversion technology which allows the recovery of waste that cannot be mechanically recycled, or other types of unsortable dry waste. The carbon and hydrogen in the waste are converted via gasification into synthesis gas, which is used to produce low-carbon methanol and hydrogen.

Alessandro Bernini, Chief Executive Officer of Maire Tecnimont Group and NextChem, commented: "This is one of the more interesting waste-to-chemicals initiatives that Maire Tecnimont is developing in Italy. This is the first application worldwide of an integrated technological scheme that allows to produce methanol from waste for sustainable mobility and hydrogen that will substitute methane in glass production processes, enabling both recycling and industrial symbiosis. It responds to the core need of the circular economy and creates the bases of a new era of waste as a resource".

UNITED STATES

JM to partner ClimeCo to develop low carbon solutions

Johnson Matthey (JM) has signed a memorandum of understanding with climate solutions company ClimeCo to accelerate the deployment of enhanced carbon capture solutions for industry. The two companies will help syngas producers, initially in hydrogen and methanol, to build the business case for reducing CO_2 emissions from existing processes by up to 95%. The partnership combines JM's experience in technology development and deployment with ClimeCo's expertise in ESG strategy and regulatory analysis, empowering customers to make informed decisions on allocating capital for the deployment of JM's *CLEANPACE*™ solutions, accelerate emissions reductions, and future-proof plants against the rising costs of carbon.

Syngas producers are responsible for approximately 70% of CO_2 emissions in the chemicals sector. JM believes that the deployment of existing technology to over 150 grey hydrogen plants in Europe and North America alone could reduce CO_2 emissions by over 100 million tons per year by 2030, equivalent to the annual emissions from approximately 40 million cars.

"Companies around the world are under pressure to reduce carbon emissions and meet net zero targets," says Jane Toogood, Catalyst Technologies Chief Executive at JM. "Creating strategic partnerships allows us to offer our customers rounded and complete solutions. By working with ClimeCo, we will enable industries such as chemicals and refining, which rely on syngas, to quickly understand the regulatory frameworks, accelerate capital decisions for decarbonisation programmes and easily deploy proven technology solutions that can have an impact today, to create a cleaner world."

BRAZIL

Unigel to build industrial-scale green hydrogen production

Unigel, one of the largest chemical companies in Latin America and the largest manufacturer of nitrogen fertilizers in Brazil, is investing $120 million in the development of a production site for green hydrogen. In the first phase of the project, Unigel will instal three 20 MW standard electrolysers from thyssenkrupp nucera, for a total of 60 MW. The plant will feed one of the largest green ammonia plants by capacity when it starts its production, at the Camacari Industrial Complex, with a capacity of 10,000 t/a of green hydrogen and 60,000 t/a of green ammonia. In future phases the company says that it plans to quadruple its production of green hydrogen by expanding the electrolyser plant to a multi-hundred MW facility, which will produce approximately 40,000 t/a of green hydrogen. The products will be offered to customers who aim to decarbonize their production chains, e.g. the steel industry, oil refining, and e-fuels. Green ammonia will also be used as a raw material in the manufacturing of fertilizers and acrylics.

"This project is the first of its kind in Brazil and reinforces the pioneering spirit of Unigel to produce green molecules on an industrial scale," said Werner Ponikwar, CEO of thyssenkrupp nucera. "As Brazil is one of the world-leading countries in terms of installed renewable energy, we are pleased to enter this partnership to make green hydrogen an affordable energy vector already today. Only through large-scale production with robust, reliable and cost-effective technologies at competitive renewable power prices green hydrogen will become market-ready with widespread use."

"Given the potential of Brazil in the generation of wind and solar energy, we believe that the country has a great opportunity to be a reference for the world in green hydrogen, a solution that brings versatility to transform renewable energy into raw materials and zero carbon fuels", said Roberto Noronha Santos, CEO of Unigel. Brazil's energy mix already has a very high share of renewables. Around three quarters of the energy used in electrolysis of the project comes from renewable sources. This makes Unigel and thyssenkrupp nucera first movers on an industrial scale in one of the most important markets in South America.

PORTUGAL

Partnership for sustainable aviation fuel

The Navigator Company and German-based developer P2X-Europe have agreed to create a joint venture, P2X-Portugal, to develop a facility for the industrial-scale production of sustainable aviation fuels based on green hydrogen and biogenic CO_2. The project will leverage Portugal's competitive renewable energy sources and biogenic CO_2 generated by Navigator's biorefineries using sustainable forests, to produce net-zero synthetic feedstocks for the chemical industry and jet fuels on an industrial scale, fostering the decarbonisation of the aviation industry. P2X-Europe is a global pioneer in power-to-liquids project development and technology based on its parent companies' H&R Group and Mabanaft's market expertise in waxes and liquid fuels.

The facility will be located at Navigator's Figueira da Foz site and will eventually capture up to 280,000 t/a of biogenic CO_2, combining this with green hydrogen from several hundred megawatts of renewable energy capacity, for a zero carbon production capacity of 80,000 t/a of kerosene and waxes using a Fischer-Tropsch polymerisation. Capex is estimated at €550-600 million for the first two development phases, with a production capacity of 40,000 t/a of synthetic products. Subject to a final investment decision by mid-2023, the project is scheduled to start commercial operations in 1H 2026.

FRANCE

Feasibility study on waste wood gasification

NextChem has been awarded a contract by Storengy to carry out an advanced basic engineering study for a waste wood and solid recovered fuel conversion plant to produce biomethane. Once the project has reached the final investment decision, targeted for the end of 2022, and has secured the required permits, NextChem will act as an EPC contractor for the methanation package of the project, which is to be implemented at Le Havre. Storengy, an ENGIE subsidiary, is a world leader in underground natural gas storage, and aims to become a leader in hydrogen storage and production of renewable gases.

NextChem will be responsible for the engineering and cost estimating for the syngas purification, methanation unit and methane upgrading of the plant, which will produce 11,000 t/a of renewable and low carbon natural gas (biomethane). French company COMESSA will be responsible for the design and supply of the chemical reactor. The technology to be used in the plant has already been successfully applied to the Gaya pilot plant near Lyon, owned by ENGIE, which validated the feasibility to produce biomethane. This will be the first commercial project in the world of its kind to inject in the grid methane produced through gasification of waste wood.

GERMANY

Joint venture for production of large-scale electrolysers

Siemens Energy and Air Liquide have formed a joint venture for the production of industrial scale renewable hydrogen electrolysers in Europe. The partnership aims to foster a European 'ecosystem' for electrolysis and hydrogen technology. Production is expected to begin in the second half of 2023 and ramp-up to an annual production capacity of 3 GW per year by 2025.

Air Liquide will a 25.% stake in the joint venture, and Siemens Energy the other 74.9%. The joint venture will be headquartered in Berlin, as will the factory that produces electrolysis modules (stacks) based on proton exchange membrane (PEM) electrolysis technology. In addition, Air Liquide and Siemens Energy have agreed to dedicate R&D capacities to the co-development of the next generation of electrolyser technologies within the framework of the partnership.

The strategic partnership will benefit from a portfolio of hydrogen projects combining both Air Liquide and Siemens Energy's pipelines, targeting large industrial-scale hydrogen projects in collaboration with customers. This will create a solid basis for the required rapid ramp-up of electrolysis capacities and thus is expected to make competitive renewable hydrogen available sooner. One of the first projects is the Air Liquide Normand'Hy electrolyser project, with a capacity of 200 MW in the first phase, in Normandy, France.

"We want to be a driving force in hydrogen technology," said Christian Bruch, CEO, and President of Siemens Energy AG. "To make green hydrogen competitive, we need serially produced, low-cost, scalable electrolyzers. We also need strong partnerships. Together with Air Liquide as a pioneer in hydrogen for over 50 years, we look forward to implementing innovative solutions and collaborating to shape this new hydrogen market."

Demonstration plant for electrically heated steam cracker furnaces

BASF, SABIC and Linde have started construction of the world's first demonstration plant for large-scale electrically heated steam cracker furnaces. By using electricity from renewable sources instead of natural gas, the new technology has the potential to reduce CO_2 emissions of one of the most energy-intensive production processes in the chemical industry by at least 90% compared to technologies commonly used today. The demonstration plant will be fully integrated into one of the existing steam crackers at BASF's Verbund site in Ludwigshafen, Germany. It will test two different heating concepts, processing around 4 t/h of hydrocarbon feedstock and consuming 6 MW of renewable energy. The start-up of the demonstration plant is targeted for 2023.

BASF and SABIC are both investing in the project, and the demonstration plant will be operated by BASF. Linde is the engineering, procurement and construction partner for the project and in the future will commercialise the technology. To support the development of the novel furnace technology, the project has also been granted €14.8 million by the German Federal Ministry for Economic Affairs and Climate Action under its "Decarbonisation in Industry" funding program. The program

PHOTO: BJÖRN WYLEZICH

Platinum group metal ruthenium offers significant potential for PEM electrocatalysts for the production of green hydrogen.

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is supporting energy-intensive industries in Germany in their efforts to achieve carbon neutrality.

Yousef Al-Benyan, Vice-Chairman and CEO of SABIC said: "Our vision is to transform our business and to help address urgent global challenges through efficient carbon management. This project holds huge potential for all of the petrochemical industry around the world in our drive for low carbon emitting processes. With the milestone we are jointly announcing today on the start of construction, we hope that our three-party collaboration can inspire many more collaborations that ultimately bring the world to net-zero greenhouse-gas emissions through a circular carbon economy."

The demonstration plant aims to show that continuous olefin production is possible using electricity as a heat source. The plant is designed in such a way that two heating concepts can be tested in parallel: direct heating applies an electric current directly to the process tubes inside the reactor; indirect heating uses the radiative heat of heating elements placed around the tubes. Testing these two concepts will make it possible to react flexibly to different customer and site requirements.

Partnership for new hydrogen electrolysis catalysts

South Africa's Sibanye-Stillwater and Heraeus Precious Metals have agreed to jointly collaborate on research and development of novel platinum group metals containing catalysts with high activity and stability for proton exchange membrane (PEM) electrolysers for the production of green hydrogen. The project will be equally funded by both parties over a three-year period and the results mutually commercialised.

Platinum and iridium are currently essential components of catalysts for the generation of green hydrogen via PEM electrolysis. Iridium, however, is one of the scarcest platinum group metals, and its limited availability is a potential constraint on the future widespread adoption of PEM electrolysers. Reducing iridium loadings in catalysts is key to ensuring a sustainable hydrogen ecosystem, enabling PEM technology to be cost competitive to make triple digit GW scale electrolysis plants a reality within the next decade. Technologies that reduce or replace iridium with, for example, ruthenium, offer significant potential. The partners aim to develop a new, robust solution based on looking at the substitution of iridium with other metals, as well as developing more sophisticated metal oxide structures.

Heraeus brings significant technical expertise in the design of catalysts for PEM electrolysis and innovative solutions for the sustainable and cost-effective use of precious metals catalysts. "With our mutual know-how and resources, we are confident to develop novel solutions that will further strengthen the role of PEM electrolysis in the hydrogen economy", said Dr. Philipp Walter, Executive Vice President New Business Development at Heraeus Precious Metals. "Without cost effective PEM electrolysis the targets for the ramp-up of the hydrogen economy cannot be achieved. We are ready to invest into a sustainable raw material strategy to make it happen."

SWEDEN

Green methanol plant secures EU funding

The European Union Innovation Fund has selected Project Air, a production facility for sustainable methanol in Stenungsund, Sweden, as one of 17 large-scale green tech projects to be granted more than €1.8 billion in EU funding. Project Air is a collaboration between Perstorp, Fortum and Uniper, and has applied for €97 million funding as part of a total investment estimated at €230 million.

Project Air is based on using CO_2 and other residue streams recovered from Perstorp's ongoing operations, biogas from new dedicated plants, and hydrogen from a new large electrolysis plant to begin large-scale green methanol production by 2026. It will produce 200,000 t/a of methanol, replacing all fossil fuel methanol used by Perstorp in its existing downstream production processes.

DENMARK

Topsoe joins Circular Industrial Plastics initiative

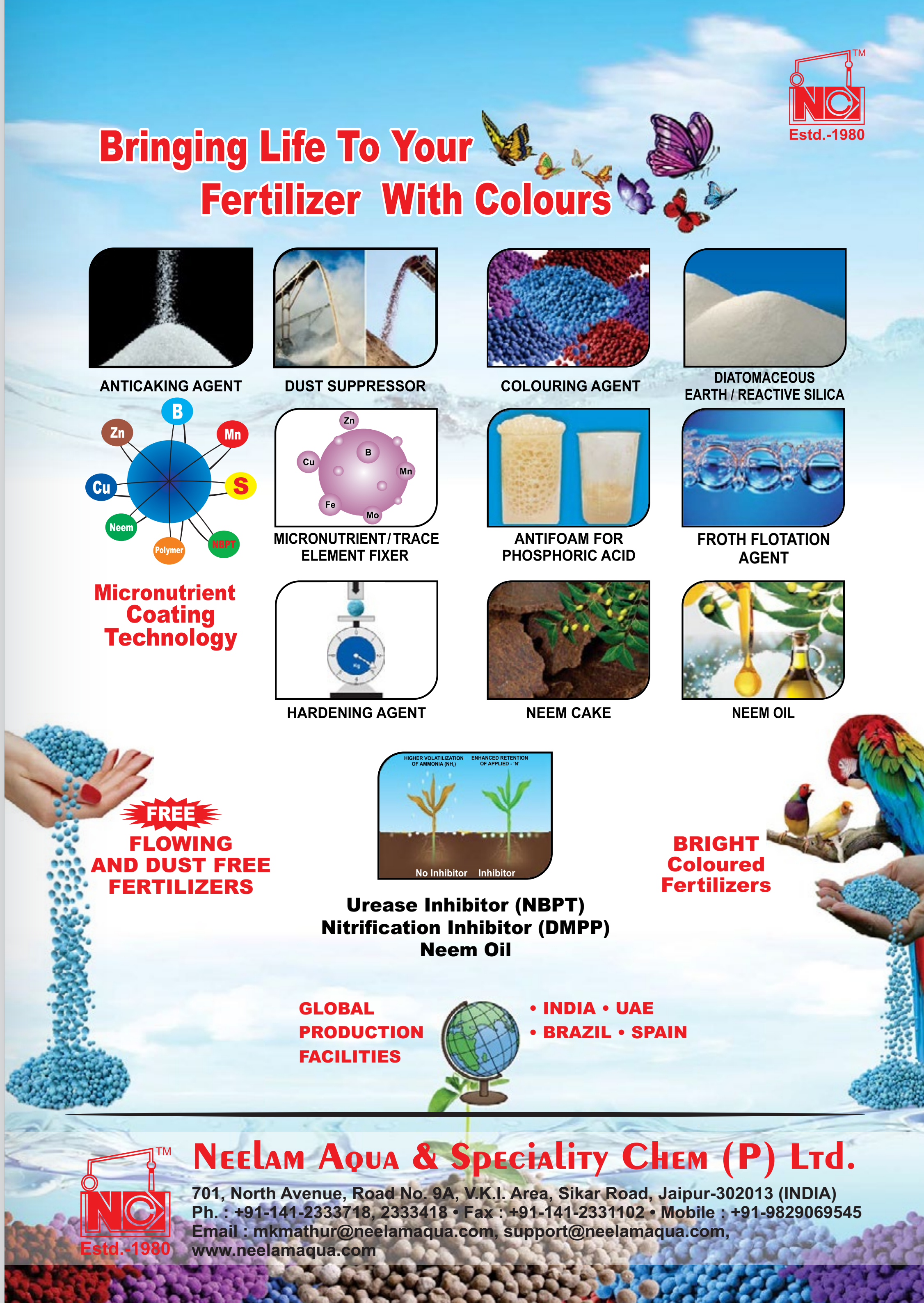
Topsoe has joined a newly formed partnership, Circular Industrial Plastics, which consists of large Danish companies, which have committed themselves to increase the recycling of industrial plastics by at least 20% before 2025. Circular Industrial Plastics has a budget of 41 million Danish krone ($5.6 million), of which 18 million ($2.5 million) were granted by the Danish Eco-Innovation Program (MUDP) under the Danish Environmental Protection Agency. The ambition is to make knowledge and technology within circular plastic available for Danish companies. Besides Topsoe, the project partners comprise Coloplast, Novo Nordisk, Danfoss, BASF, Grundfos, and COOP.

The first step in the project will be to survey and investigate the plastic materials that are currently used in the companies and then create an infrastructure for further treatment and recovery. At the completion of the project, the objective will be to demonstrate full-scale solutions for selected products within the categories of medical, technical, and consumer plastics, and to demonstrate the interaction of new recovery technologies in the circular flow.

Supply agreement for methanol plant

Anaergia Inc. has signed an agreement to supply European Energy with up to 60,000 t/a of liquid biogenic carbon dioxide over the next 10 years. Biogenic carbon dioxide is released during the decomposition of organic matter such as food waste. All Anaergia plants use organic waste material to produce biogas, which is composed of methane and carbon dioxide. European Energy, a renewable wind and solar energy producer, will produce green methanol from this biogenic CO_2. Under the terms of an agreement European Energy had previously entered into with A.P. Moller-Maersk, the green methanol will be used to power a container vessel that Maersk is having built to operate on the carbon neutral fuel. Anaergia will provide the liquified CO_2 from the anaerobic digesters that will operate at its plant being built in Tønder, Denmark.

"The benefit for us is the ability to sell the biogenic CO_2 from our plants that is produced when we convert organic materials to methane and CO_2. By selling this CO_2 instead of returning it to the atmosphere, our plants contribute to de-carbonising hard-to-abate sectors, such as shipping, while becoming more profitable, as we turn this waste gas from our plants into a useful fuel," said Andrew Benedek, Chairman and CEO of Anaergia. "This is a great example of carbon capture and utilisation, a critical step on the path towards net zero. We are looking forward to working with European Energy on this innovative endeavour, and to potentially working with them on other projects in the future as the need for green methanol rises globally". ■



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People

Clariant has announced a reorganisation into three global business units instead of the previous five, with the business unit presidents to be located in the regions with the largest customer base and highest growth potential for the respective businesses. It will also create a new executive steering committee that will include the CEO, the CFO and the presidents of the new business units.

Clariant will combine its existing Catalysts business unit and its Biofuels & Derivatives business line into a single business unit called "Catalysts". Functional Minerals and Additives will become "Adsorbents & Additives", and Industrial and Consumer Specialties and Oil and Mining Services will form the "Care Chemicals" business unit. The new units will be headed by newly appointed business unit Presidents **Angela Cackovich**, **Jens Cuntze**, and **Christian Vang**.

Angela Cackovich will become President, Adsorbents & Additives and the Europe, Middle East and Africa region. She will join Clariant`s Executive Steering Committee from Tesa, where she was a member of the Executive Committee. She gained significant industry experience in several positions, including at Henkel, Celanese, Rohm & Haas as well as Dow Corning and Hoechst. As a German citizen she holds a master's degree in chemical engineering.

Jens Cuntze has extensive experience within the company. He will become President, of the Catalysts business unit, located in the Asia-Pacific region. Previously, he was Head of Corporate Planning & Strategy after serving in various leadership roles including Head of Petrochemical Catalysts and Head of Procurement. He holds a diploma and PhD in Chemistry from ETH Zurich and is German.

Christian Vang will become President of the Care Chemicals unit and the Americas region. He has more than 14 years of leadership experience within Clariant. His most recent positions included Head of Industrial and Consumer Specialties and Head of Corporate Planning & Strategy. Prior to joining Clariant in 2008, Christian worked in leading positions at Siegwerk, SICPA and Hempel. He holds degrees from Harvard, Insead and London Business School, and is a Danish national.

With the elimination of the Chief Transformation Officer (CTO) and Chief Operating Officer (COO) roles, the new structure enables direct reporting lines of Clariant's BUs to the CEO. As a consequence of the new structure, **Hans Bohnen**, Chief Operating Officer, and **Bernd Hoegemann**, Chief Transformation Officer, have decided to step down from their current roles in the Executive Committee and will pursue their careers outside the company.

