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

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NITROGEN+SYNGAS
ISSUE 372
JULY-AUGUST 2021

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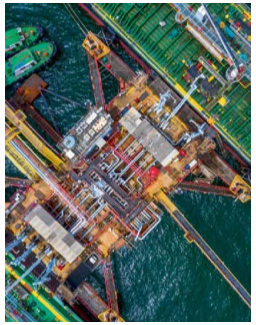

Cover: Aerial view of two fuel tanker ships at a port. AvigatorPhotographer/iStockphoto.com

12

Ammonia as a fuel

Commercial barriers still remain.

18

Corrosion control

New alloys protect against metal dusting.

Read this issue online at: www.nitrogenandsyngas.com

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CONTENTS

REGULARS

NITROGEN+SYNGAS
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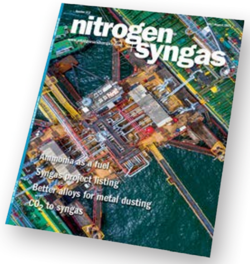
The new carbon?



At a time when green (or maybe blue) ammonia is being looked to as a way of reducing carbon emissions, substituting for hydrocarbons in a variety of potential uses, a conference held at the start of June was a reminder that nitrogen, its neighbour on the Periodic Table, is by no means off the hook on the environmental front. The Eighth Global Nitrogen Conference – held over from last year because of Covid-19, and this year held virtually, as most events are for the time being – was the latest in a series of tri-annual meetings convened by the International Nitrogen Initiative (INI), with support from the UN Economic Commission for Europe (UNECE) and the German Ministry of the Environment. The INI grew out of the 1979 UNECE Convention on Long-range Transboundary Air Pollution and 1999 Gothenburg Protocol, and is concerned specifically with 'reactive nitrogen' (i.e. nitrogen not tightly bound to itself in a triple bond, which makes up 78% of the air around us).

> **"Nitrogen management needs to be higher on the agenda of global environmental conferences.**

Many of the concerns will be familiar to the nitrogen industry – the release of nitrous oxide (N_2O) into the atmosphere, with its global warming potential, NOx pollution and its effects on health, and nitrate migration into water courses and consequent algal blooms and anoxic 'dead zones' in river estuaries, as well as deleterious effects on ecosystems and soil quality. While acknowledging the benefits that the Haber-Bosch process has brought in terms of feeding a growing global population, the INI argues that it has also led to a 100 year period where Earth's nitrogen cycle has been in imbalance, with an increasingly large load of reactive nitrogen roughly doubling the amount of nitrogen circulating in the environment over that time, and eventually finding its way into air and water.

NOx and N_2O abatement has been a success story for the nitric acid industry in particular over the past two decades. However, in spite of the success of the process industry in dealing with N_2O emissions, these have still risen globally by 30% since 1980, with most N_2O lost to the atmosphere now coming from agriculture, as a result of the breakdown of urea and ammonium nitrate in the field. N_2O is the third largest contributor to climate change after carbon dioxide and methane. Meanwhile, the effect of ammonia emissions from agriculture and other sources on human health is a subject of increasing concern.

The Global Nitrogen Conference, which was originally to have been held in Berlin, produced what it called the Berlin Declaration, which said that "better management of humanity's relationship with nitrogen is central to the success of the [UN] Sustainable Development Goals." To this end, it endorsed the 2019 Colombo Declaration to halve nitrogen waste by 2030 and called for measures to improve nitrogen management practices and technologies for use at the farm level, and the recovery of nitrogen from manures, wastewater and industrial effluents, as well as promoting foods "with lower nitrogen footprints and a higher share of plant-based protein sources". Countries should set national nitrogen targets/budgets – Germany is already on the verge of doing so, and nitrogen management needs to be higher on the agenda of global environmental conferences.

There is some evidence that this is happening. In December 2020 the UNECE adopted a draft guidance document on international sustainable nitrogen management in consultation with the INI. Much of the focus going forward will be on farming practises, and how and when and in what quantity nitrogen fertilizer and manures are applied to fields, with increasing use of precision agriculture to try and avoid volatilisation losses. But industry will also no doubt be required to play its part, via an increasing focus on slow and controlled release products – the UK's recent consultation on banning or restricting the application of urea that is not treated with a urease inhibitor is one such straw in the wind, and it may lead to an increasing move towards nitrate fertilizers like AN and CAN in Europe.

As yet, nitrogen is not the new carbon – there is nowhere near the same focus and pressure at an international level. But momentum is building for an overhaul of how we look at nitrogen and its role in the environment, and while efforts so far have been piecemeal, and mainly on a national or regional level, more coordinated and potentially far reaching policy changes may only be a few years down the line. ■

Richard Hands, Editor

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Price trends

Market Insight courtesy of Argus Media

NITROGEN

Recent ammonia market developments include a rise in the Tampa ammonia contract price to $585/t c.fr, continuing outages in the Middle East – mainly Saudi Arabia – and Ukraine exports potentially being under threat. A $50/t jump in the Tampa contract price for July shipments removed any doubt over whether there would be a slowdown in the latest price rally over the next few weeks. Cargoes continue to be lined up from the west to ship to supply customers short of product in east Asia. Buyers remained out of the market towards the end of June, weighing up potential options if the market remains tight into August.

There is still as yet no official word from Saudi Arabia over how long exports will be impacted from Ras al Khair following the fire which damaged the Ma'aden ammonia plant there, affecting 1.1 million t/a of export capacity. Traders are preparing for the region to be below capacity until August. Buyers of Saudi ammonia are facing the prospect of buying more spot ammonia, which is supporting delivered offers above last done business.

US Gulf cargoes are expected to become available next month as the regions moves further into its off-season and maintenance starts on the NuStar pipeline, but delayed turnarounds from the start of the year due to the poor weather conditions may restrict availability. In general, August offers an opportunity for some respite to the market, and lower pricing if Saudi production starts to ramp up.

Much of the urea market has been on hold toward the latter stages of June, waiting to see prices from the 24th June Indian tender. If the prices rumoured to have been offered are confirmed, the wait will have been well worth it for suppliers. Initial indications are that offer prices in the RCF tender were all above $500/t c.fr, with east coast prices rumoured close to $510/t c.fr. This would reflect netback prices above $470/t f.o.b. in China and the Middle East, marking a new step up in price.

Ethiopia is also tendering to buy over 200,000 tonnes of urea for July, squeezing available supply and most likely facing higher prices than India.

Markets in the western hemisphere have been inactive, but buyers face a new round of price increases, not only because of higher f.o.b. prices but also because freight has jumped again from the Middle East and FSU/Mediterranean origins. Recent market drivers include Indian buying and urea availability for the RCF tender, flat recent prices in Brazil, and Chinese government pressure to curtail exports due to concerns about higher domestic urea prices in China. If this does occur it will reduce availability still further. Overall market supply looks to be very tight for July and it seems that further price increases may be on the cards, especially East of Suez.

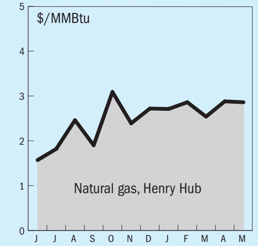
Table 1: Price indications

Cash equivalent	mid-June	mid-April	mid-Feb	mid-Dec
Ammonia ($/t)				
f.o.b. Black Sea	485-525	430-470	300-370	204-230
f.o.b. Caribbean	475-525	430-460	290-335	200-230
f.o.b. Arab Gulf	550-610	440-480	290-330	230-260
c.fr N.W. Europe	550-600	490-540	340-420	250-275
Urea ($/t)				
f.o.b. bulk Black Sea	370-435	300-340	300-380	230-250
f.o.b. bulk Arab Gulf*	435-470	320-355	350-380	260-290
f.o.b. NOLA barge (metric tonnes)	445-495	365-405	329-365	242-250
f.o.b. bagged China	400-460	320-355	320-365	270-300
DAP ($/t)				
f.o.b. bulk US Gulf	640-685	572-613	568-600	419-436
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	157	157	157	157

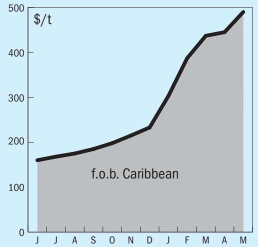
*Notes: n.a. price not available at time of going to press. n.m. no market. * high-end granular.*

END OF MONTH SPOT PRICES

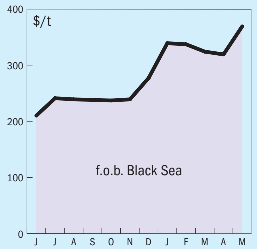
natural gas



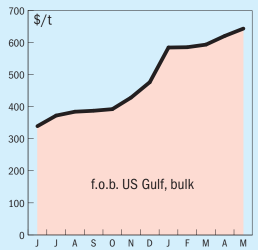
ammonia



urea

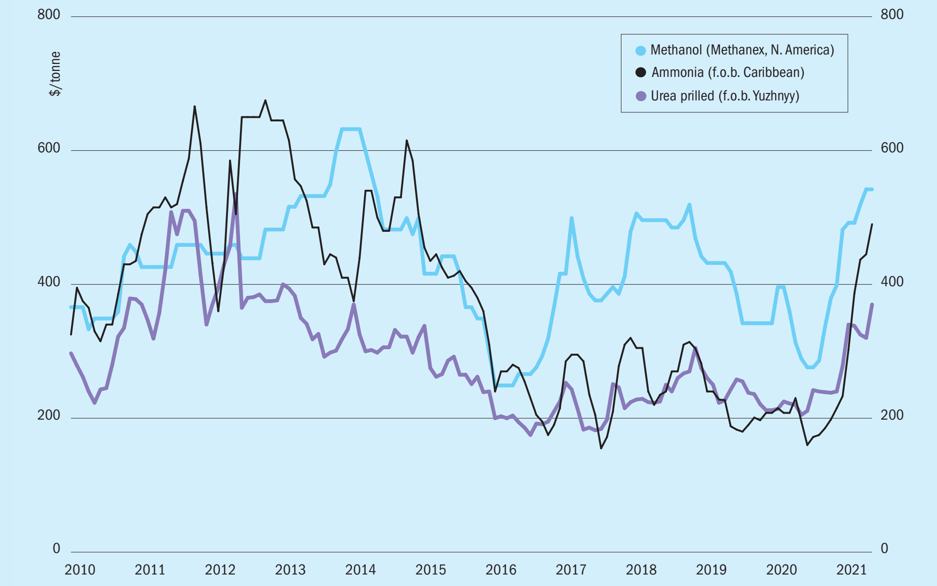


diammonium phosphate



Market Outlook

Historical price trends $/tonne



Source: BCInsight

AMMONIA

- Ammonia markets continue to be dominated by unplanned outages in Saudi Arabia (where the SAFCO 4 and one of the Ma'aden ammonia plants are both down, removing 2.3 million t/a of merchant ammonia from the market). This comes on top of other shutdowns earlier in the year on Trinidad, in the US and Australia.
- In spite of restarts at PAU in Indonesia and EBIC in Egypt, there is a shortage of ammonia availability in the short term, and this tight availability is driving higher prices in all major markets. Early June saw Black Sea prices surge $90/t to netbacks above $520/t f.o.b., and Middle East rates higher than $600/t f.o.b. Some delivered prices to India and China were reported at $670/t c.fr.
- Ammonia prices are now more than double their value at this time last year, and this pricing level is likely to drive demand destruction if it continues for any length of time.

UREA

- Urea markets have also surged. India is back in the market, having not sourced as much urea as it had hoped in the first few months of the year. A large MMTC tender was due to close on June 24th.
- Chinese authorities have become concerned over rising urea prices, which reached over $420/t in early June, with the National Development and Reform Commission (NDRC), China's state planning agency, launching an investigation into the urea market, and saying that it will "strengthen market supervision and resolutely crack down on hoarding, price hikes and fabricating and disseminating information on price increases". There was market speculation about a possible export ban.
- Rising coal prices have helped sustain Chinese prices, and while falling grain prices have been a contra-indication, continued strong Indian buying looked likely to support urea prices for the time being.

METHANOL

- Methanol prices have been stable after a ramp up of prices earlier in the year. Methanex reference prices for June were a rollover of May, at $430/t in the Asia-Pacific region.
- Russian deliveries of methanol to Europe were impacted by the Euro2020 soccer championship, with deliveries via St Petersburg halted for six weeks in June and July.
- In China, coal prices have risen by 60% from March to June, leading some methanol plants to scale back operations. At the same time, falling prices for oil and olefins lead to a squeeze on margins for Chinese MTO producers – representing half of Chinese methanol demand – with some producers idling plants. But rising energy prices may see a methanol price recovery in the second half of 2021.
- Longer term, the US infrastructure bill has lifted methanol stocks with the expectation that new construction will draw in plastics, resins and fibreboard.

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Nitrogen Industry News

KENYA

Tecnimont to work on renewable power-to-fertilizer plant in Kenya

Maire Tecnimont SpA says that its subsidiaries MET Development, Stamicarbon and NextChem have collectively begun work on a renewable power-to-fertilizer plant in Kenya. MET Development has signed an agreement with Oserian Development Company for the development of the plant at the Oserian Two lakes Industrial Park, on the southern banks of Lake Naivasha, 100 km north of Nairobi.

The plant will support Kenya's low carbon growth, agricultural output and its smallholder farmers and communities. Located near the country's largest geothermal energy basin, it will also be partly powered by on-site solar energy, displacing the need for fossil fuels and eliminating carbon from the production. The facility will reduce carbon emission with approximately 100,000 t/a CO_2 compared to a gas-based fertilizer plant. It will also reduce the country's dependency on imported nitrogen fertilizers by around 25%, as well as increasing fertilizer affordability.

Stamicarbon will provide both its Stami Green Ammonia technology and its nitric acid technology as an integrated technology package for the manufacturing of nitrate fertilizer. The technology configuration – characterised by a modular approach and therefore ideal for small scale facilities – will be the first of its kind, although based on proven technology.

The renewable power-to-fertilizer project aims to produce 550 t/a of calcium ammonium nitrate (CAN) and/or NPK fertilizers and will be the first state-of-the-art, commercial-scale nitrate fertilizer plant based on renewables. MET Development is currently engaging with local and international partners to set up the development consortium.

The project has started preliminary engineering works and NextChem aims to start the front-end engineering design (FEED) by the end of 2021. The goal is to start commercial operation of the plant in 2025. The fertilizer product is predominately produced as CAN but the facility will have the flexibility to produce NPK fertilizers in addition to meet the demand of local agricultural requirements. It will utilize approximately 70 MW of renewable power.

Pierroberto Folgiero, Chief Executive Officer of Maire Tecnimont Group commented: "We are very pleased to announce the start of this exciting project thanks to the collaboration with a pioneering player such as Oserian Development Company. With this strategic initiative we aim to unlock the potential of decarbonising the fertilizer industry using renewable energy as a feedstock. Kenya has a unique potential to provide renewable energy, making it an ideal location for local green power-to-fertilizer production, replacing imports of nitrogen fertilizer". ■

UNITED KINGDOM

CRU launches new Sustainability division

Consultancy and events company CRU has launched a new sustainability division, CRU Sustainability.

The aim is to bring together its sustainability expertise into one division and, in so doing, launch a unique service designed to give clients in the industries CRU serves data and insights to accelerate their journey to net zero. CRU Sustainability will have four focus areas: climate policy and regulation, carbon emissions and markets; the clean energy transition; and the circular economy.

"The launch of CRU Sustainability is a true game changer for tackling complex decarbonisation journeys. When it comes to supporting businesses deliver their sustainability ambitions, we have all the corners covered – data, climate policy and industry expertise," said Robert Perlman, executive chairman at CRU Group.

CRU Sustainability will be led by Dr Jumana Saleheen. Dr Saleheen is currently Chief Economist for CRU Group, where she heads up economic thought leadership and global forecasting. Having worked at the Bank of England and the Federal Reserve Bank of Boston, Dr Saleheen brings over two decades of experience to her expanded role as head of CRU Sustainability.

RUSSIA

Stamicarbon and Shchekinoazot collaboration on sustainable fertilizer production

Maire Tecnimont's innovation and licensing company Stamicarbon is to team up with Russian chemical company Shchekinoazot to jointly explore, develop and implement green technologies at Shchekinoazot's existing and new enterprises in the Russian Federation, with the common goal to contribute to sustainable fertilizer production.

The agreement captures the commitment of both parties to assist in the development and commercialization of green technologies, as a joint effort to industrialize environmentally best performing fertilizer products and processes. Stamicarbon and Shchekinoazot consider each other as a priority partner for the implementation of green technologies at the company's urea plant and other fertilizer plants in the Russian Federation.

Pierroberto Folgiero, Maire Tecnimont Group CEO, commented: "Stamicarbon is at the forefront of innovation in the fertilizer industry, and as such it is best positioned and equipped to set the pace for the development of technologies to support the energy transition. I am glad that an industry leader such as Shchekinoazot has selected Stamicarbon as the partner of choice to industrialize sustainable fertilizer production."

Pejman Djavdan, CEO of Stamicarbon, said: "We are committed to the development of technologies for Green Fertilizers, decreasing the environmental footprint of fertilizer production and use. In partnership with Shchekinoazot, I'm sure we will greatly contribute to the implementation of these new technologies and intensification of sustainable agriculture."

NETHERLANDS

Stamicarbon launches green ammonia technology

Stamicarbon has launched its Stami Green Ammonia technology, describing it as "a solution to tackle the global carbon challenge". The technology relies on renewable resources instead of fossil fuels to eliminate carbon from the process, paving the way for sustainable and green downstream fertilizer production.

Stamicarbon has signed an exclusive licensing agreement with Argentinian-based Raybite SRL for the commercialisation of this small-scale ammonia technology package. The agreement means that Stamicarbon has become an ammonia licensor for small-scale ammonia plants. By adding this technology to Stamicarbon's portfolio, installation of small-scale urea plants and mono-pressure nitric acid plants in green fertilizer projects become feasible. Stami Green Ammonia technology can also be applied in existing plants, as part of a hybrid technology solution to make existing fertilizer production more sustainable. Producers can choose, for example, to use this technology in combination with urea production based on carbon recycling, or in combination with nitrate fertilizers. In addition to delivering the technology, Stamicarbon can also assist with feasibility studies, project development and financing.

The technology condenses ammonia without the need for a large dedicated refrigerating compressor. A multi-service compressor accommodates the refrigerating compression stage instead, allowing for better plant reliability and substantial capex saving compared to other technologies. Four plants are currently in operation, and as noted above, it will be used in the development of a green power-to-fertilizer plant at the Oserian Two Lakes Industrial Park in Kenya.

The technology also differs in the pressure of the synthesis gas, which is ideal for current green ammonia applications. In addition, there are hardly any inerts present within the process, which means that the conversion per pass of the reactor is higher. Meanwhile purging can be minimised, resulting in minimal (or even redundant) need for ammonia recovery.

PHOTO: FATIMA FERTILIZERS

Fatima Fertilizers' urea plant.

PAKISTAN

Fatima Group implements digital solution at ammonia plant

Pakistani fertilizer company Fatima has implemented Topsoe's digital solution *ClearView*™ at their 1,650 t/d ammonia facility at Rahim Yar Khan. *ClearView* uses an online simulation of the actual performance of for instance an ammonia, hydrogen, or methanol plant to reveal performance variations that can be optimised. In many instances, plant performance deviates from what is immediately visible to the plant operator which can lead to unrecognized inefficiencies.

"Digitalisation is important in the strategic goals of both Topsoe and Fatima Group. It is a pleasure to collaborate with Topsoe, who is a great trusted partner, to jointly pursue our goals. Fatima remains committed to actively collaborate on the on-going development of the amazing tool and also other fields of common interests," said Fawad A Mukhtar, CEO Fatima Group.

"When we monitor the plants with *ClearView*, we achieve a new level of detailed insights that enable our customers to optimize productivity on different parameters. For now, our customers are within ammonia and our sulphur emissions solution, WSA. But… our medium-term vision is to make digital performance optimisation a part of all our technology offerings," said Amy Hebert, Chief Commercial Officer at Topsoe.

JAPAN

Yara to supply blue and green ammonia for power generation

Yara International says that it has signed a memorandum of understanding with JERA Co., Inc, Japan's largest power generation company, to collaborate on the production, delivery and supply chain development for blue and green ammonia, to enable zero-emission thermal power generation in Japan.

Japan recently announced plans to introduce ammonia into the fuel mix for thermal power generation, as part of its measures to cut CO_2 emissions and reach carbon neutrality by 2050. As part of its Green Growth Strategy, the government is targeting ammonia imports of 3 million tonnes by 2030.

JERA is the largest power generation company in Japan, producing about 30% of Japan's electricity. The company is committed to establishing green fuel supply chains to achieve zero CO_2 emissions from its operations in Japan and overseas by 2050. Under the MoU, Yara and JERA are targeting collaboration in the following areas:

- Supply and development of new ammonia demand in Japan.
- Sequestration of already captured CO_2 (CCS) at Yara's ammonia plant in Pilbara, Australia, enabling the production and supply of blue ammonia to JERA.
- New clean (blue and green) ammonia project development.
- Optimisation of ammonia logistics to Japan.

Yara produces roughly 8.5 million t/a of ammonia and employs a fleet of 11 ammonia carriers, including five fully owned ships, and owns 18 marine ammonia terminals with 580,000 tonnes of storage capacity – enabling it to produce and deliver ammonia across the globe.

"This ground-breaking collaboration aims to decarbonise JERA's power production and provide Yara with a footprint in the strategically important Japanese market. Building blue and green ammonia value chains is critical to enabling the hydrogen economy, and collaborating with a key player like JERA marks a milestone in leveraging Yara's global capabilities," said Svein Tore Holsether, president and CEO of Yara.

UNITED STATES

Bakken and Mitsubishi may buy Dakota Gasification

Bakken Energy, LLC and Mitsubishi Power have signed a strategic partnership agreement to create a world-class clean hydrogen hub in North Dakota, comprising facilities that produce, store, transport and consume clean hydrogen. It will be conn-

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The Great Plains Synfuels plant, Beulah, North Dakota.

PHOTO: DAKOTA GASIFICATION

ected by pipeline to other clean hydrogen hubs being developed throughout North America. The project would involve the potential acquisition and redevelopment of the Great Plains Synfuels Plant at Beulah, North Dakota, and Bakken and Mitsubishi say that they are currently in negotiations with the Basin Electric Power Cooperative and its subsidiary Dakota Gasification Company. The redevelopment would make the facility the largest producer of clean hydrogen in North America. The project is in due diligence, and specific details are confidential until that phase is complete.

