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IMPORTANT INFORMATION:

Number 390
July | August 2024

nitrogen+syngas

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Low carbon ammonia

Ammonia Safety Symposium, San Diego

Urea technology showcases

Primary reformer materials of construction

NITROGEN+SYNGAS
ISSUE 390
JULY-AUGUST 2024

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Cover: San Diego, California, USA
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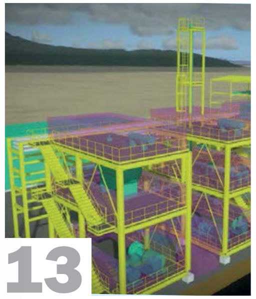
Ammonia safety

Safety considerations for maritime use



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Urea technology

Small scale urea plants

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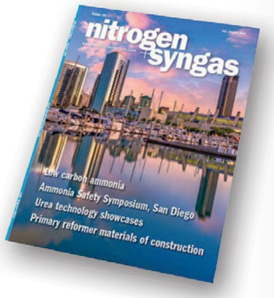
Gas is still the key



> "The good news is that the LNG market remains in robust health..."

With all of the focus on low carbon ammonia and methanol developments, one could occasionally be forgiven for forgetting that most of the syngas industry relies upon natural gas as a feedstock, and that gas pricing and availability remain the key determinants of profitability for producers. As our article this issue discusses, even low carbon ammonia is likely to be largely based on natural gas, albeit with carbon capture and storage, at least for the remainder of this decade.

The gas industry has continued to grow inexorably over the past few decades, from a series of regional markets to an increasingly global market, thanks to the massive rise of gas shipping as liquefied natural gas (LNG). This week saw the publication of the International Gas Union's 2024 report on the state of the LNG industry, and it makes for interesting reading.

The United States became the largest exporter of LNG last year, at 84.5 million t/a, up 10% on 2022, outpacing Australia, which in turn had outpaced Qatar as the leading exporter a few years ago. These three countries now account for 60% of all LNG exports between them, and adding Russia and Malaysia takes that figure to three quarters of the LNG market. On the demand side, the destination remains mainly Asia; China, Japan, Korea and India collectively take just over half of all shipments, but Europe now receives 30% of LNG cargoes, as it tries to pivot away from the pipelines from Russia that it had previously relied upon. Indeed, the US – Europe route is now the single busiest for LNG tankers.

Pricing meanwhile seems to have comprehensively decoupled from oil indexation, and fell below \$8.00/MMBtu for the Japan/Korea benchmark in February this year, after a much more subdued winter price rise for 2023-24 than the price spikes seen the previous year. The price of LNG remains of vital interest to the ammonia industry as European and Indian gas pricing is dominated by LNG markets, and these two regions represent the floor price for ammonia at present.

The good news is that the LNG market remains in robust health. As of February this year, the IGU reports that 216 million t/a of new capacity is under construction or has achieved financial closure, of which around half is in North America. The continuing cheapness of US gas makes it an ideal source of LNG. In theory that should also make it an ideal producer and exporter of ammonia, but capital costs, permitting issues and the need for carbon capture or other lower carbon technologies have slowed the pace of development there.

Floating LNG production rigs also continue to be popular. While only 12.7 million t/a of FLNG plants are currently operational, another 100 million t/a is under construction or development, over 90% of it in the US, adding operational flexibility to LNG production. Europe is also looking to floating regasification terminals as a way of rapidly boosting LNG import capacity.

All of this activity – in theory! – makes for a more stable and lower gas cost market, after the rollercoaster ride of the past few years. However, the report acknowledges that the main risks to its forecast remain political. ■

Richard Hands, Editor

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Price Trends

Ammonia markets were quiet in June, though both CF Industries and Grupa Azoty were reported to be looking for July tonnes and the enquiry will test how tight the market is going forward. Algeria has traded in the $400-405/t f.o.b. range, suggesting c.fr values in Europe might be slightly higher at $450-460/t c.fr. Supply from Algeria has been and continues to be somewhat restricted because of constraints caused by the hot weather. Gas supply however is easing in Egypt and further ammonia exports should emerge shortly.

The Middle East still awaits the return of one of Ma'aden's ammonia units which is down for a turnaround but a reduction in price in the region suggests the supply position is easing from recent tightness. PIC sold a parcel to the Far East at $330/t f.o.b. following recent sales as high as $360/t f.o.b.

Indonesia still appears to be without spot tonnes and traders believe little will emerge in July. Malaysia also has little to offer and is focused on term deliveries. The market was expecting the Tampa price to emerge at time of writing, and some anticipated a rollover from the $400/t f.o.b. agreed for June. The more bearish participants however point to the weaker domestic market in the US and in particular the aggressive fill program announced 20 June by Koch.

Trinidad saw natural gas curtailments of at least 37% from the beginning of June, with the impact on ammonia production set to vary by supplier. Yara's Tringen I plant was reported to be fully offline during the gas curtailment period, with the Tringen II unit also shutting down briefly due to a power outage. Trinidad exported 290,000 t of ammonia in May, up from 260,000 tonnes in April. Caribbean export prices were pegged at around $360/t f.o.b.

The urea market seems to be looking for a catalyst to hold current f.o.b. levels or to push the market higher. There is a definite air of softness in the market as buyers generally sit on the sidelines. Much of the speculation has centred around Egypt, which shut down several plants during June due to gas supply curtailments. Supply was restored towards the end of the month, and most plants returned to production. With about 200,000 tonnes of exports estimated by some traders to be fulfilled from earlier sales, producers in Egypt may not be pressurised to enter the export market until July. This may have triggered one producer to offer tonnes as high as $365/t f.o.b. Traders were apparently selling top-off tonnes for vessels already scheduled into Europe at $350-355/t f.o.b. netback.

Brazil has seen slightly lower levels with sales reported at $360-$370/t c.fr but numbers as low as $350/t c.fr reflect just buyer bids. There is however said to be a heavy line up of unsold tonnes. Argentina traded up to $390-395/t c.fr, but buyer interest has now faded and some traders believe numbers may have to fall to $375/t c.fr to secure fresh interest. Mexico remains on the sidelines waiting for rain and some readjustment in the price.

India's urea sales climbed 10% in May to 2.13 million tonnes. Production declined 3% to 2.57 million tonnes and urea imports fell 18% to 344,000 tonnes. ■

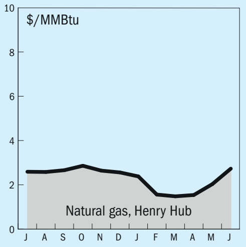
Table 1: **Price indications**

Cash equivalent	**mid-Jun**	**mid-Apr**	**mid-Feb**	**mid-Dec**
Ammonia ($/t)				
f.o.b. Black Sea	n.m.	n.m.	n.m.	n.m.
f.o.b. Caribbean	360	435	395	475-575
f.o.b. Arab Gulf	320-330	270-300	270-350	470
c.fr N.W. Europe	450-460	460-470	470-480	535-545
Urea ($/t)				
f.o.b. bulk Black Sea	340-350	250-260	300-320	273-290
f.o.b. bulk Arab Gulf*	280-350	275-290	345-352	298-302
f.o.b. NOLA barge (metric tonnes)	300	285-305	355-360	330-334
f.o.b. bagged China	n.m.	300-310	330-335	360-370
DAP ($/t)				
f.o.b. bulk US Gulf	550-570	550-570	550-570	560
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	260-265	230-240	255-260	309-310

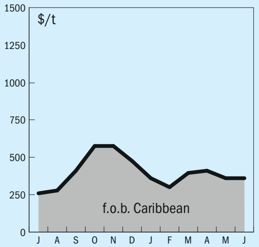
*Notes: n.a. price not available at time of going to press. n.m. no market. * high-end granular.*

END OF MONTH SPOT PRICES

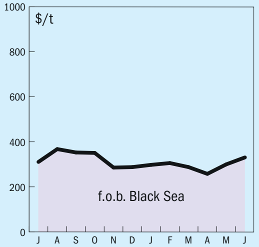
natural gas



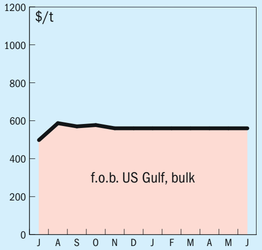
ammonia



urea

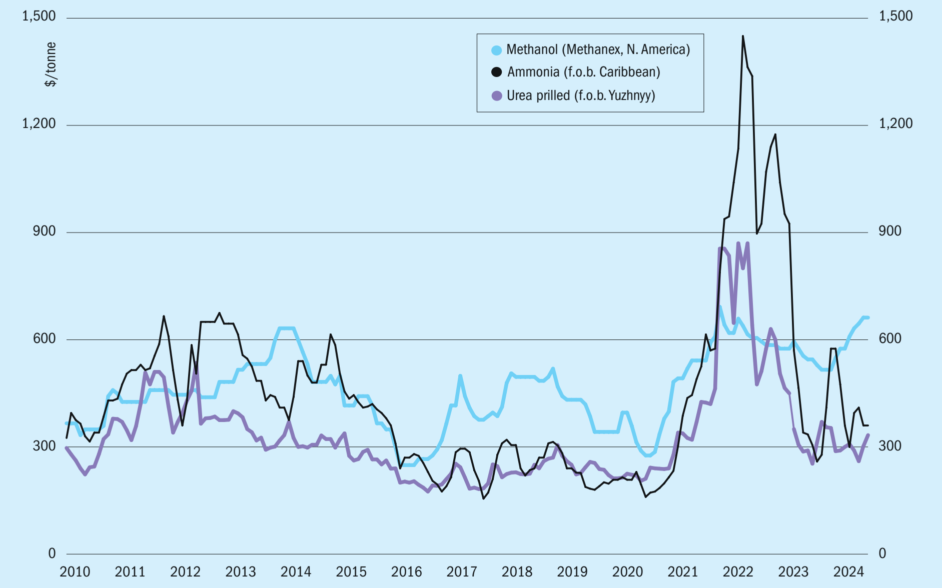


diammonium phosphate



Market Outlook

Historical price trends $/tonne



Source: BCInsight

AMMONIA

- Prices in the Eastern Hemisphere, whilst still flat-to-firm, do not appear as supported as they have been over the past month, whilst indexes. There are still no signs of softening in the Far East although demand remains underwhelming and supply improving. While production in Indonesia is said to be back up and running, traders do not expect any spot cargo to emerge in July other than possibly some small part cargoes. August could see spot offers.
- India could see higher prices as there is still demand to be covered. The resolve of suppliers West of Suez should be tested next week in Europe and when the Tampa price should also be settled for July.
- West of Suez look balanced for the time being, with regional supply issues seemingly counteracted by a lack of demand.

UREA

- Urea prices have been firmer in June due to supply-side issues, in China, Egypt and to a lesser extent Indonesia. Demand for July tonnes should in theory keep prices firm, but the market has been nervous of committing too far forward.
- The next tender from India is expected to signal the direction that the market takes. In the absence of supply from China, which is facing government restrictions, prices are likely to move higher to cover an Indian tender.
- However, if Indian buyers hold off, buyers in Latin America and Europe could see lower numbers. This slide was already apparent in Brazilian prices towards the end of June.
- There is also speculation that India may buy more urea to compensate for an apparent shortage of DAP. RCF has twice tendered for 100,000 tonnes of DAP at the end of June and start of July.

METHANOL

- US methanol pricing remained robust, driven by increased demand from downstream derivative industries. The delayed start-up to Methanex's Geismar 3 plant in Louisiana, due to refractory issues in the autothermal reformer, and its pushback to Q3 2024, has also curtailed expectations for abundant supply, particularly affecting exports to major markets like South Korea and China. Other shutdowns, including gas supply curtailments in Trinidad, have also contributed to a tight market in the Americas.
- In Asia, Methanex methanol, increased its Asian contract price (ACP) for June 2024 by $20 month-on-month to $420 per ton, the highest since March 2023.
- Egypt was also affected by gas supply curtailments, with Methanex idling its 630,000 t/a plant. However, lacklustre demand in Europe has kept prices relatively flat there. ■

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Nitrogen Industry News

UNITED STATES

Hanwha and INEOS looking at blue ammonia plant

Hanwha Corporation and INEOS Nitriles have announced their intention to collaborate in a study for a new low-carbon ammonia facility with carbon sequestration in the USA, with a capacity of more than 1 million tonnes per annum. The location of the plant is yet to be determined. The two companies have agreed heads of terms, under which Hanwha and INEOS will jointly explore the feasibility of a facility to meet the growing global demand for ammonia with low-carbon emissions. A final investment decision is planned for 2026 with planned commercial operation in 2030.