Clariant will ensure additional transparency and accountability by moving away from its current structure of an Executive Committee with a sole oversight and review role. Instead, the Company will have a new Executive Steering Committee that will include CEO Conrad Keijzer, CFO Bill Collins as well as the three BU Presidents effective July 1st, 2022.

In terms of gender equality, Clariant says that it strives to provide equal opportunities for all genders with a special focus on strengthening the gender balance at the management level by doubling the current female representation to at least 30% by 2030.

Nutrien has formally appointed **Ken Seitz** as its new president and CEO. Seitz has served as interim CEO since January 2022 and brings more than 25 years of experience in the agriculture and mining sectors. Russ Girling, chair of the Nutrien board of directors said, "Nutrien's record performance and disciplined execution of strategy during some of the most turbulent times we have seen globally underscore the strength of Ken Seitz's leadership. As president and CEO, Mr. Seitz will continue to drive positive outcomes for all of our stakeholders as we strive to safely and sustainably feed the world."

Mr. Seitz said, "I look forward to continuing the important work of safely and sustainably feeding a growing world with the executive leadership team, our employees globally and support of the Board of Directors. Growing up on a dairy farm in Saskatchewan, I am honoured and humbled to work alongside growers during these challenging times today and going forward. Nutrien is extremely well positioned to help meet the global goals of food security and climate action, partnering across the food system. Our purpose is to feed the future, and I am invigorated by the noble pursuit to help solve these critical world needs."

Calendar 2022/3

SEPTEMBER

11-15
66th AIChE Safety in Ammonia Plants and Related Facilities Symposium,
CHICAGO, USA
Contact: Ilia Kileen, AIChE
Tel: +1 800 242 4363
Web: www.aiche.org/ammonia

12-14
Argus World Methanol Forum,
HOUSTON, Texas, USA
Contact: Michelle Ladiana,
Argus Media Group
Tel: +44 (0)20 7780 4340
Email: conferencesupport@argusmedia.com
Web: www.argusmedia.com/en/conferences-events-listing/methanol-forum

OCTOBER

2-7
Ammonium Nitrate/Nitric Acid conference,
HOUSTON, Texas, USA
Contact: Hans Reuvers, BASF,
Karl Hohenwarter, Borealis.
Email: johannes.reuvers@basf.com,
karl.hohenwarter@borealisgroup.com,
annaconferencehelp@gmail.com
Web: annawebsite.squarespace.com

26-28
Global Syngas Technologies Conference,
TUCSON, Arizona, USA
Contact: Global Syngas Technologies Council, PO Box 18456, Sugar Land, TX 77496 USA
Tel: +1 713 703 8196
Email: info@globalsyngas.org

NOVEMBER

29-30
Argus Clean Ammonia Europe Conference,
HAMBURG, Germany
Contact: Argus Media Group
Tel: +44 (0)20 7780 4340
Email: conferences@argusmedia.com
Web: www.argusmedia.com/en/conferences-events-listing/clean-ammonia-europe

JANUARY 2023

30 – 1st FEBRUARY
Fertilizer Latino Americano,
RIO DE JANEIRO, Brazil
Contact: Argus Media Group
Tel: +44 (0)20 7780 4340
Email: conferences@argusmedia.com

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Plant Manager+

Handling leaks in urea plants: part 3

Leaks in the high-pressure synthesis section of a urea plant can have catastrophic consequences. UreaKnowHow.com started to collect incidents in an incident database and in 2017 AmmoniaKnowHow.com and UreaKnowHow.com introduced FIORDA, the Fertilizer Industry Operational Risk Database, a global open source risk register for ammonia and urea plants.

Part 1 of this short series of articles on how to handle leaks in urea plants explained why leaks in the high-pressure synthesis section of a urea plant are so critical and discussed corrosion and sealing challenges and what happens when there is a leak. Part 2 looked at the causes and consequences of leaks and discussed different types of critical leaks. Part 3 discusses different measures to prevent carbamate leaks.

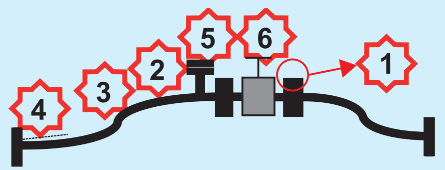
Prevention measures

As explained in Part 2 it is very difficult to stop a carbamate leak. The best practice is to prevent a leak in the first place. This can be done by the following measures:

Minimise the number of flange connections

Due to the challenges of avoiding leaks, as explained in Part 1 of this series of articles, it is good practice to minimise the number of flange connections in the urea plant.

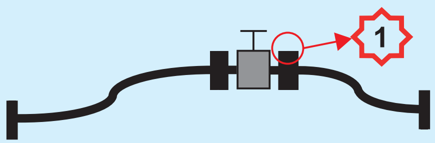
Fig. 1: **Failure modes in 316L Urea Grade high-pressure piping systems**



1. Crevice corrosion (flange connections, some accessories e.g. thermowells)
2. Condensation corrosion (gas phase piping systems)
3. Strain induced intergranular corrosion
4. Chloride stress corrosion cracking (carbon steel tracing)
5. Active corrosion (e.g. dead ends, weld-o-lets)
6. Erosion corrosion (e.g. 2-phase lines, valves)

Source: UreaKnowHow.com

Fig. 2: **Failure modes in super-duplex high-pressure piping systems**



1. Crevice corrosion (flange connections, some accessories e.g. thermowells)

Source: UreaKnowHow.com

Choose higher alloy materials of construction

A relatively high number of safety incidents occur with high-pressure 316L UG carbamate lines and NH_3 and CO_2 carbon steel feed lines. This is caused by the following:

- Many failure modes exist when using standard materials like 316L UG and carbon steel.
- Many welds of piping systems are made in the field instead of the shop.
- Welds in low-pressure parts of feed lines are typically considered a lower risk level.
- Piping systems are typically difficult to inspect and to reach.

By choosing higher alloy materials most failure modes can be avoided in high-pressure piping systems in the synthesis section of urea plants as indicated in Figs. 1 and 2.

Fig. 1 shows that besides the unavoidable failure modes, passive corrosion and possible design, fabrication, and installation failures, 316L Urea Grade high-pressure piping systems suffer from: crevice corrosion at flanges and some accessories, condensation corrosion of gas lines, strain induced intergranular corrosion, chloride stress corrosion cracking due to carbon steel tracing touching the stainless steel main pipeline in chloride containing ambient conditions, active corrosion due to loss of sufficient oxygen in the liquid phase and erosion corrosion due to high velocities.

Fig. 2 shows that most of these failure modes can simply be avoided by choosing a super-duplex as material of construction. Besides better safety and reliability, the higher strength of super-duplex saves on weight as it allows a lower wall thickness.

Choosing stainless steel as the material of construction also avoids the numerous failure modes in carbon steel ammonia feed lines like atmospheric corrosion, corrosion from inside due to carbon dioxide, erosion issues, vibration issues and weld failures.

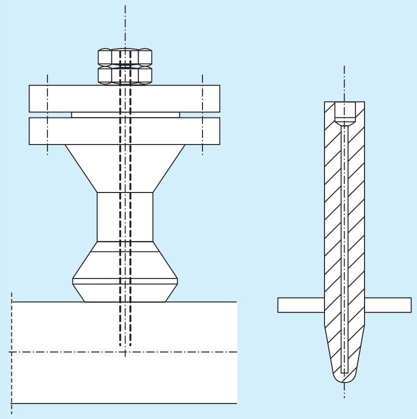
Choose a better design

Another way to prevent and/or reduce failure modes and consequential leaks is to choose a better design. Fig. 3 shows two possible designs for a thermowell.

In the design on the left a weld-o-let is applied to install the thermowell. This weld-o-let has some disadvantages, for example:

- It consist of several parts welded together, whereas each weld introduces risks to reduce corrosion resistance due to overheating;
- It forms a dead zone in liquid phase pipelines leading to higher corrosion rates as a result of lower oxygen levels; and
- It potentially forms a heat sink in gas phase pipelines leading to condensation corrosion.

Fig. 3: **Two possible designs for a thermowell**



Source: UreaKnowHow.com

The BHDT design on the right side avoids all of the above-mentioned risks and leads to higher safety and reliability levels.

Assure proper quality and experience during fabrication/installation/maintenance

Processing urea grade materials requires special knowhow and experience. It is therefore recommended to involve qualified and experienced fabricators during the fabrication, installation and maintenance of these equipment items and materials.

For high-pressure flange connections, it is recommended to minimise the number of flange connections, use of flange passports, and train mechanics how to handle these flanges. A flange passport leads to the following benefits:

- the awareness for good workmanship increases by means of a number of basic questions;
- the mechanic is triggered by a number of questions and,
- it provides the opportunity to unambiguously record deviations and to follow up.

Perform risk-based inspection programs

As equipment and materials experience continuous corrosion and several failure modes, it is recommended to perform a risk-based inspection when the plant becomes 10-15 years old. The program of a risk-based inspection should be tailormade and inspections should be performed by qualified and experienced inspectors taking into account all possible failure modes both from the process side as well as the utility and atmospheric side. ■

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PHOTO: NAVOYAZOT

Left: Navoyazot nitric acid plant.

The nitric acid market

Most nitric acid is used for production of fertilizer nitrates and ammonium nitrate explosives, but it is also used in polyamides, polyurethanes and aniline dyes as well as a number of industrial processes including ore treatment. High ammonia prices have pushed nitric acid prices to record levels this year, but growth predictions remain robust.

Nitric acid is the second most used industrial acid after sulphuric acid. Based on 100% nitric acid, total tonnage produced was about 66 million t/a in 2020. The route almost exclusively used for nitric acid production is the Ostwald process; the oxidation of ammonia over a precious metal catalyst, and nitric acid production represents about 18% of all ammonia demand globally.

In terms of end uses, nitric acid is predominantly used for the production of ammonium nitrate and its various derivatives, including urea ammonium nitrate (UAN) and calcium ammonium nitrate (CAN), as well as other specialty fertilizers and mixtures such as NPK fertilizers (Figure 1). Outside of its fertilizer use, AN is also widely used in the explosives industry as a component of ammonium nitrate-fuel oil (ANFO), a mixture that is the most common industrial blasting explosive, used in mining and quarrying, and representing around 90% of the commercial explosives market. However, while around 80% of nitric acid is used in AN manufacture, the remainder goes to a number of industrial processes, most notably nitrobenzene production, for use in dyestuffs, toluene diisocyanate (TDI), used in polyurethane manufacture, and adipic acid, used in polyamide manufacture. There is also a substantial quantity used in metal extraction and treatment, especially ferrous metal etching and cleaning, as well as the reprocessing of uranium. Highly pure (>98%) nitric acid is used in the semiconductor industry.

Geographically, nitric acid capacity is concentrated where AN is manufactured, primarily in Europe and Eurasia and North America, but capacity is also growing rapidly in China. As Figure 2 shows, these regions between them represent over 80% of all AN capacity. However, while nitric acid consumption in Europe, Eurasia and North America is focused primarily on production of ammonium nitrate and UAN/CAN, Chinese nitric acid consumption is conversely heavily biased towards chemical uses, which account for around 70% of demand. Metallurgical and pharmaceutical uses add another 20% to this, with ammonium nitrate for explosives and fertilizer use still very much a minority of consumption. China's nitric acid production is mainly (ca 50%) concentrated in the east of the country, particularly Jiangsu, Anhui, Zhejiang and Shandong provinces.

Demand

The coronavirus pandemic had a major effect on many end-use industries, from fertilizers to chemicals manufacture, with lockdowns causing disruption to production, supply and consumption. The effect was particularly pronounced on the car industry, leading to reduced demand for plastics and polyamides. This led to the first fall in nitric acid consumption for several years in 2020, though the figure for 2021 rebounded to approximately the 2019 level. Prior to this, however, demand had been growing steadily, if unspectacularly.

In terms of end-use markets, ammonium nitrate fertilizer use rose by 18% over the preceding decade to reach 17.3 million tonnes N in 2020. Europe was the largest consuming region, at 3.0 million tonnes N for the EU, with Russia and the US close behind at 2.9 and 2.8 million tonnes N respectively. However, consumption in China is rising rapidly, almost doubling over the decade to reach 2.2 million tN/a. Ammonium nitrate is preferred as a fertilizer in regions with short growing seasons, as the nitrate is present in a form readily available to the plant, unlike urea, which must hydrolyse to nitrate in the soil before it can be taken up. This has helped AN keep its share of nitrogen fertilizer consumption in spite of concerns over its safe storage and handling, as evidenced by the explosion in Beirut harbour in 2020, or any potential for misuse as an explosive by dissident groups. However, the markets in which it finds use are fairly mature in terms of fertilizer use and consumption, and so outside of its increasing use in China, growth in demand for AN fertilizer is relatively slow, with overall consumption increasing by about 1.6% per year.

The commercial explosives market, meanwhile, is based mainly based around mining and quarrying, with some used in road and other construction. Three industries have traditionally dominated demand for mining explosives; coal mining, iron ore mining, and copper mining, collectively using more than two thirds of all explosives. Of these three, coal mining has remained essentially static over the past decade, with production rising only 1% from 2011 to 2021, when it reached 167 million t/a according to BP figures. Production is concentrated in China (50%) with India, Indonesia and the US representing another 25%. Iron ore mining is an even larger industry, and production was 2.6 billion t/a of ore in 2021 (1.6 billion tonnes Fe), with Australia, Brazil, China and India the leading producers, representing around 80% of production between them. Production has risen about 8% over the past decade. Finally copper mining stood at 21.0 million t/a in 2021, with Chile by far the largest producer, followed by Peru, China and Congo. Copper is the fastest growing of the three sectors, with production having risen by over 30% from 2011 to 2021. Overall, demand for industrial grade AN has risen at about 1.4% per year over the past decade.

Industrial chemical markets are a much faster growing segment, with average annual growth rates for TDI, nitrobenzene and adipic acid ranging from 3.5% to 4.9%, and it is a similar story for some of the metal treatment segments. However, collectively they only represent 20% of nitric demand, and so growth in these segments only brings the overall growth rate for nitric acid demand to just over 2% year on year. China remains the fastest growing single market.

Nitrous oxide

The nitric acid industry has come under increasing pressure to reduce its emissions of nitrous oxide, N_2O. It is estimated that around 5 kg of nitrous oxide are produced for every tonne of nitric acid, which has turned nitric acid production into the single largest industrial process source of nitrous oxide. Because of N_2O's high global warming potential; around 270-300 times that of CO_2, even the emission of relatively lower quantities can have a significant impact on man-made climate change. The US, for example, calculated that 7% of its CO_2-equivalent emissions came from nitrous oxide in 2020, mainly from emissions form soil during the breakdown of nitrogen fertilizers.

Because of this, installation of N_2O abatement technologies has been strongly encouraged via the Kyoto Protocol, and has become mandatory in some jurisdictions: for example, since 2013 it has been obligatory for nitric acid plants in the European Union to have such abatement technology installed. Three ways of controlling N_2O emissions are recognised; primary, secondary and tertiary. Primary reduction comes during the ammonia oxidation process itself, using lower reaction temperatures, or perhaps via modification of the precious metal catalyst gauze such as substitution of cobalt, though this also makes the reaction less selective. Secondary abatement happens prior to the process stream reaching the absorption tower, and tertiary is an 'end of pipe' solution that selectively reduces N_2O. End of pipe solutions are often preferred, as many nitric acid plants are of considerable vintage (over 30 years old) and may not be as amenable to changes to the process section. Iron zeolite catalysts have proven effective at decomposing N_2O to N_2 and O_2, and form the basis of thyssenkrupp's *EnviNOx*® process, which has achieved N_2O removal rates of 98-99%, with overall NOx emissions being reduced to as low as 1 ppmv. BASF's rival *DeNOx* process uses a vanadium oxide catalyst instead for similar effect. Last year, Clariant donated 10 loads of its *EnviCat* catalytic reduction catalyst to nitric acid producers who did not have existing abatement systems.

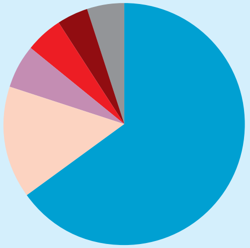
However, of the estimated 580 nitric acid plants operating globally, around half are believed to still have no N_2O abatement technology in place, mostly in countries without the appropriate emissions control legislation in place. To try and combat this, the German Environment Ministry's Nitric Acid Climate Action Group (NACAG) has been partnering with governments and nitric acid producers in these countries and providing financial support to install abatement technology. Signatories to its Declaration now include Tunisia, Argentina, Mexico, Zimbabwe, Indonesia, Vietnam, Cuba, Pakistan, Thailand, Jordan, Georgia, Uzbekistan, Colombia and Bosnia, and most recently it has assisted with a tender for abatement technology for Sable Chemicals in Zimbabwe, and a study on abatement options for the government of Thailand.

The merchant market for AN

As nitric acid is a difficult and dangerous chemical to store and transport, about 90% of it is produced for captive use on-site, integrated into downstream AN and other production. The merchant market for nitric acid is comparatively small, with China the largest importer, but production growth is gradually switching towards Asia as countries like India and particularly China try to boost domestic production for industrial uses. Chinese production is often at the higher end of the cost curve and can act as a swing producer of acid. However, the covid pandemic and associated shutdowns of chemical producers which consume nitric acid in China has impacted upon domestic demand, which has kept a lid on prices.

Nevertheless, as with virtually all commodities, the war in Ukraine and subsequent sanctions on Russia has impacted upon the nitric acid market. Rising fuel and freight charges, and particularly the surge in the price of ammonia led to nitric acid prices reaching $420/t in Europe in March 2022, $380/t in the US and $450/t in China. Since then, however, prices have peaked and weaker market fundamentals have reasserted themselves. ■

Fig. 1: **Nitric acid consumption, 2020**

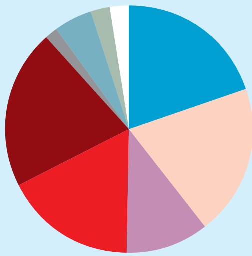


AN fertilizer	65%
AN explosives	15%
Adipic acid	6%
Toluene di-isocyanate	5%
Nitrobenzene	4%
Others	5%

Total: 66 million t/a (100% HNO_3 basis)

Source: Sabic

Fig. 2: **Ammonium nitrate capacity by region, 2020**



Europe	24%
FSU	24%
North America	13%
China	21%
Other Asia	25%
Middle East	2%
Africa	6%
South America	3%
Australasia	3%

Total: 30.3 million tonnes N per year

Source: IFA

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Ammonium nitrate markets after Ukraine

The war in Ukraine has severely affected the supply of ammonium nitrate and CAN from Russia and Ukraine, with particular potential impact on Europe and Latin America. Can urea make up the difference?

The conflict in Ukraine and subsequent international sanctions have upended many markets, but perhaps none more so than for oil, gas, food and fertilizer. Oil has been perhaps the least affected of these. The US has halted Russian oil and refined products imports, and some countries have pledged to end imports of Russian oil by the end of 2022, including the EU, UK and Australia, but by and large the oil market seems to have reconfigured itself and rearranged global flows of product, and Russian oil continues to be exported, now flowing towards China and India instead.

Natural gas is a very different prospect, however. Here Russia has sought to exploit Europe's vulnerability by stepping down exports to Europe along even the pipelines that do not cross the conflict zone, exacerbating an already tight supply situation. With the northern hemisphere winter approaching, Europe is scrambling to find LNG cargoes and switch to alternative power sources, including switching back on some closed coal-fired power plants, and gas prices have soared to truly unprecedented levels. This in turn has had a major impact on European fertilizer producers. With natural gas accounting for the bulk of operating expense in ammonia production, natural gas prices as high as $70/MMBtu such as have been seen in the Netherlands TTF price can be equivalent to a $2,500/t baseline cost in the price of ammonia. Even at the inflated prices currently being seen in the market, this makes most European ammonia production uneconomic. Producers have consequently been forced to progressively close domestic ammonia production. All UK ammonia production is now idled. German production is running at about 50%. The last line at Achema in Lithuania will close in September, and Yara reckons that overall across Europe its output is now down to only 35% of capacity. For the moment many producers are operating on imported ammonia at these record prices, but even so around half of Europe's downstream nitrogen production is currently not producing. Furthermore, it is by no means sure that there is enough ammonia to go around. Russia accounts for 23% of ammonia production globally, as well as 14% of urea and in 2021 was the world's second largest ammonia producer (after China) and the largest exporter. In 2021, Russia exported 4.4 million tonnes of ammonia, representing 30% of all traded ammonia.