MHI to supply turbomachinery to ammonia plant

Mitsubishi Heavy Industries (MHI) Compressor International Corp (MCO-I) will supply four compressors and two steam turbines for a revamp and expansion of Koch Fertilizer's ammonia production facility in Fort Dodge, Iowa. Koch has recently announced a $140 million revamp of its Fort Dodge facility to further improve reliability, environmental and safety performance. The investment will increase ammonia capacity by 85,000 st/a. In order to help meet these increased production goals, MCO-I will work in collaboration with Koch Fertilizer and its nominated EPC firm to supply turbomachinery including one syngas compressor train and one process air compressor train. Each train will be installed as 'footprint replacements' for the current trains onsite, to minimise impact to the existing facility's infrastructure.

Steve Lucchesi, account executive, MCO-I, said, "MCO-I has extensive experience working in large capacity ammonia application... MCO-I's approach to flexible frame design enabled us to meet this project's unique requirements and spatial constraints with new, state-of-the-art turbine and compressor technology that will improve the efficiency and reliability of trains critical to ammonia production."

UNITED ARAB EMIRATES

Abu Dhabi to build large-scale blue and green ammonia plants

UAE oil and gas company ADNOC says it will build a big-scale 'blue' ammonia plant at Ruwais, Abu Dhabi, extending its interests in developing a hydrogen-based infrastructure. The 1.0 million t/a ammonia facility, which has moved to the design phase, will be at the new Ta'zizz industrial and chemicals hub at Ruwais. Blue ammonia is made from conventional natural gas feedstock, with the carbon dioxide by-product from captured and stored. In recent months, ADNOC has signed a number of agreements to explore hydrogen supply opportunities with customers.

This project builds on the mandate given to ADNOC from the UAE's Supreme Petroleum Council in November 2020, to explore opportunities in hydrogen and hydrogen carrier fuels such as blue ammonia, with the ambition to position the UAE as a hydrogen leader. ADNOC is already a major producer of hydrogen and ammonia, with over 300,000 t/a of hydrogen produced at the Ruwais Industrial Complex. Wood Group has been engaged to perform pre front-end engineering and design work for the project, as well as six other chemical projects at the Ta'zizz hub.

In addition to this, the Khalifa Industrial Zone in Abu Dhabi (KIZAD) has also announced plans for the construction of a green ammonia production facility using hydrogen generated from solar power, aimed at both regional and international markets. Helios Industry, a privately owned special project vehicle company, will invest over $1 billion in the construction of the facility over several years, according to KIZAD. The project will be developed in two phases. Once completed it is intended to produce 200,000 t/a of green ammonia from 40,000 t/a of green hydrogen.

UZBEKISTAN

Financing completed for new ammonia plant

Ferkensco Management Ltd has signed two bilateral agreements with Gazprombank to finance the construction of an NPK plant in Uzbekistan's Samarkand region and an ammonia-based fertilizer facility in the Sydarya region. The ammonia project is already under way, with site surveys completed in late 2020. In March 2021, a cooperation agreement was signed with the governor of the Syrdarya region, with Casale SA licensing its ammonia technology for the project. The plant is aiming to produce 495,000 t/a of ammonia at an investment cost of $350 million.

Timur Juraev, head of Ferkensco in Uzbekistan, said: "We welcome the engagement with a reliable international partner such as Gazprombank to help us to achieve our goals. We are firmly focused on long-term cooperation with international partners to bring new opportunities that develop Uzbekistan and create jobs. These modern facilities will produce highly efficient, complex mineral fertilizers, help Uzbekistan meet domestic demand, and also enter foreign markets."

INDIA

Toyo wins ammonia EPC contract

Toyo Engineering has been awarded the EPC contract to build an ammonia plant with a capacity of 1,500 t/d (520,000 t/a), as well as associated offsite and utility facilities, by Performance Chemiserve Ltd (PCL). The plant will be built at Navi Mumbai near Taloja in Maharashtra state on the west coast of India, with completion scheduled for the first half of 2023. PCL is a subsidiary of Deepak Fertilisers and Petrochemicals Corporation Ltd (DFPCL). DFPCL was set up in 1979 as an ammonia manufacturer. The plant will not only meet the key raw material needs of Deepak, but also have excess capacity for sale in the open market. Currently, the company imports about 400,000 t/a of ammonia from the Middle East for its downstream petrochemical and fertilizer businesses. The company is also setting up a 377,000 t/a technical ammonium nitrate (TAN) plant at Gopalpur in Odisha to tap growing demand for industrial explosives in both the domestic and overseas markets, which is expected to be completed by March 2024.

Toyo has worked on more than 80 ammonia plants and is also implementing a 1.27 million t/a ammonia-urea fertilizer project for Hindustan Urvarak & Rasayan Limited (HURL) at Gorakhpur, Uttar Pradesh.

COLOMBIA

Stamicarbon remotely completes nitric acid revamp study

Stamicarbon has remotely completed a revamp study for the Monómeros Colombo Venezolanos single pressure nitric acid plant in Colombia aimed at increasing and optimizing production. Located in Barranquilla, on the country's northern coast, the nitric acid plant was designed by Stamicarbon and commissioned in 1968. In spite of over 50 years of operation, the plant has been well-maintained, with only a few heat exchangers replaced due to end of life and the boiler replaced to prepare for capacity increase. Recently, however, growing demand for NPK, which uses nitric acid as a feedstock, led Monómeros to look for ways to produce more nitric acid at their own facility.

The original plant's nameplate capacity was 225 t/d of nitric acid at 55%wt concentration, with an actual capacity of 275 t/d at 50%wt. Stamicarbon performed a revamp study and developed two revamp options for the plant: 300 t/d of nitric acid with acid concentration >50%wt, or 350 t/d of nitric acid with concentration >50%wt. After a year of technical discussions and evaluation of the scope of work, Stamicarbon signed the study agreement with Monómeros and began work on the project in October 2020. In November, the team delivered the "as-is" mass balance, reflecting the existing situation of the plant. With this mass balance, the work on designing the two revamp options began. In March, as part of the study agreement, Stamicarbon delivered datasheets for a new type of packing to be used as a replacement in the oxidation/absorption columns in the plant. Six months after the kick-off meeting, Stamicarbon delivered the final package, presenting the two revamp options, including recommendations on the improvements to be implemented in the plant to reach the desired capacities.

"It was important for the Monómeros project team that every single piece of equipment in the plant was considered in the study, to assess the complete plant behaviour," said Mauricio Medici, Licensing Manager at Stamicarbon, who took the role of project manager during the study. "Being the original licensor, Stamicarbon has a broader understanding of the overall plant configuration and operations, and our work fulfilled their request successfully because we had a complete view of the project."

AZERBAIJAN

New fertilizer terminal for Baku

The port of Baku has announced the start of construction of a fertilizer terminal at its new facility in Alat. The strategic terminal is being jointly financed by the government of Azerbaijan and the Port of Baku. It is expected to be commissioned by the end of 2022. The investment decision resulted from a feasibility study revealing a significant potential for transhipment of fertilizers from landlocked Central Asian countries to western markets via Azerbaijan. Three states of Central Asia – Turkmenistan, Uzbekistan and Kazakhstan – have production capacity for various fertilizers, including urea, sulphur, and potassium carbonate that exceeds 6.6 million t/a, including the recently inaugurated Garabogaz Fertilizer Plant on the eastern shore of the Caspian Sea in Turkmenistan, which alone produces 1.2 million t/a of urea, more than 90% of it inteded for export.

The Port of Baku's new fertilizer terminal will have the capacity to handle 2.5 million t/a. The facility will have two warehouses with a total capacity of 60,000 tonnes, and state-of-the-art conveyor systems to unload the various types of fertilizers directly to warehouses or into wagons/rail hoppers at a newly designed wagon loading station. The port authority plans to lease the terminal operation through a long-term concession and is currently in negotiations with potential bidders.

The terminal aims to increase the role of Azerbaijan as a strategic transit country for Central Asian states and boost president Ilham Aliyev's diversification strategy for turning Azerbaijan into a trade and logistics hub of Eurasia. With the completion of new port in Alat with an annual throughput capacity of 15 million t/a, the Baku-Tbilisi-Kars railway connecting European and Asian rail networks, and key infrastructure projects linking the country's transport networks along the East-West and North-South axes, Azerbaijan aims to become the top choice for foreign logistics companies and investors intending to expand their business at the crossroads of Europe and Asia.

SAUDI ARABIA

Utility completion for Ma'aden ammonia plant

The Saudi Arabian Mining Company (Ma'aden) has announced the commissioning of utilities for its $900 million, 1.0 million t/a ammonia plant in Ras Al-Khair Industrial City. Overall construction completion is expected in 4Q 2021, with full operations beginning in 1Q 2022, according to the company. The ammonia plant is the first part of Ma'aden's $6.4 billion Phosphate 3 expansion, which will add 3 million t/a of ammonium phosphate fertiliser production capacity to increase its total installed phosphate capacity to more than 9 million t/a.

Ma'aden CEO Abdulaziz Al Harbi said: "This is a tremendous milestone for our phosphate portfolio. We have been moving ahead with the construction during the COVID-19 pandemic and thanks to the dedication of the Ma'aden team and our partners, construction has been completed for the utility section and pre-commissioning activities started."

BOLIVIA

YPFB recommissioning continuing

Petroliferos Fiscales Bolivianos (YPFB) says that the plan for the repair and recommissioning of its stalled PAU ammonia-urea plant project at Bulo Bulo is 85% complete, with the restart of operations at the plant expected for June 2022. Contracts for the supply of equipment and materials have been agreed, and more than 200 plant staff hired. Companies from Brazil, Argentina, Paraguay, Peru and Uruguay are reportedly interested in buying up to 1.4 million t/a of urea, once the plant is back in operation.

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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

RUSSIA

Financing agreement for blue ammonia plant in Siberia

Russian energy company Novatek says that it has reached a preliminary agreement with Gazprombank and PJSC Sberbank to finance the construction of a gas-based ammonia plant on Siberia's Yamal peninsula. Novatek said the plant, to be built close to the town of Sabetta, will produce low-carbon ammonia using carbon capture and storage (CCS), injecting the CO_2 produced into local underground reservoirs. Novatek did not disclose the capacity of the ammonia plant, but described it as a "pilot" facility.

AUSTRALIA

Woodside considering green ammonia exports to Japan

Australian oil and gas producer Woodside is collaborating with Japanese companies IHI and Marubeni to explore the production and export of 'green' ammonia to Japan. The ammonia would be produced from hydroelectric power in the Bell Bay region in the northeast of the island of Tasmania. Woodside says that the capacity of the proposed generation plant could eventually be scaled up to as much as 250 MW to produce green hydrogen as feedstock for green ammonia exports.

The initial phase of the partners' studies will focus on deepening their understanding of Japanese and Asian ammonia markets, with technical and commercial evaluations underway. Japan is stepping up its efforts to capture opportunities for green hydrogen and ammonia in order to deliver its target of net zero carbon emissions by 2050.

Leigh Creek raises capital for UCG syngas project

Leigh Creek Energy has raised A$18 million which it says will allow it to begin construction of a commercial underground coal gasification (UCG)-based syngas and power generation project in South Australia. The project, 550 km north of Adelaide, eventually aims to become the largest UCG site in Australia and a globally significant producer of nitrogen-based fertiliser for agriculture. However, UCG has an unhappy history in Australia, with Linc Energy's project in Queensland getting the process banned in the state.

Leigh Creek says that the funds will pay for 3D Seismic surveys, drilling and construction of gasifier chambers, acquisition of power generation infrastructure and general working capital. The 5 MW syngas-based power plant is expected to be constructed by the end of March 2022. This forms Stage 1 of the company's plans, with the larger Stage 2 involving increasing syngas production, a larger power plant and the construction of a downstream 1.0 million ammonia-urea plant, all at a total cost of A$2.6 billion. A definitive feasibility study on Stage 2 of the project is due to be completed by the end of this year.

EPA approves fertilizer import project

The Western Australian Environmental Protection Authority (EPA) has approved the development of the CBH Kwinana fertilizer import project. The project involves the construction of a dedicated liquid urea ammonia nitrate pipeline on the existing Kwinana Grain Terminal jetty, crossing the shoreline and running underground to storage tanks within the proposed onshore facility. The facility will comprise three liquid urea ammonium nitrate (UAN) storage tanks with a total capacity of 48,000 t, a shed for the storage of up to 80,000 t of dry fertilizer, water management infrastructure including swales and a 3,000 m³ evaporation pond, as well as hardstand areas including access roads, truck washdown bays, a site office, amenities, and weighbridges.

CANADA

Northern Nutrients to build enhanced urea plant

Northern Nutrients, a crop nutrition company based in Saskatoon, Saskatchewan, has announced that it will build sulphur enhanced urea fertilizer manufacturing facility at its site. Construction will begin in July 2021 with expected completion early in 2022. The facility will use Shell *Thiogro* technology, a patented process for the incorporation of micronised elemental sulphur into urea, resulting in a sulphur form that is available to plants across the growing season.

Northern Nutrients is owned by Ross Guenther, along with Matt and Rob Owens of Emerge Ag Solutions, also based in Saskatchewan. The sulphur facility is another step of Northern Nutrients' long-term strategy to bring new sustainable fertilizer technologies to Western Canadian farmers. For three years, Northern Nutrients has been importing the patented Shell sulphur urea into North America, a uniquely suitable fertilizer product, which has been widely distributed to retailers in Western Canada.

"The adoption of the products by producers and the anticipated increasing demand has convinced us to produce our own form of the sulphur-enhanced urea in Canada," says Ross Guenther, president and co-owner of Northern Nutrients.

Matt Owens of Emerge Ag Solutions and co-owner of Northern Nutrients says, "We first tried the sulphur product three years ago, and all our growers who have tried it have increased their acres and moved all of their sulphur requirements over to the Shell micronized sulphur urea product. They like the product (11-0-0-75) because it is readily available to the plant early and throughout the growing season, it mixes well in any dry blend, and it has a low salt index compared to other forms of sulphur."

"Once we saw how our customers responded to it, we thought we'd like to invest in the company, so we are very optimistic about what the sulphur product and the new phosphorus product could mean for farmers. The lower salt index is important in our area, and I also like that it is much less dusty than ammonium sulphate," says Rob Owens, president of Emerge Ag Solutions and co-owner of Northern Nutrients. "We are very excited to bring these products to dealers and farmers in the West."

Curtis Bowditch from Tisdale, Saskatchewan has been using the sulphur-enhanced urea for three years. He says, "The seed safety of the product was a game changer for our farm and allows us to get both our phosphorus and sulphur in the seed-row for the first time. Logistically it was a huge time saver."

DENMARK

EUDP to support green ammonia plant

The Danish Energy Technology Development and Demonstration Program (EUDP) has awarded an 11 million euro grant to a 5,000 t/a green ammonia project being managed by the Skovgaard Invest, Vestas, and Haldor Topsoe. The project aims at building a 10 MW green ammonia plant on Jutland directly coupled to local wind and solar power generation – 12 MW from six existing Vestas wind turbines and 50 MW from new solar panels. The plant is expected to be operational by 2023.

The partnership says that green ammonia can serve as a clean fuel for for the shipping industry, potentially replacing significant volumes of fossil fuels and helping accelerate the transition to a world powered by renewable energy. The plant will be a so-called dynamic ammonia plant, where the power from wind turbines and solar panels will be connected directly to the electrolysis units, making it more cost-effective than using battery or hydrogen storage. Topsoe will design the plant to secure optimal production and adapt to the inherent fluctuations in power output from wind turbines and solar panels. The ammonia plant will interface to a green hydrogen solution developed by Vestas, integrating electrolysis with wind and solar. In addition, the renewable energy generation will be connected directly to the national grid so surplus power can be sold to the grid.

Kim Grøn Knudsen, Chief Strategy and Innovation Officer at Topsoe said: "we are proud that the Danish technology program acknowledges our project as being unique when it comes to developing and demonstrating new energy technology that holds a global potential. The green ammonia plant is a prime example of how renewable electricity can be converted to sustainable fuels via electrolysis. For us, this is one of more partnerships showing that we already today have the technologies to introduce new clean solutions showcased by this green ammonia project." ■

Sustainable Fertilizer Technology Forum

The fertilizer industry is at a defining moment, facing the need to accelerate advances in emissions abatement, energy efficiency and environmentally sustainable production in order to deliver net-zero carbon production and embrace the circular economy. Technology is underpinning this step change across the fertilizer industry. With this in mind, CRU Events has announced that it will launch a new virtual event, the CRU Sustainable Fertilizer Production Technology Forum, from 20-23 September 2021, which will focus on the technical innovations that are enabling more sustainable fertilizer production.

This cross-nutrient event will encompass the production of nitrogen, syngas and phosphates. Content will be primarily technical, focusing on new innovations in sustainable fertilizer production, as well as showcasing existing and updated technologies that improve energy efficiency and environmentally sustainable production in existing production assets. Alongside the technical presentations at the event will be presentations from industry experts and CRU's fertilizer analysis and consulting teams and the new CRU Sustainability division, exploring key drivers including economics, regulation, policy and investment.

The event will use CRU's tried and tested immersive virtual environment to allow technical and sustainability professions from around the globe to learn and connect. Content will be enhanced by multiple interaction opportunities, including meet the experts and live networking sessions. ■

For more information on the event, visit:
www.events.crugroup.com/sustainableferttech/

CONTENTS

NITROGEN+SYNGAS
ISSUE 372
JULY-AUGUST 2021

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Syngas News

OMAN

Oman plans to build the world's largest green hydrogen plant

A consortium has unveiled plans to build one of the largest green hydrogen plants in the world in a bid to make Oman a leader in renewable energy technology. The $30 billion project is being developed by Oman's state-owned oil firm OQ, green fuels developer InterContinental Energy and Kuwait government-backed renewables investor EnerTech. Construction is scheduled to start in 2028 in Al Wusta governorate on the Arabian Sea. It will be built in stages, with the aim to be at full capacity by 2038, powered by 25 GW of wind and solar energy. Two years has already been spent on solar and wind monitoring analysis for the development. According to the consortium, the site chosen has the optimal diurnal profile of strong wind at night and reliable sun during the day, and is also located near the coast for seawater intake and electrolysis.

The hydrogen is intended for export to Europe and Asia, according to Alicia Eastman, co-founder and president of InterContinental Energy, either as hydrogen or converted into green ammonia, which is easier to ship and store. The facility aims to produce 1.8 million t/a tonnes of green hydrogen and up to 10 million t/a of green ammonia.

Oil and gas currently accounts for 85% of Oman's GDP, but falling reserves and changes in the global energy industry have led to the country's Oman Vision 2040 strategy, launched in December 2020, to diversify the economy away from fossil fuels and increase investment in renewables.

MALAYSIA

Contracts awarded for new methanol plant

Following a successful front-end engineering and design (FEED) study in 2019, Air Liquide Engineering & Construction and Samsung Engineering have been awarded the contract to build a methanol plant for Sarawak Petchem, a state-owned oil and gas firm, in Bintulu, Sarawak State, Eastern Malaysia. The new facility is planned to come into operation in 2023 and will produce 5,000 t/d of methanol based on Air Liquide's Lurgi MegaMethanol™ technology. As part of the agreement, Air Liquide will be the technology licensor, also providing engineering, related equipment as well as an air separation unit with a production capacity of 2,200 tons per day of oxygen.

Cheonhong Park, vice president of Samsung Engineering, stated: "Samsung Engineering and Air Liquide co-developed this project from the pre-feasibility study stage together by implementing exceptional engineering capabilities and showing superb commitment to this project. Through this collaboration, we will successfully deliver the world-scale methanol plant in Sarawak and hope to collaborate with Air Liquide for future joint projects."

EGYPT

Abu Qir to build methanol and ammonia plants

Abu Qir Fertilizers has agreed to partner with Helwan Fertilizers Company and Al Ahly Capital Holding Company to establish an integrated industrial complex at Ain Sokhna in the Suez Canal Economic Zone. The $1.5 billion complex will have a capacity of 1 million t/a of methanol, as well as 400,000 t/a of ammonia. The move follows a feasibility study begun at the end of last year, which also considered a second phase of downstream acetic acid, dimethyl ether (DME) and ammonium nitrate or calcium ammonium nitrate production. A feasibility study on the latter, targeting a potential 2,400 t/d of AN or 3,000 t/d of CAN, is now being carried out by Nexant and expected to be complete in 3Q 2021. In other news, Abu Qir has also commissioned thyssenkrupp Uhde to conduct a study on raising capacity of the urea granulation unit at the company's Abu Qir 3 production line near Damietta from 1,925 t/d to 2,500 t/d.

NEW ZEALAND

Methanex to cut output at Motunui to save gas

Methanex says that it is temporarily cutting production at its Taranaki site to free up natural gas supplies for electricity generation over the southern hemisphere winter. The company has agreed to a short term gas supply of between 3.4 to 4.4 PJ (petrajoules) to Genesis Energy to support a secure supply of natural gas for the country's electricity system. Methanex will idle one of its Motunui plants for close to three months during the winter, and release natural gas to support the country's electricity sector, a joint company statement said.

UNITED STATES

NWIW admits defeat on mega methanol project

Chinese methanol developer Northwest Innovation Works (NWIW) has finally thrown in the towel over attempts to build a large-scale gas-based methanol plant at the port of Kalama in Washington State for export of methanol to China to feed olefins production. The company has notified port officials that it is terminating its lease on the land, effectively killing the project for now. NWIW was looking at up to 3.6 million t/a of methanol production in two stages, but ran into concerted local opposition and was tied up for years in environmental impact studies, particularly as regards greenhouse gas emissions. The company argued that using natural gas in the US with large scale import of renewable electricity for utilities would avoid far greater emissions in China from coal-based methanol production, but failed to convince local authorities, resulting in the rescinding of a shoreline use permit.

Oberon Fuels begins DME production

Oberon Fuels says that the DME production line at its facility in Brawley, California is now on-stream and producing the first commercial renewable dimethyl ether (DME) in the United States. As part of a $6 million project funded in part by a grant from the California Energy Commission, Oberon is converting waste methanol into DME at Brawley. In addition to waste methanol, other potential feedstocks include biogas from dairy waste, food wastes, agricultural waste, as well as excess electricity and CO_2, resulting in low carbon to carbon-negative DME, the company said. The plant is expected to produce 1.6 million gallons per year (4,400 t/a) of DME from more than 5,500 t/a of waste material when operating at full capacity.