Hans Casier, CEO of INEOS Nitriles said: "This project is a potentially important contributor to INEOS Nitriles' carbon emission reduction targets in 2030 and its net zero ambitions by 2050. This project would be a significant step towards a leadership position in low-carbon Acrylonitrile supply of which ammonia with low-carbon emissions is a key raw material. INEOS positions itself to find solutions to the challenges the world is facing and is looking forward to achieving a net zero economy whilst both continuing to deliver products that are essential to society and remaining competitive."

Kiwon Yang, CEO of Hanwha Corporation added: "Our collaboration with INEOS Nitriles is aimed at strengthening our strategic foothold in the global ammonia market and addressing the growing worldwide demand for clean ammonia solutions. The production of industrial materials using clean ammonia aligns well with our commitment to key sustainability principles. This technological advancement will be a pivotal turning point in realizing Hanwha's vision for a sustainable future." ■

LSB to supply low carbon AN solutions

LSB Industries says that it has entered into an agreement to supply up to 150,000 st/a of low carbon ammonium nitrate solution to Freeport Minerals Corporation. LSB will supply the ANS from its El Dorado, Arkansas facility for five years, beginning on January 1, 2025, with a phasing in of the low carbon contracted volume.

LSB's low carbon product offering stems from the carbon capture and sequestration project that it currently has under way with its partner, Lapis Energy, who will capture and permanently sequester more than 450,000 t/a of CO_2 produced from El Dorado's ammonia production. The carbon sequestration is expected to result in more than 375,000 t/a of low carbon ammonia that LSB can sell or upgrade and sell to customers in the form of other low carbon nitrogen products, such as AN solutions. The project is expected to commence operations in 2026, pending approval by the Environmental Protection Agency of LSB and Lapis' Class VI permit application, which the companies expect to receive in the second half of 2025.

"This important agreement validates our belief that our industrial and mining customers will identify the low carbon nitrogen products that we plan to produce as an important part of their decarbonisation journeys and value them accordingly," said Mark Behrman, LSB's President and CEO. "We view this contract with Freeport as a major step towards attaining our vision of becoming a leader in the global energy transition and look forward to partnering with them as a strategic supplier as they advance toward their net zero aspiration."

INDIA

Coromandel to restart ammonia pipeline

The Southern Bench of the National Green Tribunal has ruled that Coromandel International Ltd can restart its offshore ammonia pipeline after obtaining a no-objection certificate from the Directorate of Industrial Safety and Health, and subject to approvals from the Tamil Nadu Maritime Board and Indian Register of Shipping. The company shut down its ammonia offshore pipeline activity, based on TNPCB's notice, after a gas leak on December 26th left Ennore residents with breathing difficulties, eye irritation, and vomiting, and led to hospitalisation of at least 54 people.

RUSSIA

Taman ammonia terminal begins commissioning

Commissioning work has reportedly begun at the TogliattiAzot terminal for transshipment of ammonia and fertilizers at Taman, according to a press statement by General Director Anatoly Shablinsky. TogliattiAzot has been building a terminal at the port of Taman since the early 2000s. The project was put on pause for several years, with construction resuming in 2015, but stalling again due to the unsettled issue of the land lease with the Krasnodar Territory and legal disputes regarding the recognition of ownership rights to real estate.

The construction project was revived in the summer of 2022 following the shutdown of the Yuzhnyy ammonia terminal in Ukraine. The Arbitration Court of the Krasnodar Territory ruled it illegal for regional authorities to refuse to transfer land plots at the port of Taman, where the terminal is being built, to federal ownership (facilities involved in the transshipment of explosive substances can only be built on federal lands). The head of the region and the Togliattiazot senior management subsequently signed a cooperation agreement.

Togliattiazot had previously indicated that the first stage of the ammonia terminal in Taman, with a capacity of up to 2 million t/a of ammonia, was planned for launch in December 2023. The second stage of construction is planned for 2024-2025, and will increase capacity to 3.5 million t/a of ammonia and 1.5 million t/a of urea. Commissioning of the export terminal will allow TogliattiAzot to once again reach full production capacity, which was reduced due to the shutdown of the Togliatti-Odessa ammonia pipeline in 2022. TogliattiAzot operates more than 3 million t/a of ammonia and 960,000 t/a of urea capacity.

QATAR

Supply agreement with Koch Fertilizer

QatarEnergy has signed a long-term urea supply agreement with Koch Fertilizer LLC. The 15-year supply agreement, starting in July 2024, stipulates the supply of up to 0.74 million t/a of urea to Koch Fertilizer. Under this agreement, urea of Qatari origin will be supplied into the agricultural sectors of the US and other international markets.

Saad Sherida Al-Kaabi, Qatar's Minister of State for Energy Affairs, and also President and CEO of QatarEnergy, said: "We are delighted to announce the signing of this long-term sales agreement with one of our valued partners, solidifying our longstanding relationship with Koch Fertilizer. This agreement marks a significant step in advancing synergy and cooperation and fostering mutual growth and value for both sides."

Mark Luetters, Senior Vice President of Koch Industries and President of Koch Fertilizer said: "QatarEnergy has been a cherished partner of Koch Fertilizer for more than a decade and we are thrilled to cement our mutually beneficial relationship for years to come. The agreement aligns with Koch Fertilizer's long-term vision and presents an exciting opportunity to better serve our customers."

This agreement highlights QatarEnergy's strategy in establishing longstanding relationships with reliable leaders of the Fertilizers industry and its commitment to support the global agricultural sector.

Koch Fertilizer LLC is a subsidiary of Koch Industries with fertilizer plants in North America, Trinidad and Tobago, and Morocco; and distribution facilities and terminals located in the U.S., Canada, Mexico, Brazil, Australia, and other international markets.

HUNGARY

Nitrogenmuvek debt rating lowered

S&P has lowered its rating of Hungarian fertilizer producer Nitrogenmuvek's debt from CCC+ to CCC. In a statement, S&P said that "the negative outlook indicates that Nitrogenmuvek faces mounting refinancing risks; in our view, the likelihood of a debt restructuring is rising and we could lower our ratings further if the company makes no progress on its refinancing plans." Nitrogenmuvek has yet to refinance its €200 million senior unsecured notes, due May 14, 2025, and S&P says it is concerned that "options for refinancing the notes could be constrained by the difficult economy" and "uncertainty regarding the progress of Nitrogenmuvek's litigation against Hungary's emission trading system (ETS) decree and the related CO_2 quota tax."

In response, the company says that it is "working on a number of options and structures to ensure a successful refinancing strategy, which we target at the time when we have good level of visibility in respect to the industry recovery and tax issue, which is expected in upcoming months." Zoltan Bige, chief strategy officer and son of owner added that the company has "an attractive level for funding liquidity" through its bond, and that Nitrogenmuvek is now focused on finding optimal solutions for short-term needs while handling challenges including local tax, volatile markets and industry under-performance. It also aims to support a long-term funding strategy, which includes further efficiency improvements and preparing for decarbonisation.

CHINA

China to suspend urea exports?

Ten key nitrogen fertilizer manufacturers, including Jinkong Equipment, Henan XLX, Hebei Dongguang, Linggu Chemical, Yuntianhua, Hualu Hengsheng, Hebei Zhengyuan, Shandong Ruixing, and Hubei Yihua, have jointly agreed an initiative to fully guarantee the supply of domestic spring ploughing nitrogen fertilizer and stabilise the sales price of nitrogen fertilizer in China. The companies have agreed to prioritise supplying the domestic market. Export orders will be suspended and the domestic market will be fully supplied. Furthermore, the companies have agreed that the ex-factory price of nitrogen fertilizer should not be allowed to rise higher than the level as of May 21st 2024.

SENEGAL

Feasibility study on new urea plant

Petrosen Trading & Services has completed a feasibility study into the construction of a 100,000 t/a ammonia-urea plant in Senegal. Commissioning is tentatively scheduled for 2029, according to state oil and gas company Société des Petroles du Senegal. The project would be run by the Senegal Fertilizer Company (SEFCO), and would aim to monetise gas discovered off the coast of Senegal in order to achieve self-sufficiency in urea and achieved higher value for the country's phosphate production via the formulation of NPK fertilizer blends. The plant would also supply fertilizer markets in the West African region, including Mali, Burkina Faso, Ivory Coast, and Ghana, as well as potentially Europe, the United States and Brazil, two of the largest importers of urea in the world. There has also been a parallel study focusing on the carbon capture potential of this plant, which assesses that it is possible to capture nearly 17 million tonnes of CO_2 over the 30 years of operation of the plant. The CO_2 captured could be reused in food preservation, the agri-food industry, or even construction, according to Société des Petroles du Sénégal.

GERMANY

BASF appoints seller for ammonia and methanol assets

BASF and International Process Plants (IPP), a global leader in the acquisition and sale of process plants and equipment, have entered an agreement to sell the ammonia, methanol and melamine plants at BASF's Verbund site in Ludwigshafen, Germany. The plants have become available as BASF implements structural measures at its Ludwigshafen site to ensure competitiveness in a changing European market environment, as announced in February 2023. BASF says that it will continue to produce ammonia and methanol in other assets at Ludwigshafen site. The two companies have agreed not to disclose financial details of the deal.

The agreement includes integrated production assets for ammonia (380,000 t/a), methanol (165,000 t/a) and melamine (51,000 t/a). IPP is offering these production units for relocation and sale to qualified buyers with projects for such assets who are looking for opportunities for lower capex and shorter project execution timelines.

"We are excited to add these world-class ammonia, methanol, and melamine plants to our portfolio of excellent plants for relocation," said Ronald Gale, President of International Process Plants. "These facilities represent a significant opportunity for companies seeking to expand their production capacity with existing assets that operate at a high level of energy and raw material efficiency. IPP is committed to finding a new home for these assets in a location with sufficient and economic gas supply or as part of a green ammonia or methanol project where they can continue to operate efficiently and productively."

"BASF is partnering with IPP on the divestment of the idled ammonia, methanol, and melamine plants to ensure that these well-maintained assets are sustained for chemical production. The units were in operation through 2023 and only shut down in the context of the

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structural adaptation of our production setup at the Ludwigshafen site. The sale represents a more sustainable and economic approach to the deployment of these production units, and with a net benefit to the global process industry," said Ruediger von Watzdorf, Senior Vice President Technology, BASF Monomers division.

BASF expands biomass-based portfolio

In addition to the above sales, BASF is also now offering 'biomass balanced' (BMB) ammonia and derivatives with a significantly lower product carbon footprint compared to conventional ammonia derivatives. Certified renewable raw materials replace fossil resources at the start of the production process, and renewable electricity is also used to further reduce production-related emissions. The range of products includes ammonia anhydrous BMBcert™, ammonia solution 24.5% BMBcert™, urea prills BMBcert™, 40% urea solution BMBcert™, and 45% urea solution BMBcert™. The mass balanced products are certified according to ISCC (International Sustainability and Carbon Certification) PLUS standards. These measures lower the product carbon footprint of these products by at least 80% versus the average PCF of conventional fossil ammonia derivatives without compromising on quality and performance. The certified products enable customers to reduce their Scope 3 emissions as well as the product carbon footprint of their products.

Ammonia cracking project

Heraeus Precious Metals has launched a research project called AmmoCatCoat, leading a consortium with five project partners to develop technologies for efficient and sustainable hydrogen production from ammonia. The project, with a total volume of around two million euros, is funded by the German Federal Ministry of Education and Research (BMBF) and will have a duration of three years. The other project partners are Fraunhofer ISE, the Leibniz Institute for Agricultural Engineering and Bioeconomy (ATB), the Centre for Transmission Electron Microscopy (CAU), PYREG GmbH, and Purem by Eberspächer, combining expertise in catalysis, biomass conversion, material characterisation, and surface treatment. The project aims for the practical demonstration of operation under real-technical conditions at the pilot plant scale.

"We are proud to lead such a strong consortium and together make a directional contribution to realizing the hydrogen economy," says Dr.-Ing. Konrad Krois, project manager at Heraeus Precious Metals, "I am convinced that with AmmoCatCoat we will succeed in providing a more efficient and sustainable method for ammonia cracking. The energy transition needs solutions that are material-efficient and competitive in operation."

Precious metal catalysts based on ruthenium are exceptionally suitable for ammonia cracking, but Heraeus says that, in order to make the process as sustainable, efficient, and cost-effective as possible, the materials used need to allow operation at low temperatures and have high long-term stability, as well as be used as sparingly as possible, and ideally are sourced from renewable resources. In the project, a highly catalytically active ruthenium layer is applied to an electrically heatable catalyst

carrier system, which ensures direct and even heat distribution. The active layer consists of nanoparticles that are finely distributed on a specially tailored carbon material. This enables the ruthenium to be used for extended periods of time before the precious metal is recycled at the end of its useful life, allowing further energy savings. The goal is to achieve maximum ammonia conversion at temperatures below 500°C. This results in substantial energy savings in operation.