Finally, the effect on grain markets has been equally serious. In 2020 Russia and Ukraine accounted for 26% of global wheat exports (Russia 18%, Ukraine 8%), 24% of barley exports (12% each) and 14% of corn exports (Ukraine 13%, Russia 1%). While an international deal has been done to export some grain from Odessa, around 30 million tonnes of grain is still reckoned to be sitting in silos and stores in Ukraine, awaiting export. With a storage capacity of an estimated 55 million tonnes, it is by no means clear if there is sufficient space to store this year's harvest, though the production figure this year is bound to be down as the war has cut some of the through the most productive land in the southeast of Ukraine. This shock to the international market has driven up food prices, making fertilizer a little more affordable but also threatening famine in areas such as east Africa.

Above: A Gapzrom pumping station. Russia has progressively cut gas supplies to Europe this year.

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Table 1: Total AN melt capacity (million tN/year), 2020

Europe	7.4
Russia/CIS	7.3
(of which: Russia 4.5, Ukraine 0.9)	
North America	3.8
South America	1.0
Africa	1.8
Middle East	0.7
South Asia	0.9
East Asia	6.9
Australasia	0.9
Total	**30.8**

Source: IFA

Export restrictions

The restrictions on export of nitrogen fertilizer are not just down to Russia's inability to sell or Europe's and North America's unwillingness to buy. There are also domestic restrictions on sales to ensure supply to the home market. Russia had already imposed export quotas on fertilizers back in December 2021 as gas price issues in Europe led to potential production shortages. While the quota for urea was above the normal seasonal export amount, the quota for export of Russian AN for the six months from December 1st was just 744,000 tonnes; less than half the amount that would usually be exported over that period. This was followed in late January by a complete ban on AN exports during February and March, later extended to April. On May 1st exports were allowed again, but the quotas from late 2021 were still in force. Finally, by June 1st, the Russian domestic fertilizer application season having come to an end, exports were permitted at an unrestricted rate, though western sanctions on Russian banks and payment processing and consequent high shipping rates continued to complicate the actual process of exporting. There were shipments to Brazil at discounted rates of up to $50-100/t to the prevailing market price.

Meanwhile, on May 31st, the Russian government announced that it would be extending its export quotas for nitrogen and complex fertilizers. Between July 1st and December 31st 2022, only 8.3 million tonnes (product) of nitrogen fertilizers and 5.95 million tonnes of complex fertilizers will be permitted to be sold overseas; approximately 60% of what might normally be shipped. As before, the quotas will not apply to fertilizer supplies to the breakaway and largely internationally unrecognised republics of Abkhazia (Georgia), South Ossetia (Moldova) and the so-called Donetsk and Luhansk People's Republics in eastern Ukraine.

Ammonium nitrate

Russia is a key player in the ammonium nitrate market. As Table 1 shows, when total AN melt capacity (including CAN and UAN) is taken into account, Russia's share of world capacity is more like 15%, but its importance to the straight AN fertilizer market is much greater. In 2021 it exported 4.3 million tonnes of ammonium nitrate (1.5 million tonnes N), which represented almost 50% of the international market. This dominance in the AN trade is also shown in Table 2, which aggregates figures for both AN and CAN fertilizer. The net regional figures obscure a good degree of cross-border trade within regions, but Russia's exceptional position in the market is clear. It also shows that, while Europe was – prior to the current crisis at least – broadly self-sufficient in AN/CAN production, many countries outside of Europe are net importers, particularly Brazil, which takes much of the 800,000 tonnes N destined for South America.

Russia's share of the urea market is shown in Table 3. Here Russia is important though far less dominant. Russian customs figures show that 2021 exports were 7.3 million tonnes of urea (3.4 million tonnes N), slightly up on the 2020 figure in Table 3. This made it the world's single largest urea exporter, with around 18% of the global market. It is worth noting, as IFA analyst Laura Cross pointed out at IFA's annual conference in May, that of that 7.3 million t/a of urea exports in 2021, only around one third (2.4 million t/a) went to countries that have since imposed sanctions on Russia, while two thirds (4.9 million t/a) went to countries which have not, including Brazil and India. The impact of sanctions on the urea market are therefore likely to be far less severe than for e.g. potash, where Russia and Belarus supply most of Europe's needs.

Table 2: World AN/CAN production and trade, 2020, million tonnes N

	Production	Export	Import	Net export
Europe	5.7	2.9	3.1	-0.2
Russia	4.6	1.6	0	1.6
Ukraine	0.6	0	0.1	-0.1
Other CIS	1.6	0.6	0.5	0.1
North America	3.2	0.3	0.2	0.1
South America	0.5	0	1.3	-0.8
Africa	0.9	0.1	0.5	-0.4
Middle East	0.4	0.1	0.1	0
South Asia	0.4	0	0.1	-0.1
East Asia	2.6	0.1	0.2	-0.1
Australasia	0.7	0	0.1	-0.1
Total		**21.2**		

Source: IFA

Table 3: World urea production and trade, 2020, million tonnes N

	Production	Export	Import	Net export
Europe	2.2	1.4	3.0	-1.6
Russia	4.5	3.3	0	3.3
Ukraine	1.5	0.7	0	0.7
Other CIS	1.6	0.7	0.3	0.4
North America	7.2	0.8	2.5	-1.7
South America	1.4	0.4	6.0	-5.6
Africa	5.4	3.9	1.4	2.5
Middle East	10.8	8.3	1.2	7.1
South Asia	15.2	0	5.3	-5.3
East Asia	31.5	4.5	2.7	-1.8
Australasia	0.2	0	1.1	-1.1
Total		**83.5**		

Source: IFA

Russia also exports around 2.2 million t/a of urea ammonium nitrate (UAN). This became a bone of contention in July last year when CF Industries brought a case before the US International Trade Commission alleging that UAN solutions from both Russia and Trinidad had been illegally "dumped" (i.e. sold at below the notional cost of production and export) on the US market. The ITC came to its conclusions on the case in June 2022, and agreed that Russian imports had been dumped at rates ranging from 8.16% to 122.93%, and unfairly subsidised at rates ranging from 6.27% to 9.66%. In addition, the ITC found that imports from Trinidad had been dumped at a rate of 111.71% and unfairly subsidized at a rate of 1.83%. However, in its finally injury determination, and no doubt with an eye on the current international market situation, the Department of Commerce elected not to impose import tariffs on these products, presumably in a bid to at least partially cushion US farmers from rising fertilizer prices. In a press statement CF Industries said it was "disappointed" in the decision, since it was clear that "unfair trade practices from state-subsidised entities underpinning UAN imports from Russia and Trinidad… were clearly established through thorough and impartial investigations".

Europe's dilemma

The current crisis for Europe in particular is thus twofold. Firstly, sky-high gas prices have forced the largest shutdown of European nitrogen fertilizer capacity ever seen, while the continent's ability to substitute using ammonia or ammonium nitrate from overseas is greatly reduced by Russia's export quotas and financial sanctions.

European leaders are still scrambling to adjust to the new reality. The Spanish and Dutch governments have said that they have "a new focus" on treating animal manure and using it instead of traditional synthetic fertilizers. However, this would require a derogation to, or amendment of, the EU Nitrates Directive. The directive, introduced in 1991, aims to protect water quality across Europe by preventing nitrates from agricultural sources from polluting ground and surface waters and by promoting the use of good farming practices. The Dutch government has proposed a 'derogation' from the existing law for allowing the application of fertilizers with recovered nutrients from manure for a minimum period of eight years. Nevertheless, ramping up projects to recover nutrients from manure to a sufficient level to make a difference to EU nitrogen consumption is a long term plan, with gains possibly several years away.

Substitution of ammonium nitrate with urea is possible, though European farmers have traditionally preferred AN because it is more quickly available to the plant in the field during short growing seasons without having to be hydrolysed first as urea is. Urea and AN prices tend to end up linked in this way, with AN prices capped by the equivalent nitrogen nutrient value of urea. As Tables 2 and 3 show, the urea market is roughly four times larger than the ammonium nitrate market, both in terms of production/consumption and international trade, and Europe's share of it much smaller. This in theory should make sourcing urea easier than ammonium nitrate. The issue is that, given Russian export quotas, there still may not be enough spare urea capacity available around the world to supply sufficient for all that consumers wish to buy. We may have moved into a market which, rather than being demand limited as is traditional, has become supply limited. This will play out at the farm level, with crop prices, farm incomes, subsidies, crop mix etc all playing a part in deciding which farmers can and do afford fertilizer over the coming months. IFA's recent analysis of this indicated that Latin America was one of the regions with the most exposure to high market prices for nitrogen. IFA's pessimistic scenario – something which seems increasingly likely – predicts a 7% fall in global fertilizer use in the 2022-23 fertilizer year, comparable to the 8% fall in 2008-09, though this overall figure represents only a 5% fall in nitrogen consumption and up to 13% in potash consumption. South and East Asia show the sharpest total decline, followed by Latin America and Africa, but Africa shows the largest percentage decline.

Looking to the future, with the conflict in Ukraine showing no signs of winding down, the reconfiguration of the global nitrogen industry seems set to continue. Though there is new urea and other nitrogen capacity due to come on-stream in the next few years, a proportion of this is in Russia and the timescale for completion is now much more doubtful, as discussed elsewhere in this issue. Even with demand destruction this year caused by high prices, nitrogen markets look set to be tight for a couple more years to come. ■

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Syngas project listing 2022

A round-up of current and proposed projects involving non-nitrogen synthesis gas derivatives, including methanol, hydrogen, synthetic/substitute natural gas (SNG) and gas- and coal-to-liquids (GTL/CTL) plants.

Contractor	Licensor	Company	Location	Product	mt/d	Status	Start-up date
BOTSWANA							
n.a.	n.a.	Botswana Oil	Ikaegeng	CTL	2,600	FS	n.a.
CANADA							
n.a.	Greyrock Energy	Rocky Mountain GTL	Carseland, AB	GTL	70	C	2022
n.a.	Topsoe	Air Products	Edmonton, AB	Hydrogen	1,500	DE	2024
n.a.	Topsoe	Nauticol	Grande Prairie, AB	Methanol	5,000	CA	2026
CHILE							
Siemens	JM (DAVY™)	Haru Oni	Punta Arenas	Methanol	350	UC	2022
CHINA							
n.a.	Casale	Anhui Tanxin Tech Co	Hubei, Anhui	Methanol	1,500	C	2021
n.a.	Eastman/JM (DAVY™)	Jiutai	Togtoh, Mongolia	Methanol/MEG	3,000	C	2021
n.a.	JM (DAVY™)	Ningxia Baofeng	Yinchuan, Ningxia	Methanol	7,200	UC	2024
n.a.	JM (DAVY™)	Jiangsu Sailboat	Lianyungang, Jiangsu	Methanol	300	UC	2023
n.a.	n.a.	Sinopec	Tahe, Xinjiang	Hydrogen	60	UC	2023
n.a.	JM (DAVY™)	Shenhua Baotou	Baotou, Mongolia	Methanol	6,000	DE	2026
EGYPT							
n.a.	n.a.	EBIC	Ain Sokhna	Hydrogen	270	UC	2024
n.a.	n.a.	IMC	Ain Sokhna	Methanol	3,000	CA	2025
FINLAND							
n.a.	n.a.	Veolia	Äänekoski	Methanol	36	CA	2024
GERMANY							
n.a.	Siemens	Siemens	Wunsiedel	Hydrogen	900	UC	2022
INDIA							
EIL	Topsoe	Assam Petchem	Namrup	Methanol	500	C	2022
BHEL	n.a.	Coal India Ltd	Dankuni	Methanol	2,000	P	2025
INDONESIA							
Samsung	Air Liquide	Petronas	Bintulu, Sarawak	Methanol	5,000	UC	2023
n.a.	Topsoe	PT Bukit Asam	Muara Enim	Methanol	6,000	UC	2025
	Air Liquide						
n.a.	Air Products	PT Bumi Resources	Batuta	Methanol	5,000	DE	2026
IRAN							
Namvaran	Topsoe	Badr-e-Shargh Pet Co	Chabahar	Methanol	5,000	UC	n.a.
PIDEC	Casale	Apadana Methanol	Assaluyeh	Methanol	5,000	UC	On hold
n.a.	Casale	Fateh Sanat Kimia	Dayyer	Methanol	5,000	UC	On hold
n.a.	n.a.	IOC	Mathura	Hydrogen	15	BE	2024
ITALY							
n.a.	Tecnimont	Alia Servizi Ambientali	Empoli	Methanol	375	BE	2025
MALAYSIA							
Samsung	Air Liquide	Sarawak Petchem	Sanjung Kidurong	Methanol	5,000	UC	2023
Samsung	n.a.	H2biscus	Sarawak	Methanol	1,400	DE	2025
NETHERLANDS							
n.a.	Air Liquide	W2C Rotterdam	Rotterdam	Synfuels	n.a.	P	2026
n.a.	Casale	Gidara Energy	Amsterdam	Methanol	250	DE	2024
n.a.	n.a.	Gidara Energy	Rotterdam	Methanol	270	DE	2025
NIGERIA							
n.a.	Air Liquide	Brass Fert & Petchem	Brass Island	Methanol	5,000	BE	2025
RUSSIA							
n.a.	Casale	Gazprom Methanol	Tomsk	Methanol	3,100	RE	2024
China Chengda	Topsoe*	Nakhodka Fertilizer	Nakhodka	Methanol	5,400	UC	2023
Tecnimont	Topsoe*	Baltic Gas Chemical	Ust-Luga	Methanol	5,000	DE	n.a.
Hyundai/NIIK	Topsoe*	Gaz Sintez	Vysotsk	Methanol	4,850	UC	2023
TAIF	Topsoe*	Nizhnekamskneftekhim	Nizhnekamsk	Methanol	1,500	CA	n.a.
MHI	Topsoe*	GTM One	Khimprom	Methanol	3,000	BE	2025
n.a.	JM (DAVY™)*	JSC Technoleasing	Skovorodino	Methanol	3,000	BE	2025
n.a.	Casale	Metafrax					
SAUDI ARABIA							
n.a.	Air Products	Air Products Qudra	Jubail	Hydrogen	415	UC	2023
n.a.	Topsoe	Chemanol	Jubail	Methanol	+300	RE	2023
SINGAPORE							
n.a.	Air Liquide	PTTEP	Singapore	Methanol	150	FS	n.a.
SWEDEN							
n.a.	Topsoe	Liquid Wind	Örnsköldsvik	Methanol	150	DE	2024
n.a.	n.a.	Project Air	Stenungsund	Methanol	600	P	2026
TURKMENISTAN							
Sojitz, KHI	Topsoe	Turkmengaz	Ovadan-Depe	Methanol	n.a.	CA	n.a.
UNITED ARAB EMIRATES							
n.a.	n.a.	Ta'ziz	Ruwais	Methanol	5,400	P	2025
UNITED KINGDOM							
n.a.	n.a.	Equinor	Saltend	Hydrogen	380	DE	2026
n.a.	n.a.	Cromarty Clean Fuels	Nigg, Scotland	Methanol	n.a.	FS	n.a.
UNITED STATES							
Fluor	Air Liquide	YCI Methanol	Lake Charles, LA	Methanol	4,800	C	2021
Linde	Linde	Praxair (Linde)	St James Parish, LA	Hydrogen	425	C	2021
n.a.	Relocated plant	US Methanol	Charleston, WV	Methanol	480	UC	2022
n.a.	Air Liquide	Air Liquide	California	Hydrogen	30	UC	2022
Fluor	JM (DAVY™)	South Louisiana Methanol	St James Parish, LA	Methanol	5,000	UC	On hold
KBR	JM (DAVY™)	Methanex	Geismar, LA	Methanol	5,000	UC	2024
n.a.	Topsoe	Arbor Renewable Gas	Beaumont, TX	Methanol/MTG	135	DE	2024
n.a.	n.a.	Bia Energy	Shreveport, LA	Methanol	1,600	FS	2025
n.a.	Topsoe	Nacero	Penwell, TX	Methanol	5 x 5,000	CA	n.a.
UZBEKISTAN							
Hyundai	Topsoe/Sasol	Oltin Yo'l GTL	Shurtan	GTL	5,000	C	2022

Original licensors: Topsoe and Johnson Matthey have both announced their withdrawal from all new commercial activity in Russia.

KEY

BE: Basic engineering
C: Completed/commissioning
CA: Contract awarded
DE: Design engineering
FS: Feasibility study
n.a.: Information not available
P: Planned/proposed
RE: Revamp
UC: Under construction

Conversion:
1 t/d of hydrogen = 464 Nm³/h
1 t/d of natural gas = 1,400 Nm³/d

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Urea plant revamping for energy savings

Casale reviews urea plant revamping process schemes and successful case studies for energy savings and TOYO discusses its latest revamping technologies including application of the new generation low-pressure, energy-saving ACES21-LP™ process.

CASALE

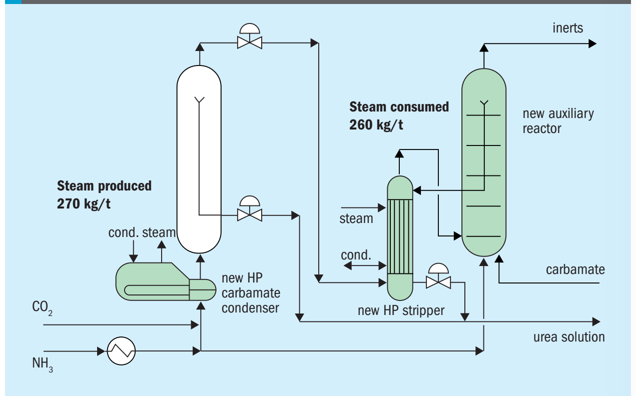
Casale urea plant revamping schemes for energy savings

Matteo Fumagalli

Since April 2021, alongside the progressive improvement of the SARSCoV-2 pandemic and consequent recovery of the economy worldwide, the price of natural gas has surged to levels not seen for almost 20 years. In some regions the high prices for energy and raw materials have had a major impact, drastically eroding the operating margin of many fertilizer manufacturers. For example, in Europe, where natural gas in August 2022 is ten times more expensive than it was in early 2021, the cost of urea production has skyrocketed.

In this scenario, which according to several analysts is not going to improve any time soon, reducing the energy intensity of fertilizer production processes is crucial for keeping operating costs under control and to recover profitability. In a typical breakdown of urea production costs, ammonia accounts for 80-85%, whereas energy (steam and power) typically accounts for "only" 10-16%. With the urea price as in 2020, the energy bill of an average urea plant would total 25-40 $/t. Even a significant reduction of the energy consumption, 20-30% less, would yield a "meagre" 5-10 $/t extra profit. In such market conditions, energy saving alone is seldom a sufficient driver for complex and costly plant revamping projects which generally require an associated relevant capacity increase to provide attractive returns. A different scenario is represented by revamping projects backed or demanded by authorities to reduce the environmental impact or carbon footprint of fertilizer production. However, in the current urea market scenario, with spot prices of urea at around 800 $/t and natural gas as high as 200 $/MWh, energy saving projects yield a very attractive return time, especially for vintage and high energy consuming plants.