"This is a critical step on the path to decarbonizing the transportation sector," said Elliot Hicks, chief operating and technology officer and an Oberon Fuels co-founder. "Our innovative approach uses waste resources to create a flexible molecule that can reduce emissions from fossil fuels, as well as create entirely new, super-clean fuels."

NETHERLANDS

Waste to methanol facility

GIDARA Energy has announced it is intending to build a waste to methanol plant in Amsterdam; Advanced Methanol Amsterdam (AMA). The plant will convert non-recyclable municipal waste into methanol which can be used in fuel blending, helping to meet governmental objectives to achieve CO_2 emission reductions as defined in RED II. The AMA facility will utilise HTW biomass gasification technology, developed by thyssenkrupp with German energy company RWE – GIDARA Energy acquired the process in 2019. AMA will produce around 87,500 t/a of methanol, diverting the waste from 290,000 households that would otherwise be landfilled or incinerated.

Wim van der Zande, CEO at GIDARA Energy, said: "We are in a unique position owning a proven gasification process with a track-record for this application, which eliminates any major process or technology risks. We purposely selected this plant's capacity and configuration because of the experiences in operated facilities, matching local feedstock availability and local blending capacity. Our focus is to establish the AMA facility and use the same configuration at future locations in The Netherlands, Europe and North America".

PHOTO: AMA

Computer rendering of the new AMA facility.

Enerkem switches to waste to fuels production

Enerkem, Shell and the Port of Rotterdam say that their Rotterdam waste-to-chemicals project will be repurposed to manufacture jet fuel instead, to meet growing demand for sustainable aviation fuels. The facility will process up to 360,000 t/a of non-recyclable municipal waste to produce up to 80,000 t/a of products, of which around 75% could be sustainable aviation fuels, and the remainder used for road fuels or to feed circular chemicals production, Enerkem said. The jet fuel would be produced via Enerkem's waste gasification technology and Shell's Fischer-Tropsch technology. The partners are looking to submit a permit application for the revised project by the end of 2021. Once the final investment decision has been taken, construction could take around three years, with production starting in 2025 or 2026. Enerkem says that Air Liquide is also interested in partnering the companies as a supplier of industrial gases.

LUXEMBOURG

Low-carbon syngas for the steel industry

Maire Tecnimont subsidiary NextChem has joined forces with Luxembourg-based Paul Wurth, part of the SMS Group and a leading technology provider for the steel industry, to promote the combined use of electrolysis and syngas production in the iron and steel industry. The collaboration is aiming to develop an advanced technological solution to convert natural gas into synthesis gas to be used during iron ore reduction. Using low carbon syngas will decrease the amount of fossil fuels required in the energy-hungry process, reducing CO_2 emissions in steel production.

The companies will combine their respective knowledge and expertise to study the integration of electrolysis technology into the syngas production scheme, with the aim of producing low-carbon steel at a competitive cost. Introducing green hydrogen into the metallurgical process allows for the further lowering of the volume of coke required and reduces the carbon footprint of steel plants.

Pierroberto Folgiero, CEO of Maire Tecnimont Group and NextChem commented: "Integrating electrolysis in the revamping of steel furnaces is one of the most interesting challenges nowadays. We are really proud of this agreement, which strengthens the existing alliance between Maire Tecnimont and Paul Wurth to develop low carbon impact solutions in a hard-to-abate sector like the steel industry."

UZBEKISTAN

Uzbekistan GTL plant now aiming for Q4 2021 start-up

Uzbekistan has plans to commence production at its first gas-to-liquids (GTL) plant in the fourth quarter of this year. The $3.6 billion plant is nearing completion in the Kashkadarya region, with state-owned oil and gas firm Uzbekneftegaz working in partnership with South Africa's Sasol, the GTL technology supplier. The plant will process 3.6 bcm of gas per year at capacity, generating 1.5 million t/a of synthetic liquid fuels, including 300,000 t/a of kerosene, 725,000 t/a of diesel, 440,000 t/a of naphtha and 50,000 t/a of liquified petroleum gases, for both domestic use and export.

UNITED KINGDOM

ScottishPower considering green hydrogen for Nigg

ScottishPower has contracted Global Energy Group to conduct a feasibility study on developing offshore wind-powered green hydrogen at the Port of Nigg on the northeast coast of Scotland. The study will assess the full potential range of processes that could be supported by hydrogen and the most efficient and innovative way of delivering an end-to-end hydrogen production facility at the port, with poten-

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tial uses including powering heavy plant machinery and vehicles used in daily operations at the site as well as powering high temperature, energy intensive processes like the manufacturing of offshore wind components. The partnership will be one of the first projects led by ScottishPower's new Green Hydrogen Business, launched in December 2020. Port of Nigg already supports some of Scotland's largest offshore wind farms and is expected to play a key role in the fabrication and manufacturing of Scotland's growing offshore wind sector.

BELGIUM

Hydrogen refuelling station

CMB.TECH has opened the first multimodal hydrogen refuelling station at the Port House in Antwerp. It is the first refuelling station in the world that produces green hydrogen, which will be used to power ships, tube trailers, cars, trucks and buses. In addition to the hydrogen refuelling station, CMB.TECH will today launch a hydrogen truck with the symbolic name: Lenoir, a reference to the French-speaking Belgian who in 1860 built the first internal combustion engine powered by hydrogen. Among the vessels served will be the Hydroville, the world's first hydrogen-powered passenger ship. Until now, the Hydroville has been supplied with hydrogen by a mobile hydrogen refuelling station, but the new station will allow it to refuel in Antwerp.

Roy Campe, CTO of CMB.TECH said: "In the future ports will become hydrogen hot spots, because they have a large concentration of applications that are difficult to electrify. In addition, many ports will have access to hydrogen, either through large electrolysis plants or through imports. We are therefore very pleased that, after two and a half years of development, we are now able to put the station into operation."

CMB.TECH's new hydrogen refuelling station.

PHOTO: CMBTECH

SPAIN

Green methanol for Galicia

Energy supplier Iberdrola and European chemical company Foresa have plans to investment in renewable hydrogen for the production of green methanol at Foreasa's site in Galicia on Spain's northwest coast. Options under consideration include construction of a 20 MW green hydrogen plant, expandable to 200 MW, and/or CO_2 capture equipment. The methanol would be used in Foresa's chemical processes for the downstream production of wood glues and resins, and a surplus could be exported in the future. The investment, which is eligible for Next Generation EU funds, would exceed €82 million in the first phase, producing 10,000 t/a of methanol, and could reach €400 million in its expansion, when up to 100,000 t/a of methanol would be produced.

Blueprint for green hydrogen revolution

Siemens Gamesa has launched an industry white paper; Unlocking the Green Hydrogen Revolution, which outlines an ambitious plan to deliver cost-competitive green hydrogen by 2030 from onshore wind and by 2035 from offshore wind. Siemens Gamesa calls for a joined-up approach to encouraging both market demand and scaling production, highlighting four key requirements to deliver low-cost green hydrogen within the next decade:

1. Increase drastically the capacity of renewables because the green hydrogen revolution relies on this. The world needs up to 6,000 GW of new installed renewable energy capacity by 2050, up from 2,800 GW today to generate the expected demand for hydrogen (500 million tonnes, according to the Hydrogen Council).
2. Create a cost-effective demand-side market for green hydrogen to drive down the costs of equipment, infrastructure and day-to-day operating costs. Currently, the main operating cost for green hydrogen production is powering the electrolysers, so a decrease in energy costs lowers the cost of the hydrogen and increases demand.
3. Develop the supply chain as no one provider can own the entire production and distribution process. At the moment, initiatives are fragmented, and therefore costly, meaning renewable energy companies, electrolyser manufacturers, network providers and water treatment specialists need to work together to build a resilient supply chain.
4. Build the right infrastructure in terms of logistics, storage and distribution. There needs to be investment in hydrogen pipeline networks to unlock the potential of green hydrogen.

Andreas Nauen, Siemens Gamesa CEO, said, "When it comes to green hydrogen, we need to act now. It took three decades for wind and solar to reach grid parity with fossil fuels, and we cannot afford to wait that long for green hydrogen to reach price parity with fossil-based hydrogen. Wind will play a powerful role in accelerating the production of green hydrogen, which is vital to decarbonizing our economy. Therefore, to unlock the potential of green hydrogen, we need to drive down costs quickly. To do this, we need a consensus between industry, policy-makers and investors to rapidly develop the demand-side market, build the supply chain and roll out the necessary infrastructure."

ITALY

Feasibility study on hydrogen plant

Maire Tecnimont's NextChem has signed an agreement with Mytilineos' Renewable and Storage Development Business Unit (RSD BU) have signed an agreement to develop engineering activities for the implementation of a green hydrogen plant via electrolysis in Italy. Mytilineos is active in the development, construction and operation of utility-scale solar and hybrid power projects, with over 1 GW of medium to large scale solar projects installed worldwide. The project, which will convert renewable energy from one of Mytilineos' solar plants into green hydrogen, is intended to be followed by other plants as well, aiming to provide local off-takers with a carbon neutral energy carrier alternative that could allow for effective decarbonisation including in hard-to-abate industrial sectors.

Pierroberto Folgiero, chief executive officer of Maire Tecnimont Group and NextChem, commented: "NextChem is a front runner in the development of a hydrogen-based green economy: we have four technological solutions for hydrogen production in our portfolio, with different levels of carbon intensity. Among these, green hydrogen is the most ambitious one from an economic and environmental point of view and we are already working on it, both in Italy and abroad. This collaboration with Mytilineos is extremely promising and gives us the opportunity to demonstrate the benefits of an approach aimed at creating integrated platforms of plant solutions for the energy transition".

DENMARK

Partnership for methanol fuel cells

Blue World Technologies is partnering with Clayton Power to develop a small-scale mobile methanol fuel cell solutions for stationary and auxiliary power. The target is to develop a solution in the 5 to 15-kW power range. The methanol fuel cell power unit can be applied to trucks to power appliances such as air conditioning and TV. The methanol fuel cell solution combines Blue World Technologies' proprietary high-temperature proton exchange membrane technology, and Clayton Power's lithium-ion batteries to provide an instant- and continuous power supply. The effort is supported by Danish Energy Agency through the EUDP (Danish Energy Technology Development and Demonstration Program) and includes Aalborg University as a key knowledge partner.

IRELAND

Green hydrogen facility for Cork Harbour

Plans have been announced for Ireland's first green hydrogen facility, located in the harbour of Cork on the southwest coast. Energy firm EI-H2 intends to seek planning permission for a 50 MW electrolysis plant in Aghada, which when operational in 2023 will produce 20 t/d of green hydrogen at an estimated investment cost of €120 million, using surplus electricity from offshore wind power.

EI-H2 is owned by Cork businessman, Pearse Flynn, who says that Ireland is starting to take leadership in tackling climate change. "The production of hydrogen from excess wind capacity will play a significant role in Ireland's decarbonisation, given that Ireland could be generating 8 GW of offshore wind by 2030. There inevitably will be 'curtailed' energy that will go to waste unless we find ways of using it. EI-H2 is planning the production of safe and environmentally sound green hydrogen that will allow industry to decarbonise."

The proposed site has been selected because of its proximity to an existing triangle of energy generation, including power generating stations, heavy industry and an oil refinery. There is also potential to export green hydrogen in the future using a fleet of environmentally friendly ships.

AUSTRALIA

Wärtsilä and Global Energy Ventures to cooperate on hydrogen engines

The technology group Wärtsilä has signed a memorandum of understanding with Global Energy Ventures (GEV) of Australia, a company specialised in delivering compressed shipping solutions for transporting energy to regional markets. The two companies will cooperate on the inclusion of Wärtsilä propulsion systems in GEV's compressed hydrogen ships. The cooperation aims at advancing GEV's approval in principle application for its new 430-tonne compressed hydrogen and is also intended to demonstrate the availability of a highly efficient, low-emissions propulsion system for the vessel.

"We look forward to working closely with Wärtsilä on this project. We have shown that C-H2 shipping is ideally suited for exporting green hydrogen with a lower delivered cost and having a technology leader such as Wärtsilä with us, we can deliver a shipping solution that is completely sustainable," said Martin Carolan, CEO, GEV. ■

NITROGEN+SYNGAS
ISSUE 372
JULY-AUGUST 2021

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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

People

The International Fertilizer Association (IFA) says that **Svein Tore Holsether** has been elected as its new chair of the Association. IFA said in its press release that the selection of Holsether, the president and CEO of Yara International, is a continuation of the industry's commitment to sustainability.

"I am honoured to be appointed Chair of IFA because the fertilizer industry has a key role in finding sustainable solutions to some of the greatest challenges the world is facing. As an industry, we need to lead the way to decarbonise food and build resilient and fair food systems," Holsether said.

Dmitry Konyaev, CEO of Russia's UralChem, has become the new vice chair of the Association. Both Holsether and Konyaev serve on the executive board of directors, which also welcomed two new appointments: **Jeanne Johns**, managing director and CEO of Incitec Pivot Ltd, and **Tony Will**, president and CEO of CF Industries. **Mostafa Terrab**, group chairman and CEO of OCP, Morocco, remains on the executive board of directors as Immediate Past Chair, along with **Zhai Jidong**, vice president international for Kingenta, and **Alzbeta Klein**, director general of IFA.

There are also five new Board Directors elected by the membership: **G. David Delaney**, CEO, Itafos; **Ahmed El-Hoshy**, Group CEO, OCI NV; **Shakeel Ahmad Khan**, CEO, Petronas Chemicals Marketing; **Suresh Krishnan**, managing director, Paradeep Phosphates Ltd and Mangalore Chemicals and Fertilizers; and **Mayo Schmidt**, president and CEO, Nutrien. IFA members also re-elected to the board of directors Raviv Zoller, president and CEO, ICL Group.

Haldor Topsoe has established a new green hydrogen organisation to accelerate all aspects of the company's business within the field of electrolysis, including development of high-performance electrolysis technology, sales, and partnerships. Cleantech entrepreneur **Chokri Mousaoui** becomes the new member of Topsoe's Senior Leadership Team and executive vice president of the new organisation.

"At the core of our efforts is our capability to turn renewable power into essential carbon-neutral fuels and chemicals. We have Topsoe's leading electrolysis technology, now we add the fully focused organization and leadership needed to realize its true potential. I am thrilled to welcome Chokri Mousaoui as Executive Vice President and head of the organization. Chokri brings great leadership and commercial experience from a highly successful tech startup and will lead our work to accelerate the commercialization of our green hydrogen business," said Roeland Baan, CEO of Topsoe.

Chokri Mousaoui co-founded Eternal Sun in 2011, which specialises in equipment for testing solar modules. Under his leadership, the company evolved from a start-up to the market leader within solar testing. In 2016, the company acquired the solar simulator division of US-based Spire Solar Corporation, and in 2019 ABN AMRO Energy Transition Fund joined as new majority shareholder.

"I am impressed with Topsoe's bold vision of being recognised as the global leader in carbon emission reduction technologies by 2024, not least because the company truly has what it takes to make an exceptional contribution to move the energy transition forward. I really look forward to working together with the talented people here to commercialise our green hydrogen offerings and bring them to the market fast. The demand for innovative solutions is significant and growing," said Chokri Mousaoui.

Nirlep Singh Rai has become the new Director (Technical) at India's National Fertilizer Ltd (NFL. He previously served as executive director in the same company, and is also chief executive officer (CEO) of Ramagundam Fertilizers and Chemicals Limited (RFCL), a joint venture between NFL, Engineers India Ltd (EIL) and the Fertilizer Corporation of India Ltd (FCIL). Rai has previously run technical services and projects at NFL's Bathinda plant. His experience includes technical services and operation and maintenance of large scale fertilizer plants.

Sergey Klyavlin, who previously headed the Belorechensk Mineral Fertilizers company, has become CEO of Nevinnomyssky Azot. Both companies are subsidiaries of EuroChem. Before working at the Belorechensk Mineral Fertilizers company, Klyavlin headed the department for the production of complex fertilizers at Nevinnomyssky Azot. **Viktor Keil**, who has managed Nevinnomyssky Azot for almost 20 years, has been appointed Deputy Head of the Fertilizers division at EuroChem.

! The following events may be subject to postponement or cancellation due to the global coronavirus pandemic. Please check the status of individual events with organisers.

Calendar 2021

AUGUST

29-SEPTEMBER 2

65th AIChE Annual Safety in Ammonia Plants and Related Facilities Symposium, SAN DIEGO, California, USA
Contact: Ilia Kileen, AIChE
Tel: +1 800 242 4363
Web: www.aiche.org/ammonia

SEPTEMBER

14-15

Argus Methanol Forum – **virtual event**
Contact: Argus Media Group
Tel: +44 20 7780 4340
Email: conferences@argusmedia.com
Web: www.argusmedia.com/en/conferences-events-listing/methanol-forum

20-23

Sustainable Fertilizer Production Technology Forum – **virtual event**
Contact: CRU Events,
Chancery House, 53-64 Chancery Lane, London WC2A 1QS, UK.
Tel: +44 (0) 20 7903 2444
Fax: +44 (0) 20 7903 2172
Email: conferences@crugroup.com

27-29

IFA Annual Conference, LISBON, Portugal
Contact: IFA Conference Service,
49 Avenue d'Iena, Paris, F75116, France.
Tel: +33 1 53 93 05 00
Email: ifa@fertilizer.org

OCTOBER

2-7 POSTPONED TO 2022

Ammonium Nitrate/Nitric Acid Conference, HOUSTON, TX, USA
Contact: Hans Reuvers, BASF,
Karl Hohenwarter, Borealis
Email: johannes.reuvers@basf.com
karl.hohenwarter@borealisgroup.com
annaconferencehelp@gmail.com
Web: www.an-na.org

NOVEMBER

16-18

39th Annual World Methanol Conference – **virtual event**
Contact: Jake Barrett, IHS Markit
Tel: +1 212 709 1316
Email: Jake.Barrett@ihsmarkit.com
www.ihsmarkit.com/events/39th-annual-world-methanol-conference/overview

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Plant Manager+

Problem No. 61 Carbamate safety valve problems

The heart of any urea plant is the high-pressure urea synthesis section. Properly functioning safety valves are vital to protect the high-pressure section against ruptures due to pressures that are too high in case of upset conditions. However, the very corrosive intermediate ammonium carbamate makes the reliable and proper functioning of safety valves more challenging.

Traditional safety valves suffer from crevice corrosion problems causing small leakages which often go undetected. These small leakages can lead to the risk of crystallisation of ammonium carbamate in the outlet line of the safety valve even when heat tracing is applied (see picture).

Furthermore, due to the increased effective seat area the safety valve can open before reaching the set pressure. This round table discussion considers options to improve the reliability of carbamate safety valves in urea plants.

Muhamad Reda of Pupuk Kujang in Indonesia kicks off the round table discussion: Does anyone have records of trouble with high pressure safety valves in the high-pressure carbamate condenser? Is it possible to add a block valve or isolation valve upstream of the high-pressure safety valve (171 kg/cm²g) in a urea plant? Does anyone have any brand recommendations for safety valves/angle valves or any valve for the high-pressure system in a urea plant?

Mark Brouwer of UreaKnowHow.com, The Netherlands replies: The safety valve company LESER in Germany has solved the reliability issues with high pressure carbamate safety valves.

Muhamad replies: Thank you Mark, our licensor also recommends LESER. But they don't recommend a block valve upstream of the safety valve, especially for high pressure ones. Has anyone installed a block valve upstream of a safety valve?

Mark continues: Indeed, it is not normal practice to have a block valve upstream of the safety valve. Please note:: 1. One should assure the block valve is open. 2. Normally a block valve is used to enable maintenance of the safety valve in case one has a spare in service. However, due to corrosion phenomena and the relatively large valve size, it is risky to rely on one block valve. A block and bleed system would be preferable, but this kind of system is not easy to make reliable due to the corrosion and crystallisation issues.

Khaled Seliem of Abu Qir Fertilizers in Egypt asks another related question: Is it possible to install a rupture disc upstream of the safety valve and is it applied with high-pressure reactor safety valves?

Mark responds: There have been some trials in the past, mainly in the US. Some risks to consider:

- Part of the rupture disc may get stuck in the safety valve.
- What happens when there is a small crack in the rupture disc?
- How do you avoid crystallisation?
- How do you ensure that no pressure will build up between the rupture disc and the safety valve?

The most reliable solution in my view is the LESER carbamate safety valve solution.

Emmanuel Ogoh of Notore Fertilizers in Nigeria provides valuable information: Installing a rupture disc upstream of the high-pressure reactor is common practice in my plant (Stamicarbon process). The rupture disc (easily replaceable) provides protection from corrosion to the safety valve.

Moreover, there have been reported cases of high-pressure safety valves passing and not seating properly after lifting. The presence of a rupture disc upstream will reduce the chance of these occurrences. However, replacing a ruptured disc requires total draining and purging of the high-pressure loop which may increase downtime. Having a block valve (normally in open position) upstream of the rupture disc will reduce replacement time.

Mark replies: Although it is in a Stamicarbon plant, I do not think the rupture discs have been there right from first start up. Best to doublecheck with Stamicarbon, but as far as I know licensors do not like rupture discs upstream of the carbamate safety valves the same goes for block valves.

Muhamad replies: You are right that there have been reported cases of high pressure safety valves passing and not seating properly after lifting. It happened twice last year in our plant, and now some safety valves are passing. But is it really OK to install a rupture disc and block valve upstream a safety valve?

What if the rupture disc gets ruptured and stuck in the safety valve? We asked our licensor (TOYO) but they don't recommended a block valve.

Mark replies: LESER in Germany has solved the reliability issues with high pressure carbamate safety valves. They have developed two successful improvements: the LESER flush system, which eliminates passing after blow off and a support loading system, which reduces the blow off amount with some 75% and increases the blow off pressure to a level very close to the set pressure. LESER safety valves have been the standard in all new Stamicarbon plants for more than ten years.

Andreas Caldonazzi of LESER in Germany adds valuable information: There is a strong recommendation in the relevant standards not to use isolation valves upstream of the safety valve.

Some extracts from the relevant standards are shown below: For example, ISO 4126-9: "Isolation of safety devices, 8.4.1 Basic requirement, The equipment shall be protected against excessive pressure at all times during operation. There shall be no isolating valve in a pressure relief system, except for the cases in 8.4.2, 8.4.3 and 8.4.4."

Also, in API 520-2 there is a relevant specification on this topic: "8 PRD Isolation (Stop) Valves, 8.1 General, Isolation block valves may be used for maintenance purposes to isolate a PRD from the equipment it protects or from its downstream disposal system. Since improper use of an isolation valve may render a PRD inoperative, the design, installation, and administrative controls placed on these isolation block valves should be carefully evaluated to ensure that plant safety is not compromised. A PRD shall not be used as a block valve to provide positive isolation.