OMAN

Consortium to develop green hydrogen project in Oman

Actis and Fortescue have been awarded exclusive rights to develop major green hydrogen project in Oman. At a signing ceremony in Muscat, Hydrogen Oman SPC (Hydrom), an independent entity founded by the Omani government to orchestrate and deliver the nation's green hydrogen strategy, announced the consortium was a winning bidder in the second round of a green hydrogen tender process.

The project, which is currently in feasibility stage, is expected to involve construction of up to 4.5 GW of wind and solar renewable energy resources that will power electrolysers with the potential to produce up to 200,000 t/a of green hydrogen per year. Under the current plan, this is expected to be sold to local industrial offtakers as well as processed into derivatives such as green ammonia for export via the existing port of Salalah.

Speaking at the signing ceremony, Salim bin Nasser Al Aufi, Oman's Minister of Energy and Minerals and Chairman of Hydrom, said: "Oman is strategically located between two key green hydrogen demand centres in Europe and Asia. This, in addition to, our tier-1 infrastructure and logistics capabilities, have enabled us to leverage our first mover advantage in the global hydrogen industry. The availability of renewable natural resources in Oman coupled with the country's favourable geopolitical positioning, investor-friendly policies and progressive energy transition strategies make it one of the most suitable countries for green hydrogen production. I would like to congratulate Actis and Fortescue on their awarding and look forward to working together to realise our collective vision."

CHINA

Stamicarbon to revamp urea plant

Maire Group's NextChem Sustainable Technology Solutions division, via its subsidiary Stamicarbon, has been selected by Qinghai Yuntianhua International Fertilizer Co., Ltd. to provide the process design package for the revamping of a dual-line urea plant in Qinghai Province, China, with a capacity of over 1,200 t/d each. The proprietary medium pressure flash design, part of the *EVOLVE Energy™* series, significantly lowers steam use and optimises the use of feedstock, reducing the overall energy consumption of the plant by over 25%. In particular, Stamicarbon says that the addition of a medium-pressure recirculation section enables the maximisation of energy savings without any modification to the existing high-pressure equipment. This results in a significant decrease of the carbon footprint while generating savings in maintenance and operating expenses.

FRANCE

Low carbon nitrogen plant announcement

FertigHy says that it will build its first low carbon fertilizer facility France's norther Hauts-de-France region. The €1.3 billion CAPEX investment build is expected to be in operation by 2030 and will produce 500,000 t/a of low-carbon fertilisers. The production process will use renewable and low-carbon electricity to produce hydrogen for ammonia production. FertigHy is a consortium of founding investors EIT InnoEnergy, RIC Energy, Maire Group, Siemens Financial Services, InVivo, and Heineken, and plans to build, own and operate several large-scale fertiliser factories across Europe producing cost-competitive, low-carbon fertilisers for European farmers - starting in France.

José Antonio de las Heras, CEO of FertigHy, said: "A long-standing agricultural base and strong governmental support were principale triggers for FertigHy to choose Northern France to develop its first fertiliser manufacturing plant. Running on renewable and low-carbon electricity, this plant is a decisive step towards the production of European-made fertilisers and towards reducing imports of mineral nitrogen fertilisers. FertigHy will therefore contribute to the decarbonisation of French agriculture, where fertilisers production and use currently account for 30% of the sector's total greenhouse gas emissions."

AUSTRALIA

Mubadala to invest in Perdaman urea project

Mubadala Investment Company, the Abu Dhabi sovereign investor, has announced its decision to invest in Perdaman's A$6.4 billion Western Australia Urea project at Karratha in Western Australia. The new investment, which is in line with the wealth fund's target of doubling its exposure in Asia by 2030, represents the largest investment ever made in the Australian fertiliser industry, with the facility expected to produce up to than 2.3 million t/a of urea. It will incorporate solar energy and green hydrogen to replace coal-based urea imports, as well as ensure optimised energy efficiency and low emissions. Around half of production will be exported to Asia, Brazil and the US. The value of the investment was not disclosed. The project is already being funded by US-based infrastructure investment fund Global Infrastructure Partners (GIP), who have committed more than A$2.1 billion (US$ 1.4 billion) last year.

Dyno Nobel extends contract with BHP Mitsubishi Alliance

Dyno Nobel's products and technology solutions division has secured a long-term contract extension with BHP Mitsubishi Alliance (BMA) in the Bowen Basin region in central Queensland. The five-year agreement will see Dyno Nobel supply its explosives products and services to BMA's Goonyella, Saraji, Peak Downs, and Caval Ridge mines. In addition, Dyno Nobel will continue to supply the Daunia mine which BMA recently divested to Whitehaven Coal. Ammonium nitrate and premium emulsion products will be locally manufactured at Dyno Nobel's Moranbah plant in the Bowen Basin. The Moranbah plant has a secure and sustainable long-term future following the finalisation of a gas supply agreement until 2033, with the option to extend to 2041.

Dyno Nobel Asia Pacific President Greg Hayne said: "We expect to supply around 20% more ammonium nitrate each year from July as part of the new agreement… the long-term gas supply agreement we have secured with Queensland Pacific Metals (QPM) ensures that our team at Moranbah can safely provide our customers with domestically manufactured bulk explosives protected from volatile global ammonia pricing. The possible use of waste mine gas from our customers' coal mining operations has the potential to further enhance the sustainability of our Moranbah plant and provide environmental benefits for our customers and the community."

UNITED ARAB EMIRATES

Notice to proceed for low carbon ammonia plant

Tecnimont says that Fertiglobe has given it notice to proceed with construction activities related to the low-carbon ammonia plant under development in the Ta'ziz Derivatives Park near Ruwais, Abu Dhabi. Fertiglobe is developing the low carbon ammonia plant with its project partners Ta'ziz (a joint venture between ADNOC and Abu Dhabi sovereign wealth fund ADQ), Mitsui and GS Energy Corporation. Once in operation in 2027, the ammonia facility will produce 3,000 t/d (1 million t/a) of ammonia. The plant will be one of a series of global-scale chemical and industrial facilities that Ta'ziz is developing in the area.

UNITED KINGDOM

Uhde and Johnson Matthey to offer integrated solution for blue ammonia

Johnson Matthey (JM) and thyssenkrupp Uhde say that they have signed a memorandum of understanding to jointly offer a fully integrated blue ammonia solution. The technology combines Uhde's proven ammonia process and JM's hydrogen expertise through its LCHTM technology, which will enable the production of blue ammonia with up to 99% CO_2 capture. thyssenkrupp Uhde has licensed, engineered, or constructed over 130 ammonia plants worldwide since 1928 and is the market leader for plants with a capacity greater than 3,000 t/d via its dual pressure technology. JM's LCH technology, which utilises JM's autothermal reformer alone or in conjunction with JM's gas heated reformer, has been selected for several of the world's first large scale blue hydrogen projects including bp's H2Teesside, a 700 MW low carbon hydrogen production plant, and the H2H Saltend project with Equinor and Linde for a 600 MWt low carbon hydrogen production plant.

Alberto Giovanzana, Managing Director – Catalyst Technologies at Johnson Matthey, said: "We know multiple routes are needed in the energy transition, and ammonia provides several options because it can be used directly in power and shipping industries, and as a hydrogen carrier to safely transport hydrogen to areas it is not easy to produce. Combining our expertise and over two decades worth of partnership with thyssenkrupp Uhde, we are excited to offer this technology which will allow our customers to produce ammonia with significantly lower CO_2 emissions."

NORWAY

Electricity supply secured for large-scale green ammonia plant

Norwegian green ammonia production firm North Ammonia AS has secured 171 MW of grid capacity for a large-scale green ammonia production plant in Eyedehavn, near Arendal, Norway from energy company Glitre Nett. The supply agreement ensures that Eydehavn Green Ammonia will have sufficient electricity capacity to produce around 145,000 t/a of green ammonia. Targeting a start-up in production in 2028, the firm is working towards a final investment decision for the project in 2025.

"This is an important milestone and gives us a good basis for continuing the development of our facility in Eydehaven and reinforces Arendal's position as an attractive location for green industrial development in Norway," said Mikkel Torud, CEO of North Ammonia.

In mid-2023, the company partnered with Oslo-listed shipping company Hoegh Autoliners for the supply, distribution, delivery and consumption of green ammonia.The partnership aims to power at least 5% of their deep-sea operations with green ammonia by 2030. ■

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Syngas News

URUGUAY

HIF to license JM methanol technology

Johnson Matthey (JM) has been selected by HIF Global, as the methanol licensor for HIF Global's Paysandú eFuels project in Uruguay. The facility would be the largest e-methanol plant in South America and will use electrolytically produced green hydrogen and waste CO_2 from an ethanol plant to produce e-methanol. JM's *eMERALD*™ technology has been proven as a route to decarbonise methanol production and this technology will be deployed at the HIF facility, with expected production capacity of 700,000 t/a of e-methanol. The methanol will be used to support rapidly growing demand from the marine market, as well as as a feedstock to produce e-gasoline (via a methanol to gasoline process) which will facilitate the decarbonisation of over 150,000 vehicles.

This collaboration builds on the successful demonstration of the *eMERALD* technology in the HIF Haru Oni eFuels facility, where JM licenses its technology and supplies the catalyst. The demonstrator plant has successfully operated for over 12 months, producing methanol that is further processed into gasoline. Additionally, HIF Global has announced other planned eFuels projects to be built in the US, Tasmania, and Chile. JM is already working with HIF Global to support the development of these projects. HIF Global will invest $4 billion in the facility. Construction of the plant is planned for 2025.

Victor Turpaud, CEO HIF Latam, said: "eFuels are a replacement for fossil fuels and are a necessary solution for decarbonising global transport. We have already demonstrated the capability to produce eFuels with green hydrogen and recycled CO_2, using Johnson Matthey's technology at our Haru Oni eFuels facility in southern Chile. Expanding our collaboration with Johnson Matthey represents the importance of long-term relationships to HIF and to achieve our common goals". ■

UNITED STATES

Wind power for renewable hydrogen

Hy2gen, a developer, financier, builder and operator of plants for the production of renewable hydrogen and hydrogen derivatives has signed a memorandum of understanding (MoU) with offshore wind energy developer Ocean Connect Energy Inc. (OCE) for the mutual investigation of the potential to power renewable hydrogen production from offshore wind. The MoU formalises a collaboration between the two companies to identify, evaluate, and develop favourable locations to power Hy2gen's renewable fuel production from the gigawatt-scale offshore wind energy generation that OCE develops in the USA and worldwide.

The companies have formed a 10-month working group to identify and mature high-capacity offshore wind energy areas where project development may be held back by constrained grid transmission, low electricity demand, or other factors. "Where renewable hydrogen production can be built near the point of interconnect from offshore wind energy generation, we have the potential to create predictable and lasting demand for the energy. This makes the need for new grid transmission less urgent and the need for infrastructure investment less substantial, while accelerating wind energy project execution," said David White, president of Hy2gen USA Inc. "Renewable hydrogen can change the paradigm of where offshore wind is developed," added Kevin Banister, chief executive officer of Ocean Connect Energy.

Worley wins contract for GTL project

Worley has secured the front-end engineering and design (FEED) contract for Cerilon's gas-to-liquids (GTL) project in North Dakota. Cerilon's facility will be the first of its kind to use large-scale carbon capture and sequestration (CCS) technology. This approach aims to minimise the project's environmental footprint. The GTL plant will convert natural gas into approximately 24,000 bbl/d of high-quality synthetic products, including advanced lubricants, ultra-low sulphur diesel, and naphtha.

Worley plans to leverage a standardised design approach for this project, enabling efficient replication in the future. Worley has already completed the preliminary engineering phase (pre-FEED) for the GTL project, and this new agreement signifies the official start of the FEED stage. Engineering services will be delivered from Worley's Calgary office, Canada, with additional support from their global network, including integrated delivery teams.

GERMANY

NextChem completes acquisition of GasConTec

NextChem has finalised the acquisition of 100% of GasConTec GmbH (GCT), an innovative company specialising in technology development and process engineering. GCT has over 80 patents and extensive expertise in the synthesis of low-carbon products such as hydrogen, methanol, olefins, gasoline and integrated methanol-ammonia processes. The company's portfolio includes autothermal reforming, which can generate low-carbon hydrogen with high carbon capture rates. This achieves high hydrogen yields while reducing external energy needs, ensuring efficiency and cost-effectiveness, especially for large-scale plants. The company also has access to a German-based industrial-scale demonstration plant for high-pressure partial oxidation.