Fig. 1: **HEC process synthesis section**



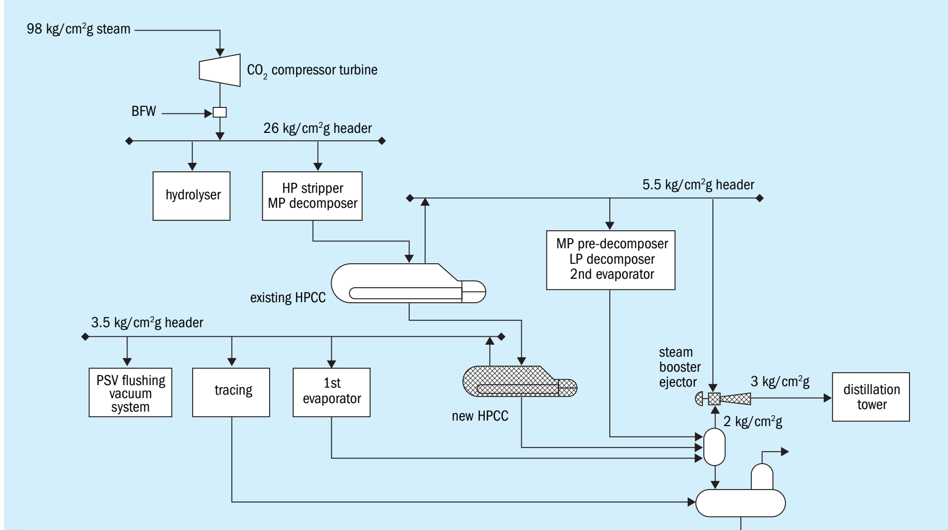
Source: Casale

Revamping of urea plants has always been part of Casale's DNA, which led to the development of specific process schemes for energy saving. During almost four decades of activity in the urea business, Casale has implemented its revamping schemes to vintage plants of different design, covering almost all process technologies. In the following review, a few process schemes are presented together with the mention of cases studies where they have been successfully applied.

Revamping Total Recycle plants: The HEC process

The High Efficiency Combined (HEC) process was developed in the 1990s specifically for the revamping of vintage Total or Partial Recycle plants. Its name refers to the main feature of the process scheme, which foresees the combination of a once-through high-conversion synthesis step with a reactor fed only by recycled carbamate. Fig. 1 shows the overall scheme of the synthesis section with the new items of equipment marked in green, consisting of a new auxiliary reactor, a HP carbamate condenser and a HP stripper. The HP stripper requires 20 bar(g) steam, but the HP carbamate condenser generates LP steam at 5.5 bar(g) which is used in the downstream purification sections. The overall CO_2 conversion of the HEC synthesis section is about 72-73% which represents a drastic improvement compared to a typical Total Recycle averaging 60-64%. Thanks to the increase in conversion of the synthesis section, the demand for MP steam reduces from 1550 kg/t to 1,100 kg/t (about 30% saving).

Fig. 2: **Modified steam network for self-stripping plant**



Source: Casale

Another major advantage of the HEC process is the possibility to maintain the entire existing purification section. The scope of revamping can thus be limited to a few pieces of equipment in the HP section which can be conveniently installed with the plant in service. The shutdown time needed to implement the modifications can be narrowed down to slightly more than a conventional turnaround. The increase in conversion of the synthesis section also allows easy plant capacity increase of up to 30-40% without affecting the purification and recovery section. The combination of energy saving and, if desired, capacity increase leads to extremely attractive investment return time due to the relatively low investment cost.

Energy savings for self-stripping plants

The so-called "self" or "ammonia" stripping plants represent a major share of the urea plants currently in operation. Since their introduction in the 1970s the conceptual process scheme has maintained the original features, but a few modifications have been gradually implemented to improve the specific energy consumption. Nowadays, modern self-stripping plants have reached a degree of heat integration that allows specific MP steam consumption below 700 kg/t (excluding the consumption of the CO_2 compressor). Since the backbone of the most efficient plants is pretty much the same as vintage plants, the modifications required to upgrade old high-energy consuming plants to the state of the art can be carried out without major capex allocation.

Casale has applied its experience in several total or partial revamping projects of ammonia stripping plants. Among the latest of relevance, it is worth mentioning the revamping of Trombay, India, urea plant. The plant, commissioned in 1982, in common with many plants of its kind built throughout the mid-1990s, did not implement any heat recovery strategy and relied upon the HP stripper to maximise the decomposition of unreacted carbamate to maintain the recycle of carbamate, and consequently water, from the downstream sections as low as possible. The operating philosophy required the bottom temperature of the titanium HP stripper to be as high as 210°C, generating a massive quantity of vapours to be condensed in the kettle HP carbamate condenser. The production of LP steam in the HP carbamate condenser was such that all the downstream 3.5 kg/cm²g demand was fully covered. By contrast, the consumption of 22 kg/cm²g steam in the HP stripper was proportionally high leading to an overall energy consumption above 1.1 Gcal/t (including the CO_2 compressor). The revamping project, focused on energy saving, required the energy consumption to be decreased by 25% minimum.

To achieve such a demanding target the revamping strategy was based on maximising the integration of heat sources and consumers to implement the highest heat recovery allowed by the temperature profiles. Meanwhile the demand for

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steam was shifted from medium pressure, extracted from the turbine, to low-pressure steam generated by the HP carbamate condensers. In the original plant design only two steam pressure levels were foreseen, 26 and 3.5 kg/cm²g. The former level was used in the HP stripper and hydrolyser, whereas the LP steam was deployed to the decomposition stages, evaporators and distillation tower. In the revamping project an additional kettle-type HP carbamate condenser was installed downstream of the existing one. With a second HPCC it was possible to generate LP steam at 5.5 kg/cm²g, deployed to users requiring higher temperatures, and 3.5 kg/cm²g used for tracing, flushing and in exchangers requiring lower temperatures. Additionally, a steam condensate tank at 2.0 kg/cm²g was installed on the LP condensate return header. The low-low pressure generated steam is now thermo-compressed in a booster ejector using 5.5 kg/cm²g and delivered to the process condensate distillation tower. Fig. 2 shows a schematic of the modified steam network.

A major advantage of steam produced internally at 5.5 kg/cm²g is the possibility to add a new decomposition step directly downstream of the HP stripper. Urea solution from the HP stripper after flashing at 18 kg/cm²g is subject to a new carbamate decomposition step carried out in a medium-pressure pre-decomposer. The pre-decomposer removes the additional carbamate due to the lower HP stripper bottom temperature, thus debottlenecking the existing MP decomposer. Thanks to the MP pre-decomposer, the MP decomposer can still be operated solely with steam condensate from the HP stripper, without the need for MP steam injection. For such purposes, Casale has designed a pre-decomposer with special internals for phase separation which avoids increasing the water entrained in the MP vapours.

To reduce LP steam requirements so that the entire plant consumption could be entirely satisfied with internally generated steam, a vacuum pre-concentrator was installed on the first stage evaporator. This solution has been widely applied in modern ammonia stripping plants where the heat released by carbamate vapours at medium pressure can be conveniently exploited for urea concentration in place of LP steam. Besides steam savings, adding a vacuum pre-concentrator has the added advantage of drastically reducing the duty required by the MP carbamate condenser and consequently the consumption of cooling water. The heat recovery performed by the vacuum pre-concentrator reduces the consumption of 3.5 kg/cm²g steam by approximately 200-230 kg/t urea. This reduction is not enough to close the gap between consumed and produced LP steam. Therefore, two additional recovery steps were added. A new exchanger was installed to exploit the heat of condensation of low-pressure carbamate vapours and a second heat recovery exchanger was installed upstream of the reflux condenser in the wastewater treatment. The former is used for ammonia feed pre-heating, the latter as recycled carbamate preheater. The main purpose of these items is to increase the production of steam in the HP carbamate condensers and meanwhile debottleneck condensers in the LP and wastewater treatment sections with consequent saving of cooling water.

The revamping project was completed between December 2020 and February 2021. During the guarantee test run, the measured MP steam flow rate from turbine extraction (which accounts for all the process users including the hydrolyser) was lower than the guarantee value, achieving a reduction of specific energy consumption of about 27%. The recorded value is in line with the most modern urea plants, which places the revamped process scheme among the best available technology on the market. If compared only with ammonia stripping plants with prilling towers, the achieved specific consumption is the best performance commonly measured in India. Together with energy savings, the revamping project also attained a reduction of the ammonia specific consumption and a drastic improvement of the quality of the treated water which is now at BFW grade.

Revamping CO_2 stripping plants: The MP section

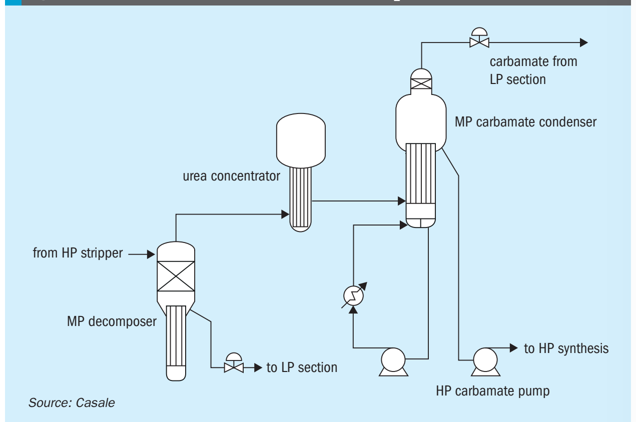
One of the intrinsic features of the CO_2 stripping process as it was introduced in the 1960s is the absence of a purification stage at medium-pressure. The removal of free ammonia (not bonded with CO_2 in ammonium carbamate salts) carried out in the HP stripper allows the recovery of the remaining carbamate in a single low-pressure stage. At 3.5 bar(g) the temperature of carbamate formation is such that recovering the heat of condensation for any process use is scarcely practical. In most cases, such heat is lost to the cooling water. Moreover, the HP stripper requires up to 850-900 kg/t of steam at 20 bar(g) which is balanced by an even higher LP steam generation in the HP carbamate condenser; still, in the traditional CO_2 stripping process, especially if granulation is the finishing method selected, excess LP steam is either exported or reinjected into the turbine.

For reasons such as these, in recent years several licensors have been adopting process schemes based on CO_2 stripping technology, but with an intermediate purification step in between the HP stripper and the LP section. The advantage of these intermediate sections operating at medium pressure can be summarised as follows. Having a carbamate recovery step at a pressure intermediate between 10 to 20 bar(g), the stream from the HP stripper can contain a higher fraction of carbamate and a fraction of free ammonia is also tolerated; this translates into the possibility to lessen the degree of decomposition and consequently the steam consumption in the HP stripper. Additionally, carbamate decomposition at medium-pressure can be carried out with steam at 4-8 bar(g) and carbamate formation follows a temperature profile which allows the implementation of a heat recovery strategy, for example, to concentrate urea solution.

Fig. 3 shows the process scheme of the MP section adopted by Casale for new or revamped CO_2 stripping plants. The pieces of equipment included in the section are a MP decomposer, a MP carbamate condenser with its dedicated tempered cooling water loop and a urea concentrator. This section is operated at approximately 10 bar(g) which allows use of LP steam (generated or mildly thermo-compressed) in the MP decomposer and exploits the heat of condensation of the carbamate vapours to promote urea solution concentration in a vacuum evaporator. This process scheme was adopted for the revamping of a CO_2 stripping plant in Russia in 2018 where it was desired to reduce the high MP steam consumption, due to integration with a melamine plant, by at least 200 kg/t (approximately 20%). For such revamping, the equipment installation cost was contained by repurposing an idle HP stripper and an idle HP carbamate condenser, which were conveniently recycled as an MP decomposer and MP condenser respectively. In addition, the existing HP carbamate pumps were maintained and revamped to increase the suction pressure, which was considerably less expensive than replacing them with new machines.

In the same revamping project, together with the MP section addition, heat recovery was implemented on the tempered cooling water loop of the HP scrubber. Specifically, tempered water at 130°C has been used for pre-heating the urea solution upstream of the final concentration in the vacuum section. Such schemes are nowadays commonly applied in modern plants and can be an attractive option for vintage plants. ■

Fig. 3: **Casale MP section for new or revamped CO_2 stripping plants**



Source: Casale

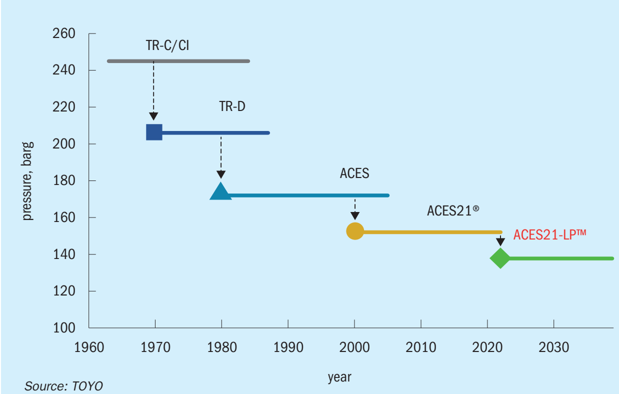
TOYO ENGINEERING CORPORATION

Revamping urea plants with ACES21-LP™ for energy savings and plant cost reductions

Kenji Yoshimoto

Toyo Engineering Corporation (TOYO), a global leading engineering contractor and urea process licensor, has developed TOYO's proprietary urea processes since the development of the partial recycle process in the 1950s. Using its expertise, advanced technology and novel thinking, TOYO established ACES21® in the late 1990s and has since been awarded 16 ACES21® projects, including two 4,000 t/d urea projects for Indorama Eleme Fertilizer and Chemicals Limited (IEFCL) which is the world's largest single train urea plant. TOYO has been working on further improvements and innovations in its proprietary urea processes and has developed ACES21-LP™, the next generation ACES21®, which was introduced in *Nitrogen+Syngas* July-August 2022. This article introduces TOYO's idea and experiences for revamping a conventional urea plant, including an example of utilising ACES21-LP™ technology.

Fig. 1: **History of lowering urea synthesis pressure**



Source: TOYO

Upgrading existing ACES21® urea plants with the ACES21-LP™ concept

TOYO has developed the next generation ACES21® process, ACES21-LP™, to realise further energy savings and plant cost reductions, while maintaining all salient features of the current ACES21® process. Fig. 1 shows the history of how TOYO has lowered urea synthesis pressure over the past 60 years. The urea synthesis pressure has been lowered step-by-step from around 240 bar to 152 bar through technology advances. The ACES21-LP™ concept lowers the urea synthesis pressure one step further to 136 bar. The key to realising the benefits of ACES21-LP™ is the sophisticated application of DP28W™, conventional duplex SS and 316L SS to the synthesis section in combination with reduced passivation air. The simple and sophisticated concept of ACES21-LP™ enhances the well-known features of the current ACES21® process in terms of the following aspects:

- lowest synthesis pressure among commercial urea processes owing to the uniquely optimised synthesis conditions and reduced passivation air requirement;

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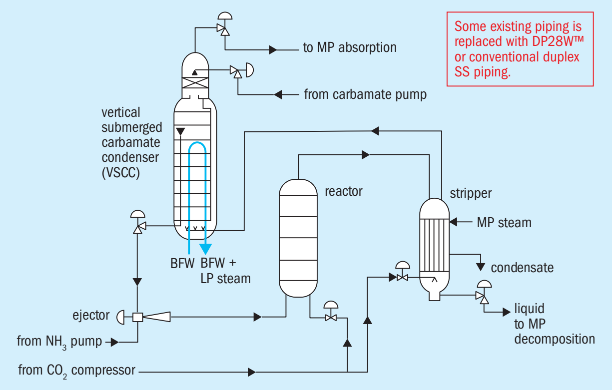
Fig. 2: **ACES21® synthesis section**



Source: TOYO

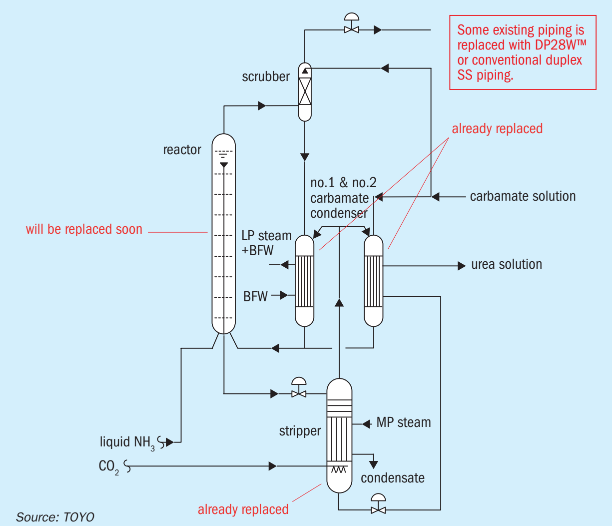
Table 1: **Opex reduction by ACES21-LP™**

	ACES21®	ACES21-LP™
Electricity*	base	3-5% reduction
Steam	base	3-5% reduction

**For ammonia feed pump, carbamate feed pump and other pumps/blowers inside battery limits*

Source: TOYO

Fig. 3: **Modification scheme to low-pressure concept**



Source: TOYO

- highest CO_2 conversion among advanced modern urea processes;
- further energy savings (less opex) due to 5-10% lower power requirements of the CO_2 compressor, ammonia and carbamate pumps;
- less capex owing to the milder mechanical design conditions of the synthesis equipment (synthesis section HP equipment cost reduced by 5-10%).

Since the basic process scheme of the current ACES21® process is retained in ACES21-LP™, this concept can be easily applied to currently operating ACES21® plants with minor modifications. As shown in Fig. 2, to convert the process to ACES21-LP™ requires some replacement of stainless steel piping material with DP28W™ or conventional duplex SS in areas that are most corrosive. Since the material selected in other areas of ACES21®, including the existing synthesis equipment, shows sufficient corrosion resistance even under the new operating conditions, only minor modifications are required.

Thanks to the lower operating pressure, opex can be reduced compared to the original ACES21® condition. Table 1 shows a comparison of the expected power and steam consumption between ACES21® and ACES21-LP™. Both are lowered by 3-5%, which is remarkable considering the conventional ACES21® process has been the most energy-saving process among the licensors.

TOYO's concept to apply ACES21-LP™ is to tailor the selection of a suitable and reliable material according to the service conditions, specifically considering the corrosiveness of the environment, and not to employ costly material to all parts unnecessarily.

Upgrading CO_2 stripping urea plants with the low-pressure concept

The ACES21-LP™ concept can also be applied to currently operating conventional CO_2 stripping urea plants like the TOYO ACES process. Fig. 3 shows a typical modification scheme to upgrade the existing ACES plant using the ACES21-LP™ concept. All TOYO ACES plants have been operated for more than 20-30 years; therefore, the synthesis equipment needs to be replaced with new equipment in which DP28W™ is selected as the material of construction for the lining or tubes. For instance, in one ACES plant, the stripper and carbamate condensers were replaced with new ones made of DP28W™ based on the above

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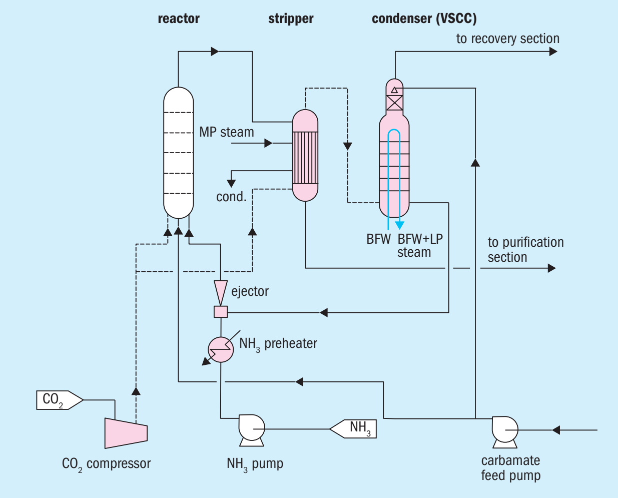
Table 2: **Predicted process performance after renovating to low-pressure process**

	Conventional urea stripping	Low pressure process
Passivation air	base	significant reduction
Synthesis pressure	base	10 bar decrease
Overall steam consumption	base	2-3% reduction
CO_2 compressor capacity	base	2-3% increase

Source: TOYO

Fig. 4: **Revamp of the Total Recycle process**



Source: TOYO

concept and the reactor will soon be replaced with a conventional duplex steel-lined reactor. In such a case, the plant can be upgraded to the low-pressure process by replacing only some limited piping with piping made of DP28W™ or conventional duplex stainless steel piping.

By making modifications to lower the synthesis pressure, plant owners will enjoy energy savings. Table 2 shows a comparison of the expected process performance before and after renovation to the low-pressure process. As shown in the table, the synthesis pressure is reduced by 10 bar while maintaining the N/C and H/C ratios in the reactor as in the present condition, and the overall steam consumption is reduced by 2-3%. It should be noted that, instead of energy savings, the plant capacity can be increased by 2-3% by using the extra margin of the CO_2 compressor because the head and power of the compressor are reduced thanks to the lower synthesis pressure.