8.2 Application: If a PRD has a service history of leakage, plugging, or other severe problems that affect its performance, isolation and sparing of the PRD may be provided. The use of isolation valves and/or sparing permits the PRD to be inspected, maintained, or repaired without shutting down the process unit. However, there are potential hazards associated with the use of isolation valves. The ASME Boiler and Pressure Vessel Code, Section VIII [7], Appendix M, Section M-5.6 discusses proper application of these valves and the administrative controls that shall be in place when isolation valves are used. Local jurisdictions may have other requirements."

Conclusion: The LESER view is to minimise all possible risks in the upstream line. The exceptions should not be used for a very critical application like a high-pressure carbamate condenser protection.

Prem Baboo in India joins the discussion with a valuable contribution: ASME code does not allow operating any equipment without a pressure safety valve (PSV) on-line. If you have two PSVs then you can have car seal open isolation valve. Isolating the PSV when the plant is in operation is unsafe and risky.

Isolation valves upstream and downstream of PSVs are usually only required if there are two PSVs in parallel. The interlock also appears in the DCS system of both PSVs. This then allows one PSV to be removed for maintenance / recalibration / certification while the other remains in service.

Of course, it is necessary to interlock the isolation valves in such a manner that the vessel is always connected to a PSV. Be careful that the downstream valve is specified for the correct duty or ensure that both the upstream and downstream valves around the PSV are either both open, or both closed. The off-line PSV should never sit there with its inlet open and outlet closed while the other PSV is in line.

The function of rupture is different, generally used for burst disc, bursting disc, or burst diaphragm, it is a non-reclosing pressure relief safety device that, in most uses, protects a pressure vessel, temperature system equipment or system from over pressurisation or potentially damaging vacuum conditions.

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An ammonia tanker being loaded at Dharan, Saudi Arabia.

PHOTO: SAUDI ARAMCO

Ammonia to burn

Plans to decarbonise power production and shipping are leading to increasing interest in using ammonia as a fuel, but technical and economic barriers still remain to be overcome.

Ammonia burns. In some ways it is as simple as that. Not as energetically as hydrocarbons – its energy density (higher heat value) is about 22.5 MJ/kg; about half that of a typical hydrocarbon like gasoline or diesel – but nevertheless about the same as methanol and significantly more than hydrogen, and certainly close enough to existing fuels that it could be used to run a vehicle. Ammonia-powered engines have a long history, and in the 1930s and 40s there were some experimental ammonia-powered cars. Ammonia Casale actually built an engine designed to run on a mixture of ammonia and coal gas in the 1940s, and which was used to run buses in Belgium during World War II when gasoline was in short supply. Gasoline currently costs around $700/tonne in the US ex-refinery, before taxes and distribution costs, while ammonia on a tanker can currently be had for $300/tonne f.o.b., before shipping and handling costs, so per unit of energy, it's even roughly on a par.

These facts alone however are not enough to encourage the use of ammonia as a vehicle fuel, because it also has significant drawbacks. While gasoline is flammable to the point almost of explosion, ammonia in gaseous form is highly toxic if breathed in, and in order to maintain it as a liquid it must be cooled and stored below -33°C at atmospheric pressure or compressed to around 10 bar (raising the boiling point to about 25°C), or some combination of the two, increasing both the dangers and costs of its transport and storage. Furthermore, while the basic equation for combustion of ammonia looks quite clean:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

producing in theory only inert nitrogen and water, in practice nitrogen oxides (NOx) are also produced in significant quantities, equally toxic if breathed in, as well as being, in the case of N_2O, a gas with a very high global warming potential. These must be scrubbed from any ammonia engine exhaust, although selective catalytic reduction using ammonia generated from a solution of urea is now a standard part of most large goods vehicles in North America and Europe, and increasingly of diesel passenger cars, and adds only marginal additional cost.

But what has brought about ammonia's current vogue as a potential fuel source is the potential for it to be made with low carbon emissions, either from hydrogen generated from water electrolysis using renewable energy, or from conventional coal or methane feedstock with carbon capture and storage – 'green' and 'blue' ammonia respectively. While at present very little ammonia is actually made this way, the number of new low carbon ammonia projects continues to multiply almost daily, with some like Yara's projected conversion of its Porsgrunn plant, and large scale projects in the Middle East such as those in this issue's Industry News section in the UAE, Oman and Saudi Arabia, as well as interest in Australia, there could by several million t/a of renewable ammonia being produced by 2030. Industries like shipping, as well as the Japanese power sector, which are looking towards a zero carbon future but puzzling over how to get there, have begun to fix on low carbon ammonia as the solution to their problems.

Power generation

If ammonia can be burned, then presumably it can be used in a gas turbine to drive electricity production. However, there had been little practical work done on this until a few years ago. Then in 2014, Hideaki Kobayashi, professor at the Institute of Fluid Science at Tohoku University in Sendai, Japan, in conjunction with the country's National Institute of Advanced Industrial Science and Technology (AIST), built the first working direct ammonia-powered gas turbine which generated electricity. As ammonia's range of combustion in air is fairly limited (between 15-25%) he had to develop a spiral mixing system to ensure a stable concentration of ammonia in air, and the turbine uses extra turbine blades that generate a high-pressure, high-temperature fuel mixture.

Japan is interested in ammonia as a potential energy carrier, and plans to introduce ammonia into the fuel mix for thermal power generation, as part of its measures to cut CO_2 emissions and reach carbon neutrality by 2050. As part of its Green Growth Strategy, the government is targeting ammonia imports either for conversion back to hydrogen and nitrogen (using ammonia as a hydrogen carrier) or by burning ammonia directly in power production.

The government push is leading to major players committing large sums on research and development. Dr Kobayashi's gas turbine generated 40 kW of electricity, but in March 2021 Mitsubishi Power, part of Mitsubishi Heavy Industries (MHI), announced that it had begun development work on a 40 MW 100% ammonia powered gas turbine system. The company says that it is targeting commercialisation in or around 2025. Among the challenges it admits it needs to overcome is dealing with the generation of nitrogen oxides, and Mitsubishi Power says that it is aiming to resolve this by combining selective catalytic reduction with a newly developed combustor that reduces NOx emissions, for installation in the Company's H-25 Series gas turbines.

Meanwhile, in May 2021, Yara International signed a memorandum of understanding with Japan's JERA Co., the country's largest power generation company, to collaborate on the production, delivery and supply chain development of blue and green ammonia, to enable zero-emission thermal power generation in Japan. Yara is aiming to sequester CO_2 at its ammonia plant in the Pilbara region of Western Australia, enabling the production and supply of blue ammonia to JERA, as well as potentially jointly developing new green and blue ammonia capacity and optimising the logistics of shipping ammonia to Japan. JERA produces about 30% of Japan's electricity.

Japan's Green Ammonia Consortium, which includes Kansai Electric Power, Shell Japan, trading houses such as Mitsui and Marubeni, as well as Mitsubishi Heavy Industries, says that it expects 1% of Japan's electricity to come from blue and green ammonia combustion by 2030, potentially rising to 10% by 2050. Initially, this will involve burning ammonia alongside coal to generate electricity. An experiment at Chugoku Electric Power in 2017 successfully burnt ammonia and coal in an existing power station, and JERA says that it will convert its 1 GW Hekinan coal-fired power station in Aichi, central Japan, to a 20% ammonia feed during 2024-25. By 2030, Japan expects to be importing an extra 3 million t/a of ammonia for power generation. Developments outside Japan are still limited at present, however, and the country is becoming something of a guinea pig for the development of renewable ammonia as a power plant feed.

Marine fuel

The International Maritime Organisation (IMO) has set a goal of reducing the total greenhouse gas (GHG) emissions from international shipping by at least 50% by 2050, compared to 2008 levels. In addition, a target has been set to reduce the carbon intensity of shipping by 40% by 2030, thus emphasising the need for the rapid introduction of existing and new low carbon technologies. This in turn seems to have galvanised some segments of the maritime industry to start looking seriously at renewable ammonia as a fuel candidate. Among the prime movers in this has been Finnish marine engine manufacturer Wärtsilä, which, in conjunction with the European Commission and European research initiative the Waterborne Technology Platform, has been working on four-stroke ammonia internal combustion engine designs, hoping to reach the stage of field tests as soon as 2022. The company is also developing ammonia storage and supply systems to install ammonia fuel cells on Eidesvik Offshore's supply vessel Viking Energy by 2023, part of the EU project ShipFC. After its conversion, Viking Energy is expected to become the first carbon-free ammonia-powered vessel in the world. Equinor will use it for supply operations on the Norwegian continental shelf to help cut its supply-chain emissions. Yara will supply the ammonia using renewable power as part of the ShipFC consortium.

Meanwhile, MAN Energy Solutions is expecting to have a two-stroke ammonia engine ready to deliver by early 2024, Kirkeby said. By the following year, the company aims to offer retrofit conversions to allow existing two-stroke engines to use ammonia.

As with power plant developments, Japan has also been working on ammonia as a shipping fuel. Japanese trading house Itochu has signed a memorandum of understanding with Dutch oil storage and terminal operator Vopak for a feasibility study concerning the development of ammonia supply infrastructure for use as a marine fuel for vessels in Singapore. Itochu already operates an ammonia storage and handling facility at Singapore's Banyan terminal, and is now looking at the possibility of building offshore facilities such as a floating storage tank and an ammonia fuel supply vessel. Itochu is also already involved in a project in Japan to develop ammonia supply infrastructure and launch ammonia-fuelled commercial vessels. Last year, Japanese shipping company NYK Line, shipbuilder Japan Marine United Corporation (JMU), and ClassNK signed a joint research and development agreement for the commercialisation of an ammonia-fueled ammonia gas carrier that would use ammonia as the main fuel, in addition to an ammonia floating storage and regasification barge.

Finally, shipping leviathan Maersk said in a 2019 report that it sees ammonia, along with biogas and alcohol, as one of its three main "commercially viable" candidate fuels for low carbon shipping.

The potential for ammonia in the marine industry is great; the International Energy Agency (IEA) has suggested that its use for shipping could reach 130 million t/a tonnes by 2070 – on the same scale as its use for fertilizer. Figure 1 shows estimates from the American Bureau of Shipping, which suggests that one third of all shipping fuel consumption could be represented by ammonia by 2050, which would again be well over 100 million t/a at current fuel consumption rates. At the moment, however, its use is limited to a few research and development vessels, and its eventual uptake, as with the power sector, is very much dependent on the availability of blue and green ammonia – while 'grey' ammonia is cheaper than most alternative marine fuels, blue and green ammonia are not, and the use of ammonia

AMMONIA FUEL

Nitrogen+Syngas 372 | July-August 2021
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CONTENTS

NITROGEN+SYNGAS
ISSUE 372
JULY-AUGUST 2021

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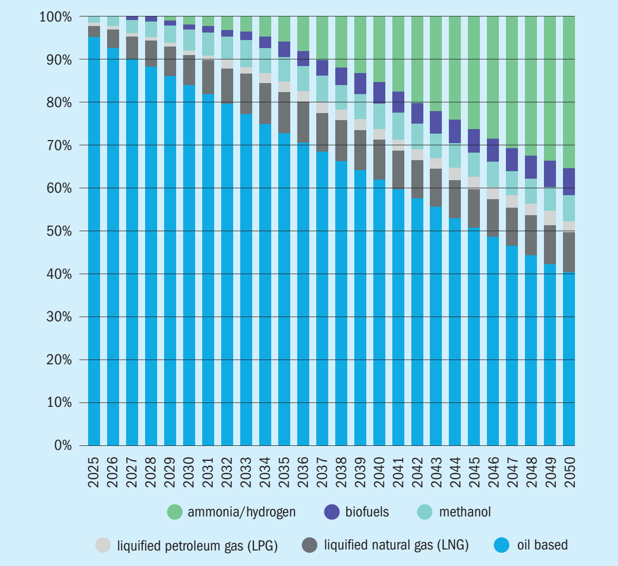
Fig. 1: **Projected use of alternative fuels for shipping (percentage), 2025-50**



Source: American Bureau of Shipping

does not justify the expense of a switchover from a conventional fuel unless it is a zero carbon fuel option.

Barriers to commercialisation

The main barriers to commercialisation of green/blue ammonia as a low carbon fuel are threefold; technical, economic and ensuring sufficient supply. Of these three, the technical seems to be the least daunting; there is a considerable amount of research and development under way by some major players in their respective industries – companies like MAN and Wärtsilä on the shipping side, and Mitsubishi and JERA on the power plant front. The question is merely one of engineering, and there do not seem to be any insuperable barriers on the horizon. Removal of nitrogen oxides from an exhaust stream is already a well understood and proven technology.

The economic side is potentially more challenging. At present, fully 'green' ammonia costs two to four times as much to make as conventional ammonia. CF Industries is currently planning to convert part of the feed for an ammonia train at its Donaldsonville plant in Louisiana by 2024, by which time it will be producing 20,000 t/a of green ammonia using hydrogen from electrolysis with electricity provided from renewable sources. CF puts the cost of producing green ammonia at \$500/t, significantly more than the present f.o.b. cost. The company suggests that it could reap a reward in terms of premium prices for green ammonia. But this in turn pushes the cost onto downstream consumers and could raise the price of, e.g. shipping, were it to become a shipping fuel. Still, electrolyser costs have already come down tenfold over the past decade, and as renewable power continues to be introduced at scale, so unit costs are likely to come down still further. BP suggests that by 2050, the cost of renewable energy will have fallen by 30-70% compared to its current value – already cheaper than conventional fuels in many markets.

In the meantime, blue ammonia might be a cheaper bridging option in the short term, and CF Industries, along with Nutrien in North America, is also looking at large scale conversion to CCS for its ammonia production. Plants in the US Gulf Coast are near to established oil and gas fields and so could use CO_2 for enhanced oil recovery, while taking advantage of tax credits for CCS. Since 2013, Nutrien has been selling about 250,000 t/a of CO_2 into the EOR market from its Geismar fertilizer plant in Lousiana. Saudi Arabia, Russia, and several other countries are either already producing or actively converting capacity to CCS, mainly for enhanced oil recovery. Saudi Aramco recently shipped 40 tonnes of blue ammonia as part of a demonstration shipment to Japan, with 30 tonnes of CO_2 captured during the process designated for use in methanol production at SABIC's Ibn-Sina facility and another 20 tonnes of captured CO_2 being used for enhanced oil recovery at Aramco's Uthmaniyah field. While piping to handle acidic CO_2 and pump it back into oil reservoirs is an expense, it is only a marginal increase in cost to the cost of producing conventional ammonia. It seems likely that we will see many more such projects over the next few years, as a market develops for low carbon ammonia.

The third barrier, however, may be the most significant – that of producing sufficient low carbon ammonia to meet anticipated demand. Japan is looking at 3 million t/a of ammonia demand for power generation by 2030, and JERA is working with Yara to source ammonia for Japan's power industry. Taken with other blue and green ammonia developments, such as Yara's Porsgrunn conversion, and the recently announced projects in the UAE to add 1.2 million t/a of blue and green ammonia before the end of the century, this looks achievable. But if ammonia did take off as a shipping fuel in the way that Figure 1 suggests, the prospect of 100 million t/a of demand by 2050 would require a wholesale change in the industry, and that in turn might require the economics, and possibly even the demand, to come first. And, just as ammonia production must currently compete with the power industry for natural gas and coal feedstocks, so in future it might have to compete with the power industry for renewable electricity. Still, if the shipping industry feels it has no alternative (developments in electrically powered vessels are even more in the experimental phase than ammonia) in order to achieve the IMO low carbon goal, that might just be enough of a push to develop blue and green ammonia plants at the scale required to achieve it. ■

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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

Syngas project listing 2021

PHOTO: CGCL

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.

Above: The CGCL methanol and DME plant at La Brea, Trinidad, during construction.

Contractor	Licensor	Company	Location	Product	mt/d	Status	Start-up date
AUSTRALIA							
n.a.	n.a.	Coogee Chemicals	Darwin, NT	Methanol	1,000	FS	2024
BELGIUM							
n.a.	n.a.	North C Methanol	Ghent	Methanol	135	P	2024
BOTSWANA							
n.a.	n.a.	Botswana Oil Ltd	Dumela	CTL	2,700	P	n.a.
CANADA							
n.a.	Greyrock Energy	Rocky Mountain GTL	Carseland, AB	GTL	70	UC	2022
CHINA							
n.a.	Casale	Anhui Tanxin Tech Co	Hubei, Anhui	Methanol	1,500	UC	2021
n.a.	JM (DAVY™)	Shenhua Yulin Energy	Yulin, Shaanxi	Methanol	6,120	UC	2022
n.a.	JM (DAVY™)	Ningxia Baofeng	Yinchuan, Ningxia	Methanol	7,200	DE	2024
n.a.	Eastman/JM (DAVY™)	Jiutai	Togtoh, Mongolia	Methanol/MEG	3,000	UC	2022
EGYPT							
n.a.	n.a.	Abu Qir Ferts	Ain Sokhna	Methanol	3,000	FS	n.a.
GERMANY							
n.a.	Siemens	Siemens	Wunsiedel	Hydrogen	900	UC	2021
INDIA							
n.a.	TechnipFMC	HPCL	Vishakhpatnam	Hydrogen	2 x 340	C	2020
n.a.	Haldor Topsoe	RCF	Trombay	Methanol	242	C	2020
EIL	Haldor Topsoe	Assam Petchem	Namrup	Methanol	500	C	2021
n.a.	n.a.	Coal India Ltd	Dankuni	Methanol	2,000	P	2024
INDONESIA							
n.a.	Air Liquide	Pertamina	Balikpapan	Hydrogen	260	UC	2021
Samsung	Air Liquide	Petronas	Bintulu, Sarawak	Methanol	5,000	UC	2023
n.a.	Haldor Topsoe/Air Liquide	PTBA	Tanjung Enim	Methanol	6,000	CA	2025
IRAN							
Namvaran	Haldor 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	Bushehr Pet Co	Assaluyeh	Methanol	5,000	UC	On hold
n.a.	Casale	Fateh Sanat Kimia	Dayyer	Methanol	5,000	UC	On hold
MALAYSIA							
MHI	Air Liquide	Sarawak Petchem	Sanjung Kidurong	Methanol	5,000	DE	2023
NETHERLANDS							
n.a.	Air Liquide	W2C Rotterdam	Botlek	Synfuels	n.a.	P	n.a.
NIGERIA							
n.a.	Haldor Topsoe	Brass Fert & Petchem	Brass Island	Methanol	5,000	DE	n.a.
RUSSIA							
China Chengda	Haldor Topsoe	Nakhodka Fertilizer	Nakhodka	Methanol	5,400	UC	2023
Tecnimont	Haldor Topsoe	Baltic Gas Chemical	Ust-Luga	Methanol	5,000	DE	2024
Hyundai/NIIK	Haldor Topsoe	Gaz Sintez	Vysotsk	Methanol	4,850	DE	2023
TAIF	Haldor Topsoe	Nizhnekamskneftekhim	Nizhnekamsk	Methanol	1,500	CA	n.a.
MHI	Haldor Topsoe	GTM One	Khimprom	Methanol	3,000	BE	2023
n.a.	JM (DAVY™)	JSC Technoleasing	Skovorodino	Methanol	3,000	BE	2023
SAUDI ARABIA							
n.a.	Air Products	Air Products Qudra	Jubail	Hydrogen	415	UC	2023
SWEDEN							
n.a.	Haldor Topsoe	Liquid Wind	Örnsköldsvik	Methanol	150	DE	2023
TRINIDAD AND TOBAGO							
MHI	MGC	Caribbean Gas Chemical	La Brea	Methanol	3,000	C	2021
MHI	MGC	Caribbean Gas Chemical	La Brea	DME	300	C	2021
n.a.	Sasol	NiQuan Energy	Pointe a Pierre	GTL	250	C	2021
TURKMENISTAN							
Rönesans, KHI	Haldor Topsoe	Turkmengaz	Ovadan-Depe	Methanol/MTG	5,225	C	2020
Sojitz, KHI	Haldor Topsoe	Turkmengaz	Ovadan-Depe	Methanol/MTG	5,225	CA	2023
UNITED KINGDOM							
n.a.	n.a.	Equinor	Saltend	Hydrogen	380	P	2024
UNITED STATES							
n.a.	Relocated plant	US Methanol	Charleston, WV	Methanol	480	UC	2021
Fluor	Air Liquide	YCI Methanol	Lake Charles, LA	Methanol	4,800	C	n.a.
Linde	Linde	Praxair (Linde)	St James Parish, LA	Hydrogen	425	UC	2021
n.a.	Air Liquide	Air Liquide	California	Hydrogen	30	DE	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	DE	On hold
n.a.	Haldor Topsoe	Nacero	Penwell, TX	Methanol	5 x 5000	CA	n.a.
n.a.	Oberon Fuels	Oberon Fuels	Brawley, CA	DME	13	C	2021
UZBEKISTAN							
Hyundai	Haldor Topsoe/Sasol	Oltin Yo'l GTL	Shurtan	GTL	5,000	C	2021

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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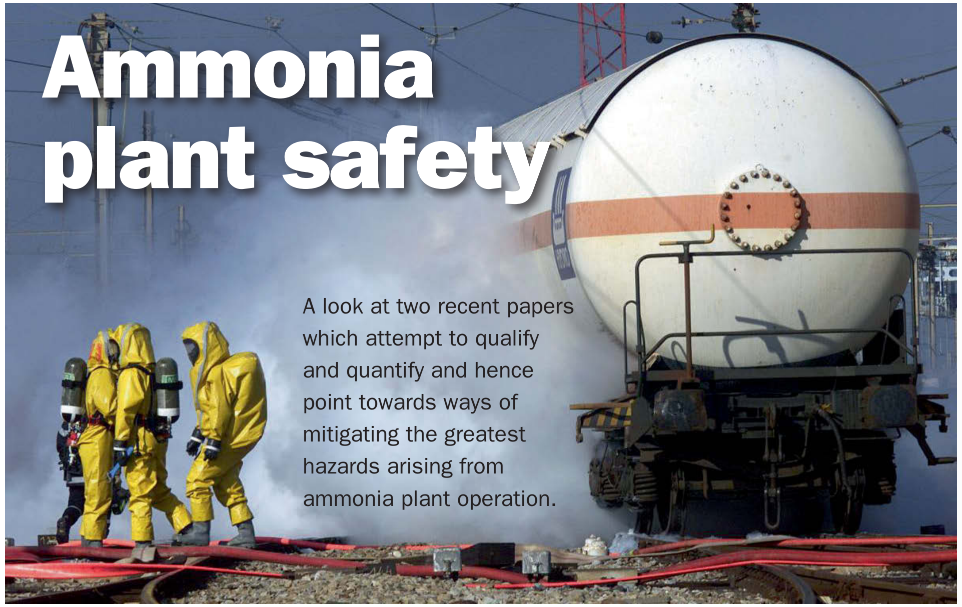
Ammonia plant safety



A look at two recent papers which attempt to qualify and quantify and hence point towards ways of mitigating the greatest hazards arising from ammonia plant operation.