Alessandro Bernini, CEO of NextChem parent Maire Group, commented: "This acquisition marks an important step in NextChem's path to enhance and expand its unique technology portfolio. GasConTec brings distinctive solutions able to effectively meet our clients' current and future decarbonisation needs."

DENMARK

Methanol valves for dual-fuel shipbuilding

Pres-Vac Engineering has announced the successful certification of its innovative high-velocity methanol valves. These valves, essential for the safety and efficiency of methanol tank systems, are now certified under the IMO 1621 standard, among other regulatory benchmarks. The valves enable greater flexibility in ship design, accommodating long vent-pipes up to 128 meters for DN 65 size, with allowances for even longer pipelines. This development offers shipbuilders and owners unique options in creating more efficient and compliant dual-fuel systems. The valves incorporate features such as improved flow control and minimised gas emissions. These mechanical valves operate without electronic controls, adding a layer of safety to their functionality.

Agreement on methanol storage

SRC Group and advisory and project management firm Green Marine have signed a collaborative agreement to develop and deliver SRC's Methanol Superstorage solution to market. Methanol Superstorage uses the SPS Technology Sandwich Plate system instead of traditional cofferdams that separate tank walls, boosting shipboard tank volumes by 85% and in part compensating for methanol's significantly lower energy density than conventional heavy fuel oil.

Hannes Lilp, CEO, SRC Group said: "With Green Marine's extensive experience in methanol projects and overall technical knowledge of the entire process, combined with SRC's expertise in methanol storage and over 23 years of experience in ship refits and conversions, we are well-placed to onboard Methanol Superstorage for both retrofit and new build vessels, and establish a mature sales framework to enable global adoption."

Green Marine continues to drive development of the methanol supply chain in the marine market, with recent agreements including preparations for projected supplies of green methanol from Chinese partners. The firm also recently named Singapore-based former Methanol Institute Chief Commercial Officer Chris Chatterton as Managing Director and Partner, with effect from 1st July, 2024.

Methanol Superstorage has already received approval in principle from a leading IACS society, which indicates that no conceptual issues have been identified relating to ship regulatory requirements. "In parallel to class approvals, SRC and Green Marine will also oversee and manage 3rd Party technical development" said Lilp.

PHOTO: PRESS-VAC

Press-Vac's methanol valves.

ITALY

NextChem and JM to license waste to methanol solutions

NextChem's MyRechemical subsidiary and Johnson Matthey (JM) have agreed to partner for the commercialisation of the *Circular Methanol*™ technology package worldwide. Following the joint cooperation agreement of July 2021, aimed at integrating MyRechemical's waste-to-syngas technology with JM's syngas-to-methanol technology, the two companies have reached a new agreement to jointly commercialise the integrated technology under MyRechemical's proprietary *Circular Methanol*™ trademark.

SWEDEN

Permit for green methanol plant

Liquid Wind has received an environmental permit for its second green hydrogen-based e-methanol plant in Sweden. FlagshipTWO, planned for Sundsvall, is expected to produce 130,000 t/a of e-methanol by combining green hydrogen and captured carbon dioxide (CO_2) from 2027. Having been granted an environmental permit by the Land and Environmental Court in Östersund, the plant has been slated as a key supplier of lower-carbon fuels to the maritime sector. It will capture biogenic CO_2 from Sundsvall Energi's Korstaverket plant to reduce an estimated 283,000 t/a of CO_2 emission – primarily by cutting marine fossil fuel use, saving some 199,000 t/a of CO_2. Around 84,000 t/a CO_2 will also be stored in a parallel project run by Sundsvall Energi.

EGYPT

Consortium to develop green methanol plant

AD Ports Group, the operator of industrial cities and free zones in Abu Dhabi, is leading a consortium to develop a green methanol plant in Egypt. The group has signed a preliminary agreement with container shipping line Transmar and Orascom Construction, both based in Egypt, for the development, which will include storage and export centres for the synthetic fuel. AD Ports said the new centre in Egypt will provide bunkering solutions for operators who have ordered green methanol-powered vessels. Several shipping majors, including Maersk and Hapag Lloyd, are integrating green-methanol-fuelled ships into their fleets as part of decarbonisation efforts.

AUSTRALIA

UK-Australian collaboration on green hydrogen

The UK and Australian Governments have awarded a combined £480,000 (A$610,400) to a consortium looking to reduce renewable methanol costs with efficient green hydrogen production. HAMR Energy and Supercritical Solutions' project plans to demonstrate high efficiency and high-pressure green hydrogen production could reduce renewable methanol costs by up to 20%. In the first stage, the pair will deliver a techno-economic feasibility study looking at the integration of high-pressure hydrogen from UK-based Supercritical's electrolysers into HAMR's hybrid methanol plant design. The project has secured £480,000 in funding from the Australia-UK Renewable Hydrogen Innovation Partnership to de-risk the concept for progression to pilot stage, deploying Supercritical's technology in Australia as part of a renewable methanol facility from 2026. The companies estimate that electrolysis technology could reduce the cost of renewable methanol by up to 20% compared to current technologies.

UZBEKISTAN

Air Products to buy GTL plant

Air Products and Chemicals has announced a $1 billion investment deal with the government of Uzbekistan and Uzbekneftegaz JSC to acquire, own and manage a natural gas-to-syngas processing facility in Qashqadaryo Province. Uzbekneftegaz's gas-to-liquid (GTL) facility includes a natural gas-to-syngas industrial complex that converts natural gas into synthetic fuels with a high added value for domestic use and possibly export.

Air Products will purchase, own and operate two large-scale air separation units, two large-scale auto-thermal reforming units and a hydrogen production unit within the Uzbekistan GTL complex under the terms of the purchase agreement. Air Products will additionally provide oxygen, nitrogen, hydrogen and syngas under a long-term, take-or-pay/fixed fee contract. ■

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People

The International Fertilizer Association (IFA) elected seven new representatives to its Board of Directors at its Annual General Meeting, held in Singapore on 22 May. The AGM took place on the final day of the IFA Annual Conference 2024. The seven new Board Directors elected by the membership are: **Bruce Bodine**, Mosaic; **Soufiyane El Kassi**, OCP Nutricrops; **Xiaofeng Hou**, China BlueChemical; **Dmitry Konyaev**, Uralchem JSC; **Jahangir Piracha**, Fauji Fertilizer Company Ltd; **Edward Weiner**, Trammo, Inc.; and **Kelvin Wickham**, Ballance Agri-Nutrients.

Alzbeta Klein, CEO and Director General, IFA, said: “I warmly welcome each of our new members to the IFA Board of Directors. I am looking forward to working with them all in support of IFA’s mission to help feed the world sustainably.”

IFA welcomed 34 new members to the Association – five Ordinary Members, 24 Associate Members, two Affiliate Members and three Correspondent Members, and awarded its 2024 Green Leaf Award for outstanding safety, health, and environmental practices to Engro Fertilizers in Pakistan for nitrogen production, and to IMACID (a joint venture of OCP, CFCL Group, and TATA Chemicals) in Morocco for phosphate/potash production. Applicants for the Green Leaf Award undergo an extensive evaluation of performance indicators by an independent panel of experts. IFA runs the award every two years and received a record 47 eligible applications from 27 member companies in 2024.

IFA noted that Engro Fertilizers’ application exemplifies a comprehensive approach to safety, health, and environmental (SHE) management in its fertilizer manufacturing division. Through robust SHE programs and strategic initiatives like the ECO-GREEN project (a 60-day project aimed at enhancing plant energy efficiency, including the inspection and repair of 400 equipment pieces and installation of low NOx burners) Engro Fertilizers demonstrates a commitment to reducing emissions and promoting sustainability.

IMACID holds integrated ISO certifications (Quality 9001, Environment 14001, Health and Safety at work 45001, and Energy 50001), renewed in 2023 after achieving zero non-conformities in 2020. Its pioneering of a proactive safety culture using the Bird pyramid approach (a theory of industrial accident prevention), engages all employees in hazard reporting. By enhancing SHE management among its 200 daily subcontractors through the GEEX standard IMACID ensures strict compliance and impressive performance evaluations.

The Goth Macchi plant of Fauji Fertilizer Company in Pakistan achieved second place in the nitrogen producer category. Judges cited exceptional environmental initiatives including NH_3 and H_2 recovery, N_2 plant replacement and installation of solar power.


Magda Chambriard, new CEO of Petrobas

“It is the right thing to do, and it makes sound business sense to reach for the highest standards of safety and health in the workplace and to protect the environment,” said Alzbeta Klein, CEO and Director General, IFA. “Congratulations to the winners of the IFA Green Leaf Award 2024.”

Brazilian state oil company Petrobras has appointed **Magda Chambriard** as its new Chief Executive Officer. Chambriard has spent four decades in the industry and is a former head of oil and gas regulator ANP. She was chosen by president Luiz Inacio Lula da Silva to replace former CEO Jean Paul Prates after he was dismissed on May 14th, the day after the publication of results showing a 38% drop in profits year on year for Petrobras. The results and turbulence at the top of the company led to a sharp drop in Petrobras share price. However, Brazilian Mines and Energy Minister Alexandre Silveira has sought to allay fears about political interference, stating that Chambriard would execute the firm’s existing $102 billion investment plan for the 2024-2028 period. ■

Calendar 2024/2025

JULY

9-11

IFA Global Markets Conference,
LONDON, UK
Contact: Kate Ashby, International Fertilizer Industry Association
Tel: +33 1 53 93 05 25
Email: conference@fertilizer.org
Web: http://www.ifaglobalmarkets.org/

SEPTEMBER

9-12

AIChE Ammonia Safety Symposium,
SAN DIEGO, California, USA
Contact: Ilia Kileen, AIChE
Tel: +1 800 242 4363
Web: www.aiche.org/ammonia

16-18

World Fertilizer Conference,
WASHINGTON DC, USA
Contact: The Fertilizer Institute
Tel: +1 202 962 0490
Email: info@tfi.org

29 – OCTOBER 4

Ammonium Nitrate/Nitric Acid Conference, MONTREAL, Canada
Contact: Sam Correnti, DynoNobel, Karl Hohenwarter, LAT Nitrogen, Michael Gill, Orica
Email: sam.correnti@am.dynonobel.com, karl.hohenwarter@lat-nitrogen.com, michael.gill@orica.com, annaconferencehelp@gmail.com
Web: annawebsite.squarespace.com/

OCTOBER

7-9

Global Syngas Technologies Conference,
SAN DIEGO, California, USA
Contact: Global Syngas Technologies Council
PO Box 18456, Sugar Land, TX 77496 USA
Tel: +1 713 703 8196
Email: info@globalsyngas.org

22-24

World Methanol Conference 2024,
COPENHAGEN, Denmark
Contact: Mike Nash, Chemical Market Analytics
Tel: +44 20 8544 7860
Email: events@chemicalmarketanalytics.com

NOVEMBER

11-13

Ammonia Energy Association Annual Conference, NEW ORLEANS, Louisiana, USA
Contact: Ammonia Energy Association
Email: meetings@ammoniaenergy.org
Web: https://ammoniaenergy.org/conferences-events/2024-annual-conference/

JANUARY

26-29

Fertilizer Latino Americano, RIO DE JANEIRO, Brazil
Contact: CRU Events
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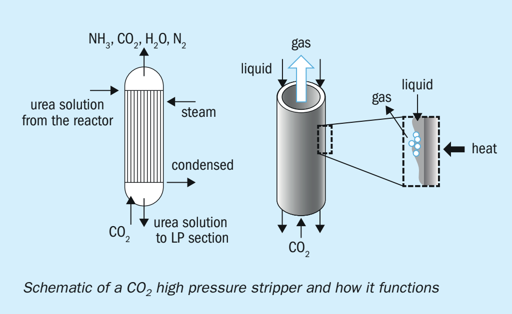
Plant Manager+

How to solve stripper efficiency issues (part 1)

Mr Petrus Kaasenbrood



Schematic of a CO_2 high pressure stripper and how it functions

A ruptured 316L Urea Grade stripper tube

In 1967, Stamicarbon revolutionised the urea production process with the invention of the HP CO_2 stripper by Mr Petrus JC Kaasenbrood. At a time when there was an energy crisis in many parts of the world, the HP CO_2 stripper led to three main benefits:

- the carbamate could be recycled at synthesis pressure so no extra water needed to be added to recycle the carbamate;
- a medium pressure recirculation section was no longer needed and;
- with the condensation of strip gases in the high pressure carbamate condenser, low pressure steam could be produced, which could be used in the downstream sections leading to a reduction of the steam consumption of a urea plant by a factor of approximately two.