Conversion of existing total recycle urea plants to ACES21®/ACES21-LP™

ACES21® and/or ACES21-LP™ can also be applied for the renovation of old vintage total recycle urea plants. Fig. 4 shows the modification scheme in the synthesis section to convert the total recycle plant to ACES21® or ACES21-LP™. The equipment illustrated in pink (the stripper, carbamate condenser and HP ejector) is added to the synthesis section; however, the existing reactor can be reutilised as it is. By virtue of this modification, a capacity increase of 50% can be achieved with energy savings of more than 30%, keeping the existing ammonia feed pump and carbamate feed pump without any modifications. The option to replace or modify the CO_2 compressor to increase its capacity depends on the revamping concept. For example, if the aim is to increase the production capacity or to improve the maintenance frequency of the existing reciprocating compressor, replacement of the compressor with a new centrifugal type may be selected.

Utilising the opportunity to renovate the urea synthesis section, TOYO can recommend converting the existing crystallisation process to a new vacuum evaporation process to concentrate the urea solution. Many vintage urea plants have applied the crystallisation process and such an aged system needs frequent cleaning which requires periodic shutdown of the urea plant. In the case of the vacuum evaporation process, continuous operation is achieved without cleaning, which improves the operability and maintainability of the plant. Besides being easier to operate with less maintenance for cleaning there is also reduction in power consumption compared to the crystallisation system.

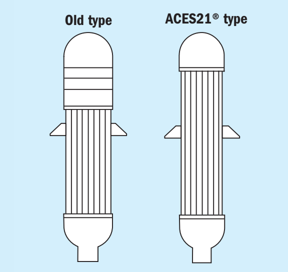
Efficiency/reliability increase by replacement of urea synthesis equipment

The synthesis equipment in urea plants that have been operated for more than 20-30 years will have inevitably deteriorated and require replacement according to the circumstances. In such a replacement case, TOYO has applied the following concept offering its best solutions to plant owners:

- selection of suitable and robust materials, such as DP28W™, to make new equipment more reliable;
- application of the latest design for internals, such as an improved baffle plate in the reactor and/or a swirl in the stripper, to increase efficiency and reliability;
- procurement by TOYO itself, depending on conditions, to assure the quality of all the details required to eliminate unexpected flaws caused by manufacturers, through advanced and efficient inspection.

The following typical example refers to excellent experience for a stripper replacement. In this case, a plant owner had faced difficulties caused by an aged stripper installed in a conventional CO_2 stripping process and wanted to replace it. TOYO

Fig. 5: **Application of ACES21® stripper**



- Simplified internals
- Improved swirl tube
- Improved liquid distributor design
- Same height keeping the same nozzle orientation
- Equipment weight reduction by 15%

Source: TOYO

Table 3: **Process performance: ACES vs ACES21® stripper**

	Before stripper relacement	After stripper replacement
Stripping efficiency	base	2% increase
Recovered carbamate flow	base	12% reduction
Urea conversion in reactor	base	2% increase
Overall steam consumption	base	3% reduction

Source: TOYO

made recommendations for a new stripper according to the following concept:

- application of the latest type of stripper for ACES21® to enhance reliability and efficiency;
- selection of DP28W™ as the material of construction for parts in areas that are most corrosive.

The plant owner agreed with all of TOYO's recommendations.

Fig. 5 shows the outline of a general drawing for an old and a new stripper. To reutilise the existing foundation and the nozzle orientation, the dimensions of the new stripper was adjusted to fit the existing dimensions. Remarkably, the weight of the new equipment is 15% lighter because of its simple internals while providing 20% additional capacity compared to the old stripper. Thanks to its compactness, maintenance work is significantly simplified.

The new stripper was installed in 2018 at the site and the initial start-up operation proceeded smoothly. The performance has been very stable owing to the improved design for the internal liquid distribution system. Table 3 summarises the process performance before and after the stripper replacement. The performance of the ACES21® stripper shows not only its stability but also energy savings due to its excellent efficiency.

In another example, an old reactor in the total recycle process was replaced with a new one in Japan. The lining material of the old reactor was titanium and the plant owner had struggled to repair the lining defect when it leaked which had occurred frequently. Therefore, the plant owner decided to replace it with a new one lined with DP28W™; the intention was to operate the new reactor under the same operating conditions as the existing one (i.e., 250 bar, 200°C). These operating conditions are severe for any material because titanium requires little passivation air even at high temperatures. Nevertheless, it is notable that the actual corrosion rate of DP28W™ has been actually far lower than titanium. The new reactor fabricated with DP28W™ has been in service since 2006 and the plant owner has reduced its maintenance cost drastically by 90% as shown in Fig. 6. Maintenance activity during each turnaround has been mainly visual inspection only and to date there have been no major repairs caused by the material.

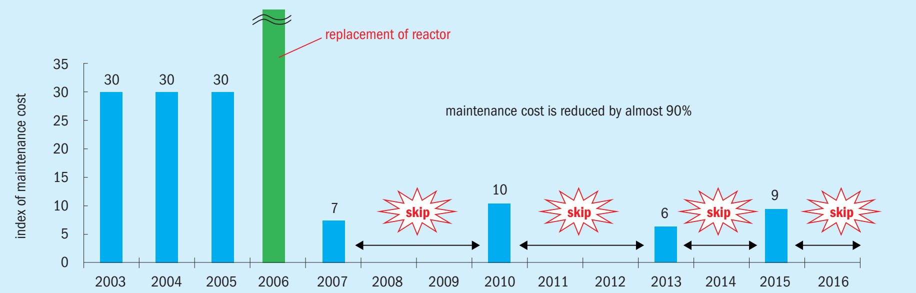
Other modern technologies

TOYO also offers various other modern technologies to assist or enhance operability/maintainability for the modernisation of existing urea plants as summarised below.

Online leak detection system

TOYO has developed an online leak detection system for detecting leaking from the lining plate of urea synthesis equipment. This system has the advantage of being

Fig. 6: **Index of maintenance cost**



Source: TOYO

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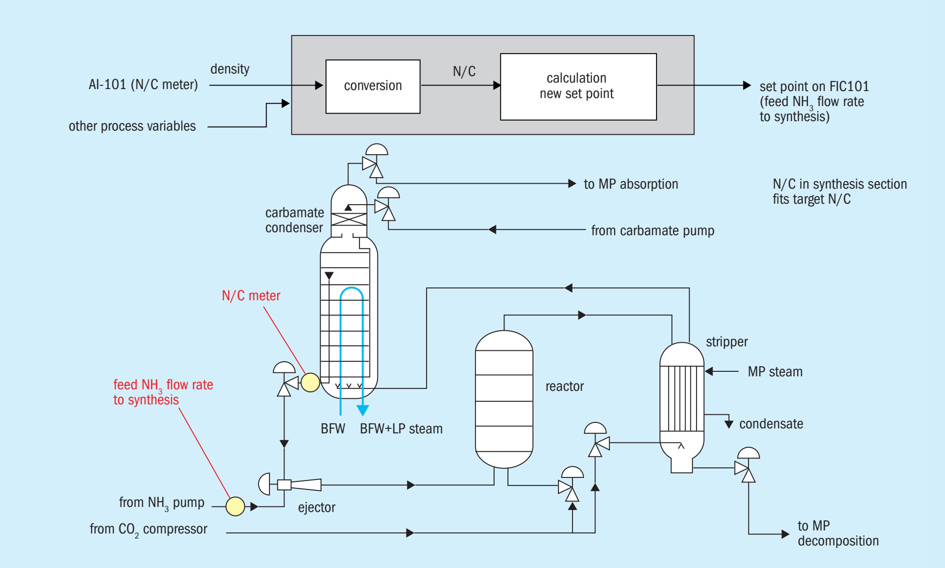
Fig. 7: **TOYO's advanced process controller**



Source: TOYO

able to detect tiny amounts of leakage and to identify the location of defects before the damage becomes severe, which contributes to making maintenance work easier, and increases the reliability of the urea plant. It can be installed for existing and/or the renewal of urea synthesis equipment to enhance reliability.

Online process condensate analyser

Process condensate is the largest by-product of the urea production process and its quality control is essential for enabling it to be used as boiler feed water make-up. However, a conventional conductivity meter, which is typically installed in existing urea plants, does not show the level of urea content because urea is not an electrolyte in aqueous solution. Therefore, TOYO and Mitsui Chemicals Inc. (MCI) have developed a proprietary online process condensate analyser for the treated process condensate, which analyses not only ammonia but also urea continuously in real time in the range from 1 ppm to hundreds of ppm. As the TOYO-MCI online urea analyser is simply configured and does not require any chemicals and reagents, its initial and running costs are low. Installation of this online analyser improves quality control around the clock for existing plant owners.

Advanced process controller (APC)

Conventionally, the N/C ratio (NH_3 to CO_2 molar ratio) of synthesis solution is obtained by laboratory analysis with results delayed be a few hours after taking the sample. Plant operators need to control the N/C ratio by monitoring the conditions of the synthesis section and periodic but non-real-time laboratory analysis results of the synthesis solution. In other words, plant operators have had to change set points of flow controllers for ammonia feed to the synthesis section when operators think it necessary based on their experiences. TOYO's APC system offers real-time monitoring of the N/C ratio of the synthesis solution with multi-variable control, as shown in Fig. 7; it enables savings in energy consumption, i.e., maximum CO_2 conversion can be realised by regulating the optimum N/C ratio in the synthesis section at the optimal point.

DX-PLANT®

In 2016, TOYO launched a digital transformation service named DX-PLANT® in the field of chemical and industrial plants by leveraging IoT and big data analysis technology. Through the development of DX-PLANT®, TOYO has provided unique solutions for the maximum benefit of plant owners. TOYO takes pride in realising the veritable "digital twin" of a real plant by DX-PLANT® and deployment of this service to existing urea plants will contribute to the improved opex and reduction of maintenance costs incurred by plant owners.

Advanced online corrosion monitoring (AOCM™)

Corrosion monitoring of high-pressure equipment and piping in the urea synthesis loop on a real-time basis is beneficial for plant owners not only in establishing optimised inspection plans but also in enabling reliable operation. Assessing the real-time condition of stainless steels exposed to ammonium carbamate is particularly challenging. TOYO developed AOCM™ (advanced online corrosion monitoring) utilising ultrasonic testing sensors, providing a solution that predicts the condition of equipment and piping (see *Nitrogen+Syngas* March-April 2021). ■

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Process optimisation and emissions abatement in nitric acid production

Optimisation of the nitric acid process depends on good process visualisation tailored to the specific process parameters of the plant, improvements in combustion efficiency, reduction of N_2O emissions and the optimal use of platinum group metals.

UMICORE AND THYSSENKRUPP INDUSTRIAL SOLUTIONS

GreenSalpeter project: For a better understanding of Pt-catalysed ammonia combustion

Artur Wiser (Umicore) and Johannes Dammeier (thyssenkrupp Industrial Solutions)

With a production of more than 60 million tonnes per year, ammonia oxidation via the Ostwald process is the main route to producing nitric acid production and has a large economic and environmental impact. Due to the energy intense Haber Bosch process, which is applied to produce the feedstock ammonia (NH_3), there is a great potential to increase overall sustainability by reducing the formation of byproducts (N_2 and N_2O) and thus increasing the yield of nitric acid per tonne of ammonia.

Despite the fact that the Ostwald process has been in use for over a century, there is still a knowledge gap concerning the complex interaction of chemical kinetics and process parameters (p, T, flow field, catalyst geometry). The harsh reaction conditions, very fast kinetics, strong influence of mass and heat transport limitations and especially the strong coupling of all phenomena complicate studies of the system under industrial conditions.

To investigate this complex process and to get a more detailed understanding of the interaction of different influencing factors governing the selectivity and efficiency of the process, catalyst provider Umicore, together with thyssenkrupp Industrial Solutions, the largest process licensor for nitric acid plants, and Umesoft, a data science company, are working together in a joint development project, the GreenSalpeter project, funded by the German Federal Ministry for Economic Affairs and Climate Action. The main development subjects are the improvement of the combustion efficiency, the reduction of N_2O emissions and the usage of platinum group metals. Big progress has been achieved in the field of computational fluid modelling coupled with detailed kinetics of the ammonia oxidation reaction[1-3].

Experimental setup

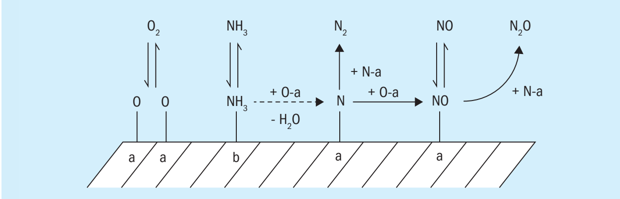
In order to study the Ostwald process on a laboratory scale, key parameters of the industrial process have to be met. This includes short residence times and thus high volume flows up to 5,000 lN h^{-1}, pressures up to 5 atm, preheating temperatures up to 450°C, reaction temperatures over 850°C and ammonia volume fractions in air up to 13%. The laboratory setup not only meets the criteria, but also uses separate preheating of the reaction mixtures as well as chemically inert catalyst fixation and gas sampling to prevent undesired side reactions. The product stream can be fully analysed using an integrated quadrupole mass spectrometer. Various industrial platinum group metal gauzes varying in compositions, mesh geometries and stacking can be studied. Process conditions can also be varied[2].

CFD modelling

The kinetic model (model C) previously published by Kraehnert and Baerns was chosen for the implementation in a CFD simulation, because it provided the best correlation between experimental and computed rates of product formation in the Kraehnert work[4]. Fig. 1 shows the mechanistic scheme and parameter of the model for ammonia oxidation used. The reaction mechanism contains ten reactions, six gas species, and six surface species. The adsorption reactions for oxygen, ammonia, and nitrogen oxide are reversible. The adsorption of the formed by-products N_2 and N_2O is not included. Possible gas phase reactions are neglected in this work. There is no agreement in the literature about the role of gas phase reactions during ammonia combustion. Solid lines show elementary reactions and the dashed line shows a lumped reaction[4].

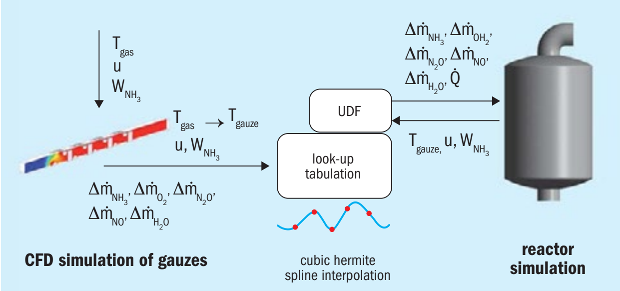
The Kraehnert-mechanism is a further advancement based on the kinetic model on Pt/Al_2O_3 near atmospheric pressure. In the mechanism, the polycrystalline Pt surface of the catalytic gauze is assumed to be similar to Pt (1 1 1) surface. The energetic data for adsorption of species on a Pt surface were provided by DFT calculations. Kinetics for oxygen desorption is assumed to be coverage independent. The

Fig. 1: Mechanistic scheme of reaction steps of ammonia oxidation



Source: Kraehnert and Baerns

Fig. 2: Data flow in the CFD simulations combining the different scales of reactor and catalyst



Source: Umicore/tkIS

stepwise activation of ammonia (hydrogen stripping by oxygen atoms) is simplified to one stoichiometric reaction with the assumption that the first step (NH_3 + O) is rate determining. The production of water is also included in that step. The mechanism includes two different adsorption sites on Pt surface: sites "a" for O, N, and NO and sites "b" for NH_3. Hence, a competition for adsorption sites between oxygen and nitric oxide can be concluded. This fact is also supported by spectroscopic evidence.

The mechanistic surface kinetic model has been implemented in CFD simulations using the rate mapping approach previously published by Votsmeier[5]. The purpose of the rate mapping procedure is to provide source terms for the gas species by interpolation of a spline function between a certain number of points in a rectangular grid. The spline function represents a functional relationship between the input parameters and the gas phase source terms. The grid points are computed in a pre-processing step and saved in so-called "look-up tables". During the simulation, the software interacts with look-up tables to get the source terms for the gas species by interpolation of the spline function between the grid points. This approach decouples the calculation of the fluid flow and the numerical treatment of the surface kinetic and provides a faster convergence of the solution in the CFD model requiring less computational time[1].

A similar approach allows for investigation of the interplay of reaction conditions, reactor design and the micro kinetics at the platinum gauze surface. A scheme of the calculation procedure is shown in Fig. 2.

First, CFD simulations including the kinetic mechanism described above of a small excerpt of a Pt gauze are performed at different process and flow conditions. The results of these calculations concerning the conversion of mass by the ammonia oxidation reactions are stored in look-up tables. Cubic Hermite splines are used. An orthogonalisation procedure ensures a rectangular grid in the dimension of gauze temperatures. Process and flow conditions of the ammonia oxidation reactor are simulated by CFD as shown in Fig. 3.

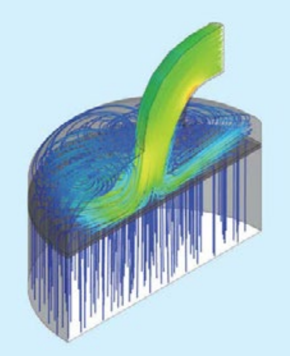
User defined functions (UDF) trigger a mapping process, which maps the mass conversions from the look-up tables to the suitable process and flow conditions from the CFD simulation. The result is a locally resolved map of the resulting mass flows of NO, NO_2 and N_2O as well as reaction temperatures at the catalyst surface. These results help to optimise the reactor design with regard to a uniform temperature distribution and maximised NO selectivity.

Gas phase reactions

Chemical processes in the gas phase during the ammonia oxidation have been studied. These processes involve the species included in the Ostwald process, for instance the homogeneous oxidation of NH_3 or the selective non catalytic reduction of nitrogen oxides (NOx) by NH_3. One of the key features of the homogeneous schemes is its reliance on the characteristics of each process variable. Therefore, it is of interest to determine the role of such reactions in the gas phase of the ammonia oxidation process.

Due to the complexity of the chemical mechanisms of the processes in the gas phase, reduction and implementation through computational simulation tools is necessary. While catalytic reactions favour NO formation, the gas phase reactions promote N_2 and N_2O formation due to NO reduction. The simulations will allow the route to be established by which

Fig. 3: CFD analysis of the flow distribution inside a simplified ammonia oxidation reactor



Source: Umicore/tkIS

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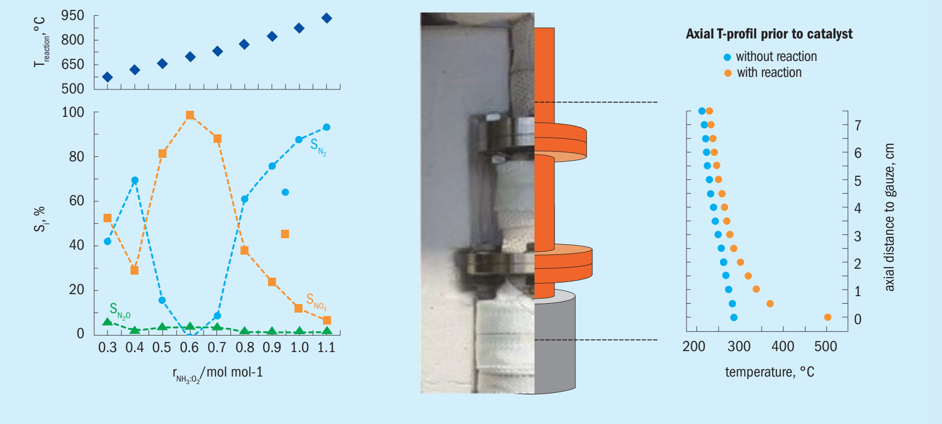
Fig. 4: The influence of NH_3-O_2 ratio and temperature increase on the product distribution within the laboratory scale reactor



Source: Umicore/tkIS

these sub-products are formed and help to reduce their negative impact on the process efficiency, and the environmental impact of the Oswald process[6].