PHOTO: REUTERS

While the chemical process industries have a generally good safety record, the catastrophic potential consequences of any failure, particularly in the ammonia industry, mean that there is a constant need by operators to try and identify and mitigate any potential hazards in advance. Two papers published in the past few months attempt to do that, the first from a personnel work process point of view, the second from an overall site perspective.

PT X Gresik

PT X operates two ammonia plants at its site in Gresik, Indonesia, with a combined capacity of 1.1 million t/a. The company conducted its own hazard survey in 2018, which concluded that the activities that posed the greatest threat to the health and safety of workers at the site were the supervision of welding and oil level checking in the ammonia plant section of the site, the former because of the sparks generated and potential for fire, and the second because of the potential for spillage of dangerous materials.

A follow-up study was conducted to apply risk management to the activities and this was published in the Indonesian Journal of Occupational Safety and Health in August 2020[1]. The research was a descriptive study which was carried out by observation using a cross-sectional design, with analysis and data collection performed at the same time. The study aimed to identify hazards, perform a basic risk analysis and identify any risk control or existing risk analysis that has been done, as well as a risk reduction assessment. The tools used for the data collection were mainly obtained from interviews with plant staff, with the aid of observation sheets, interview guide sheets, and job safety analysis sheets. Data that was obtained through observation and interviews was then processed using a semi-quantitative technique.

Hazard identification found six main hazards; three associated with welding (sparks, gas leakage, and fire from the reaction of oil with hydrogen) and three with oil level checking (exposure to hot oil droplets, slippery floors, and again flame due to oil reaction with hydrogen). The basic risk analysis then attempted to quantify this via likelihood and potential consequences. This showed that the initial risk level consisted of three risks with a 'very high' level, two risks with a 'substantial' level and one risk with a priority 3 level. Methods to mitigate and control these risks were then determined. After the risk control effort was applied, the results of the assessment on the existing risk analysis showed that the level of risk decreased significantly; by between 67% and 95%.

OCI Nitrogen

Following several major process-related incidents at the Chemelot site in Geleen, Netherlands, the Chemelot Board initiated an external investigation which concluded that the potential hazards of the plant and the chemical processes do not receive as much attention as they might due to a natural focus on occupational safety. This chimes with other similar reports on incidents in the chemical industry, including a gas explosion at the Esso Longford plant in Australia, and the 2005 explosion at the BP Texas City refinery.

OCI, one of Chemelot's largest site users, and the operator of two ammonia plants at the site, had faced its own safety incidents at the site, caused by incorrect choice of materials, accelerated wear, incorrect design, and unrecognised risks during work. Although no injuries were suffered in any of the incidents, in some cases the ammonia plant had to be shut down for a longer period, and there was both hardware damage and loss of production. While awaiting the results of an external investigation, OCI began its own study in conjunction with the Safety and Security Science Group, Faculty of Technology, Policy and Management, at the Technical University of Delft, with the aim of being able to monitor process safety and take targeted measures at an early stage to stop the development of a major accident.

The study was published in the Journal of Loss Prevention in the Process Industries earlier this year[2], and concentrated on which process equipment items had the largest potential adverse impact on people in the event of failure. This boiled down to four questions:

i) Which intrinsic hazards are connected to the ammonia production process?
ii) Where in the ammonia production process can an event of failure occur?
iii) What adverse impact can the hazards have in the event of failure?
iv) How can the adverse impact on humans be measured?

The research modelled the effect of a loss of ammonia containment using DNV GL's *Phast*™ dispersion model. *Phast* can calculate thermal radiation, concentrations such as upper and lower explosion limits, overpressure and toxic concentrations of individual components as well as mixtures, under the predominantly prevailing weather conditions.

The first step was to select the main process equipment to be studied, by dividing up the ammonia process into 64 items or collections of process equipment significant and representative of the ammonia production process (and including associated pipework). Process pressures, temperatures and substances were then used, along with height of any potential release and the assumed response time before any mitigating action could be taken by plant operators or emergency staff. Effects were then calculated showing radii within which there was a chance of death of at least 95%. Pressure and overpressure was also used to calculate the chance of blast/pressure waves, flying debris etc being encountered, and upper and lower explosion limits used to model potential flash fires/explosions.

The calculations showed that the ammonia production process comprises several intrinsic hazards related to the presence of steam, flammable gas and ammonia. A release of a hazardous substance can give rise to burns, internal injury or poisoning from exposure to heat radiation, flames, overpressure or toxic concentration respectively. In the front end of the ammonia production process loss of containment scenarios may lead to heat radiation from jet fires, flame contact from flash fires or to overpressure from explosions due to the presence of flammable components. In the back end there is also ammonia present which release may lead to high toxic concentration levels resulting in poisoning. Releases of steam were not considered as their effects are much smaller than those from jet or flash fires. The largest adverse impact on humans in the event of failure is expected from the syngas compression to the ammonia separation sections (exposure to heat radiation, flame contact and overpressure) and from the ammonia product pumps and buffer tanks (exposure to a toxic ammonia concentration). In general, it was concluded that higher pressures, temperatures and mass led to higher adverse impacts on humans. This results in effect radii from which maximum distances from the point of release can be determined. By taking the maximum distance as a (relative) measure, the effects of a release of both flammable and toxic substances can be compared. If the central event cannot be avoided, there is a 1 to 1 relationship between the central event and the consequences of burns, internal injury, and poisoning resulting in death.

The authors state that the effect calculation results can be used for risk mapping of an entire chemical plant or be employed and applied in a layer of protection analysis (LOPA) to establish risk mitigation measures. The results from this research provided new insights for OCI Nitrogen into the current method of equipment classification and the investment in preventive measures. It is suggested that a path forward for future process safety research can be the link of the equipment ranking results with barrier management and as such, further optimisation of safety investments. ■

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NITROGEN+SYNGAS
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Nitriding in ammonia converters: behaviour, experience, and solution

The internals of ammonia synthesis converters are generally made of austenitic stainless steel to withstand the harsh operating conditions (high temperature, high pressure and synthesis gas containing hydrogen and ammonia). Since nitriding is the most critical material degradation for the converter internals, Casale has set up a large nitriding analysis campaign. In the last decade, samples of materials operated under different pressures and temperatures and for different time spans have been tested and analysed. The data obtained has been used to increase nitriding knowledge and to establish a correlation to predict nitriding rate to allow the most suitable material and relevant thickness to be selected. **L. Redaelli** and **G. Deodato** of Casale report on how this correlation was established and provide valuable insight on this phenomenon and how to predict and control it.

One of the key items in an ammonia plant is the synthesis converter. Besides the efficiency of its performance, reliability is essential, as a plant cannot run if the converter is down and the risk involved in its failure is significant because of the high pressure, flammable gas it contains. In addition, the ammonia synthesis converter is the reactor with the longest run between catalyst changes, usually more than ten years, but sometimes up to 25 and more. Ammonia catalyst, once reduced, is highly pyrophoric and should not be allowed to come into contact with oxygen. Therefore, any maintenance activity is only possible when the catalyst is replaced and converters should operate between catalyst changes without repairs or internal inspections.

To achieve this, several aspects need to be considered since converters are subject to different metallurgical deterioration phenomena, and they have a complicated mechanical design with multiple catalyst beds and internal heat exchangers to improve efficiency.

Ammonia converter environment

The ammonia converter operating environment is characterised by an aggressive combination of high pressure and high temperature gas composed of hydrogen, nitrogen and ammonia, which implies the concurrence of hydrogen related damage and nitriding.

To reduce these problems the catalytic bed where the ammonia is generated at high temperature is usually separated from the pressure bearing shell. In most designs and in all multi-bed solutions the catalytic beds are enclosed in a protective shell inside the pressure retaining vessel, which separates the pressure bearing function from the high temperature environment. Cold flushing of the external vessel is provided by the inlet gas, which is low in temperature and ammonia content. This arrangement is called a cold wall design, while in the absence of a cartridge the converter arrangement is defined as a hot wall design.

The latter design avoids the cartridge by inserting the catalytic bed directly in the pressure vessel with the aim of reducing capital cost. It was used in the past and is sometimes still used when an additional single bed converter has to be added downstream of the main converter, but several of these vessels have faced problems during their operating life.

A brief introduction to the metallurgical phenomena that affect the ammonia converter is required to understand the different choices in the design of ammonia converters, the problems related to these choices and the solution proposed.

As already mentioned, the combination of a high content of hydrogen and ammonia implies the concurrence of hydrogen-related damage and nitriding, exacerbated by high temperature and high pressure.

Hydrogen related damage refers mainly to high temperature hydrogen attack (HTHA) and hydrogen debonding.

High temperature hydrogen attack occurs in hydrogen-rich environments where, under certain conditions of temperature and pressure, carbon and low alloy steels can suffer irreversible damage. Its mechanism is described in International recognised standards such as API 941 and it is dealt with in ammonia converter pressure vessels by using the cold wall design and by proper material selection. In this design the converter cartridge and all of its internals are made of austenitic materials that are not affected by HTHA.

Hydrogen debonding affects welding between dissimilar metals, including weld overlays of stainless steels and nickel alloys on ferritic steels. Cracking commonly occurs at the interface between the austenitic weld material and the heterogeneous base metal, due to hydrogen, which has penetrated the metal during fabrication or operation, remaining entrapped up to saturation levels at cooling down cycles. The faster the rate of cooling, the higher the likelihood of entrapped hydrogen causing debonding. In general, stressed heterogenous welds should be avoided, especially when involving thick sections.

Nitriding

Nitriding is the introduction of atomic nitrogen in the surface of a metallic component. Atomic nitrogen forms solid solution and several nitrides with iron, but also nitrides with other elements with an affinity for nitrogen such as chromium. Since atomic nitrogen is required, molecular nitrogen is not a nitriding agent unless it is ionised, but gaseous ammonia mixtures with hydrogen are. Above a certain temperature ammonia decomposes over steel according to the reaction

$$NH_3 \rightarrow [N] + \frac{3}{2} H_2$$

where [N] represents the nitrogen dissolved in the steel.

This reaction occurs on the surface of the steel. Depending on the type of steel, temperature, pressure and gas composition, different types of solid solution and nitrides can form on the surface, creating an external nitride layer. This layer can increase in thickness over time and typically comprises a compound layer and an underlying diffusion zone. The compound layer is richer in nitrogen and harder, while the diffusion zone is softer with fewer nitrides, but overall the nitride layer is much harder than the base metal. This characteristic has been widely used to increase resistance against wear and fatigue of components such as engine cylinders.

While controlled nitriding is a technological process used to improve specific features of steel components, uncontrolled nitriding can be a problem due to its intrinsic characteristics. The nitride layer is hard but also brittle and involves structural modifications that causes volumetric changes.

The penetration rate of this layer will slow down after an initial fast growth since the layer itself acts as a barrier to further diffusion.

This layer does not cause any problem until it remains compact and does not crack.

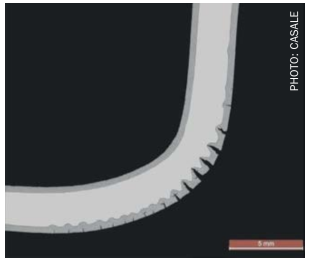

Fig. 1: Effect of increasing penetration of nitriding (darker layer) due to cracks in a thin bended plate.

The main characteristic of a hard and brittle material compared to a ductile one is that there is little or no plastic deformation before rupture.

For this reason, in case of stress concentration, there is no plasticisation and consequently stress cannot redistribute over a larger area and can easily reach high local peaks. Therefore, a brittle material will more easily reach its rupture limit in areas of stress concentration. When the rupture stress is exceeded, a brittle material will crack.

In a nitriding environment, when cracks appear, further surface is exposed leading to further penetration of the nitride layer (Fig. 1). The apex of the cracks is subject to high stress concentration, even ten times higher than nominal stress. When nitriding progresses, these high stresses cannot be accommodated by plasticisation of the material and the rupture limit is again exceeded leading to further propagation of the crack. This propagation, cycle after cycle, can lead to the component failure.

Experience shows that components designed to avoid any stress concentration, preventing any abrupt geometrical change, sharp corners, temperature induced peak stress and sharp transitions can withstand moderate nitriding because the brittle layer remains compact.

It should be noted that, since nitriding generally involves a volume increase in steel it also generates internal stresses that could lead to cracks even in the absence of external loads.

In ammonia converters nitriding will occur to a degree depending on the combination of pressure, temperature, ammonia content and steel composition.

Nitriding develops on carbon steel, low alloy steels and on stainless steels, however, on the latter at a much reduced rate and at higher temperatures.

According to the literature and Casale experience, nitriding of carbon steel and low alloys starts at temperatures above 370-380°C and becomes significant above 400°C. As a consequence, carbon steel and low alloys are not recommended in ammonia atmospheres above 370-380°C, instead austenitic stainless steel or even nickel alloy should be used.

This limitation is the main reason, together with hydrogen attack, for the selection of the cold wall design of the ammonia converter, where the pressure retaining vessel is cold flushed by the inlet gas, poor in ammonia, and an internal stainless steel cartridge encloses the hot part of the process.

At higher temperature and reduced rates, nitriding also affects austenitic stainless steels, converting the comparatively ductile, moderate strength austenitic matrix to a very hard and brittle magnetic microstructure. It is the most critical material degradation phenomenon for the internals of ammonia converters, affecting the design and limiting the useful life of many components. However, due to the limited industrial application of nitriding on stainless steel and the differences between the controlled nitriding of the industrial process and the long term effects of uncontrolled nitriding in the ammonia synthesis environment, data about the effects of nitriding inside ammonia converters are scarce and difficult to correlate with actual operating conditions. No detailed data are available in the literature and it is not easy to simulate the effects of high temperature and pressure over an exposure time of 10 to 20 years in a laboratory.

Casale approach

Casale, as a leader in ammonia plant design and specifically ammonia converter design for one hundred years, has gained a wide experience in the effects of nitriding on the design of converter internals. In the continuous effort to develop ever more efficient and reliable technologies, Casale implemented a specific program to review the knowledge of nitriding in the ammonia synthesis environment for the purpose of optimising the design of critical components. Samples of materials which operated under different pressures and temperatures and for different

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PHOTO: CASALE

Fig. 2: Nitrided sample after traction test. Cracks occurred in the nitrided layer


PHOTO: CASALE

Fig. 3: Effect of nitriding in a 20 year old perforated plate.

time spans from ammonia converter components replaced in revamps, were analysed in laboratories, and mechanically tested over the last decade.

This knowledge supplemented by laboratory testing has provided valuable insight into this phenomenon and how to predict and control it in newly designed components as well as how to assess existing components in order to advise plant owners about the safety of their plant.

As a leader in converter revamping, Casale has modified all types of existing ammonia converters and therefore during this survey samples from different operating conditions and design were collected.

Some numbers from the survey are helpful in understanding the extent of this effort.

Of all samples collected about one hundred were examined in specialised laboratories, for visual analysis, nitriding thickness measurement and chemical composition. The oldest sample was about 45 years old, while the youngest was about four years old. The thickness of samples varied from 2 mm to more than 20 mm. The maximum nitride thickness measured was about 1.6 mm, as expected in the oldest sample. Since the tendency to crack increases with nitride layer thickness, measurements were taken in unaffected areas.

Several of these samples were also mechanically tested to verify the behaviour of the material under traction loads (Fig. 2).

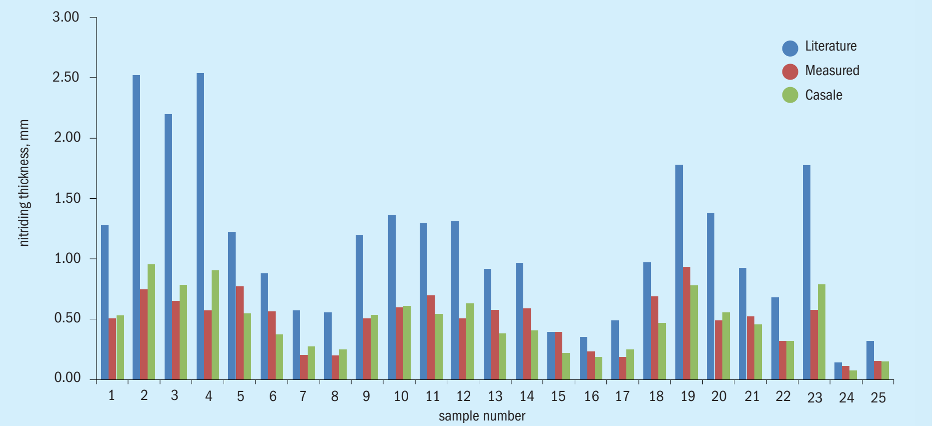
In addition, samples of different chemical composition were submitted to a controlled nitriding atmosphere for comparison with real life results.

Fig. 3 shows the effect of nitriding in a 20-year-old perforated plate.

Some of the results of this survey are summarised here. It is understood that these considerations are valid only for operating conditions within the range of the tested samples, since based on an empirical analysis, but for practical purposes, the operating range represented covers the conditions found in practically all ammonia converters still in operation.

For reference, the samples analysed cover a timespan from four years to 45 years, and a temperature range from 400°C to 540°C. The ammonia content varied from about 2-3% to 21%, and the absolute pressure was also considered.

Fig. 4: **Predicted values of nitriding depth from available literature (blue) and Casale method (green) compared to measured values (red)**



Source: Casale


PHOTO: CASALE

Fig. 5: Nitrided sections of an interchanger tube. Cracks start at high nitride thickness

Results

In general, it was found that, for any set of operating conditions, the nitriding rate (increase of nitride layer thickness versus time) is initially high, then progressively decreases but does not stop in the timeframe considered. As an indication, the nitriding thickness reached after eight years will take three times as long to double.

Regarding the operating conditions, the survey shows that the rate of nitriding depends markedly on operating temperature, increasing exponentially with temperature in the field considered.

It depends less markedly on ammonia, increasing with content. The increase is less than linear, and nitriding become significant above about 5% with a thickness which will not double even at concentrations as high as 20%. Of course, the higher the absolute pressure the higher the relevant thickness, since the effective parameter is the ammonia partial pressure, which is the product of ammonia concentration and absolute pressure.

The data obtained has been used to establish a correlation which allows the extent of nitriding over time to be predicted, thereby allowing the most suitable design and relevant material thickness to be selected. This correlation improves previous rationalisations that can be found in the literature, thanks to the huge quantity of specific data that covers the complete operating range of the ammonia converter (see Fig. 4).

It is known that the nitriding rate decreases with increasing nickel content, but it was not possible to address this effect in the correlation by retrieved data only, because all of the samples collected were mainly made of stainless steel grade 304, 316 and 321, which have limited variation of nickel content, or Inconel, which is virtually immune to nitriding.

For this reason, laboratory tests of accelerated nitriding were set up to compare different grades of stainless steel. While accelerated industrial nitriding environments cannot be easily compared to that in an actual ammonia converter, and therefore laboratory tests cannot be used to predict actual nitriding in operating conditions, the behaviour of different grades of stainless steel in tests can be evaluated versus those of grades that have a known behaviour in operating conditions.

From these tests it has been observed that doubling the percentage of nickel has a relevant impact on the nitriding rate and therefore selecting suitable stainless steel grades for critical components in the ammonia converter permits significant improvement in the design, increasing reliability and extending operating life.

Another important issue that has been substantiated by this survey, is the effect of the volumetric change due to nitriding. In stainless steel, the absorption of nitrogen involves an increase in volume in the compound layer that generates stresses due to the geometrical constraints of the unmodified core material. In smooth geometries, when the nitriding layer is small compared to the base material, this effect usually goes unnoticed, but when the thickness of the nitriding layer is high compared to the overall thickness, especially where there are abruptly changes of geometry, cracks will occur in the brittle nitrided layer (see Fig. 5). These cracks will expose the unaffected material, which will be subject to initial fast nitriding of the new material. This phenomenon will lead to a higher nitriding rate due the mechanism of crack progression described previously. For this reason, frequent temperature changes such as in start-up and shutdown, which increase the thermal stress and accelerate the progression of cracks, are much more critical than continuous service at high temperature where the nitriding rate is generally low for some years.

Beyond volume changes, mechanical stresses can also lead to cracking of the nitrided layer. To assess the effects of stresses on the nitrided samples, a series of tension tests were performed on operated samples. As expected, the nitrided layer, which is harder but brittle and therefore cannot accommodate excessive strain by plasticisation, will always fail first. This should be taken into account in ammonia converter design.

A final point to be noted is that the nitrided layer becomes magnetic and subject to oxidation. While the operating atmosphere of ammonia converter is reducing and therefore this phenomenon is not a problem, it should be considered when ammonia converter internals are subject to a long shutdown in an unprotected atmosphere.

Conclusion

The huge amount of data from collected samples and tests have allowed Casale to refine its understanding of the effects of nitriding in the ammonia converter, to establish a correlation which allows the extent of nitriding to be predicted over the years, and to incorporate all of this knowledge in the material selection and design of its converters, improving their reliability and operating life. ■

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Intelligent material design

T. Hentrich and **B. Nowak** of VDM Metals provide an overview of the development of VDM® Alloy 699 XA, a new generation, metal dusting resistant alloy, available in a wide range of product forms, for demanding applications in the chemical process industry.

PHOTO: VDM METALS

Fig. 1: Alloy 601 showing metal dusting pits.

VDM Metals founded in 1930 in Germany (since 2020 a company of Acerinox) produces high performance alloys for use in extreme conditions – high temperatures, icy waters, soaring heights and deep underground. VDM materials are made to last, resisting heavy mechanical, thermal and chemical stresses, sometimes all three simultaneously. In many key technologies, high performance alloys from VDM Metals are indispensable for the industrial-scale implementation and safe control of essential processes in hot or corrosive environments. Safety and reliability are very important for any project in the chemical process industry. VDM Metals fulfils customers' needs for demanding materials concepts in plant engineering, the development of new processes or in the field of maintenance.