US patent 3,356,723 describes the invention of the HP CO_2 stripper:

"In a continuous process for the preparation of urea wherein NH_3 and CO_2 are reacted at elevated temperature and pressure to continuously provide an ammonium carbamate melt, thereafter in an autoclave, said melt being converted into a urea solution containing ammonium carbamate and the carbamate being stripped from said solution by decomposing said carbamate into NH_3 and CO_2 by heat and expelling NH_3, CO_2 and H_2O from said solution, the improvement which comprises continuously stripping the urea solution with CO_2 in a stripping zone outside said autoclave and at a pressure of at least 50 atmospheres up to urea synthesis pressure wherein the urea solution flows downwardly along the inside of externally steam heated tubes in the stripping zone and CO_2 stripping gas passes upwardly in said tubes in contact with said urea solution, the pressure of the heating steam being in the range of 15-30 atm., whereby NH_3 and CO_2 are expelled from said solution, condensing the resulting mixture of CO_2 gas and gases expelled from said urea solution after addition of further NH_3 and at a pressure of at least 50 atmospheres up to urea synthesis pressure to form a carbamate solution and returning the thus formed carbamate solution to said autoclave for further urea synthesis."

In the HP CO_2 stripper, urea reactor effluent is thus treated counter currently with CO_2 in a stripper at high pressure in order to dissociate carbamate and at the same time enable easy condensation of the carbamate gases without the addition of water. Preferably, this is done at the same pressure as the reactor operating pressure. The condensation of strip gases will produce steam leading to a significant reduction in steam consumption to produce urea.

This patent from 1967 has revolutionised urea technology and nowadays all modern urea processes operate an HP stripper.

The first stripper (1960s) had tubes made out of 316L Urea Grade but soon after the start-up several tubes ruptured due to high corrosion rates (refer to the picture). It was concluded that this material was not sufficiently resistant to ammonium carbamate corrosion at these severe process conditions in the tubes (high temperatures and low partial pressure of oxygen). A new material, austenitic stainless steel 25-22-2, was developed with a higher chromium content which proved to have much better corrosion resistance and could achieve long lifetimes. The world record has been set by SKW Piesteritz in Germany with a lifetime of 35 years with Sandvik (now Alleima) 2RE69 25-22-2 tubes.

The efficiency of the CO_2 HP stripper in Stamicarbon plants is typically around 80% and is a critical process parameter for safe, reliable and efficient operation. This is especially true for austenitic stainless steel tubes as these can experience active corrosion.

There are many causes that can lower stripper efficiency, such as:

1. High liquid load
2. Fouling liquid dividers
3. Bad installation liquid dividers
4. High delta-P range liquid dividers
5. Fouling inside tubes
6. CO_2 distributor issues
7. Entrainment of condensate with steam
8. Steam not saturated
9. High N/C ratio of liquid entering stripper
10. Not vertical installation of HP stripper
11. Large size stripper and old design baffles shell side

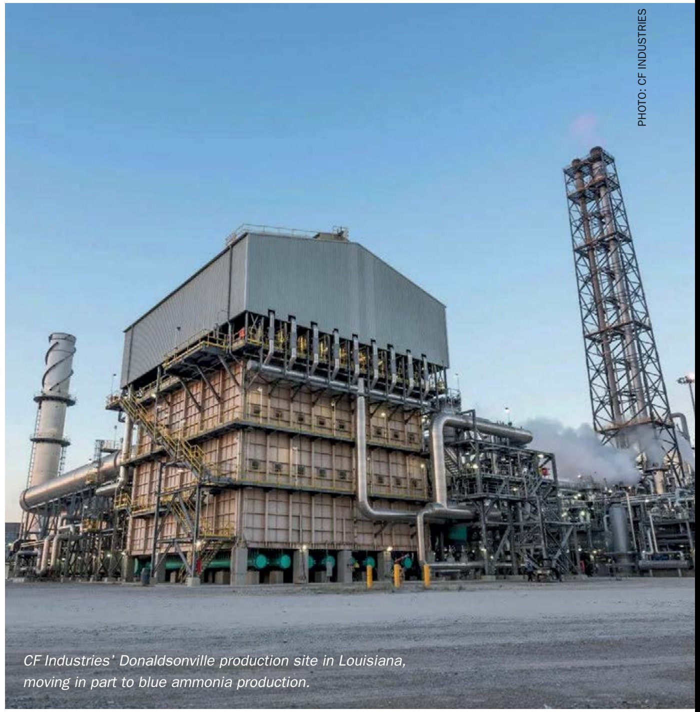
All of these causes will be discussed in detail in future instalments of Plant Manager+ ... ■

Low carbon ammonia capacity

A review of the current slate of plans for green and blue ammonia production.

Demand for low carbon emission hydrogen and ammonia is expected to accelerate as decarbonisation quickens over the coming decades. Both will play a significant role in decarbonising hard-to-abate sectors including steel, shipping, aviation and fertilizers, and within the wider energy transition generally. But after a flurry of project announcements, the number moving towards final investment decisions (FIDs) remains small. Costs have often been revised upwards, sometimes by substantial amounts, and while the subsidies now available in places like the US and EU have generated a great deal of interest and project activity, they do not appear to have been decisive in driving FIDs.

The Hydrogen Council says that there have been a total of 45 million t/a of low carbon hydrogen capacity announcements with a target completion date before 2030. However, current production remains less than 100,000 t/a, and final investment decisions have only been taken on 3 million t/a of production capacity. Overall, CRU calculates that green ammonia project announcements total 180 million t/a of capacity, but only 2% have reached FID, while blue ammonia project announcements total 60 million t/a of capacity, with 4% having reached FID.



CF Industries' Donaldsonville production site in Louisiana, moving in part to blue ammonia production.

Costs

One major reason for this is that costs have been higher than anticipated. For green projects, electrolysis capacity has not fallen as rapidly as expected. Indeed, recently in markets such as the US, Europe and China, the cost of electrolysers has risen by more than 50% in the past year, due to a combination of inflation, labour costs, increases in utility prices and bottlenecks in production. An increase in the cost of materials and labour means that associated costs for electrolysers such as pipes, cables, coolers, pumps, water-purification facilities etc have also gone up. The price of renewable electricity also remains roughly double what it had been hoped it would.

This has led to a greater focus upon blue projects, which use carbon capture and storage/sequestration (CCS) to defray the carbon intensity of conventional fossil fuel based production. CRU's Hydrogen Cost Model puts the cost of conventional grey hydrogen at around \$2.00/kg H_2. CCS requires additional investment and is energy intensive, but the added cost of carbon capture is only around \$0.40–0.50/kg H_2 in a steam reforming plant, because fossil-based hydrogen production processes already separate CO_2 process streams. However, hydrogen produced via electrolysis with low-emission electricity, assuming full costs of electricity are borne, is upwards of \$5.00–6.00/kg H_2.

Nor is there much sign of this reducing. CRU's model projects that most countries are still expected to exhibit green hydrogen

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costs above blue and grey costs by 2050, ranging between ~ $3.00–7.00/kg in real terms – even before the addition of necessary storage and distribution costs. Green ammonia costs also follow the same trajectory, with the cost of green hydrogen forming the largest part of its overall cost structure. Furthermore, as ammonia production requires a constant supply of hydrogen, additional costs associated with overcoming this challenge – if relying on the underlying intermittency of renewable energy – can also be presumed.

The conclusion is that aside from those countries that are expected to have access to low-cost renewable energy, green hydrogen and ammonia costs will still be prohibitively high by 2050, with implementation of subsidy or a carbon price likely needed for the industry to develop. It also indicates that the focus is likely to remain on hard to abate sectors such as steel, fertilizers, refining, aviation and shipping, with other sectors looking to alternative solutions.

Carbon capture

With blue ammonia favoured in the short to medium term, there will be increasing focus on carbon capture. The number and volume of projects had been climbing rapidly, with the US the most favoured area thanks to the Inflation Reduction Act credits, though the delay in finalising 45Q guidelines is stalling projects. One wrinkle with CCS is that it remains difficult to assess how long term the removal of a tonne of carbon dioxide is. The captured CO_2 must be monitored to see whether or not it returns to the atmosphere and if it does, how long that process takes. While there are over 400 million t/a of CO_2 capture projects on the books for completion by 2035, there has been a pause in new project activity in recent months due to uncertainties regarding policy, financing, and transport and storage permits. Most of this capacity is for power generation or hydrogen and downstream chemical use.

Demand for low carbon ammonia

Existing uses of hydrogen, including refining, methanol and ammonia production, are forecast to be the most significant demand markets for low-emissions hydrogen, driven by decarbonisation. Uptake in these sectors poses less of a technical challenge, and end-users are able to leverage existing hydrogen infrastructure, supporting a switch to low-emissions alternatives sooner. Demand for methanol and ammonia production will be supported by existing uses, as well as their uptake into new markets, such as marine fuels. Low-emissions ammonia demand is forecast to surpass 200 million t/a by 2050, driven by substitution into existing uses and uptake into new demand markets. However, most of this demand will come in the late 2030s and 2040s, as fuel substitution in aviation and marine uses gathers pace. Near-term demand will be focused on existing markets, including fertilizer and industrial uses, as these present the least technical hurdles for adoption, although co-firing ammonia with coal to reduce emissions from coal-fired power generation will be important in Japan and South Korea.

As a substitute product, the main advantage low carbon ammonia offers is a reduction in CO_2 emissions compared with alternatives. The value delivered is therefore dependent on the carbon savings from its use in a specific end-market. Today, the best value proposition for green ammonia based on its low carbon credentials is in Europe. However, it is important to consider that the application of emission taxes is not global. Many countries are opting not to use taxation schemes to encourage decarbonisation. This adds downside to the value of green ammonia in markets outside of these jurisdictions.

Table 1: **Major blue ammonia projects**

Company	Site	Capacity, t/a	On-stream
CF Industries	Donaldsonville, USA	1.7 million	2025
LSB Industries	Houston, USA	1.1 million	2027
OCI	Beaumont, USA	1.1 million	2025
QAFCO	Mesaieed, Qatar	1.1 million	2026
Tarafert	Durango, Mexico	200,000	2026
Wabash Valley	Terra Haute, USA	550,000	2026
Yara	Sluiskil, Netherlands	378,000	2026
Yara	Gulf Coast, USA	1.4 million	2028
Total		**7.53 million**	

Source: CRU

Table 2: **Green ammonia projects**

Company	Site	Capacity, t/a	On-stream
ACWA Power	Chirchiq, Uzbekistan	15,000	2025
ACME Cleantech	Duqm, Oman	100,000	2027
Baofeng Energy	Ningxia, China	100,000	2024
CNNC Huineng	Inner Mongolia	122,000	2024
CF Industries	Donaldsonville, USA	20,000	2024
Enaex	Tocophila, Chile	18,000	2025
Enaex	Mejillones, Chila	682,000	2030
NEOM Co	NEOM, Saudi Arabia	1.3 million	2026
Jilin Power	Jilin, China	200,000	2024
Tarafert	Durango, Mexico	200,000	2026
Unigel	Bahia, Brazil	60,000	2025
Vision Energy	Inner Mongolia, China	1.5 million	2028
Yara	Porsgrunn, Norway	20,500	2024
Total		**4.3 million**	

Source: CRU

Based on CRU's calculations, the value of green ammonia in the power sector will not exceed the cost of delivering it to the market until 2040, necessitating additional incentives to encourage uptake.

In the near term, low-emissions ammonia capacity is forecast to increase by 11 million t/a by 2030, based projects that are expected to be firm additions announced for the period. Capacity additions from green ammonia projects are expected to be 4 million t/a, the majority of which are in China, as shown in Table 2. Blue ammonia projects represent 7 million t/a, concentrated in the US, as shown in Table 1. The Inflation Reduction Act (IRA) legislation has incentivised CCS projects, with blue ammonia producers now eligible to claim $85 and $60 for each tonne of CO_2 that is permanently stored or utilised, respectively. There are now 17 projects under development in the US totalling 33 million t/a of ammonia capacity, with half of those announced in 2023. Greenfield projects make up the majority of announced capacity (27 million t/a), with the remainder coming from CCS conversions of existing production.

Most new supply in the build-out is expected to feed into traditional fertilizer production, with uptake in new end uses more limited in the short term. If new demand fails to materialise in e.g. the marine sector, the traditional ammonia market could become oversupplied.

The missing key for project financing remains the committed offtake, with potential end-users still unconvinced by the lack of policy clarity, high costs and infrastructure requirements of adopting hydrogen or ammonia.