Results

Experiments

The study reveals that the lab setup allows for reproducible, time resolved experiments. Proper use of the quadrupole mass spectrometer together with a calculation routine combining complete detection of species-sensitive ion currents and consideration of cross-intensities due to isotopes and fragmentation turned out to be key. On this experimental basis parameter influences beyond traditional industrial plants could be studied as shown e.g., for the molar NH_3 to O_2 inlet ratio (Fig. 4). To build the foundation for further simulation and statistical data analysis the axial and radial temperature gradients of the reactor setup were determined. Additionally, geometrical and chemical modification of catalyst formulations can be quantified with regard to their N_2O emission within hours instead of weeks or even months.

Modelling

In the Ostwald process ammonia is catalytically oxidised to NO in short contact times on platinum/rhodium gauzes. Besides NO as the main product, N_2 and N_2O are also produced. The formation of N_2O is particularly critical because of its large environmental influence as a greenhouse gas.

Motivated by its large industrial importance, substantial fundamental research has been directed towards the mechanistic understanding of the process. The individual steps contributing to the overall reaction have been studied in numerous surface science studies. Furthermore, a number of mechanistic kinetic models have been published based on the surface science information. More recently, the individual steps of the mechanism were studied by quantum mechanical methods and a surface kinetic model was assembled based on this work.

Surprisingly, despite all this fundamental research, there seems to be very little published works which consider the effect of mass transfer limitation and no published work that applies the existing reaction mechanisms in a flow simulation of the platinum gauze reactor. This is even more surprising, since the reaction is known to be strongly heat- and mass-transfer controlled so that only a combined treatment of surface chemistry, flow, diffusion and heat conduction can reveal how realistic the existing kinetic models are at providing a realistic picture of ammonia oxidation under relevant industrial conditions.

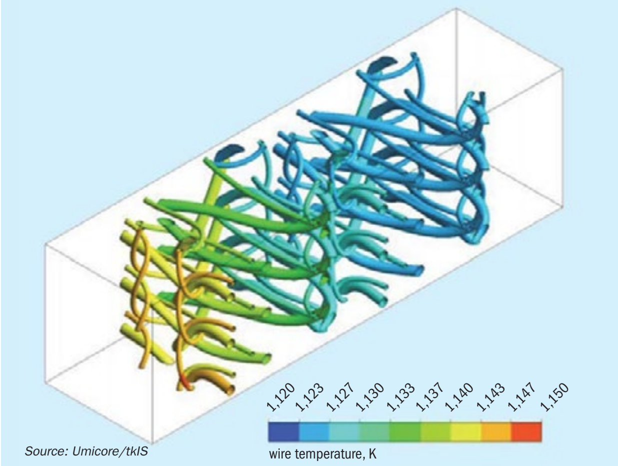
This paper describes a modelling approach where a mechanistic model of ammonia oxidation on platinum previously published by Kraehnert and Baerns was implemented in a CFD simulation using the rate mapping approach. Three main application fields for this modelling approach have been handled in this work:

- geometry influence on the process performance of the catalytic gauze;
- influence of the catalyst surface restructuring on the process performance;
- CFD modelling of the laboratory scale reactor including complex chemistry on the wire gauzes.

Since ammonia oxidation is a mass transfer limited process, the geometry of the catalytic gauzes plays an important role in reaction product selectivity. Although very little scientific relevant studies have been performed in this area, investigations of different wire and gauze geometries using the combination of CFD and detailed kinetics modelling can be summarised as follows:

- Realistic temperature (900°C wire temperature) and concentration fields are obtained by the CFD simulation (Fig. 3).
- On each single wire, the N_2O selectivity varies along the perimeter of the wire.
- The N_2O selectivity is highest on the front side of the wire and decreases towards the rear side.
- Thicker wires show a lower N_2O selectivity than thinner wires.
- The relative angle of the wire to the fluid flow has an influence on the product selectivity. Higher attack angle of the fluid on catalyst surface results in lower N_2O selectivity.
- In complex industrial gauze, the selectivity on the individual wires depends on the relative position of the wires in the gauze structure and is determined by local mass transfer effects.
- Finally, it is shown, that the simulation predicts a reduced N_2O selectivity for current industrial gauze designs, compared to conventional woven gauzes.

Fig. 5: Temperature profile of the Umicore's Multinit® gauze structure[1]



Source: Umicore/tkIS

The next application field for coupled CFD and detailed kinetics modelling is the investigation of the role of catalyst surface reconstruction during the ammonia oxidation process. The surface of PtRh catalytic wires is originally smooth and became reconstructed during the reaction. So-called "cauliflower" structures can be observed on used wires after several hours under reaction conditions. A CFD model based on computer tomography images has been developed for this investigation. The simulation results show that the product selectivity (NO and N_2O) is not uniform on the restructured surface. The excrescences protruding in the reaction mixture are much more involved in the reaction and the selectivity of N_2O on these areas is much higher than on the wire body. It leads to a significant difference between smooth wire and restructured wire models. Although it has been shown that a surface factor, which influences the catalyst surface concentration, for smooth wire models can be adjusted in a way to reproduce the results of restructured wire model. The complex restructured wire model has to be made and calculated just once to validate the surface factor, which can be implemented then for much more simple models with a smooth wire surface (Fig. 6).

Furthermore, multi-scale simulations such as those presented in this work might offer the possibility to validate kinetic mechanisms even with imperfect laboratory reactor data, by including the imperfections of the reactor in the model and then comparing lab measurements to the model predictions.

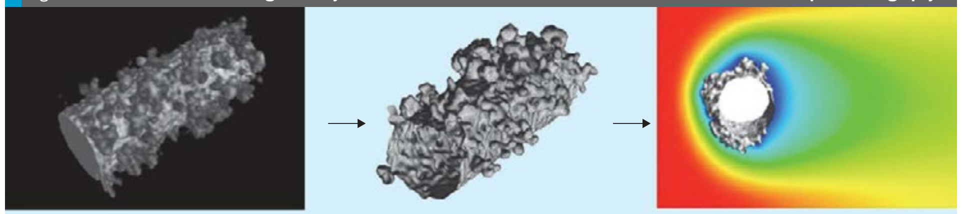
Transfer to industrial application

The development of a technique for coupling the CFD modelling with reaction kinetics of ammonia oxidation made possible scientific based optimisation of the catalyst structure. Based on the knowledge achieved in the GreenSalpeter project a unique so-called twisted wire has been developed and patented by Umicore (Fig. 7). Intertwisting of several single wires into one string increases the active area of catalyst. The modelling of such geometry shows an increase in NO selectivity and a decrease in the selectivity of undesired by products such as N_2 and N_2O. This effect can be explained by a lower surface concentration of N species which leads to a suppression of reactions, where two nitrogen species take part.

The twisted wire prototype has been tested in several experimental campaigns in a laboratory scale reactor at the Technical University of Darmstadt and also in a pilot plant at Łukasiewicz Research Network – New Chemical Syntheses Institute in Pulawy. Experiments have confirmed the results achieved by CFD modelling and further steps toward the industrial test has been made.

The industrial test was carried out in a medium-pressure plant in a campaign lasting for six months. During the campaign the combustion efficiency increased by 0.8 % (see Fig. 8), which is very significant considering the already very high efficiency

Fig. 6: Workflow for CFD modelling of catalytic oxidation of ammonia on restructured wire based on microcomputer tomography[1]



µ-computer-tomography → 3D CAD model and meshing → CFD geometry with 5 Mio. cells → Simulation of flow + surface chemistry

Source: Umicore/tkIS

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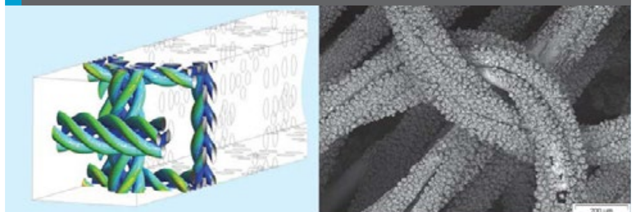
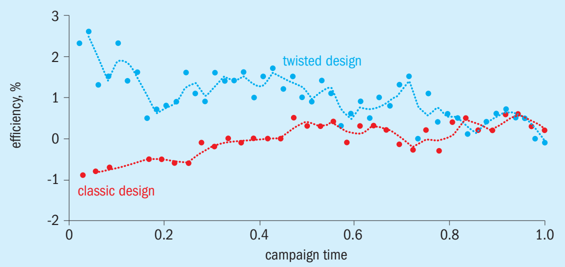
Fig. 7: **CFD model of twisted wire (left) SEM image of twisted wire gauze after an industrial campaign**



Source: Umicore/tkIS

Fig. 8: **Comparison of the oxidation efficiency achieved using Umicore's novel twisted wire designs and classic gauze designs in a medium-pressure nitric acid plant**



Source: Umicore/tkIS

levels of the Ostwald process. A drop in N_2O emissions was also observed.

After the first successful industrial test a special industrial-scale process for wire twisting was developed by Umicore and further nitric acid plants including UKL-7 type and some high-pressure reactors were equipped with twisted wire, increasing the efficiency of the process and making it more environmentally friendly and economically attractive.

Impact on the nitric acid process and CO_2 emissions

To investigate the impact of these optimisations on the nitric acid process and CO_2 emissions associated with the production of nitric acid, consumption figures for typical mono medium- and mono high-pressure processes as well as a dual pressure process have been examined. The overall efficiency of a nitric acid process depends not only on the selectivity at the catalyst gauze, but also on the efficiency of the absorption.

Typically, the absorption is more efficient at higher pressures, whereas the NO yield at the catalyst gauze is lower at higher pressures. Moreover, nowadays nearly all nitric acid plants have a tail gas treatment system using additional ammonia to reduce NOx emissions. Many plants even use ammonia to reduce nitrous oxide (N_2O) emissions. Therefore, the complete processes have been examined to calculate absolute NH_3 savings by enhancing the NO selectivity of the catalyst by 0.8%.

Due to varying details of the processes and different plants, the accuracy of the considerations is limited. Assuming typical consumption figures of 282 kg NH_3/t HNO_3 for a dual pressure process, 284 kg NH_3/t HNO_3 for a mono medium-pressure process and 286 kg NH_3/t HNO_3 for a mono high-pressure process, savings of more than 2 kg NH_3/t HNO_3 is technically feasible (consumption figure without additional ammonia consumption for tail gas treatment). For a 1,000 t/d nitric acid plant running 350 days per year, this adds up to 700 t NH_3/a. Economic savings depend on the price of ammonia, but can be expected to be in the order of 200,000 €/a.

The impact on the climate can be assessed by considering the CO_2 emissions associated with the ammonia production. Despite new developments, literally all ammonia is still produced by the Haber-Bosch process using hydrogen generated by steam reforming of natural gas. Therefore, the production of 1 t NH_3 generates 1.9 t of CO_2 emissions (average value, lower emission figures e.g., with modern Uhde technology). Considering the 700 t of ammonia savings of the 1,000 t/d nitric acid plant, more than 1,300 t of CO_2 emissions can be saved by this single plant in one year.

However, to create a global impact it is of course not enough to equip one single plant with these optimised technologies. The global nitric acid production has already been discussed in the introduction. Assuming a minimum of 60 million tonnes of nitric acid produced per year, equipping one third of the nitric acid plants with the new technology would result in potential savings of 76,000 t of CO_2 emissions per year.

Conclusion

Scientific methods such as state-of-the-art mass spectrometry for product analysis, carefully designed experimental set-ups, statistical methods for experimental designs and sophisticated computational methods involving CFD and modern kinetic models are being used to improve the understanding of the ammonia oxidation mechanism in nitric acid production technology.

Based on the results of these methods, new and optimised products are being developed. The first application of a "twisted wire" catalyst shows noticeable advantages over the conventional design. Implementation of these developments in the nitric acid industry can lead to significant cost reductions and significant CO_2 emission reductions. ■

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SABIN METAL CORPORATION

Optimising ammonia oxidation over platinum gauzes

Brad Cook and Juergen Neumann

Despite its long history, there have been hardly any developments and advances for the gauze catalyst for ammonia oxidation. The most notable change took place in the 1990s with the introduction of knitting technology, which resulted in greater flexibility of the catalyst gauzes at lower production costs.

Little attention has so far been paid to the link with the plant design, which, with its specific reaction environment, places fundamentally different demands on the catalyst. For decades science has devoted itself to the kinetic investigations of the surface reaction on the catalyst as well as the interpretation of recrystallisation processes and precious metal losses of the catalyst. While this may satisfy scientific curiosity, it is of little use to the plant operator to find a satisfactory answer to the question of how to optimise his individual process.

A really satisfying solution approach is the visualisation of the specific process and an individual layout design of the catalyst gauze pack based on this in order to achieve a real increase in the performance of the catalyst system.

Process visualisation

The three images in Fig. 1 include examples of Sabin's visualisation tools, the process visualisation in process modelling and simulation (Fig. 1a), the visualisation of the individual flow characteristics using computational fluid dynamics (Fig. 1b) and the visualisation of the reaction process in the catalyst package itself using SEM/EDX analysis (Fig. 1c).

The difficulty of process evaluation is mainly due to the fact that different process parameters are correlated with each other and in addition a temporal effect is added by the aging of the catalyst. In most cases it is not possible for the plant operator to evaluate the impact of each individual influencing factor in order to draw conclusions for optimising his process.

Especially in mono-pressure plants, the effects of absorption efficiency and catalyst selectivity are correlated via the operating pressure. In addition, the aging of the catalyst also has a temporal effect on the nitric acid process yield.

Using the three-dimensional regression analysis, the individual influencing variables can be separated from one another and brought together again in the process simulation in order to derive an optimal operating mode of the reactor.

The images in Fig. 2 visualise such an approach using a case study. In Fig. 2a, the time-independent absorption efficiency (grey area) is plotted against the resulting nitric acid process yield (coloured area). The difference between the two areas results in the time- and pressure-dependent aging of the catalyst (Fig. 2b), expressed in the change in its selectivity. A time/pressure selectivity map (Fig. 2c) results from the top view, with which the course of the nitric acid process yield to be expected is shown as a function of pressure and time.

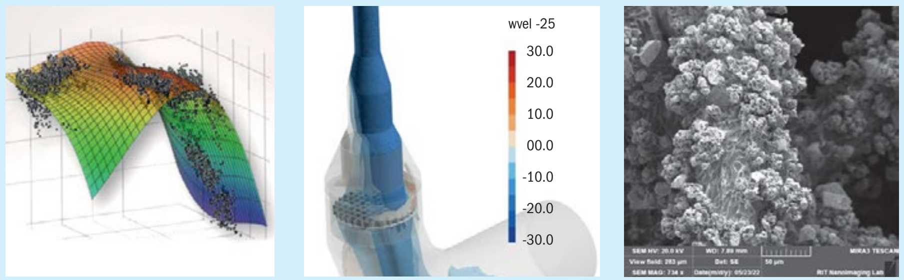
Process modelling and simulation offer the possibility of separating individual parameters from their correlations and, by combining them in the process simulation, making reliable predictions about the course of the process and the nitric acid process yield. Process modelling and simulation thus form an indispensable basis for process optimisation.

Computational fluid dynamics (CFD) enables the visualisation of the influence of flow effects on the catalyst and thus on its selectivity and aging behaviour. Indications of an inhomogeneous flow distribution over the catalyst are recurring shadows that migrate across the catalyst surface, regions with a continuously darker colour temperature, or the occurrence of hotspots.

Cracking in the catalyst pack, far from the edge zone of the catalyst pack (Fig. 3a) is due to material fatigue due to a high ammonia load, while cracking in the edge area (Fig. 3b) and the occurrence of hotspots (Fig. 3c) have their causes in thermal stresses, traced back to an inhomogeneous flow distribution.

By means of computational fluid dynamics, flow effects and inhomogeneities can be visualised, a modified pipe layout as well as internals can be designed that prevent flow separation from the reactor

Fig. 1: **Process visualisation tools**



a) Process simulation **b) Computational fluid dynamics** **c) SEM/EDX analysis**

Source: Sabin

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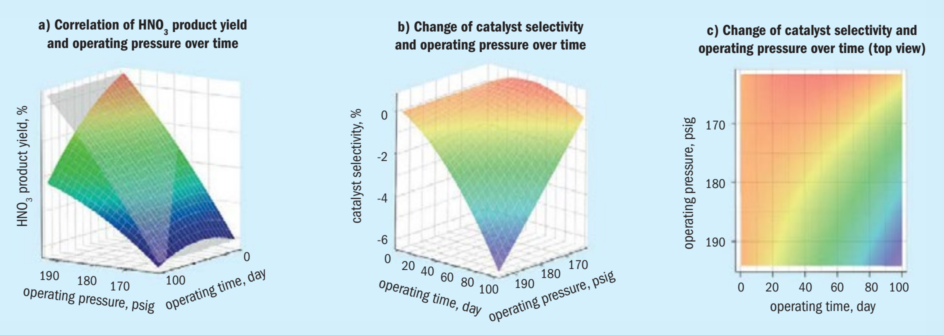
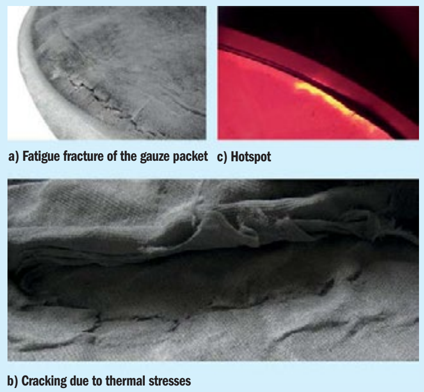
Fig. 2: **Process evaluation using 3-dimensional regression analysis**



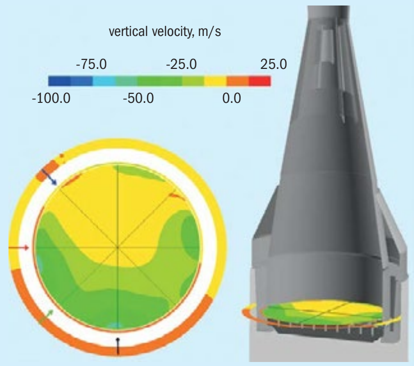
Source: Sabin

Fig. 3: **Influence of flow effects on the catalyst**



Source: Sabin

Fig. 4: **Computer-aided design study for gas distribution installations**



Source: Sabin

wall, particularly at the reactor inlet. Fig. 4 shows such a calculation for a flow distributor in the reactor inlet and the resulting velocity distribution of the flow over the catalyst pack.

All the operator of a nitric acid plant sees of his process is the glowing red surface of the gauze package. With the process gas, air and ammonia are introduced into the catalyst package at a comparatively low mixed gas temperature, which react with one another on the gauze catalyst, releasing heat that is dissipated with the product gas.

The main conversion of the ammonia contained in the process gas takes place on the top layers of the gauze pack. The high heat release by the reaction results in the highest surface temperature with the highest temperature difference between the catalyst surface and the surrounding process gas. As it penetrates further through the catalyst package, the process gas becomes increasingly depleted of ammonia, while its temperature rises and the temperature difference between the catalyst and the process gas continues to decrease.

Using the SEM/EDX analysis, the course of the reaction described can be visualised in the various gauze layers of the catalyst package. The higher the surface temperature of the catalyst gauze, the more volatile platinum (IV) oxide forms on the surface, which decomposes again into oxygen and elementary platinum at significantly lower temperatures of the process gas. If this decomposition occurs close to the surface of the catalyst, agglomerates with a cauliflower-like structure are deposited on it, which become visible in the SEM analysis. From the number, size and structural composition of these cauliflower-like agglomerates, conclusions can be drawn about the ammonia conversion and the corresponding heat release on the gauze surface, as well as the temperature difference between the gauze surface and the surrounding process gas.

The images in Fig. 5 illustrate this relationship between the position of the gauze layer in the catalyst package and the resulting surface morphology for increasing

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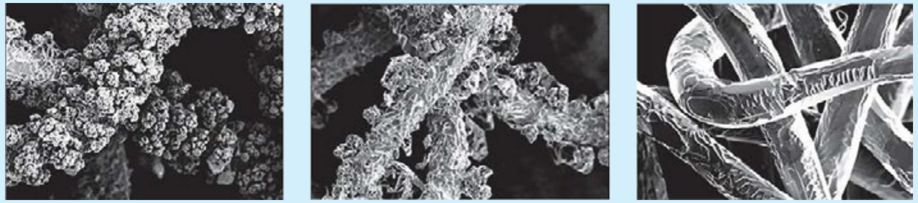
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31

Fig. 5: **Surface morphology according to gauze layer position**



a) SEM image of a top gauze layer — b) SEM image of a middle gauze layer — c) SEM image of a bottom gauze layer

Source: Sabin

gauze layer positions in the flow direction of the process gas.