Pressure equipment such as vessels, piping and their accessories, assemblies and other safety equipment is strictly regulated throughout international markets. In addition to achieving certification for the quality assurance system in compliance with the European Pressure Equipment Directive (97/23/EC), these requirements have also helped to gain a deeper understanding of customers' needs through the material development process for all product forms and probably following the production steps too.

As an integrated manufacturing producer VDM keeps all major production steps in-house – a vital prerequisite for a robust and stable manufacturing process, based on the knowledge that the quality and safety of construction goes back to the metallurgy and even beyond, to management and quality of raw materials. The results of these efforts are: maximum purity, homogeneity, reproducibility and optimum further processing characteristics of metal products.

VDM Metals offers high performance materials in the main semi-finished product forms plate, sheet, strip, rod, bar, wire and additionally as powder. These various product forms exhibit excellent fabricability into vessels, heads, trays, tubes, pipes, fasteners, fittings and flanges, etc. which are subsequently manufactured into the different pieces of equipment required by the chemical industry as pressure vessels, reactors, columns, heat exchangers and filters.

The constantly increasing requirements of the petrochemical industry regarding efficiency demand the application of new materials in diverse product forms. The big challenge is the combination of high-temperature corrosion resistance and workability. Workability is an important factor, not only for end-users in case of maintenance work, but also for material producers for further processing because availability on schedule is also an important "material property". Additionally, due to the global trend for CO_2 reduction or neutrality by production processes in the chemical process industry, an intensification of production conditions to achieve greater process efficiency causes an occurrence of different corrosion types.

For many years, customers in the petrochemical industry have reported a particular problem in their plants, known as metal dusting. This type of corrosion occurs, for example, in hydrogen, ammonia, methanol and synthetic fuel production plants. For affected companies, metal dusting typically results in increased maintenance costs or running processes less efficiently.

Metal dusting can be highly detrimental. It is a high-temperature form of corrosion damage in iron, nickel or cobalt alloys, which are exposed to a carbon-bearing atmosphere with a carbon activity greater than one (i.e. mixtures of CO, H_2, H_2O and CO_2) typically between 500°C and 800°C. CO from the gas atmosphere reacts at the metallic surface to form atomic carbon, which diffuses into the metal. The metal supersaturates in carbon and decomposes into a mixture of graphite, carbidic, oxidic, and metallic particles ("metal dust"). The corrosion attack takes place by the formation of pits (see Fig. 1), but general attack is also possible.

Table 1: **Nominal composition of tested alloys in weight percent**

Alloy	UNS	Alloy No.	Cr	Ni	Fe	Al	C	Others
600	N06600	2.4816	16	72	8	0.2	0.07	0.3 Ti
601	N06601	2.4851	23	60	14	1.4	0.06	0.4 Ti
800 H	N08810	1.4958	20	31	45	0.4	0.08	0.3 Ti
690	N06690	2.4642	29	60	9	0.3	0.01	0.3 Ti
602 CA	N06025	2.4633	25	60	9	2	0.18	0.2 Ti, 0.06 Y, 0.08 Zr
699 XA	N06699	2.4842	30	Bal.	≤2.5	2	0.02	0.2 Nb, 0.05 Zr

Source: VDM Metals

In many traditional designs, the process parameters that could lead to metal dusting were avoided due to safety requirements as well as the lack of "ideal" material for these applications. "Ideal" material means a good combination of corrosion resistance, creep properties and workability (possibility to produce seamless tubes as well as good weldability). A well-balanced chemical composition is crucial for achieving this combination of properties.

A lot of research work has already been done in order to understand the influence of the chemical composition of wrought alloys on resistance to metal dusting[1]. It is related to the ability of the alloy to form a protective oxide scale on its surface that should be dense enough to delay the diffusion of carbon. Therefore, a high Cr, Al or Si content improves the resistance of an alloy against metal dusting. Reducing the Fe content is also beneficial.

However, a high Si content could decrease weldability properties.

Furthermore, the influence of the microstructure and the surface conditions and treatment such as machining, pickling and grinding on material behaviour under metal dusting conditions was investigated and reported as important influencing parameters[2].

The workability of new and existing alloys is also important. In some applications, it is required to use seamless tubes and/or complicated thick wall welded constructions. For these needs, it is important to assure good hot and cold workability. Expansion and extrusion processes during tube production involve high temperatures and high strain rates. It is therefore crucial that alloys show good ductility at high temperatures. Generally, tube production also includes a metal working process with high deformations at room temperature, such as cold pilgering. New alloys must therefore withstand the required deformations without failure.

The design and control of the whole tube manufacturing route, hot and cold forming processes, solution annealing treatment, finishing operations and inspection procedure, is essential to obtain final tubes with an optimised microstructure and surface quality, which guarantees the optimal mechanical, oxidation and corrosion properties. In this sense, it is very important to achieve a microstructure free of undesirable precipitates, with an adequate and homogeneous grain size, and to avoid depletion of these chemical elements that enhance metal dusting resistance, such as Cr and Al, at the tube surface.

Good weldability under argon is a necessary property for the realisation of complex constructions, but also for additive manufacturing processes (new parts or repair jobs).

Based on the abovementioned aspects and wide material expertise, VDM Metals started the development of a new alloy especially for application under metal dusting conditions. In addition, benchmark alloys for each requirement were determined and used to compare the results achieved during the development process. In order to meet the needs of its customers the following requirements for alloy development were defined:

- higher metal dusting resistance than Alloy 602 CA;
- creep strength at least as good as Alloy 601;
- room temperature ductility better than Alloy 602 CA, in the range of Alloy 601 to produce seamless tubes;
- good weldability (under argon) similar to Alloy 601.

Table 1 shows the nominal composition of the tested alloys in weight percent.

In 2012, a patent application (author: Dr H. Hattendorf, from VDM Metals R&D department) was finally filed for a new type of nickel-based alloy with approx. 30% Cr, 2% Al and less than 2.5% Fe.

In 2013, the laboratory phase for the new material Alloy 699 XA was successfully completed. The improved metal dusting resistance of the new alloy was experimentally confirmed by a significantly longer incubation time, i.e. the period until the first pit attack by metal dusting.

Further optimisation and the necessary preparations for large-scale tests followed. In 2015, the first large-scale batch was melted, from which tube feedstock and forged bars, sample sheets of various thicknesses and welding rods were produced at VDM Metals. In 2016, seamless tubes made of VDM® Alloy 699 XA were successfully produced at Tubacex in Spain.

Tubacex Group, as a leading multinational company devoted to the production of seamless tubes in stainless steel and high-nickel alloys, is constantly working on improvement of technological processes and product quality. This approach helps customers from different industry areas to meet strongly increasing process requirements. Due to their chemical compositions with a high content of nickel, chromium and aluminium to impart superior characteristics, high performance materials, such as Alloy 699 XA, are more complex than standard stainless steels to process. Tubacex Group possesses long-term experience in manufacturing tubes of special alloys and assures a robust production process. During the most critical steps on the tube production route, such as piercing, extrusion, cold-pilgering and solution annealing, the required process parameters are carefully defined and controlled.

NITROGEN+SYNGAS
ISSUE 372
JULY-AUGUST 2021

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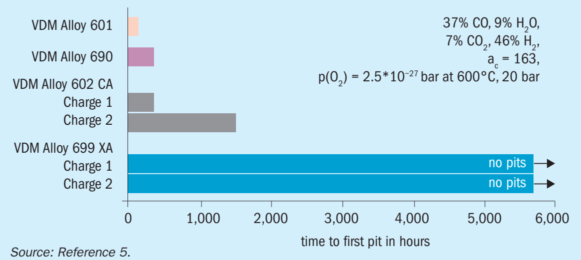
Table 2: **Gas composition, oxygen partial pressure and carbon activity at 600°C and 20 bar pressure**

Gas	Composition, vol.-%				pO_2, bar	Carbon activity, a_c		
	CO	H_2O	CO_2	H_2		CO reduction	Boudouard	At water gas shift equil.
2B	37	9	7	46	$2.5\ 10^{-27}$	163	452	253

Source: VDM Metals

Fig. 2: **Time to first pit (no matter where)**



Source: Reference 5.

Metal dusting resistance is enhanced by surface working. Tubacex Group can deliver Alloy 699 XA tubes with ground outer and inner surfaces to maximize the potential against metal dusting corrosion.

Both the strict control during the manufacturing process and the optimisation of the final surface quality, guarantee high-quality Alloy 699 XA tubes with successful performance in service.

The main goal of this development was the design of an alloy that is highly resistant to metal dusting. The methodology and detailed sample description of the metal dusting test rig at Netherlands Organization for Applied Scientific Research (TNO) in Eindhoven has been reported in previous papers[3,4].

A temperature of 600°C was chosen to investigate corrosion resistance, since at this temperature the metal dusting attack is most severe. In order to test material performance at close to industrial conditions, and due to the understanding that the total pressure has a significant effect on the severity of the metal dusting attack[3], a high pressure of 20 bar was used for the whole test duration. Long-term exposures were run using the so-called gas 2B (see Table 2). This is a gas with a high carbon activity used by TNO to rank very high metal dusting resistant alloys. The entire test conditions are more aggressive than expected in common industrial application in order to prove a worst case scenario. Moreover, customers' exact process conditions are strictly confidential and cannot be used as an example for investigation conditions. After each exposure of about 125 hours the test was paused, the samples were cleaned ultrasonically, examined for pits and optical documentation was taken.

Fig. 2 shows the time to first pit, no matter where it forms (on the surface or edge of the specimen) for the different materials and Table 3 shows pictures of alloy samples after the appearance of the first pit or at the end of the exposure time[5,6]. The sample of Alloy 601 shows many pits after the first test stop at 123 hours. The number of pits after this short time proves that this material is not suitable for use under severe metal dusting conditions due to a Cr and Al content that is too low and a Fe content that is too high.

For Alloy 602 CA there are a few pits up to about 1,499 hours, and for Alloy 690 only one pit up to 754 hours is visible.

Alloy 699 XA, as a low Fe material with a Cr + Al content ≥30 wt-%, shows no pits and no attack on the surfaces or edges up to 5,693 hours (many different specimens with a slightly different chemical composition, but all within Alloy 699 XA specification were tested in the same experimental setup). Based on this remarkable test result, the goal of the first requirement "higher metal dusting resistance than Alloy 602 CA" was clearly achieved.

Table 3: **Samples after appearance of the first pit or end of exposure respectively**

Alloy	Photos taken after	Photo	Pits
VDM Alloy 601	123 hours		many pits
VDM Alloy 690	754 hours		1 pit
VDM Alloy 602 CA	1,499 hours		few pits
VDM Alloy 699 XA Charge 1	5,963 hours		no pits
			only surface discolouration
VDM Alloy 699 XA Charge 2	5,963 hours		no pits
			only surface discolouration

Source: VDM Metals

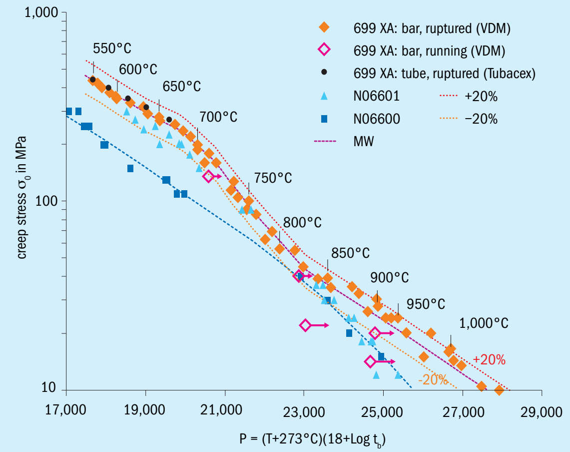
Mechanical properties

Balanced mechanical properties of the material over the whole temperature range is another important aspect for successful alloy application. Components as well as the whole construction should be able to withstand the thermo-mechanical load over the whole lifetime.

In general, high temperature mechanical properties compete against workability in metallic materials. All of the mentioned alloys in this article are wrought or rolled alloys and undergo cold and/or hot deformation treatment during production. During the deformation process some small defects after melting and remelting like pores are closed and hence beneficial microstructures and homogeneous grain sizes are realised. This is only possible if the deformation of the material is feasible without cracks or damage due to its too high mechanical strength and low ductility at room as well as high temperatures. While the focus for the development of most wrought Ni-base alloys has generally been on processing properties such as workability and weldability, the development of materials that are highly resistant to creep for very high temperature application (close to the alloy melting point) has primarily concentrated on end-part performance. Consequently, some manufacturing steps such as production of seamless tubes are not available, for example, for wrought Alloy 602 CA. These factors were the main drivers when defining the requirements to meet the balance between mechanical properties and workability:

- usability of a new material;
- creep strength at least as good as Alloy 601;
- room temperature ductility better than Alloy 602 CA, in the range of Alloy 601, to produce seamless tubes;
- good weldability (under technical pure argon) similar to Alloy 601.

Fig. 3: **Larson-Miller plot**



Source: VDM Metals

Table 4: **Mechanical properties at room temperature**

Alloy	Yield strength $R_{P0.2}$, MPa	Tensile strength R_m, MPA	Elongation A_5, %
Alloy 699 XA	255 - 395	650 - 750	47 - 68
Alloy 602 CA	270 - 390	675 - 780	30 - 54
Alloy 601	220 - 300	550 - 710	44 - 68
Alloy 690	240 - 400	610 - 740	40 - 63

Source: VDM Metals

The most important mechanical characteristic for application in CPI at high temperature is creep resistance. Non-interrupted uniaxial creep tests in tension with strain measurement were done on solution annealed samples from a forged bar for Alloy 699 XA. Creep tests on annealed tubes of Alloy 699 XA were also performed during the alloy development project. For the reference alloys, Alloy 601 and Alloy 600, interrupted creep tests were carried out on samples from solution annealed hot rolled plate.

The data on Alloy 699 XA, Alloy 601 and Alloy 600 were analysed according to the Larson-Miller approach. C=18 was used in the Larson-Miller parameter P based on data for Alloy 602 CA.

In Fig. 3 lines are shown for the mean value, the mean value –20% and the mean value +20%. Fig. 3 confirms, that the second requirement "creep strength at least as goo as alloy 601" has been achieved.

NITROGEN+SYNGAS
ISSUE 372
JULY-AUGUST 2021

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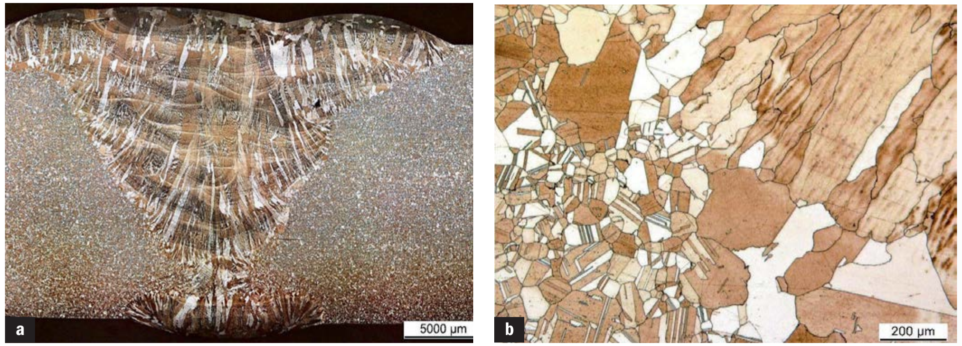
PHOTOS: VDM METALS

Figs 4(a) Macroscopic (above left); and 4(b) microscopic picture of the weld respectively the heat-affected zone (above right).

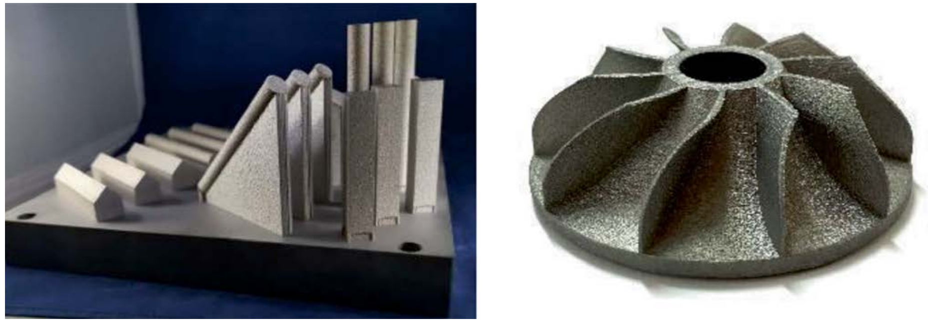
PHOTOS: VDM METALS

Fig. 5: Examples of printing specimens and parts.

Another important aspect are mechanical properties at room temperature due to its influence on production processability. For Alloy 699 XA, tensile tests were performed at room temperature on bar and plate as well as on tube. All samples were solution annealed. The ranges of the results are shown in Table 4. This shows that the third requirement "room temperature ductility better than Alloy 602 CA, in the range of Alloy 601 to produce seamless tubes" has been achieved.

For the successful introduction of a material into the market, the weldability of an alloy is an essential requirement for complex parts and in case of repairs.

Plates of Alloy 699 XA of 16 mm thickness were welded with gas tungsten arc welding method (GTAW) with 2.0 and 2.4 mm rod under argon using matching filler metal. Afterwards a welding procedure test according to DIN EN ISO 15614-1 was successfully performed. Fig. 4a shows a macroscopic picture of the weld and Fig. 4b a microstructure of the weld, i.e. the heat-affected zone can be seen. Hence, also the fourth requirement "good weldability under argon" was also achieved.

Alloy 699 XA for additive manufacturing (AM)

Since Alloy 699 XA shows an excellent combination of high temperature corrosion resistance and weldability, this alloy should be considered as 'ready-to-use' for AM. During a current powder project outstanding results were achieved: crack free, as well as uniform microstructure, even in complicated design parts, and good mechanical properties in an as-built condition, as well as in annealed condition (see Fig. 5). ■

Acknowledgement

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NITROGEN+SYNGAS
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JULY-AUGUST 2021

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Metal dusting attack on steam reformer components

Metal dusting corrosion damage on steam reformers is no longer a major issue in modern methane steam reformer units. Nevertheless, failures related to metal dusting corrosion attack still take place in some specific designs and configurations that are more prone to experience this damage. Poor maintenance or deterioration of insulation components on transition areas might expose metallic surfaces to metal dusting attack. In this article, **Dr P. Cardín** and **P. Imízcoz** of Schmidt+Clemens Group describe different case studies, where the end users benefited from the experience of a collaboration to address potential risks and improve plant reliability against metal dusting corrosion damage.

Metal dusting is a type of corrosion damage similar to oxidation attack of carburised metal, reported in Fe, Ni and Co alloys. It is typically observed in industrial furnaces, boilers, and heat exchangers that operate in strongly reducing atmospheres (CO/H_2). Final corrosion products are powdery graphite-metal mixtures. Compared with normal corrosion, it occurs randomly and progresses much faster. Ellipsoidal pits, found on the metal surface, are a characteristic indication of metal dusting [1, 2].

Metal dusting occurs due to the absorption of carbon into the metal, leading to the precipitation of metastable carbides and later decomposition of these carbides into metal particles and carbon (graphite). Metal dusting requires carbon activities greater than one ($a_c>1$), to allow carbide formation and involve no-equilibrium gas compositions. Additionally, metal areas where a carbon-rich gas atmosphere (CO/H_2) becomes stagnant, are more prone to suffer from this severe corrosion attack[2, 3].

Steam reformer process gas, with its high carbon activity (a_c), can induce metal dusting corrosion attack on "cool" reformer zones. Modern steam reformer designs tend to avoid critical temperature areas where metal dusting attack might take place.

Nevertheless, damage or deterioration of insulation equipment in the outlet portions of tubes can produce metal dusting corrosion attacks as seen in Fig. 1. In this case, a standard material 25Cr35NiNbTi in a process gas heater, experienced severe pitting (maximum pitting depth up to 100 mm) after a relatively short period of time (1-2 years). Lower process gas temperatures, due to production restrictions, placed part of the heater into the critical temperature range for metal dusting corrosion damage.

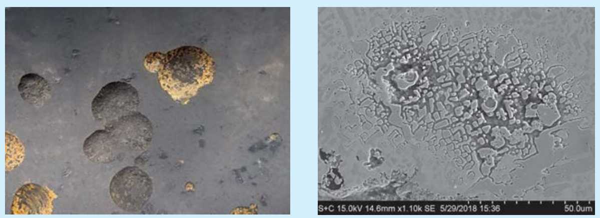


Fig. 1: **Metal dusting attack on a 25Cr35NiNbTi (HP-Nb MA) sample – surface "pitting" (left); internal corrosion, SEM image transversal section (right)**

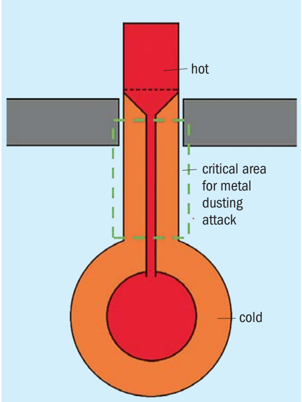
Source: Schmidt+Clemens Group

Factors influencing metal dusting damage

The metal dusting attack mechanism was widely described by Grabke *et al* and other authors, for different types of steel materials. For high alloy steels and Ni-alloys, several steps lead to metal dusting damage incidence[4,5,6,7,8]:

- The presence of local defects or damage to the protective oxide layers allowing the transfer and dissolution of carbon into the metal phase.
- Inward carbon diffusion causes carbide precipitation within the alloy material.
- Carbon concentration rises, leading to carbon activity values higher than one.
- For iron-based alloys, metastable carbides (Fe_3C) form as an intermediate phase that decomposes to graphite and metal particles. For Ni-alloys, graphite formed on the supersaturated solid solution destroys the alloy into graphite and metal particles.
- Metal particles formed by alloy disintegration act as catalysts for further carbon deposition and coke growth on affected areas, leading to an extension of the corrosion attack.

Fig. 2: **Critical areas for metal dusting damage on typical "cold" collector designs**



Source: Schmidt+Clemens Group

As mentioned, several factors influence the incidence of metal dusting on alloy materials:

Temperature and pressure: It is commonly accepted that the temperature range where metal dusting takes place is within the range 480 to 815°C and the maximum rate of attack occurs at around 600 to 620°C. The lower temperature indicated should be taken as a practical temperature limit below which the rate of metal dusting damage will be acceptable/negligible for a wide range of steel materials[8].

Pressure has a direct influence on carbon activity in the gas phase. Higher pressures lead to more severe metal dusting attacks.