Energy transition

Longer term, the energy transition will lead to far more renewable electricity production and gradually begin to bring the cost of green projects down to one comparable with blue production. CRU's Power Transition Service forecasts that energy generation will slightly more than double by 2050, with additional capacity mainly coming from wind and solar generation. Economic growth will support rising electricity generation, while the use of new technologies, including AI, will push electricity generation growth higher. By 2050, most people will have swapped fossil-powered vehicles and boilers for EVs and electric heat pumps, respectively.

Solar PV and wind turbine manufacturing costs are declining and CRU carbon abatement curves show that replacing fossil-fired generation with solar and wind power is among the least expensive steps to decarbonise. Many countries are planning to significantly reduce fossil-fired generation and increase solar and wind power over the next decade; and a rise in carbon taxes will help incentivise this transition. While many renewable energy targets and ambitions may not ultimately be realised within the timeline expected, there will still be a significant shift to solar and wind power.

However, increasing solar and wind power reduces grid stability. To address this, intermittent power needs to be supplemented by battery energy storage systems (BESS) or other means, which will increase costs. Indeed, energy storage costs will become more important as solar and wind generation begins to comprise a larger proportion of power mixes. ■

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Syngas project listing 2024

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

Contractor	Licensor	Company	Location	Product	mt/d	Status	Start-up date
AUSTRALIA							
n.a.	n.a.	Bell Bay Powerfuels	Tasmania	Methanol	600	DE	2027
CANADA							
n.a.	Greyrock Energy	Rocky Mtn Clean Fuels	Carseland, AB	BTL	15	DE	2025
n.a.	Topsoe	Air Products	Edmonton, AB	Hydrogen	1,500	DE	2024
CHINA							
n.a.	JM (DAVYTM)	Ningxia Baofeng	Yinchuan, Ningxia	Methanol	7,200	UC	2024
n.a.	JM (DAVYTM)	Jiangsu Sailboat	Lianyungang, Jiangsu	Methanol	300	C	2024
n.a.	n.a.	Sinopec	Tahe, Xinjiang	Hydrogen	60	UC	2023
n.a.	JM (DAVYTM)	Shenhua Baotou	Baotou, Mongolia	Methanol	6,000	DE	2026
n.a.	CRI	Henan Shuncheng	Anyang, Henan	Methanol	330	C	2023
DENMARK							
Technip	Topsoe/Sasol	Arcadia e-Fuels	Vordingborg	Green F-T	240	DE	2026
EGYPT							
n.a.	n.a.	EBIC	Ain Sokhna	Hydrogen	45	UC	2024
n.a.	n.a.	Scatec	Ain Sokhna	Methanol	120	DE	2026
FINLAND							
n.a.	n.a.	Veolia	Äänekoski	Methanol	36	UC	2024
INDIA							
EIL	Topsoe	Assam Petchem	Namrup	Methanol	500	C	2023
BHEL	n.a.	Coal India Ltd	Dankuni	Methanol	2,000	FS	2026
INDONESIA							
Samsung	Air Liquide	Petronas	Bintulu, Sarawak	Methanol	5,000	C	2023
n.a.	Topsoe	PT Bukit Asam	Muara Enim	Methanol/DME	6,000	UC	On hold
IRAN							
Namvaran	Topsoe	Badr-e-Shargh Pet Co	Chabahar	Methanol	5,000	UC	2025
PIDEC	Casale	Apadana Methanol	Assaluyeh	Methanol	5,000	UC	2023
n.a.	Casale	Fateh Sanat Kimia	Dayyer	Methanol	5,000	UC	On hold
n.a.	n.a.	IOC	Mathura	Hydrogen	15	BE	2024
ITALY							
n.a.	Tecnimont	Alia Servizi Ambientali	Empoli	Methanol	375	BE	2025
MALAYSIA							
Samsung	Air Liquide	Sarawak Petchem	Sanjung Kidurong	Methanol	5,000	UC	2024
Samsung	n.a.	H2biscus	Sarawak	Methanol	1,400	FS	2027
NETHERLANDS							
n.a.	Casale	Gidara Energy	Amsterdam	Methanol	250	DE	2025
NIGERIA							
n.a.	Air Liquide	Brass Fert & Petchem	Brass Island	Methanol	5,000	DE	2025
RUSSIA							
China Chengda	Topsoe*	Nakhodka Fertilizer	Nakhodka	Methanol	5,400	UC	2026
n.a.	n.a.	Baltic Gas Chemical	Ust-Luga	Methanol	5,000	DE	On hold
CNCEC	n.a.	GTM One	Khimprom	Methanol	3,000	BE	2025
SAUDI ARABIA							
n.a.	Air Products	Air Products Qudra	Jubail	Hydrogen	415	UC	2023
n.a.	Topsoe	Chemanol	Jubail	Methanol	+300	RE	2023
SINGAPORE							
n.a.	Air Liquide	PTTEP	Singapore	Methanol	150	FS	n.a.
SPAIN							
Tecnicas Reunidas	n.a.	Nascar	Almeria	Methanol	110	FS	2026
SWEDEN							
n.a.	Topsoe	FlagshipONE	Örnsköldsvik	Methanol	150	UC	2025
n.a.	JM (DAVYTM)	Perstorp (Project Air)	Stenungsund	Methanol	600	DE	2026
TURKMENISTAN							
Sojitz, KHI	Topsoe	Turkmengaz	Ovadan-Depe	Methanol	n.a.	CA	n.a.
UNITED ARAB EMIRATES							
n.a.	n.a.	Ta'ziz/Proman	Ruwais	Methanol	5,400	P	2025
UNITED KINGDOM							
Linde	JM (DAVYTM)	Equinor	Saltend	Hydrogen	380	DE	2027
n.a.	n.a.	Cromarty Clean Fuels	Nigg, Scotland	Methanol	n.a.	FS	n.a.
UNITED STATES							
n.a.	Relocated plant	US Methanol	Charleston, WV	Methanol	480	C	2022
n.a.	JM (DAVYTM)	HIF	Matagorda, TX	MTG	1,840	DE	2026
KBR	JM (DAVYTM)	Methanex	Geismar, LA	Methanol	5,000	UC	2024
Technip	Topsoe	ExxonMobil	Baytown, TX	Hydrogen	2,700	DE	2028
n.a.	Topsoe	Nacero	Penwell, TX	Methanol/MTJ	5 x 5000	CA	n.a.
n.a.	n.a.	Beaver Lake	Louisiana	Methanol	1,300	FS	2027
UZBEKISTAN							
Hyundai	Topsoe/Sasol	Oltin Yo'l GTL	Shurtan	GTL	5,000	C	2023
n.a.	Air Products	GCC MTO	Karakul	Methanol/MTO	3,360	DE	2025

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

Right: Methanex's Geismar 3 plant, Louisiana, under construction.

PHOTO: METHANEX

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Ammonia safety at sea

A look at the safety challenges that face developers of ammonia-powered shipping vessels before it can become used more widely as a low carbon fuel.

As the nitrogen industry begins to slowly turn its output towards lower carbon ammonia production so the interest in using it as a relatively clean fuel increases, mainly from the shipping industry. As we noted in our editorial in the previous issue, the Det Norske Veritas (DNV) count of orders for new ammonia-powered ships this year reached four in April 2024, bringing the total currently under order to nine; much smaller than methanol, LNG or conventional powered vessels, but still significant. Current projections foresee that demand from the power sector and bunkering for ammonia will account for up to 4% of total ammonia demand in 2030, and possibly to as high as 29% in 2050.

The interest from ship builders and operators is due to International Maritime Organisation (IMO) targets which aim to reduce 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. Ammonia has a number of characteristics which make it attractive as an alternative fuel, from producing no carbon emissions when burned, to a relatively high octane rating of 110–130, and a small flammability range, making it relatively safe in terms of explosion risk. It also has a relatively high power-to-fuel-to-power efficiency, and there is already a large scale global distribution network in place.

It has required some re-engineering to make it feasible, however. Development of an ammonia powered ship engine has taken some time, but Finnish marine engine manufacturer Wärtsilä now commercially offers its new Ammonia 25 four stroke engine, and while MAN Energy Solutions has put back the date for the launch of its own two-stroke ammonia marine engine from 2024 to 2027, it remains confident that it will be able to offer retrofit conversions to existing two-stroke engines from that date. Itochu and Vopak are looking at ammonia bunker fuel infrastructure for Singapore, and Japanese shipping company NYK Line, shipbuilder Japan Marine United Corporation (JMU), and ClassNK are developing an ammonia-fuelled gas carrier, in addition to an ammonia floating storage and regasification barge.

Challenges

But ammonia does face several challenges before it becomes more widely taken up by the shipping industry, however. On a technical level, ammonia combustion generates nitrous oxides which must be scrubbed from exhausts, and it must be stored as a refrigerated and/or pressurised liquid. Green ammonia also remains extremely costly, although if some of the large carbon capture and storage projects currently under development come to fruition, large volumes of blue ammonia should be available at a relatively competitive cost with conventional shipping fuels like diesel. But the largest concern for ship owners, operators and ports, is safety.

Ammonia safety at sea

Ammonia chiefly presents three main hazards; toxicity, fire risk, and corrosion risk. Corrosiveness is perhaps the least immediately concerning from a safety perspective, but complicates ammonia operations. Ammonia reacts with water to form ammonium hydroxide, which is strongly alkaline and which can corrode metals and cause embrittlement of plastics or rubber, damaging components and possibly leading to failures. This necessitates proper storage and handling procedures, as well as the use of protective coatings and materials that are resistant to alkaline substances.

Flammability

Ammonia burns – that is the whole point of using it as a fuel. However, the auto-ignition temperature of ammonia under atmospheric conditions is 651°C, and it requires considerable energy to auto-ignite. The main flammability hazard comes from dispersions of ammonia vapour in air. Ammonia is lighter than air and diffuses relatively quickly, especially if released at high pressure. Without ignition, ammonia dissipates by vaporisation and forms a vapour cloud that disperses in the air. However, in the event of ignition, there are four potential risk scenarios for ammonia, including a vapour cloud flash fire, jet fire, pool fire, and vapour cloud explosion. Compared to LNG and LPG, ammonia has a lower risk of fire due to its lower burning rate; liquid ammonia does not burn continuously, as the heat emitted from the flames is not sufficient to reach the liquid, but if an external heat source is present, enough ammonia can vaporise to keep the fire burning.

The use of water spray, fog, or foam can be effective in extinguishing large ammonia flames, while dry chemicals or CO_2 are more appropriate for small ammonia fires. However, it is important to avoid directing a water jet directly towards a leak or liquid ammonia source as this may cause a hazardous reaction. Responders must wear protective equipment with an oxygen supply.

Toxicity

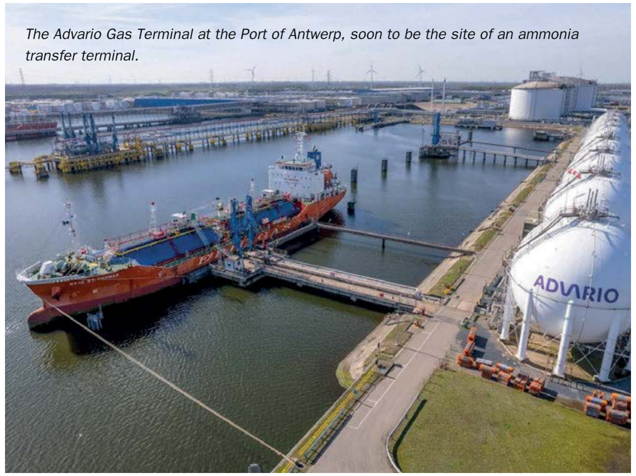
The main concern of an ammonia release is its toxicity. Ammonia concentrations above 1700 ppm (0.17%) cause coughing and oedema, and concentrations of 2500-4500 ppm (0.25-0.45%) can be fatal in approximately 30 minutes. Above 0.5% concentration usually produces rapid respiratory arrest. The concentration at which the gas is immediately harmful to life or health (IDLH) is 300 ppm. The human nose can detect ammonia concentrations as low as 5ppm. This means that a low level threat can be readily identified and action taken to withdraw from the ammonia contaminated area. However, the danger can be higher on a ship due to the number of small compartments where ammonia could build up without dispersing.

Shipboard operation

Lloyd's Register Maritime Decarbonisation Hub and the Maersk Mc-Kinney-Møller Center for Zero Carbon Shipping (MMMCZS) have produced a multi-disciplinary assessment of the design challenges and risks to seafaring personnel from the use of ammonia as a marine fuel. The analysts chose three ammonia-fuelled reference ship designs to model, including a 3,500 TEU feeder container ship with a liquid ammonia tank at ambient pressure and a temperature of minus 33°C; an 80-100,000 dwt bulk carrier with a fully pressurised ammonia fuel tank at ambient temperature and a pressure of 18 bar; and a 50,000 dwt medium-range tanker with a semi-refrigerated tank on deck at a pressure of 4 bar.