The formation of the different surface morphologies in the various gauze layers as well as the accumulation of rhodium compounds provide the gauze manufacturer with important information about the performance of the respective catalyst gauze layer according to the process conditions and thus form an important basis for the optimisation of the catalyst package with regard to the specific process conditions of a plant.

Summary

The performance of the catalyst for ammonia oxidation can only be as good as the ambient conditions allow. These environmental conditions primarily include the correlation of the process parameters and the specific flow characteristics in the reactor, which ultimately have a significant influence on the performance of the catalyst.

For the plant operator, these influencing factors result in the size of his process yield and the service life of his catalyst, without being able to establish a correlation between cause and effect.

Only the process visualisation by means of process simulation, computational fluid dynamics and the SEM/EDX analysis of gauze samples of the catalyst package after its service life provide both the plant operator and the manufacturer of the catalyst gauzes with fundamental knowledge, which enables an optimisation of the process and a layout design of the catalyst package that is tailored to the specific process parameters of the plant. ■

HERAEUS PRECIOUS METALS

FTC Flex designs improve catalyst gauze packs for ammonia oxidation

Dr Uwe Jantsch and Jens Hesse

Catalyst gauze packs are widely used for industrial ammonia oxidation. As an expert in platinum group metals, Heraeus is an industry leader in the production of catalyst gauze packs, focusing its activities on providing products and services for the nitric acid industry. By working closely with its customers during the life cycle of their product, Heraeus strives for constant improvement for their benefit.

The economic and ecological challenges in the markets have been increasing and the nitric acid industry needs flexible answers to run its plants according to the quick changing market requirements, such as volatile raw material prices, as well as tighter environmental targets.

Increased market challenges

Platinum, rhodium and palladium are the major components in catalyst gauze packs. The high price level and the price volatility of palladium and rhodium versus platinum as well as the high raw material costs are very challenging for nitric acid producers and require a constant review of their overall costs.

In addition, there is an increasing impact of N_2O emission regulations on the overall economical balance of nitric acid plants in more and more countries. Prices for CO_2 certificates seem to increase continuously. New emission regulations coming into force also affect the cost benefit calculation, their cost and credits have to be taken into account for future taxes or CO_2 emission prices.

All of these marked prices have a strong influence on the opex of nitric acid plants and need to be considered carefully by the catalyst supplier.

FTC Flex – quick adaptation to changing market requirements

Ammonia oxidation is the core process in nitric acid production, utilising catalyst gauze packs which provide high catalytic activity and necessary low residence time of a few milliseconds for highly efficient conversion of ammonia with air. The Heraeus "Functional Total Control (FTC) system" is a concept for the catalytic oxidation of ammonia. Heraeus introduced the FTC technology in 1995 and has been developing it continuously to meet the market challenges.

Heraeus FTC gauze packs are based on varying physical parameters and metal alloys in different gauze layers. Each gauze layer of these catalyst systems is made up of fine wires which are knitted to create 3D structures. Changing geometric structures and alloys downstream the catalyst gauze pack provide optimum performance at every catalyst gauze layer and provide high product yield as well as low N_2O emissions. Each catalyst gauze design has to be tailored to the operating conditions of the specific plant and customer requirements. A schematic representation of the FTC Flex catalyst design is shown in Fig. 1. The FTC Flex concept not only considers the plant operating conditions, but also the cost

NITRIC ACID PRODUCTION

Table 1: **Flexible customisation with the FTC Flex system**

Customer challenge	Solution
Cost-benefit balance in the precious metals inventory.	Investment cost of purchasing the precious metals for the following gauze campaign can vary considerably caused by large market price fluctuations. Considering this precious metal price situation, the amount and the distribution of precious metals in the catalyst gauze pack will be adopted according to the FTC Flex systematics. High product yield and low precious metal losses will also be considered.
Sustainable usage of precious metals.	The customised FTC Flex design considers the whole precious metal loop.
Highest possible ammonia conversion into the end product to reduce raw material cost	CFD simulation of FTC Flex systems with multiple gauze layers each adjusted to the temperature and concentration profile from top to bottom of the catalyst gauze pack to maximise conversion efficiency.
Stricter N_2O emission regulations by companies or governments or participation in an CO_2 emission trading system.	Catalyst gauze pack FTC Flex with focus on low N_2O emissions by application of special catalyst gauze layers in the right order from top to bottom of the catalyst gauze pack. This helps to reduce N_2O emissions as a primary measure. Additionally, a secondary catalyst solution, provided by Heraeus as a tailored solution, will be suggested for further N_2O emission reduction.

Source: Heraeus

factors from market conditions to provide the catalyst gauze design with the best economic benefit for nitric acid plants.

FTC Flex system for flexible customisation

The high level of complexity of influencing parameters in the ammonia oxidation process can be mastered by computational fluid dynamics (CFD) simulation software to find the best solution for catalyst gauze designs.

Considering the catalyst reaction kinetics, the gas flow dynamics and the changes of catalyst micro-surfaces during the operating time, the catalyst simulation software allows Heraeus to find the best alloy composition and the best 3D geometrical structure of each gauze layer located at the different positions from top to bottom of a catalyst gauze pack.

By entering the specific operation parameters of a nitric acid plant, the respective current market prices of precious metals and raw materials and including specific customer requirements, based on the CFD simulation software the most economical catalyst gauze pack is computed (Table 1).

The typical challenges nitric acid plant operators are faced with are shown in Table 1. However, the influence of the different cost factors can vary considerably. For instance, raw material prices can differ depending on the geographic locations of nitric acid plants, N_2O emission regulations may be tightened or newly introduced in a country and have to be considered for the next gauze change. Hence the challenges that nitric acid plants face can vary significantly and have to be considered during the catalyst design simulation.

Corrugated catalyst gauze packs in high-pressure plants

Typically, the diameter of ammonia oxidation reactors in high-pressure plants is less than 200 cm and the plants are operated at pressures well above 10 bar absolute and at temperatures above 920°C. Because of the high gas velocity in the ammonia converters, the number of gauzes can easily require 30 to 40 layers to provide enough surface area for 100% NH_3 conversion. These operating conditions cause a high pressure drop in the catalyst gauze pack and in some cases can lead to a limitation of the production throughput, if the compressor is already working at its maximum.

Heraeus has extensive experience with the global use of catalyst gauze pack corrugation in high-pressure ammonia oxidation reactors. With the wave-like shape of the corrugated gauzes a gauze design is possible which provides improved gas flow conditions throughout the catalyst gauze pack. The catalyst surface area for NH_3 oxidation can be strongly increased compared to flat catalyst gauze packs. The resulting low pressure drop over the catalyst gauze pack allows the plant to be run at a higher production capacity or there will be hardly a reduction of throughput if the plant is already running close to its maximum capacity.

Under the specific operating conditions of high-pressure plants catalyst gauze packs suffer from elevated precious metal evaporation losses, leading to a significant decrease of conversion efficiency in the end of the gauze campaign.

Therefore, the typical time period between catalyst gauze changes is in a range between 70 to 90 days depending on the specific operating conditions of the nitric acid plant. The special FTC Flex design of the corrugated catalyst gauze pack provides better gas flow conditions and higher conversion efficiency, in particular at the end of the gauze campaign, which leads to longer service time of the catalyst gauze packs and improves average HNO_3 yield. Fig. 2 shows the conversion efficiency over operation time in an industrial high-pressure plant using standard gauze design which resulted in a service time of about 80 days, compared to an FTC Flex gauze design that extended the service time to 100 days.

N_2O emission reduction

During ammonia oxidation a minor amount of N_2O is produced in undesired side reactions. The formed N_2O cannot be absorbed downstream and hence is released into the atmosphere as a byproduct. N_2O is well known as one of the greenhouse gases and has roughly 300 times the global warming potential of carbon dioxide and is therefore a major factor in global warming. More than 60 million tonnes of nitric acid are produced around the world annually, with an estimated 500,000 tonnes of nitrous oxide generated as a byproduct – equivalent to the carbon dioxide emissions from over 60 million mid-sized cars.

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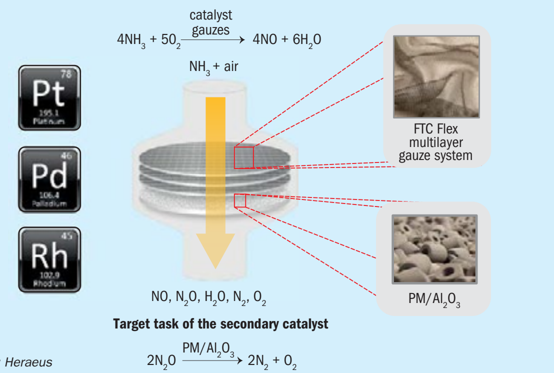
Fig. 1: **Multilayer FTC Flex gauze design with secondary catalyst**



Source: Heraeus

In more and more countries N_2O emission regulations will come into force in the near future, and others continuously tighten the emission limits or increase the costs for environmental emissions. This puts additional pressure on nitric acid producers to reduce the N_2O emissions in their plants.

Good experiences with technical solutions to reduce N_2O emissions have been available for many years. All technical solutions use special N_2O reduction catalysts which can be positioned either directly under the primary catalyst gauze pack or in the tail gas of the plant.

If there is enough space between the catalyst gauze pack as primary catalyst and the cooling system of the product gas, a secondary catalyst can be applied directly under the catalyst gauze pack as shown in Fig. 1.

Using the design principles of FTC Flex, Heraeus catalyst gauze packs in combination with an iron-oxide based secondary catalyst can achieve average N_2O emissions of less than 50 ppmv in the tail gas of medium-pressure plants. This catalyst combination is being used successfully in many nitric acid plants worldwide.

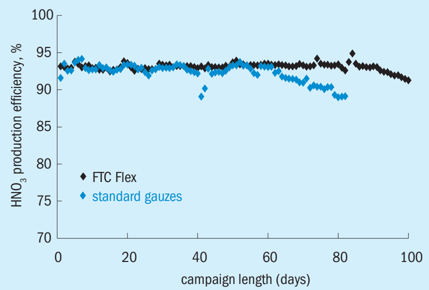
However, since N_2O is generated on the catalyst gauze pack, the most cost-effective solution will be a further reduction of the N_2O formation directly at this stage. Nowadays, N_2O emission reduction has become an important parameter for the cost evaluation of nitric acid production in many countries.

While N_2O emission reduction technology is often used in medium-pressure plants, there are only a few high-pressure plants which use an N_2O emission reduction technology. The production capacity is smaller compared to medium-pressure plants and the absolute figures of N_2O emissions are lower. However, more and more operators of high-pressure plants are requesting technologies to reduce the N_2O emissions from their plants because of rising costs of emissions or to affirm the green image of the companies. Heraeus has been developing a combination of primary and secondary catalyst technology with relatively low pressure drop for this application.

Heraeus has more than ten years of experience with this N_2O reduction technology in high-pressure reactors. During this time the primary FTC-HR gauze technology in combination with precious metal coated Raschig ring catalyst, as shown in Fig. 1, have been developed. This resulted in the new FTC Flex gauze type with a focus on high N_2O reduction during the CFD simulation process.

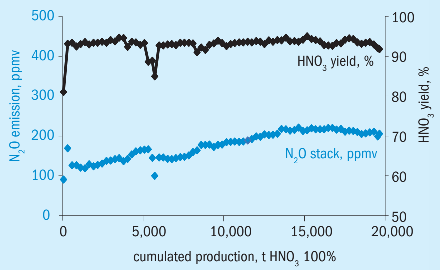
Because of the special operating conditions of high-pressure plants, the pressure drop arising from the primary and secondary catalyst system is an important parameter which limits the amount of the secondary catalyst. Nevertheless, in some industrial high-pressure reactors the combination of primary and secondary catalyst systems could be used successfully to reduce N_2O emissions. In those plants N_2O reduction rates of 80-90% could be achieved without limitation of the HNO_3 throughput and at expected HNO_3 yield (see Fig. 3). In general, the application of this type of N_2O reduction system depends on the reactor design and acceptance of a certain pressure drop at the ammonia conversion reactor and needs to be adjusted for each high-pressure plant. ■

Fig. 2: **Extended lifetime of a high-pressure plant using FTC Flex corrugated catalyst gauze packs**



Source: Heraeus

Fig. 3: **N_2O emission reduction in a high-pressure plant based on a FTC Flex catalyst gauze pack and secondary catalyst**



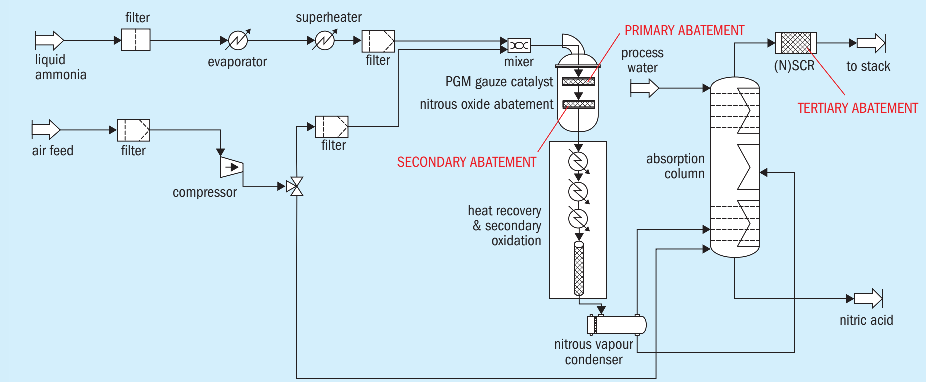
Source: Heraeus

JOHNSON MATTHEY

Nitrous oxide emissions reduction from nitric acid plants

Iain Hepplewhite

Fig. 1: **Flowsheet for the nitric acid process showing locations for primary, secondary and tertiary N_2O abatement**



Source: Johnson Matthey

Nitrous oxide (N_2O) is a recognised greenhouse gas with a global warming potential 265-298 times that of carbon dioxide. Nitric acid plants contribute a significant part of the greenhouse gas emissions from industry with N_2O emissions estimated at 350,000 tonnes per year corresponding to 100 million tonnes of carbon dioxide (CO_2e). For industrial nitric acid production, the most effective method of producing the desirable nitric oxide gas (NO) is by combustion of ammonia and air over a platinum group metal (pgm) catalyst.

On an industrial scale this reaction is normally performed over a platinum group metal (pgm) gauze in pressure vessels of up to 5m in diameter. A highly desirable solution is the in-burner destruction of N_2O using a world beating ceramic catalyst developed by Yara (YARA 58-Y1). The operating conditions immediately below the pgm catalyst create mechanical challenges that must be overcome and the paper describes how Johnson Matthey (JM) has overcome these challenges to deliver system solutions that allow greater than 90% abatement. The system solutions are widely used throughout the world with JM's experience contained in a range of highly engineered units covering a wide range of applications, where development of designs allow successful operation of the catalyst in the diverse range of existing plants.

JM's global marketing and engineering capabilities coupled with the catalyst with Yara's expertise in N_2O abatement catalyst offers the world's nitric acid industry the leading N_2O secondary abatement technology.

The nitric acid production process

Nitric acid is produced through contacting NO_2 with water. The NO_2 is produced by combusting ammonia with air using a platinum/rhodium gauze to create NO. The combustion itself has three possible reactions

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \ \text{-906.1 kJ/mol}$$

$$4NH_3 + 3O_2 \rightarrow 4N_2 + 6H_2O \ \text{-1267.2 kJ/mol}$$

$$4NH_3 + 4O_2 \rightarrow 4N_2O + 6H_2O \ \text{-1103.1 kJ/mol}$$

Two of these reactions do not produce NO and are therefore undesirable. They are avoided by running the combustion at a high temperature and at a low residence time. The ammonia combustion takes place at a temperature of around 850°C. Once the main combustion is done NO is oxidised to NO_2 non-catalytically and the resulting NO_2 is contacted with water to produce the nitric acid.

The creation of N_2O happens not only in the combustion itself, as seen above, but also in reaction with the produced NO, as shown below.

$$2NH_3 + 8NO \rightarrow 5N_2O + 3H_2O \ \text{-945.7 kJ/mol}$$

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \ \text{-2403.4 kJ/mol}$$

A flowsheet of a nitric acid process is shown in Fig. 1.

Although most of the NOx is recovered in the absorption tower some leaves the top of the absorber in the tail gas and must be treated, as its release is considered unacceptable. Two main processes for catalytic NOx removal are currently used, selective (SCR) and non-selective catalytic reduction (NSCR). Many older plants used NSCR, which removed both NOx and N_2O. However, as NSCR is both costly and leads to cross media emissions, most modern plants use selective catalytic reduction which does not remove N_2O.

Although it possible to add an additional end-of-pipe abatement step (tertiary N_2O abatement), the capex required to modify existing plants can be significant.

This article discusses a solution in which N_2O abatement catalyst is placed immediately under the primary catalyst platinum/rhodium gauze – so called secondary catalyst N_2O abatement.

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Abatement options

There are three main N_2O abatement approaches.

The first option is to ensure that the primary catalyst being used is based on the best available technology.

Secondary nitrous oxide abatement catalysts have been available for over 20 years. The catalyst is generally in the form of ceramic pellets and is installed directly under the primary catalyst. As high temperatures are generated from the oxidation of ammonia, relatively small volumes of secondary catalyst can achieve high levels of abatement. This high temperature does, however, present some difficulties in maintaining uniform gas flow through the pelleted bed, preventing gas by-passing the pelleted catalyst and minimising the movement of pellets through thermal cycling.

Tertiary nitrous oxide abatement remains a popular option and although very high levels of performance can be achieved the capital costs for such installations can be prohibitive.

Innovation

The Kyoto Protocol was the world's first climate change agreement that attempted to limit and reduce greenhouse gas emissions. Nitrous oxide (N_2O) is a recognised greenhouse gas with a global warming potential 265-298 times that of carbon dioxide (CO_2) for a 100-year timescale[1]. According to the 5th Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) from 2013, the concentration of N_2O in the atmosphere has increased by a factor of 1.2 since pre-industrial times and N_2O has become the third largest contributor to climate change[2]. The two industrial processes contributing most to N_2O emissions are the production of nitric acid and that of adipic acid. N_2O emissions from nitric acid and adipic acid production contribute to about 0.2% of global emissions (roughly 100 $MtCO_2eq$), which is equivalent to 24% of non-CO_2 greenhouse gas (GHG) emissions from key industrial processes[3].

On an industrial scale this reaction is performed in pressure vessels typically from one to five metres in diameter, with the catalyst supplied in the form of gauze. Even with the best oxidation catalyst some by-product N_2O will always be formed and emitted into the atmosphere. Abatement technology will reduce, but not eliminate these emissions. Although end-of-pipe technologies can remove N_2O from the gas system before venting to atmosphere, such installations are not always feasible and have a high capital cost. A more desirable solution was recognised as in-burner destruction of N_2O. To achieve this, some fundamental problems had to be overcome. The ammonia oxidation reaction is exothermic and results in catalyst temperatures in excess of 800°C. A pelleted catalyst was developed by Yara that could operate under such conditions to abate more than 90% of the N_2O generated across the gauzes. However, at these temperatures, the burner in which the gauzes are contained undergoes considerable expansion. Although gauzes can readily accommodate such expansion, this is not always the case with pellets and an engineered solution was therefore required that would prevent the potential for gas by-passing if the catalyst is not free flowing.

JM's marketing and engineering capabilities were combined with Yara's cooperation to offer this N_2O abatement technology to the world's nitric acid industry.

Today the catalyst is widely used throughout the world and is installed in a range of highly engineered units. JM's experience across a wide range of catalyst applications combined with extensive design knowhow in this and other sections of the chemical industry, allowed the development of designs for the mechanical modifications which allow successful operation of the catalyst in a diverse range of nitric acid plant designs. These modifications vary from minor changes to prevent loss of catalyst, to a unique design which can be retrofitted easily into plants with the most arduous operating conditions for the abatement catalyst. This innovative technology combines high catalytic activity and long-term stability under conditions of high temperature and thermal stress. The catalyst withstands normal impurities present in the gas and has no impact on the combustion reaction taking place in the burner.