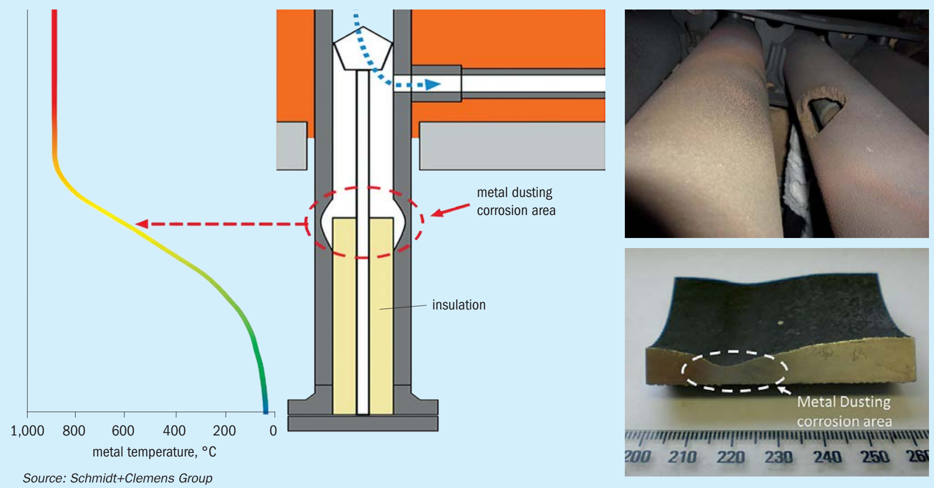
Protective oxide layers: In high alloy materials, oxide scales play a significant role in providing metal dusting resistance as carbon diffuses at a much lower rate through these protective layers. High Cr and Si contents favour the formation of strongly protective spinel/chromia/silica layers. Disruption/damage of these protective layers leads to alloy corrosion damage incidence. Cyclic operation between carburising and oxidising atmospheres could lead to metal dusting occurrence as oxide layers are no longer protective[4, 6, 8].

High nickel contents: Ni-base alloys tend to exhibit a better resistance to metal dusting attack than Fe-base alloys, due to lower carbon diffusivity in Ni alloys. The lattice of Fe_3C almost perfectly matches the lattice of graphite, indicating that carbon atoms moving from the lattice of Fe_3C to the lattice of graphite is easier than that from Ni to graphite. Consequently, the energy barrier for the precipitation of carbon on the surface of Ni is higher than that needed for precipitation on the surface of Fe_3C, which leads to a lower carbon precipitation rates in Ni-alloys[7].

Sulphur addition: It is also generally accepted that sulphur additions into the process gas can inhibit or delay the incubation of metal dusting damage on metal surfaces. Sulphur (S) deactivates metal surface catalytic activity and prevents carbon ingress and graphite nucleation by stabilising carbide structures formed. Nevertheless, S presence is mostly unwanted due to its impact on the activity of the steam reforming catalyst[4,8].

Gas composition: Most studies described in the literature indicate that metal dusting is only driven by carburisation. Nevertheless, syngas in real plants is far more complex than laboratory metal dusting experiments. Steam (oxygen potential) in syngas mixtures is playing a major role in metal dusting. Consequently, metal dusting should not only be considered as

Fig. 3: **Metal dusting damage in transition area of a "hot" collector design**



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a catastrophic carburisation, but as an active corrosion mechanism where both carbon and oxygen play a role in material degradation[8].

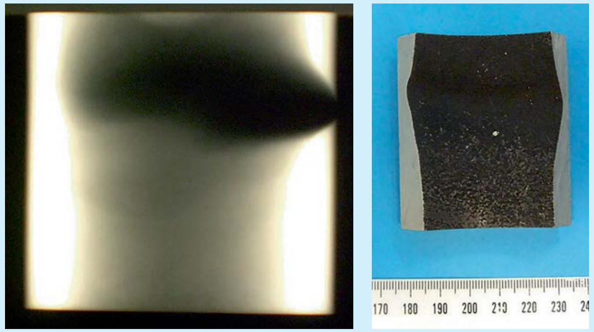
In industrial plants, the gas composition often remains relatively constant, and equipment suffering metal dusting corrosion is exposed to non-equilibrium gas. Areas where process gas becomes stagnant are more susceptible to metal dusting corrosion damage as in these areas, gas composition is most likely to shift to CO generation, increasing gas carbon activity[9].

Metal dusting attack on steam reformer components

Metal dusting damage is not a problem for "hot" steam methane reformer components (SMR) like reformer tubes and outlet manifolds. Metal temperatures are either much higher than the equilibrium temperature of carbon deposition reactions (Boudouard reaction) or much lower on the metal shell of refractory-lined outlet manifolds (cold collectors).

"Cold" outlet manifold designs are in principle more prone to suffer metal dusting corrosion damage. Problematic areas for metal dusting corrosion are located between "cold" and "hot" zones (see Fig. 2), like transition areas from the hot reformer tubes to refractory-lined manifolds or cold collectors. In such transition areas (see Fig. 3), metal temperatures might reach a critical temperature of 600°C. Modern "cold" outlet manifold designs make extensive use of a refractory lining system to maintain metal temperatures well below 450°C. Nevertheless, metal dusting corrosion issues still take place in such designs. Refractory components suffer deterioration over time, requiring inspection and maintenance to ensure they remain capable of controlling metal temperatures. Excessive thermal cycling also affects refractory components on a larger scale than metallic ones, opening cracks and cavities between refractory lining and metal components, leaving stagnant gas zones where tube metal temperatures reach the critical range of 600°C and the stationary gas is more aggressive due to CO enrichment. Consequently, initial pitting takes place on these metal surfaces. Further process gas recirculation increases the incidence of metal dusting corrosion on affected surfaces. Some designers are considering high Ni-Cr materials (like Schmidt+Clemens' Centralloy® ET 45 Micro), to minimise metal dusting damage incidence on these critical transition zones.

Fig. 4: **Radiographic inspection of metal dusting affect areas**



Source: Schmidt+Clemens Group

Although "hot" outlet manifold systems are in principle less susceptible to metal dusting damage, some designs may experience such corrosion damage in transition areas, as shown in Fig. 3. Critical areas for metal dusting damage are transition zones where temperatures might reach the critical metal dusting range and gas flow restrictions could lead to metal dusting damage incubation. Although actual design is intended to prevent these critical points, process issues like refractory deterioration could leave some gaps, as illustrated on Fig.3, between the insulating refractory and the tube metal surface. Lack of insulation of these transition areas, leads to an increase in tube metal temperature, approaching the critical temperature of 600°. Gaps created between the refractory and tube are filled with a stationary process gas. Since gas recirculation rate is relatively limited, it becomes more aggressive due to CO enrichment. Both effects combined promote metal dusting damage incubation. In many cases, end users are not aware of this damage incubation until the part fails due to corrosion damage. Replacing tube material with more resistant high Ni-Cr alloys might mitigate the incidence of metal dusting damage in these transition zones. Design modifications, re-designing these critical areas, could also minimise metal dusting in such specific cases.

Damage awareness is complicated due to the relative complexity of these transition areas. The presence of refractory insulation complicates access to metal surfaces, as these refractories may not be easily removed and inspection work could induce further damage on them, increasing the risk of metal dusting damage. Non-destructive inspection techniques (NDT), like radiography and ultrasonic inspection, can be used to assess metal dusting damage presence within these transition areas, without the need to perform more complicated operations (see Fig. 4). Frequent maintenance of critical insulation components, helps to minimise metal dusting occurrence on steam reformer transition zones.

Schmidt+Clemens experiences in metal dusting corrosion

Process gas heaters (PGH) in the direct reduction of iron, suffer from severe metal dusting damage. For such applications high chromium and nickel cast alloys, like Centralloy® ET 45 Micro, provide excellent corrosion and creep resistances. Schmidt+Clemens has also supplied high Ni alloys for steam reformer components (SMR) suffering from metal dusting corrosion damage, replacing standard cast tube materials, like alloy Centralloy® G4852 Micro. Based on Schmidt+Clemens' extensive experience, sufficient metal dusting resistance can be achieved if the following criteria are met:

- High chromium contents (>25 wt-%) are required in order to form fully protective an stable oxide layers. Lower contents might not be able to provide enough resistance for more demanding applications.
- Presence of other additions like Si, Mn and Al could improve the formation of stable oxide layers. Additions of selected rare earth elements would enhance oxide layer adhesion, thus increasing metal dusting resistance.
- High Ni contents reduce inward diffusion of carbon into alloy material. Consequently, protective alloy effect is strongly favoured, as well as high temperature resistance.
- Sulphur (S) additions in the range of 35-50 ppm delay incubation of metal dusting damage. Carbide decomposition in metal dusting atmospheres is effectively retarded by the presence of S, while coke formation might be delayed. Unfortunately, process gas "contamination" with S additions is undesired on steam reforming applications, due to catalyst deactivation issues.

Table 1: **Centralloy® ET 45 Micro nominal alloy composition**

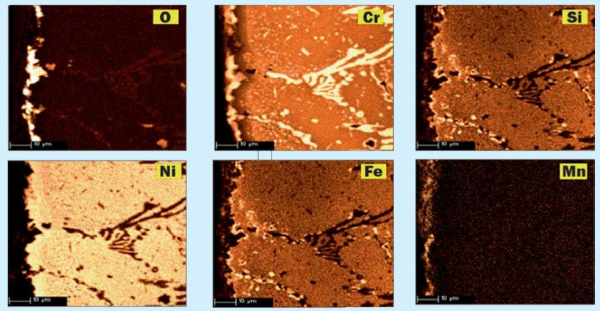
Centralloy® ET 45 Micro	C	Si	Mn	Cr	Fe	Nb	Ti	Zr	Ni	Rare earth elements
Mass Percent.	0.45	1.60	1.00	35.0	16.0	1.00	Add	Add	Bal	Add

Source: Schmidt+Clemens Group

Centralloy® ET 45 Micro is a high alloyed nickel base material consisting mainly of a Cr-Ni-Fe-Si matrix (see Table I). High chromium level, rare earth additions and primary carbide formation provide the best compromise between good high temperature corrosion resistance and high temperature creep rupture strength, offering a superior metal dusting resistance than standard reformer tube material Centralloy® G4852 Micro (25Cr35NiNbTi) (Table 1).

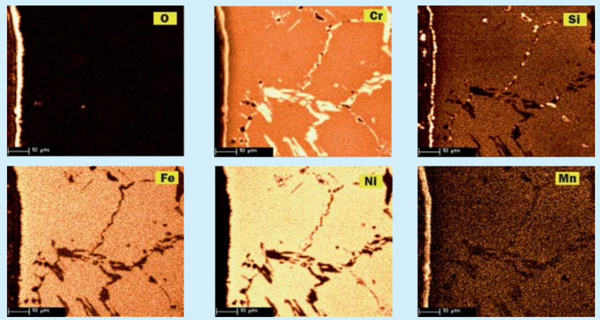
Alloy ability to maintain a protective and stable oxide layer under metal dusting conditions is the main barrier to prevent material corrosion[4,6,7,8]. Once this protective oxide layer is penetrated, lower diffusion of C within material can delay the incubation of metal dusting damage. Superior corrosion resistance of alloy Centralloy® ET 45 Micro versus alloy Centralloy® G 4852 Micro is summarised on the following SEM images (see Figs 5 and 6), exhibiting more protective oxide layers after several corrosion cycles. While Centralloy® ET 45 Micro alloy is capable of maintaining a fully protective oxide layer after these corrosion cycles, alloy G 4852 Micro was unable to maintain a protective oxide layer under the same aggressive conditions, showing unprotected metal surfaces that could incubate metal dusting damage.

Fig. 5: **SEM mapping of a G 4852 Micro alloy after several corrosion cycles**



Source: Schmidt+Clemens Group

Fig. 6: **SEM mapping of an ET 45 Micro alloy after several corrosion cycles**



Source: Schmidt+Clemens Group

Schmidt+Clemens has worked in a research programme at TNO Science and Technology Research Centre (Netherland), studying the incidence of metal dusting corrosion on typical alloy materials used for high temperature applications. As an example, a comparative corrosion test between alloys Centralloy® ET 45 Micro and G4852 Micro is presented. Samples of both alloys were exposed to a typical metal dusting gas at 600°C and 9 bar, with the following gas composition: 10% CO, 2% H_2O, 4% CO_2 and 76% H_2 (a_c = 226).

Centralloy® G4852 Micro samples were pre-oxidised in order to form a protective oxide layer and indications of metal dusting corrosion damage were detected after 24 hours of exposure. After 1,500 hours of exposure, severe pitting was detected (pit depth up to 300 μm) as illustrated in Fig. 7, with relevant mass loss after this exposure.

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Pre-oxidised Centralloy® ET 45 Micro (see Fig. 8) exposed to this highly corrosive atmosphere for 1,500 hours of exposure, showed carburisation related with carbon ingress into alloy material, but no pitting or mass change was measured. Consequently, higher Ni and Cr alloyed material offer a superior metal dusting corrosion resistance that less alloyed elements.

Conclusions

Transition areas from "hot" to "cold" metal surfaces are susceptible to exhibit metal dusting corrosion damage. Methane steam reformer component designs tend to minimise incidence of metal dusting corrosion by avoiding metal exposure to temperature ranges where high rates of metal dusting corrosion damage occur. Use of refractory insulation components, keep metal temperatures below critical metal dusting zones. However, poor maintenance or deterioration of insulation components could lead to part failure due to corrosion damage. Subsequently, metal dusting related failures in steam reformer components still take place nowadays.

Frequent inspection and maintenance of critical areas where metal dusting damage might take place, could minimise appearance of such corrosion damage. Non-destructive techniques, can help the inspection of critical areas where access to the metal surface is complicated or restricted.

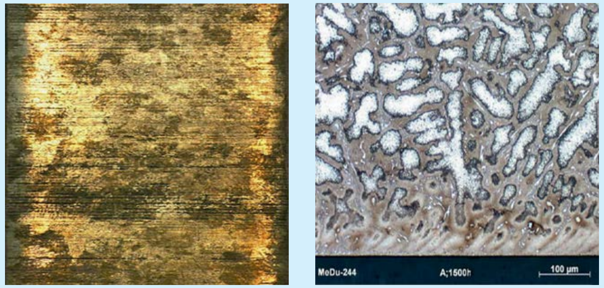
In specific cases, where metal dusting damage incidence cannot be avoided easily, replacement of standard steam reformer materials like 25Cr35NiNbTi (HP-Nb) with more resistant 35Cr45NiNbTi (Centralloy® ET 45 Micro) materials, helps to minimise metal dusting damage extent. Metal dusting corrosion damage in high alloy steels takes place due to the presence of defects or damages on protective oxide layers allowing transfer and dissolution of carbon into the metal phase. High chromium contents, help to maintain strongly protective chromium oxide layers. Additions of selected elements in our alloy Centralloy® ET 45 Micro enhance oxide layer adhesion, thus increasing metal dusting resistance

High Ni contents play a significant role in metal dusting, as Ni helps to reduce inward diffusion of carbon into alloy material. Alloy Centralloy® ET 45 Micro has a 45 wt-% nominal content of nickel. Consequently, protective alloy effect against metal dusting damage is strongly favoured, as well as high temperature resistance.

Fig. 7: **Metal dusting trials on alloy Centralloy® G 4852 Micro**

Source: Schmidt+Clemens Group

Fig. 8: **Metal dusting trials on alloy ET 45 Micro**



Source: Schmidt+Clemens Group

Centralloy® ET 45 Micro has been selected in several steam reformer designs, where higher metal dusting resistance was demanded.

Risk of metal dusting occurrence on steam reformer components can be minimised by identifying those transition areas where metal dusting incubation is favoured. Inspection/maintenance of these critical areas, including refractory insulation components, help to prevent unexpected metal dusting related failures. Specific cases where metal dusting damage cannot be easily avoided, might require upgrading existing alloy to more protective ones like our alloy Centralloy® ET 45 Micro.

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NITROGEN+SYNGAS
ISSUE 372
JULY-AUGUST 2021

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New heat exchanger allows operation below the acid dew point

To comply with stricter stack emission obligations, industries are required to recover more heat from flue gas and to clean it before it can be discharged into the atmosphere. **J. Kitzhofer** of APEX Group discusses the challenges and limitations of the majority of current heat recovery systems and reports on a new family of acid resistant tubular and plate-type heat exchangers developed by APEX Group that overcomes these problems. The new heat exchangers are resistant to dew point corrosion. The heat transfer elements are constructed from an acid resistant polymer composite with high thermal conductivity, allowing the design of new trouble-free heat recovery systems and the upgrade of existing systems to meet heat recovery and stack emission targets.

The current penalties imposed on greenhouse gas emissions are incentivising various industries to recover more heat from the flue gas and to clean it before it is discharged into the atmosphere. Heat recovery typically aims to increase the overall efficiency of the process by preheating the combustion air, which has a direct effect on reducing harmful emissions by reducing fuel consumption. Lowering the flue gas temperature is also an important factor for the overall efficiency of flue gas cleaning systems.

Industries have introduced new processes and are improving existing techniques at an accelerated pace with the objective to achieve clean air for a green environment for present and future generations. Industries which rely on fossil fuels have not been exempt from these developments. Although those industrial processes are already highly optimised for the reduction of emissions, there is still room for improvement. One area for improvement is the use of the remaining heat and the cleaning of the flue gas from hazardous components (e.g. SOx or CO_2).

A key limitation in the use of heat coming from fired heaters is found in the heat exchanger, in between the fired heater and the stack, namely the air preheater. The maximum extractable heat from the flue gas is typically defined by the minimum heat transfer surface temperature maintained above the acid dew point of the flue gas. Air preheaters are sometimes operated below the acid dew point, causing corrosion issues. Precautionary measures can be taken to extend the lifetime of the air preheater on such occasions, such as through expensive glass or polymer coating techniques applied to its sensitive metallic parts. Constant operation below the acid dew point will however cause severe corrosion issues for economical heat exchangers constructed from metallic materials. Emerging technologies for cleaning the flue gas like wet flue gas desulphurisation (WFGD), mercury recovery or post combustion carbon capture require operating with flue gas temperatures below the acid or water dew point.

Constant operation below the acid or water dew point requires a heat exchanger constructed from acid resistant materials at an affordable cost. Polymers are a category of materials that offer resistance to acids. However, the drawback of most polymers is their low thermal conductivity and the consequent thin wall thickness required for efficient heat transfer. This drawback results in a lower mechanical strength of heat transfer elements. A polymer composite overcoming this drawback is PPS-GR.

Acid condensation and subsequent corrosion

Flue gas consists of many condensable components generated during the combustion of air/fuel mixtures, such as H_2SO_4, HCl, HF, H_2O, CO_2, SO_2. In combustion technology, the sulphuric acid dew point, which has the highest temperature of all these dew points, is traditionally known as the acid dew point.

All sulphur contained in the fuel is converted to sulphur dioxide gas during combustion in the presence of oxygen:

$$S + O_2 \rightarrow SO_2$$

Only a small fraction of this sulphur dioxide is converted to sulphur trioxide. In the high temperature range, part of the sulphur dioxide reacts with atomic oxygen to form sulphur trioxide:

$$SO_2 + O \rightleftharpoons SO_3$$

At lower temperatures, an additional part of the sulphur dioxide reacts with molecular oxygen to form sulphur trioxide:

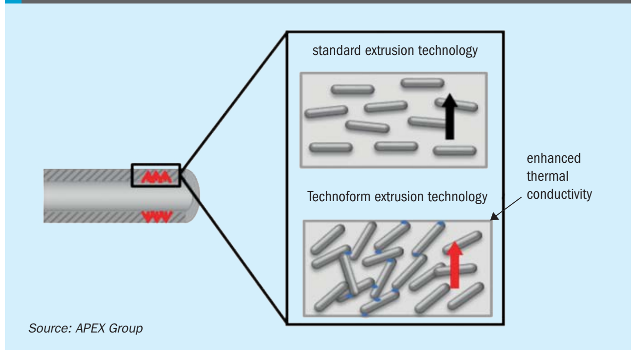
$$2SO_2 + O_2 \rightarrow 2SO_3$$

The conversion of sulphur dioxide to sulphur trioxide depends on many factors such as fuel sulphur content and composition, excess air, gas kinetics, combustion and mixing process, temperature and pressure in the system, flue gas residence time, presence of catalysts, soot, ashes, and other solid particles.

Fig. 1: **Corroded metallic APH**

SOURCE: APEX GROUP

Fig. 2: **Comparison of extrusion technologies**



Source: APEX Group

Sulphur trioxide has a high affinity for water molecules, and as the flue gas usually contains a large water vapour content (5-25 vol-%) virtually all SO_3 vapour combines with H_2O vapour to form H_2SO_4 vapour in the temperature range between 400°C and 200°C:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

At temperatures lower than the acid dew point, sulphuric acid vapour starts to condense as sulphuric acid liquid on the surface or on nuclei. Different models for the prediction of flue gas acid dew point temperature have been reported in the literature based on empirical and semi-empirical correlations, experimental analysis, neural networks, numerical analysis, etc. The acid dew point is a function of the partial pressure of sulphuric acid and the partial pressure of water. A well-known correlation for H_2SO_4 acid dew point is the one described by Verhoeff and Banchero.

Condensation of sulphuric acid

The flue gas enters the heat exchanger with a certain amount of sulphuric acid vapour at temperatures above the acid dew point. When the heat transfer surface temperature on the flue gas side drops below the acid dew point, sulphuric acid vapour condenses on this surface and builds a highly corrosive acidic film (liquid). Due to the condensation on the surface, the sulphuric acid vapour concentration of the flue gas decreases. The liquid film will grow over time. The rate of growth is dependent on the flow rate of sulphuric acid vapour, the capture efficiency of the heat exchanger and the material of construction of the heat exchanger. As soon as the flue gas bulk temperature falls below the acid dew point, sulphuric acid vapour starts to condense on solid particles (or nuclei) present in the flue gas, thus the condensation rate on the heat transfer surface decreases. A corresponding portion of sulphuric acid vapour remains in the gaseous state and is released as sulphuric acid vapour out of the heat exchanger. This is the portion of sulphuric acid vapour which determines the actual acid dew point of the flue gas at the heat exchanger outlet.

The lower the temperature of the condensate (attached to heat transfer surfaces or attached to solid particles), the more diluted the condensate is. Following the phase diagram for the binary mixture of H_2O-H_2SO_4 the typical acid concentration of the condensate is in range of 80% H_2SO_4 at the start of the acid condensation band down to about 50% H_2SO_4 at the end of the acid condensation band.