The recommendations from the report were that;

- Lower storage temperatures and pressures both reduce the safety risk from ammonia fuel. This has been borne out by other studies which show that releases from high pressure storage (>12 bar) lead to the formation of a visible, aerosol gas cloud which is heavier than air with ammonia concentrations >20,000 ppm (2%). Ship fuel storage is likely to be lower pressure (ca 4 bar), at which the risk of gas cloud formation does exist but at a far reduced level. Conversely, a release of fully refrigerated ammonia presents a more benign scenario, where a slowly-evaporating pool produces a fast-dissipating, lighter-than-air cloud, although at sea there is the risk that release onto the sea surface will result in vigorous evaporation, as it reacts both chemically and thermally with the water.
- The fuel preparation room should be divided into two or more separate spaces containing different groups of equipment that could leak ammonia.
- Access to and length of time spent in spaces containing ammonia equipment should be minimised, monitored, and controlled.
- Ventilation outlets from spaces containing ammonia equipment should be placed in a safe location adequately separated from areas accessed by crew to avoid accidental release of toxic concentrations of ammonia affecting personnel
- Multiple sensors of different types should be installed to detect ammonia.


The Advario Gas Terminal at the Port of Antwerp, soon to be the site of an ammonia transfer terminal.

SOURCE: ADVARIO

Containing ammonia releases is important. Secondary containment mechanisms, such as double-walled piping, used for ammonia-related equipment outside of already-restricted areas, have been proven to significantly reduce risk.

Where ammonia does leak, good ventilation of spaces containing ammonia equipment can provide mitigation of toxic effects for many smaller, but not all, potential ammonia leaks, and particularly for smaller leaks. Small ammonia concentrations or leaks will likely drive workers out of the confined space because of ammonia's pungent smell. Due consideration should be given to additional precautions for personnel entering these spaces.

Ventilation of spaces containing ammonia equipment also reduces the risk of ammonia concentrations reaching a flammable level. Ammonia leak alarms should be installed in both controlled areas (for example, the fuel preparation room) and near potential leak sources, and the fuel system should be subject to rapid and reliable manual and automated shutdown in the event of an ammonia leak.

In its work on ammonia engines, Wärtsilä identified ammonia leak risk zones in and around ammonia engines, including: the gas inlet or liquid fuel injection system, which is mitigated by use of ventilated double wall piping, and a low pressure return line for the liquid system. Another vector for exposure was unburnt ammonia in the exhaust at very low levels, which can be removed along with NOx in the catalytic absorber. Wärtsilä is developing PPE use profiles for working with and near marine ammonia engines. Ammonia handling PPE is already well-defined, both in regulatory terms and in commercial availability. ASTI details levels of protection from A to C, with the minimum level being an "ASTI vest", including a detector, goggles and respiratory mask, likely to be worn in an engine room under normal operating conditions.

Bunkering

Outside of day to day ship operation, the other major area subject to hazards is storage and transfer of ammonia fuel. Compared to conventional liquid fuels, ammonia bunkering is associated with possible risks related to cryogenic liquid/

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high-pressure liquid transfer and vapour return. It is relatively easy to imagine an ammonia fuel line becoming disconnected during fuel transfer, resulting in potentially lethal concentrations of ammonia at the dockside, and the potential for ignition.

A Korean joint study by the Korea Maritime Transportation Safety Authority and research partners looked at safety in ammonia bunkering based on an analysis of 118 research papers and 50 regulations and guidelines. It considered experience gathered from ammonia's prior use in chemical plants, large refrigeration units, and at farms. According to US statistics, from 1985 to 2019, there were approximately 71 fatal accidents involving anhydrous ammonia. The primary causes of deaths and injuries were identified as either fire or inhalation. Accidents involving ammonia release are generally due to human error, operational mistakes, and maintenance and inspection failures during storage tank operations, the bunkering process, and pipeline operations.

One of the chief mitigation steps against accidents during bunkering is the imposition of a safety zone; a designated area surrounding the bunkering operation where access is restricted and the necessary safety measures are implemented. However, the study found delineating such a zone problematic due to the number of factors which can influence an ammonia release, including the proximity of other vessels or structures, weather conditions, and potential environmental impacts, and factors such as the direction of a leak, leak area configuration, wind direction, ship structure, and cargo state all affect the determination of a safe zone. Because ammonia bunkering is a fairly new thing, there are currently no well-defined industry guidelines, regulations, or standards in place regarding safety zones.

Weighing up deterministic and risk-based methods in delineating the area of a safety zone, the study concluded that a hybrid approach yielded a more consistent safety zone design compared to the deterministic approach across various bunkering situations, and highlighted the usefulness of combining deterministic and risk-based elements in safety zone planning to create a more adaptable and robust approach.

Overall, their safety assessment of the ammonia bunkering process had the following recommendations;

- Strict safety regulations must be followed for the storage and handling of ammonia due to its hazardous nature. Storage containers for ammonia must be specifically designed and certified for this purpose. Trained personnel who wear suitable protective gear are responsible for handling and transferring ammonia. Appropriate personal protective equipment (PPE) and safety equipment, such as gas detectors, respirators, protective clothing, and eye and face protection, should be used.
- It is crucial to plan and carry out the bunkering process meticulously with trained personnel. The crew of the receiving vessel should be notified about the procedure and any necessary safety precautions. The process should be monitored closely to ensure it is executed safely.
- A safety zone should be established. To prevent unauthorized access, it is necessary to place clear signs and barriers.
- Proper ventilation is essential during the bunkering process to avoid the accumulation of ammonia vapours. The area where the bunkering is carried out must have adequate ventilation to disperse any leaks or spills swiftly.
- In the event of an accident or spill during bunkering, there must be emergency response plans in place. The crew should be trained to handle an ammonia spill, and necessary equipment, such as personal protective gear and spill containment equipment, should be easily accessible.
- Additionally, all equipment, pipelines, and storage tanks used during bunkering should be properly maintained and inspected.

Fuel quality specifications

A final area for consideration is the development of fuel quality specifications for ammonia. These relate particularly to its water content. Ammonia absorbs water easily, and although a small amount of water in ammonia (up to 0.5%) is needed to improve the safety of storage by reducing the risk of stress corrosion cracking (SCC). Too much water will lead to poor combustion. Commercial ammonia is available at range from 99.5% to 99.995% purity, with most bulk chemical/agricultural grade ammonia at 99.5% purity – sufficient for fuel use, but bunkering will need to control water ingress into ammonia storage.

MAN Energy Solutions has developed its own preliminary guidance for ammonia going into its dual-fuel ammonia engines once these reach the market. It notes that particles in the fuel could come from particles breaking free from catalyst used in ammonia production and from transportation of the ammonia. This raises a consideration about the need for the ammonia fuel standard to control particulate matter, and possible requirements for onboard fuel filtering between fuel tank and engine.

Evolving regulations

While ammonia has been carried safely as freight for many years, the shipping industry is still adjusting to its use as a fuel. The International Maritime Organisation has been playing its part, and has reported "significant progress" on the development of draft interim guidelines for the safety of ships using ammonia as fuel. The Sub-Committee on Carriage of Cargoes and Containers (CCC) has agreed to convene a working group from 9 -13 September 2024, which will aim to finalise these guidelines for approval by the IMO's Maritime Safety Committee in December 2024.

The IMO's International Code of the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk ('IGC Code') currently states that toxic cargoes shall not be used as fuels on gas-carrying vessels, which prevents the use of ammonia. However, last September the CCC agreed to develop guidelines to ensure ships using ammonia and other toxic cargoes as fuel are designed and operated to the same level of safety as a ship carrying and using natural gas as fuel. As for ships not carrying ammonia, Lloyd's Register published rules for ammonia-fuelled non-gas carrier vessels in July 2023, based on the alternative risk-based design pathway allowed for under the IGF Code, and hopes to publish Rules for Ammonia Gas Carriers consuming its own cargo in July 2024. Rules for gas carriers using ammonia as fuel will be published once IMO requirements and any interim prescriptive requirements become clear.

In general, none of the barriers to ammonia's commercialisation as a bunker fuel – technical/engineering, cost, or regulatory – appear to be insuperable, and there is considerable will to overcome them in the industry. However, developing a new regulatory structure is not a fast process, and it remains to be seen whether this will impede the uptake of this promising use for ammonia. ■

Urea technology showcases

Casale, Saipem, Stamicarbon & Toyo Engineering Corporation showcase a selection of innovative technologies that have recently been brought to the market.

CASALE

HYPER-U – a novel high efficiency self-stripping urea process

Matteo Fumagalli

Since the 1970s, the ammonia- or self-stripping process has served as an alternative to the CO_2-stripping process for industrial urea synthesis, favoured for its competitive energy consumption and operational costs. The CO_2-stripping process decomposes carbamate at synthesis pressure using CO_2, whereas the self-stripping process relies on heating, leading to excess ammonia in the urea solution, necessitating purification at medium pressure.

Initially seen as more complex compared to CO_2-stripping, the efficient steam consumption and ease of operation determined the success of the self-stripping process. A major advancement in steam consumption was achieved implementing heat recovery from medium-pressure carbamate vapours. Soon recognised as essential for improving efficiency, this heat integration became standard in new and revamped plants since the 1990s. However, no significant improvements have been made for years, seemingly reaching an energy optimisation plateau.

Casale developed an improved self-stripping process to further reduce medium-pressure steam and cooling water needs. The main innovation is an additional carbamate decomposition step before the conventional medium-pressure section, allowing heat recovery to be extended, reducing the need for LP steam and cooling water.

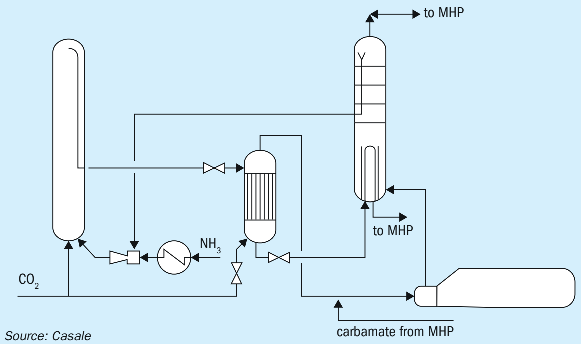
The advantages of the self-stripping process include its horizontal layout, smaller high-pressure equipment, reliable operation, and excellent energy performance. However, it also has drawbacks like dual-pressure purification stages, separate ammonia recovery, and the need for noble materials in the HP stripper.

Modern CO_2-stripping processes include a medium-pressure purification stage in their flow sheets since it is recognised as a key feature to lower the MP steam consumption. Conversely, the traditional self-stripping process appears to have hit an energy efficiency limit. Improving the self-stripping efficiency involves reducing MP steam consumption in the HP stripper without destabilising the steam network. This is possible only by increasing the extent of heat recovery which must nearly double to compete with the best CO_2-stripping processes.

HYPER-U process

HYPER-U is a self-stripping process with innovative peculiarities. Among others, the most distinctive are "hybrid-stripping" and the "combi-reactor". In the conventional self-stripping process, the HP stripper is a thermal decomposer, in HYPER-U a minor portion of CO_2 is fed to the HP stripper to reduce free ammonia in the urea solution leaving the HP section. This drastically reduces the amount of ammonia to be recovered at medium-pressure and allows carbamate vapour condensation along a higher temperature profile which favours deep heat recovery. This hybrid approach blends the best aspects of both CO_2-stripping and self-stripping processes, resulting in higher efficiency.

Fig 1: **HYPER-U high-pressure loop**



Source: Casale

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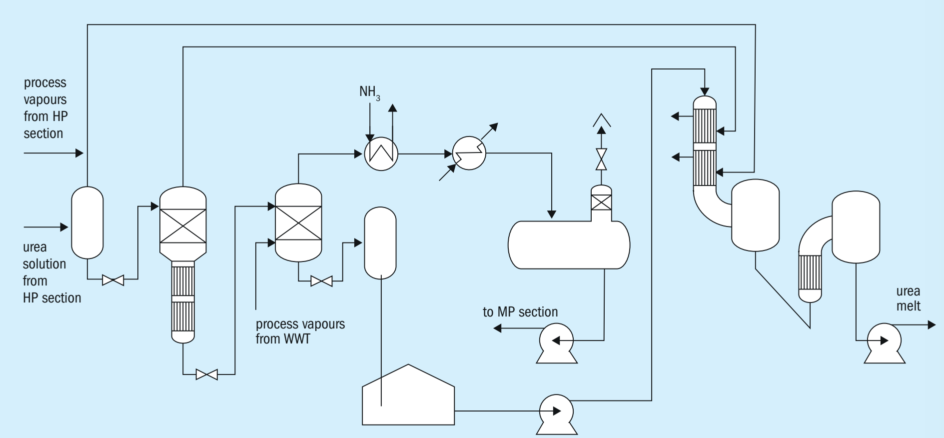
Fig 2: **HYPER-U urea solution purification and concentration sections**



Source: Casale

Vapours from the HP stripper are partially condensed in a kettle-type heat exchanger generating steam at 5.0 to 6.0 barg, but most of the condensation occurs in a "combi-reactor". The combi-reactor is a vertical vessel comprising a tube bundle and trays which makes it an actual combined vertical HP condenser-reactor. The volume of the combi-reactor is sufficiently large to ensure an adequate residence time to initiate the conversion of CO_2 into urea. The excess heat of carbamate condensation is removed with direct process-process heat transfer; namely, the heat released by condensing high-pressure carbamate vapours is used for carbamate decomposition at 30 barg. A simplified flowsheet of the high-pressure loop of HYPER-U is shown in Fig. 1.