Main considerations

As with any investment in technology several considerations need to be made in order that the correct discussions are made on the best available technology and if this technology can be futureproofed to protect any investment against subsequent changes in legislation.

- Will this technologies performance meet current and likely future legislation?

Fig. 2: Leading secondary N_2O abatement catalyst Yara 58-Y1.

- What other investment costs are there?
- What operational costs are there?
- Will there be monitoring costs?
- Will the N_2O abatement technology adversely impact nitric acid production?

Yara 58-Y1 N20 abatement catalyst

Yara's N_2O abatement catalyst (Fig. 2) is a cerium oxide-based catalyst with a cobalt compound as the active component and has been optimised for decomposing N_2O to nitrogen and oxygenx at temperatures of 800-900°C. The catalyst is offered as a multi holed cylindrical pellet with excellent thermal stability and a 2,000°C melting point.

JM have successfully installed N_2O catalysts into a range of low-, medium- and high-pressure plants worldwide, with abatement of over 90% being achieved. The Yara 58-Y1 N_2O abatement catalyst has no impact on nitric acid production and can be easily installed.

As well as high levels of abatement, this stable catalyst offers several benefits, including:

- low pressure drop;
- long lifespan;
- resistance to sintering;
- no risk of downstream pollution.

JM provides technical support throughout the whole process, including detailed analysis of the burner support structure, with the catalyst bed needing to be accommodated as a uniform layer across the burner diameter immediately beneath the gauze as shown in Fig. 3.

Abatement basket engineering

JM are experienced in successfully designing robust, stable containment baskets specifically customised for the burner in conjunction with the N_2O catalyst. This avoids preferential flow, which improves the performance of the abatement catalyst, and helps to increase the conversion efficiency and to minimise operational costs.

Fig. 3: Secondary catalyst bed of Yara 58-Y1 immediately below gauze burner hood.

The design achieves the following:

- process gas is evenly distributed through the catalyst bed;
- the required catalyst bed depth is maintained throughout the campaign;
- edge effects are minimised as a source of bypass without interfering with the flow of gas through the gauze pack above.

Thermal expansion coefficients for most of the materials used within a nitric acid burner are around 15 mm per metre, therefore the radius of a 2 m basket would expand by 15 mm. If the catalyst pellets do not move to fill the resulting gap, then this 15 mm gap becomes a route for substantial gas bypass.

As the pressure drop through the pelleted secondary catalyst can be 1.5 to 10 times higher than that of the platinum gauze pack, lower pressure drop around the edge would result in significantly higher gas flow rates, which could be in the region of 3 to 30 times higher than the bulk gas flow rate.

Thermal cycling, which occurs during repeated shutdowns and start-ups of the plant can cause some pellets to move upwards which leads to doming towards the centre of the bed. This increases the pressure drop at the centre and exacerbates the above-mentioned effect.

Containment system

The design of any containment system is dependent on the plant loading, which is defined as the ratio of tonnes per day of nitrogen per square metre cross sectional area.

For high loading plants >30tN/m²/d extensive modifications are usually required to the existing baskets.

For low and medium loading plants <30tN/m²/day containment requirements fall into three categories:

- no modifications required;
- moderate modifications;
- extensive modifications.

High loading plants

Specially designed containment is required as in general there is no space for the catalyst to be installed without some form of modification.

Introducing abatement into high loading plants introduces several key considerations when designing a containment system and a degree of compromise is therefore required between abatement performance and the effect on the burner and plant.

One of the most notable issues with high-pressure plants is that the gas velocity is significantly higher than is the case for lower-pressure plants. As a result, more catalyst is required than would be the case on lower-pressure plants. Consequently, there are two interrelated issues, the lack of useable space within the burner and the need for a larger volume of catalyst. Both need to be overcome to optimise abatement.

The optimum volume of catalyst cannot always be installed in a high-pressure plant for two reasons: physical space and pressure drop. In most burners the design of the basket would not facilitate the installation of a secondary catalyst, so space must be created.

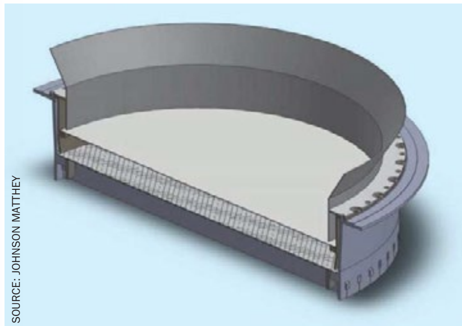

Fig. 4: Typical installation of a high loading containment creating space by moving the position of the gauzes upwards from its original position within the basket.

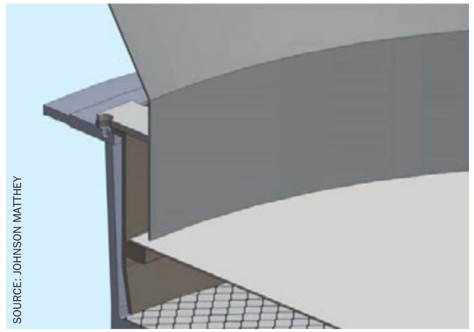

Fig. 5: Close-up of the high loading containment creating space by moving the position of the gauzes upwards from its original position within the basket.

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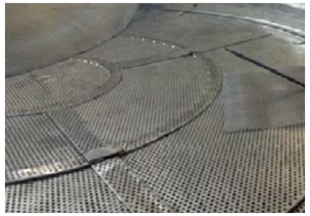

Fig. 6: Inside of a basket in good physical condition and with an even and level support.


Fig. 7: Inside of a basket in poor physical condition and with an uneven support.

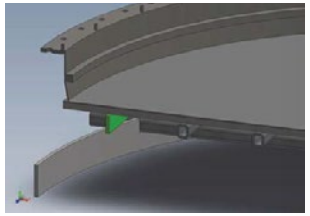
Fig. 8: New basket and honeycomb support.

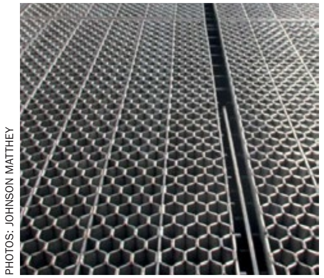

Fig. 9: Honeycomb support.

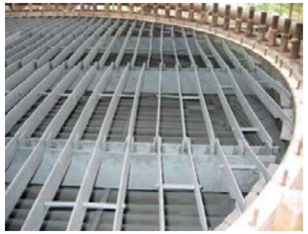
Fig. 10: Medium loading plant with no space for a pelleted secondary N_2O abatement catalyst.

Due to the lack of space in high load plants, it is necessary to engineer space into the burner to create the required room to fit the required amount of catalyst. Typically, gauzes are supported around the middle of ammonia burners, so a common strategy to create additional space in the burner is to move the reaction zone further up the in burner by means of a new containment ring, thus leaving space below (Figs 4 and 5). However, moving the reaction zone can cause the intensity of radiant heat to shift, causing damage to the burner interior and housing. Johnson Matthey has always strived to ensure that exposure of radiant heat to the main basket flange and other internals is limited as much as possible, reducing the risk of damage through thermal deformation. A second strategy is to utilise any space below the basket and above the boiler tubes. If this can be achieved, then the position of the gauzes is maintained and any risk of radiant heat causing damage to the burner interior eliminated.

Low and medium loading plants

To optimise the performance of the abatement catalyst, and to reduce the impact on plant operation and conversion efficiency a bespoke containment system is essential. The options are outlined below.

- Good physical condition: low or no modification is required, a wire mesh screen and skirt is installed to prevent catalyst loss.
- Poor support system: Support system requires redesign and replacing to support catalyst weight.
- Basket design: analysis and re-design required of support beam and the installation of containment system required. Beam simulations can be carried out using simulation software.

The containment of the secondary abatement catalyst and the maintenance of bed depth are key to maximising abatement performance.

Option 1: no modification

Generally, no modifications are required if the burner basket is in good physical condition, and the bottom support of the basket will allow good flow distribution through the pelleted bed of catalyst. At most, a flat circular mesh screen and skirt or grill would be required to prevent the loss of catalyst pellets. Fig. 6 shows an example of the inside of a basket in good physical condition and with an even and level support. The inclusion of a flat circular mesh screen prevents the loss of catalyst pellets through the 10 mm perforated plates.

Option 2: moderate modification

Moderate modifications would be required if the basket was in poor physical condition or if poor support of the catalyst resulted in an uneven bed depth affecting gas distribution. This may require a new basket and/or replacement of the existing support with a metal honeycomb.

Fig. 7 shows an example of the inside of a basket in poor physical condition and with an uneven support. Not only are the supporting plates dished which would result in differing heights of catalyst being installed, but the design of the C-shaped clamps holding the plates together also presents a problem when trying to install a consistent bed depth of catalyst.

Fig. 8 shows an example of a new basket and honeycomb support. The benefits of a honeycomb support are that the cellular shape resists thermal distortion; it presents a uniformly flat surface onto which secondary abatement catalyst is installed and it can be segmented for easy installation.

Fig. 9 shows an example of a honeycomb support.

Option 3: major modification

For some plant designs there is no space into which a pelleted catalyst can be installed and instead central support for the gauzes is offered by a series of beams. In such cases the position of the beams needs to be lowered to create space. A means of containing the catalyst is required with the installation of a new containment ring. In addition, the existing beam arrangement would have originally been designed to support the weight and pressure drop from the primary gauzes. As the beams now need to support the additional loads imposed by the pelleted catalyst, the depth of the beams may need to be increased. The material of construction may also need to be changed to a material with improved creep and rupture strength.

Summary

Johnson Matthey's experience across a wide range of catalyst applications combined with knowledge of process design in this and other sections of the chemical industry, resulted in the development of a number of engineered solutions which allow successful operation of N_2O emission reduction catalysts across the diverse range of design of existing nitric acid plants. These modifications vary from minor changes, to prevent loss of N_2O abatement catalyst, to a unique and patented design which can be retrofitted easily into plants operating under the most arduous of conditions.

Today this innovative technology is widely used throughout the world and combines leading edge catalysis and engineering designs suitable for retrofit into all nitric acid plants. ■

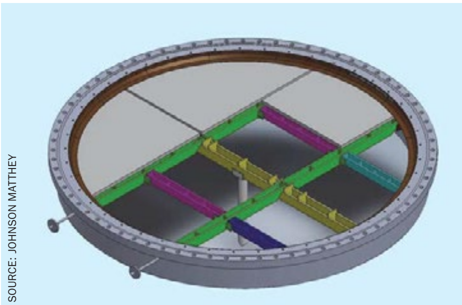

Fig. 11: Creating space, containment and support necessary for the installation of secondary N_2O abatement catalyst.

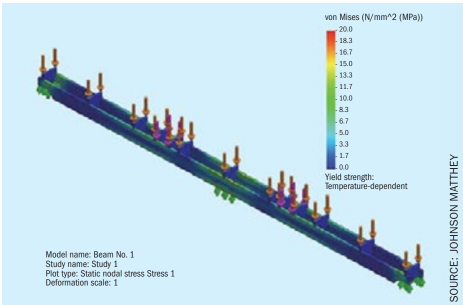

Fig. 12: Beam stress analysis being carried out using SolidWorks.

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KBR

KBR sustainable N_2O abatement

Partha Pratim Chowdhury and Rit H. Desai

Since 1954, KBR and its affiliates have licensed over 76 grassroots nitric acid plants globally and is the technology leader in the US market. KBR has experience in successfully revamping plants and fulfilling client requirements across the globe.

Nitrous oxide emissions

Industrial nitrous oxide (N_2O) is generated from undesirable side reactions in the production of nitric acid. In 2019, N_2O accounted for nearly 7% (457.14 million tonnes) of all US greenhouse gas emissions, resulting from agriculture, fuel combustion, wastewater management, and industrial processes.

Table 1 shows emissions of N_2O per tonne of nitric acid produced.

KBR N_2O abatement

Primary abatement

Primary abatement systems conceptually try to reduce N_2O generation during NH_3 oxidation at the converter. This is basically spontaneous destruction of N_2O by high temperature and time. This is a relatively slow destruction process and with longer residence time more N_2O can be destroyed. Old KBR-Weatherly nitric acid plants with a horizontal train had more residence time compared to newer plants with a vertical train. This is because in horizontal trains the gas passes through an elbow before entering the heat exchanger. This elbow allows increased residence time leading to primary abatement of N_2O.

Since it is not desirable to keep the hot gas at such a high temperature, an exchanger is connected immediately downstream to bring the gas temperature down. This design is followed in current KBR vertical train nitric acid plants. This addresses the maintenance issues faced by the mechanical components exposed to the high temperature.

Abatement of N_2O by primary measures are limited and the process has limited efficacy to achieve the acceptable emission norms.

Secondary abatement

Secondary abatement systems work on the principle of installing abatement catalyst after the platinum gauge. This targets N_2O reduction from the process stream from the NH_3 oxidation stage to HNO_3 production stage. The catalyst undergoes several extreme thermal exposures and is susceptible to damage/cracking. The performance of the catalyst has not been very successful at these operating conditions. KBR has not yet guaranteed any removal efficiency with secondary abatement, even though there are KBR plants where they are in operation.

KBR tertiary N_2O abatement

KBR's N_2O abatement process employs tertiary abatement technology and achieves ~95% removal efficiency at an operating temperature range of 350°C to 660°C (Table 2).

KBR's tertiary N_2O abatement system employs a catalytic reactor upstream of the tail gas expansion unit. Fig. 1 shows two possible locations of the abator vessel in the KBR nitric acid process. In the tertiary control system, N_2O is catalytically decomposed into N_2 and O_2:

$$N_2O \rightarrow N_2 + \tfrac{1}{2}\,O_2$$

The process uses a proprietary Fe/zeolite based catalyst, which can be bought in pellet form or as monolith bricks. The tertiary N_2O abatement can remove up to 98% of the N_2O content in the tail gas stream. The catalyst is housed in a pressure vessel suitable for continuous operation. The catalyst is expected to remain active for a period of five to seven years.

The biggest advantage of the catalyst is that it is highly efficient in N_2O abatement up to an operating temperature of 660°C. The nitric acid plants designed by KBR feature the unique expander gas heater that heats the tail gas up to 650°C. The high tail gas temperature improves the power recovery in the expander and maximises the steam export, making the KBR design highly energy efficient. This enables the retrofit of a N_2O abatement system between the expander gas heater and the expander.

Alternatively, a unit can be placed upstream of the expander gas heater, thus reducing the operating temperature of the abatement system.

Another significant feature of the design is the low pressure drop in the tertiary N_2O abatement system, approximately 20 kPa or less. This is further improved if a radial flow design is used. However, this leads to higher mechanical costs due to the intricate internal basket design inside the vessel.

The N_2O abatement system (Fig. 2) can be coupled with a NOx abatement system if required. The NOx abatement system can be provided as independent equipment or can be combined in a single reactor with N_2O abatement (Fig. 3).

Table 1: **Default N_2O emission factors**

Production process	Approximate pressure (atm)	N_2O emissions (kg N_2O/t HNO_3) Low	Average	High
Plants with NSCR		1.9	2.0	2.1
Plants with process-integrated or tail gas N_2O destruction		2.25	2.5	2.75
Atmospheric pressure (low pressure)	1	4.5	5.0	5.5
Medium-pressure plants	4-8	5.6	7	8.4
High-pressure plants	8-14	5.4	9	12.6

Source: IPCC 2006 Guidelines for National GHG Inventories & https://www.epa.gov/sites/default/files/2015-12/documents/nitricacid.pdf

Table 2: **KBR reference data for N_2O abatement**

Plant capacity, t/d	N_2O at inlet, lb/h	N_2O at outlet, lb/h	Abatement efficiency, %
624	170.1	8.5	95
835	281	4.9	98.3
1,200	409.2	7.2	98.3

Source: KBR

Equipment design

The N_2O abator vessel is designed as a hot-wall down-flow reactor. The tail gas enters the vessel from the top and is uniformly distributed over the monolith bed. Computational fluid dynamic analysis helped KBR to design the proprietary inlet distributor, which ensures smooth distribution of the tail gas above the catalyst bed. This helps in maintaining a uniform operating pressure profile across the reactor bed. Uniform distribution of tail gas helps achieve a linear temperature gradient during start-up and shutdown, thus reducing the thermal loads on mechanical components.

The catalyst bed is supported by the support beam and grid. A 24-inch manway is provided above the catalyst bed to allow for easy installation of the monolith bricks and the support grid.

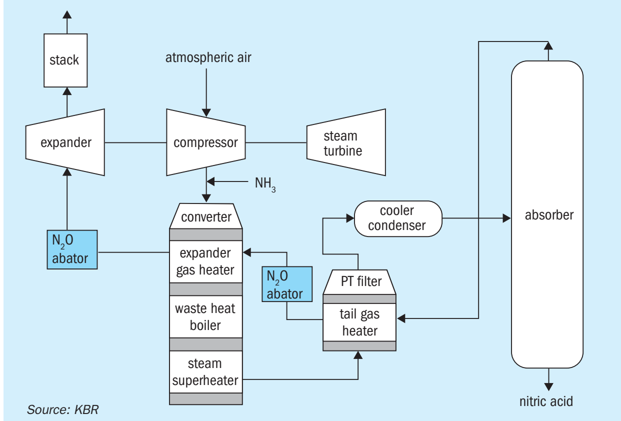
The equipment is made of special stainless steel with stringent chemistry restrictions. This enables a longer life suitable for the harsh operating conditions including temperature and pressure cycles. Being in cyclic service, the equipment is subjected to fatigue stresses. This is carefully addressed by the mechanical design with compliance to all ASME requirements. The support skirt is designed with a hot box to address the thermal cycles. The inlet and outlet nozzle design addresses the temperature and pressure cycles for a minimum life of 25 years.

The benefit of the proven hot wall design is the reduction in weight compared to a cold-wall refractory-lined design. KBR can provide a cold wall design if requested by the client. This will however lead to higher capital cost due to higher weight and the more complex design.

While a radial flow design provides better pressure drop control across the bed, the simpler axial down-flow design leads to a reduction in weight by 40%. The axial flow design enables use of monolith brick design catalyst, which can be easily installed during turnarounds. The simpler design of the reactor internals offsets the slightly higher cost of a monolith catalyst compared to pelletised extrudate catalyst. This translates to a lower capital cost for the client for installing a new N_2O abatement unit.

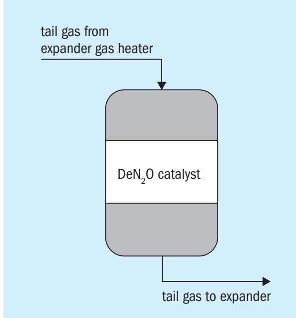
Also based on client requirements, the equipment can be sized or rated for a higher capacity in the future. This additional margin can be used later with additional catalyst as and when to meet future requirements.

Fig. 1: **Possible locations of the N_2O abator**



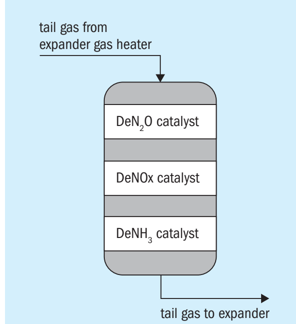
Source: KBR

Fig. 2: **Standalone N_2O abator with DeN_2O catalyst**



Source: KBR

Fig. 3: **N_2O abator coupled with NOx abatement using NH_3**



Source: KBR

Summary

With multiple units operating successfully and meeting N_2O emission restrictions, KBR's tertiary N_2O abatement system is helping nitric acid producers worldwide to meet governmental environment regulations as well as providing a sustainability commitment to society in general. The technology license is further enhanced by proprietary equipment supply by KBR which meets the best design, fabrication, and quality control industry standards. Thus, KBR is able to support clients with an end-to-end solution from design to delivery. By operating at a higher temperature range up to 660°C, the increased energy efficiency at the expander is an added advantage for the KBR process. KBR's proprietary reactor is designed to withstand the severe operating conditions and have a design life of up to 25 years. With relatively easy installation, the KBR process is suitable for both grassroots projects and brownfield retrofits. ■

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