Depending on the process operating conditions, the sulphuric acid vapour content entering the heat exchanger is divided into three distinct portions at the outlet of the heat exchanger:

- sulphuric acid liquid on the surface;
- sulphuric acid liquid on nuclei;
- sulphuric acid gas in the flue gas bulk stream.

Fig. 1 shows a typical metallic heat exchanger constructed from carbon steel which corroded due to the operation of the heat transfer surface at temperatures below the acid and water dew point. It has been observed in the field that carbon steel corrodes at a rather high corrosion rate in water-diluted acids. In such conditions, stainless steels show better performance; however, these materials also suffer greatly from corrosion due to attacks by sulphuric acid condensate at temperatures close to its boiling point at concentrations above 50 wt-%.

The solution

To operate heat exchangers under the previously mentioned harsh conditions, APEX Group has developed an acid resistant heat exchanger constructed from heat transfer elements made of a composite known as PPS-GR. The PPS-GR-made heat exchangers have been successfully tested in the field, in applications such as a water/gas heat exchanger in a waste incineration plant, a gas/gas heat exchanger in a heat recovery system of a steel mill plant and in a water/gas heat exchanger of a heat recovery system in a biomass power plant. The PPS-GR composite consists of 30% polyphenylene sulphide and 70% graphite (a heat conductive filler), and thus features the chemical attack resistance of polymers and thermal conductivity close to that of metals. Due to the high thermal conductivity of

CONTENTS
What's in issue 372
COVER FEATURE 1
Ammonia as a fuel
COVER FEATURE 2
Syngas project listing
COVER FEATURE 3
Better alloys for metal dusting
COVER FEATURE 4
C0₂ to syngas

NITROGEN+SYNGAS
ISSUE 372
JULY-AUGUST 2021

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Fig. 3: **Left: tubular heat exchanger from PPS-GR material. Right: plate-type heat exchanger from PPS-GR material**

Source: APEX Group

graphite, the heat transfer walls can be designed thicker in order to ensure better mechanical strength, while at the same time overcoming the thermal resistance of the polymer. The high thermal conductivity of the composite results from the special extrusion technology, which allows a controlled graphite flakes arrangement oriented in the direction of the heat transfer flux as shown in Fig. 2.

APEX Group has integrated the PPS-GR material into its tubular and plate-type heat exchanger, see Fig. 3.

The cross flow tubular PPS-GR heat exchanger (Fig. 3, left) is custom made and can be designed to the customer's needs, e.g. in-line or staggered arrangement of tubes, variable tube diameters and variable tube lengths.

The plate-type PPS-GR heat exchanger (Fig. 3, right) is also custom made and provides an even greater flexibility in design. The heat exchanger can be arranged in cross flow, co-current or countercurrent flow (for highest thermal effectiveness), with variable process channel gaps and variable heat transfer plate thickness and dimensions. APEX Group's well-known APEX® Free-flow Technology is integrated in the PPS-GR plate-type heat exchanger to provide operation with low fouling and low plugging tendency.

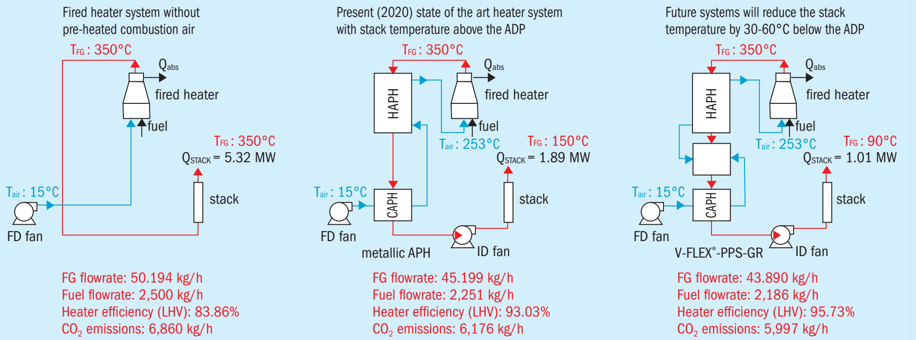
Applications

Air preheater for fired heaters

In industrial processes, heat exchanger systems are often applied as air preheaters for fired heaters, which constitute the process heart of oil refineries. For example, in syngas, ammonia, methanol and hydrogen plants, steam methane reformers (SMR) incorporate such air preheating systems. Due to the pre-heated combustion air, the efficiency of the combustion process is greatly increased. Overall, the installation of a heat exchanger as a part of a fired heater system considerably reduces the operational expenses (opex) and CO_2 emissions due to a lower fuel consumption.

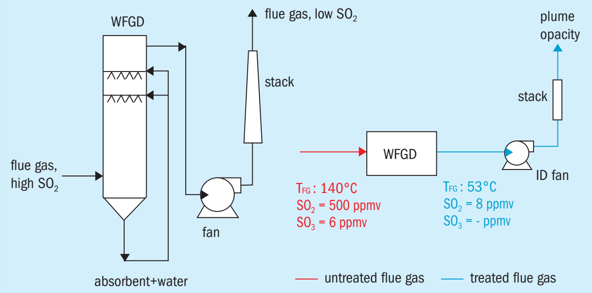
Fig. 4 shows three fired heater systems, with a variation in the stack temperature from 350°C to 90°C. The heat exchangers are traditionally designed to operate with minimum heat transfer surface temperature close to, but above the acid dew point (in the range of 120°C to

Fig. 4: **Fired heater systems: (left) with a stack temperature of 350°C, (centre) with a stack temperature of 150°C, (right) with a stack temperature of 90°C. All calculations based on required heat for the process of Qabs = 29.45 MW**



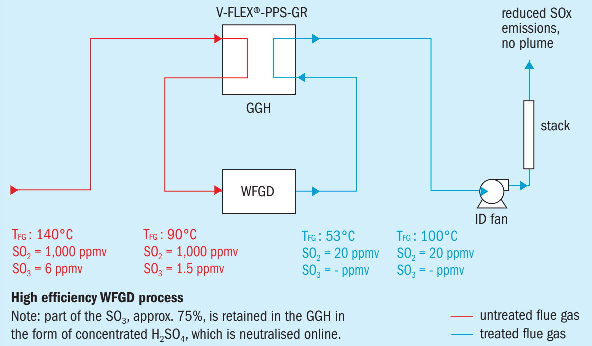
Source: APEX Group

Fig. 5: **Wet flue gas desulphurisation unit without heat recovery system**



Source: APEX Group

Fig. 6: **Wet flue gas desulphurisation unit with heat recovery system**



Source: APEX Group

140°C, resulting in a stack temperature of about 150°C) to avoid condensation of H_2SO_4 and as a result corrosion occurs on the heat transfer surface. Recently, driven by stricter stack emissions regulations, the air preheating system operators tend to further decrease the flue gas stack temperatures to as low as 90°C, to further increase the overall fired heater efficiency (e.g. 95.73% as shown in the example in Fig. 4) and to reduce the emissions. Flue gas temperature well below the acid dew point make the condensation of H_2SO_4 on the heat transfer surface of the air preheater unavoidable. The solution to this problem can be the installation of the PPS-GR heat exchanger modules in the "cold end" of the (existing or new) air preheating systems, or as a part of any other flue gas heat recovery or cleaning system.

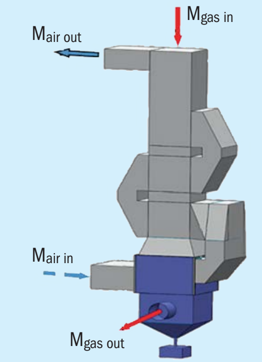
Gas-gas heat exchanger (GGH) for scrubbers

Scrubbers are used to clean the flue gas from harmful components such as Hg, CO_2, SO_2 and to a lesser degree SO_3. Fig. 5 shows a wet flue gas desulphurisation unit for cleaning the flue gas from SO_2. Flue gas enters the scrubber at 140°C, above the acid dew point. Cleaning is performed by, for example, spraying a water-lime mixture, after which the flue gas with reduced SO_2 content leaves the scrubber unit at 53°C.

Certain issues are known with this approach such as the required large water flow rate, formation of H_2SO_4 mist due to rapid cooling and consequent flue gas super saturation which greatly limits SO_3/H_2SO_4 retention in the system, and environmental restrictions with respect to the plume opacity.

The integration of a gas/gas heat exchanger made of PPS-GR composite overcomes these issues as illustrated in Fig. 6. A considerable amount of the SO_3/H_2SO_4 can be retained in the PPS-GR heat exchanger and the temperature difference between the inlet and the outlet of the WFGD scrubber can be decreased, which supresses the formation of H_2SO_4 mist in the WFGD scrubber itself. Furthermore, the temperature exiting the stack can be increased and thus plume formation can be eliminated. Additionally, the SO_2 removal efficiency of the WFGD scrubber is increased due to the lower flue gas temperature entering the WFGD unit (Fig. 6).

Fig. 7: **Heat recovery system with metallic heat exchangers in the hot part and PPS-GR heat exchanger in the cold end**



Source: APEX Group

Conclusion

Current limitations in cooling the flue gas below its acid or water dew point due to consequent corrosion issues can be overcome with the use of APEX Group's newly developed tubular and plate-type heat exchangers constructed from heat transfer elements made of the PPS-GR composite. PPS-GR presents field proven excellent chemical resistance to virtually any acid attack up to boiling temperatures, as well as good mechanical strength and thermal conductivity close to that of the metals. APEX Group heavy duty heat exchangers, capable of handling large volumes of gases, can be easily integrated into any kind of flue gas heat recovery or cleaning systems, such as air preheaters, mercury recovery, wet flue gas desulphurisation, post combustion carbon capture and similar, see Fig. 7. ■

NITROGEN+SYNGAS
ISSUE 372
JULY-AUGUST 2021

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Converting CO_2 to valuable synthesis gas

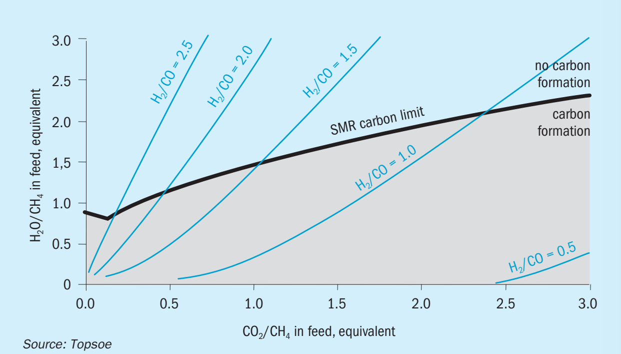
M. Østberg and **M. Rautenbach** of Haldor Topsoe describe ReShift™ technology, a new high temperature CO_2 reforming process, where preheated CO_2 is added directly downstream of a main reformer and then equilibrated in an adiabatic reactor. This new technology makes use of the high temperature of the reformer effluent to circumvent carbon formation, while at the same time maintaining an overall minimum steam to hydrocarbon carbon ratio, depending on process specific conditions. An increase in the amount of CO_2 added to the process will result in an increased fraction of CO in the produced synthesis gas. Synthesis gas with H_2/CO ratios in the range 0.5-3 can be produced. These CO-rich gases are typically utilised in the production of functional chemicals and synthetic fuels.

Important bulk chemicals such as hydrogen, ammonia and methanol are produced in a multiple step process. The first step is typically conversion of natural gas, or a similar feedstock, to produce hydrogen or synthesis gas (a mixture consisting of mainly hydrogen and carbon monoxide). This is followed by the actual synthesis and purification. The synthesis gas production step is often carried out by reforming of the feedstock with mixtures of steam and carbon dioxide (henceforth referred to as CO_2 reforming).

CO_2 reforming is an environmentally interesting process as it offers a way of utilising CO_2, which is a polluting greenhouse gas, and in many industries often considered as a waste product. CO_2 reforming is a process which can be designed with overall negative CO_2 emissions, or in other words can be designed to utilise more CO_2 than what is emitted. It is therefore expected to play an important role in combination with CO_2 capture technologies.

The technology presented in this article is a promising solution within the area of CO_2 utilisation, converting CO_2 to valuable synthesis gas with a high content of CO, but without the traditional limitations requiring large amounts of steam addition. It can be used to retrofit an existing unit for more CO production or included in new projects and is an excellent match in cases where excess CO_2 is available.

Fig. 1: **Carbon limits for steam / CO_2 reforming at a pressure of 25.5 barg and exit temperature of 950°C**



Source: Topsoe

The CO_2 reforming reaction (1), also referred to as dry reforming, is an ideal way to obtain a 1:1 ratio of hydrogen and carbon monoxide in the product synthesis gas. Obtaining a catalyst that would enable dry reforming has therefore always been pursued by the scientific community. However, formation of carbon by any of the given reactions (2)–(4) remains a challenge.

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2O \quad (1)$$

$$2CO \rightleftharpoons C_{(s)} + CO_2 \quad (2)$$

$$CH_4 \rightleftharpoons C_{(s)} + 2\,H_2 \quad (3)$$

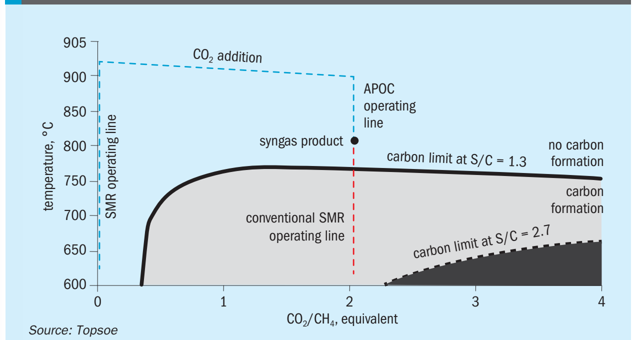
$$CO + H_2 \rightleftharpoons C_{(s)} + H_2O \quad (4)$$

Some catalyst systems have allowed for operation inside the traditional carbon forming area using, for example, noble metal catalyst or sulphur passivation (the SPARG™ process), but carbon formation has remained an issue and addition of steam a necessity. Therefore, CO_2 reforming will always occur together with steam reforming (5) and water gas shift, or in the case with addition of large amounts of CO_2, reverse water gas shift (6).

$$CH_4 + H_2O \rightleftharpoons CO + 3\,H_2 \quad (5)$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad (6)$$

Fig. 2: **Illustration of the ReShift™ process approach**



Source: Topsoe

Looking at a traditional reforming process with CO_2 addition, the operation window as limited by carbon formation is shown in Fig. 1. Here it is indicated that the lowest allowable H_2O addition is around 0.8 (illustrated as H_2O to C ratio, with all hydrocarbons as CH_4, i.e. S/C). As more CO_2 is added, more steam is required. So, if the desired product is a syngas with H_2:CO ratio of 1, it is necessary to operate with a S/C ratio of at least 2 and an addition of CO_2 corresponding to a CO_2:CH_4 ratio of about 2.4. Usually, some safety margin is added for process fluctuations, feed variations etc. and therefore the industry applied steam and CO_2 additions will be higher.

The ReShift™ technology introduced by Haldor Topsoe is a new process approach to achieve a CO-rich synthesis gas, while operating at lower S/C and with less CO_2 addition without getting into the carbon formation area dictated by thermodynamic affinity as graphite, meaning that it is a process wise very safe approach.

Introducing the ReShift™ process approach

In this new process approach being introduced to the market, it is made possible to keep a low S/C ratio by introducing the CO_2 to the process after the main part of the steam reforming has occurred and a high temperature syngas has been obtained (at this point still with a high H_2:CO ratio). This is illustrated in Fig. 2, which shows the operation line of a steam reformer (SMR) operating at S/C 1.3 with an exit temperature of 920°C. At this point, preheated CO_2 is mixed with the product gas from the SMR and the mixed process gas is equilibrated in an adiabatic reactor, named an adiabatic post converter (APOC), producing the final syngas with a low H_2:CO ratio (CO-rich).

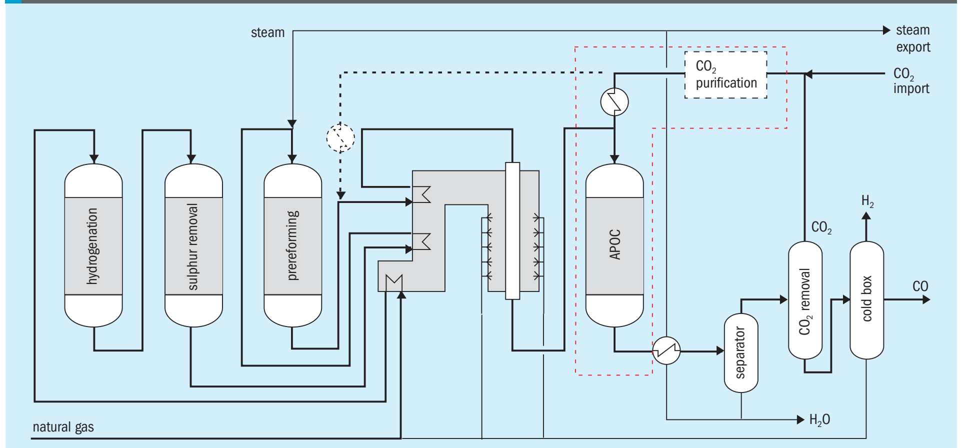
To produce the same synthesis gas in the traditional way by mixing the CO_2 upstream of the SMR, it would require a S/C ratio of 2.7 to avoid carbon formation.

The lay-out shown in Fig. 3 indicates by means of the dashed line, the changes required compared to a traditional synthesis gas unit based on tubular reforming. All it requires to introduce the ReShift™ process is the APOC reactor, with the addition of high purity, preheated CO_2. This enables introduction of the ReShift™ for revamps of existing plants with a possibility to expand the capacity with increased CO production.

Features of the APOC

A core element in the ReShift™ technology is the APOC (Fig. 4). This has been designed based on industrially proven technology. The catalyst used is a nickel-based catalyst, working as a hybrid between

Fig. 3: **Process lay-out of a ReShift™ synthesis gas unit**



Source: Topsoe

CONTENTS
What's in issue 372
COVER FEATURE 1
Ammonia as a fuel
COVER FEATURE 2
Syngas project listing
COVER FEATURE 3
Better alloys for metal dusting
COVER FEATURE 4
C0₂ to syngas

NITROGEN+SYNGAS
ISSUE 372
JULY-AUGUST 2021
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a traditional tubular steam reforming catalyst and a secondary / autothermal reforming catalyst, with more activity than the high temperature catalyst, but keeping the thermal robustness of these catalysts. The high temperatures require a refractory-lined reactor similar to the well-known secondary reformers.

The last important feature is the outlet flow distributor, not trivial to the design of a fixed bed reactor operating at these high temperatures. Also here features of the industrially proven Topsoe SynCOR™ technology are used. As for secondary reactors, the footprint of the APOC is limited compared to the associated tubular reformers.

The conversion in the reactor will be a combination of methanation (reverse steam reforming) and reverse water gas shift reaction (rWGS), having the methanation dominating the upper part giving a slight temperature increase because of the highly exothermicity of this reaction. Subsequently, the rWGS will take over leading to an overall temperature decrease in the reactor. Besides the production of CO from CO_2 and H_2, a slight increase of CH_4 also takes place.

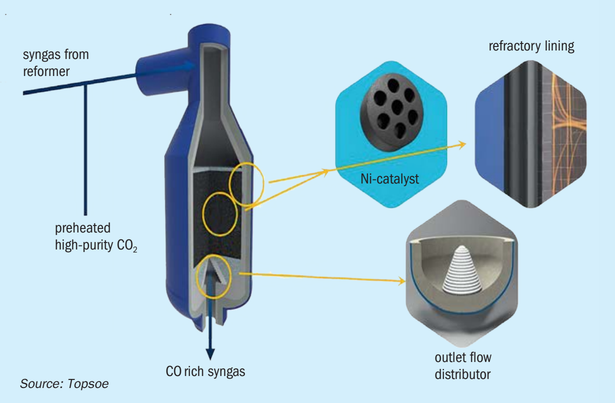
Advantages of the ReShift™ technology

The ReShift™ technology introduces the possibility to make a CO-rich synthesis gas based on a tubular reforming step operating with an absolute minimum steam to carbon ratio, while at the same time having no affinity for forming carbon according to any of the given reactions (2)–(4). The process uses traditional nickel based catalyst and all features of the additional reactor are industrially proven in secondary or autothermal reactors.

The steam addition to the tubular reformer can be significantly reduced, either resulting in a smaller tubular reformer or a possibility to increase capacity. CO_2 import is needed and as the energy needed for the tubular reforming in terms of fuel requirements are reduced at the same time, this also gives lower overall CO_2 emissions from the plant, as emitted through the flue gas.

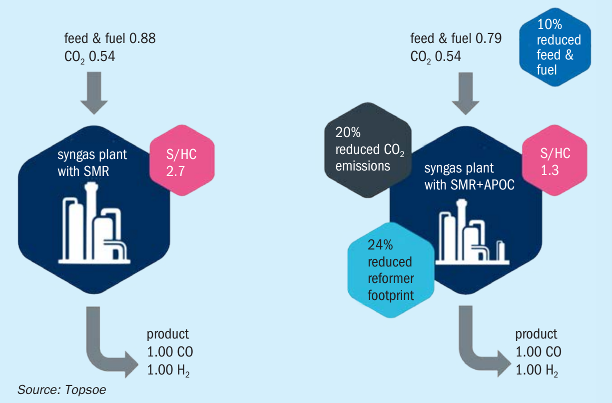
To make a 1:1 H_2:CO ratio syngas, the amount of feed + fuel can be reduced by 10%, producing the same amount of syngas. The reformer footprint can be reduced by 24% or a similar capacity expansion can be achieved (Fig. 5).

Fig. 4: Features and sketch of the APOC reactor



Source: Topsoe

Fig. 5: Advantageous of the ReShift™ technology



Source: Topsoe

Conclusions

It has been the objective of this article to present the advantages of the new ReShift™ technology offered by Haldor Topsoe if a CO-rich synthesis gas is desired. The technology is based on introducing an adiabatic post converter (APOC), equilibrating a low CO containing syngas, after mixing with preheated CO_2, to produce a CO-rich product. All elements of the APOC stem from industrially proven technology.

> "Significant savings on feed + fuel are possible, reducing the CO_2 emissions from the plant.

The technology is available for both new builds and revamps of existing plants, for now mainly focusing on tubular reformers. It enables significant reduction of the steam to carbon ratio of the main reformer and is a great fit where import CO_2 is available. Significant savings on feed + fuel is possible, thereby reducing the overall CO_2 emissions from the plant.

As the APOC reactor is compact compared to a tubular reformer, the overall footprint of the reforming section itself is also significantly reduced which is an advantage especially in revamp cases. ■

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