A critical aspect of the HYPER-U process is indeed the inclusion of an extra carbamate decomposition stage. The urea solution from the HP stripper is first expanded to 30 barg and fed to the tube bundle (tube side) inserted in the combi-reactor. Direct process-process heat exchange, not relying on an intermediate utility stream, allows carbamate to be decomposed more effectively even at 30 barg. Following the 30 barg purification stage, urea solution is then fed to the conventional medium-pressure sections for final purification.

The final carbamate decomposition stage at 3.5 barg also adopts an innovative concept. Instead of a shell-and-tube exchanger which adopts LP steam to heat up the urea solution, carbamate decomposition occurs in a column with a packed bed. The heat of reaction is provided by process vapours from the waste water treatment (WWT) section. This represents a direct heat integration since the heat of condensation of the water in the WWT vapours is used for carbamate decomposition. Using WWT vapours for LP carbamate decomposition has another major advantage: several pieces of equipment normally present for this service, such as the LP decomposer bundle, steam drum, WWT reflux condenser with its tempered water loop and carbamate reflux pumps, can be avoided.

Urea solution concentration to 96.5-99.7 wt-%, depending on the product finishing technology, is carried out in a single or double vacuum evaporation section. The first stage evaporator employs as heat source carbamate vapours at 30 and 18 barg respectively from the medium-high and medium-pressure carbamate decomposers. The condensation curve of the 30 barg vapours follow a temperature profile higher than the conventional MP vapours which allows the urea solution to be concentrated up to 95% using only heat recovered from process streams without relying on steam. Compared to the conventional self-stripping process, where MP carbamate vapours are used to concentrate the urea solution typically up to 84-85 wt-%, the steam saving attained in HYPER-U is 60% higher. A simplified flowsheet of the purification and concentration sections of HYPER-U is shown in Fig. 2.

The heat integration strategy also foresees the traditional ammonia pre-heating step utilising the heat of condensation of the low-pressure carbamate vapours. HYPER-U also features an intrinsic carbamate pre-heating; carbamate recovery downstream of the HP loop occurs at 110-115 °C which is made possible by the operating pressure at 30 barg. With respect to the conventional self-stripping process, where carbamate solution is recovered at 80-85°C, the higher temperature causes an increase of steam production in the HP carbamate condenser of approximately 40 kg/tonne.

Steam and cooling water saving strategy

The overall heat integration strategy of HYPER-U is intended to maximise the use of process heat sources to replace where possible the use of low-pressure steam. Using 30 barg carbamate vapours, condensing along an elevated temperature profile, makes it possible to exploit their enthalpy to an extent not possible in the conventional self-stripping process. As a result of this innovative heat integration and the other heat recovery stages, the overall steam demand for urea purification and concentration is drastically reduced.

A lower demand of steam in the downstream plant sections opens up the possibility to limit the duty of the HP stripper without upsetting the steam network. Lower medium-pressure steam consumed in the HP stripper, de facto leads to less 5.0 barg steam produced in the HP carbamate condenser. In order to keep a balance between LP steam demand and production, it is paramount to minimise the demand for purification and concentration. The heat integration strategy implemented in HYPER-U allows the supply of 20 barg steam to the HP stripper to be limited without the need to make up the 5.0 barg header. The consumption of 20 barg steam of the HP stripper is approximately 20% lower than in the conventional self-stripping processes.

Another significant positive effect of the deep heat recovery strategy implemented in HYPER-U is the drastically lower cooling water consumption. Maximising the amount of heat recovered for process use causes a corresponding reduction of heat normally wasted to cooling water. An overall saving of 14% cooling water can be achieved.

Other advantages

The hybrid-stripping concept has an impact on the size of the HP stripper; in a conventional modern self-stripping process, the temperature within the tubes of the HP stripper follows an approximately linear profile from 189°C at the top to 203-204°C at the bottom. In HYPER-U the bottom temperature is kept at 196-198°C and the duty is 20% lower. Maintaining the same pressure of steam, the required surface area can be decreased accordingly which positively affects the cost of the item.

Also the cost of the ammonia recovery equipment, such as the ammonia condenser and MP absorber, are reduced because of hybrid-stripping, due to the fraction of free ammonia in the urea solution leaving the HP stripper in HYPER-U being 40% lower. The flow rate of ammonia to the HP ammonia pumps is also reduced, by 20%, which is reflected in the cost of the HP ammonia pumps, but also in the overall power consumption.

Conclusions

The HYPER-U process marks a drastic improvement compared to the consolidated self-stripping technology in terms of energy performance. Among the most relevant features are the hybrid design of the HP stripper which employs a minor stream of CO_2 to lower the free ammonia and the combi-reactor, a submerged HP carbamate condenser combined with a reaction vessel. The combi-reactor enables a direct process-process heat exchange used to decompose carbamate at 30 barg. These two peculiarities allow an efficient heat integration strategy in the purification sections resulting in reduced demand of LP steam. Consequently, the duty of the HP stripper is reduced by 20% compared to state-of-the-art self-stripping processes as is the consumption of MP steam extracted from the CO_2 compressor turbine.

The thorough heat recovery carried out in the carbamate recovery section also reduces the consumption of cooling water by 15% with consequent benefit in terms of raw water make-up and electricity absorbed by cooling towers and pumps.

The overall performance of the HYPER-U process makes it competitive with all urea processes currently available, either based on self-stripping or CO_2 stripping technology. Moreover, the excellent energy performance is not obtained at the expense of augmented capex due to fewer and smaller pieces of equipment. ■

SAIPEM SpA

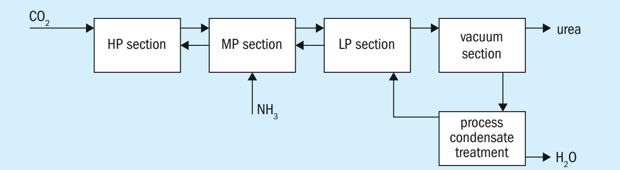
Compact urea plant for green hydrogen and CO_2 valorisation

Luca Edoardo Viganò, Morena Mottironi, Tiziano De Paolis

As the world moves towards tackling climate change, there is a surge in renewable energy installations worldwide. The progressive reduction in cost of renewable energy will lead to a new revolution in green chemistry applications. Technical advancements and environmental restrictions are also giving impetus to the development of CO_2 capture solutions.

In this scenario of worldwide change Saipem as owner and licensor of the Snamprogetti™ Urea Technology has developed a modularised solution for small-scale urea plants which fits perfectly with the portfolio of green technologies and CO_2 capture solutions that Saipem has developed and secured.

Fig. 1: **Urea production block flow diagram**



Source: Saipem

Small scale urea plant by Saipem

Applying decades of experience in licensing, engineering and construction of urea plants having capacities ranging from 300 to 4,000+ t/d, Saipem has re-thought its proven process scheme for applications up to 100 t/d of urea.

The Snamprogetti™ urea process is renowned and recognised by users worldwide for its operating flexibility, hence the first aim was to extend such

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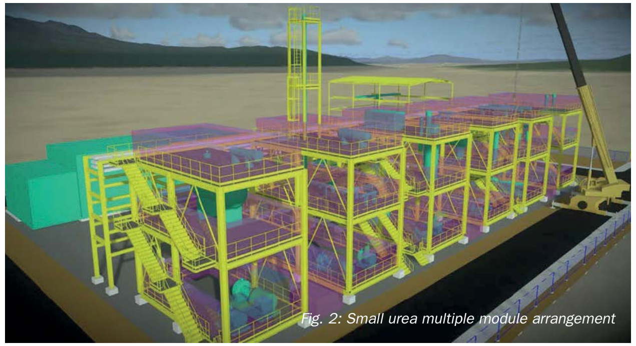


Fig. 2: Small urea multiple module arrangement

PHOTO: SAIPEM

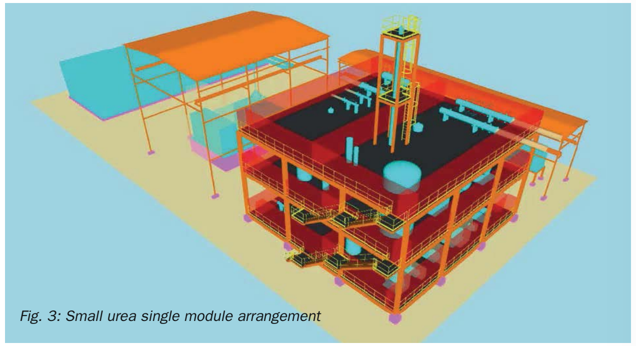


Fig. 3: Small urea single module arrangement

PHOTO: SAIPEM

flexibility to the small plant; to do so, the classic configuration with its five sections at decreasing pressure have been maintained (Fig. 1).

However, by decreasing the plant capacity, thus moving against the economy of scale, the capital investment is another important factor to be considered during the design. To minimise the time from first production to the break-even point, in a context where energy comes from renewable sources, it was decided to optimise energy recovery along the process scheme thus reducing the number of costly items.

Due to the presence of buffer volumes and the peculiarity of Snamprogetti™ urea technology being able to keep the HP bottled in for up to 48 hours, another approach applied to minimise overall bulk quantities was, e.g., for pumps, to consider installation of a single item with a second identical item kept as spare, stored in a warehouse.

These optimisations to the process scheme and approach to number of installed items, also help to reduce the plant footprint. The scheme fits perfectly with a modularised approach even though it is also applicable for a stick built construction.

Two options have been foreseen for the modular approach. The first option foresees multiple small modules, with module size and weight limited in consideration of possible limitations on road transportation. The configuration modules shown in Fig. 2 have dimensions as per Table 1.

In the second option (Fig. 3) a single module in a configuration that could be easily transported by ship and installed near the seashore is considered.

For a small scale plant it is extremely important to push the conversion in the reactor as much as possible, because a higher conversion in the reactor has the direct consequence of minimising the recycles within the plant (with benefits on overall consumptions) as well as minimising the equipment dimensions.

SuperCups, as demonstrated in different plants worldwide, are the selected solution for boosting the conversion to urea.

Due to the small capacity these plants may fit with DEF production or in general with the production of technical urea for specific applications.

In terms of finishing, the small scale urea plant can be coupled with a traditional prilling tower or a granulation plant, but the choice also extends to a pastillation unit which fits perfectly with the limited production capacity and with low capital investment also providing easy implementation in the modularisation case.

Table 1: **Module dimensions for modular configuration option 1.**

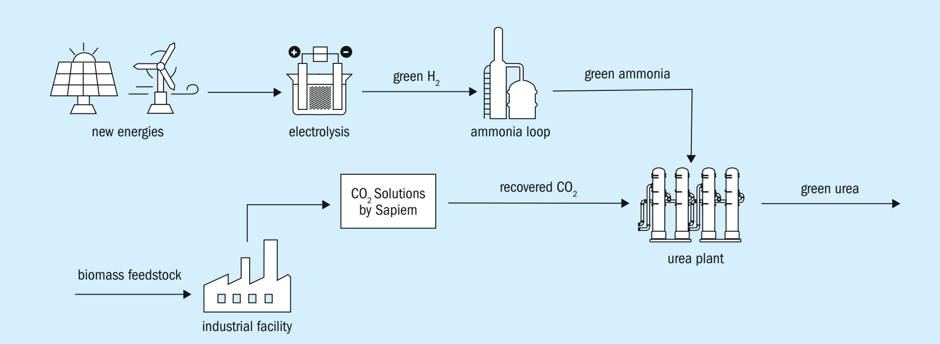
Weight:	< 100 tons
Length:	< 15 m
Width:	< 7 m
Height:	< 15 m with reactor installed stick built. If no limitation on maximum height reactor can be included in a module.

Source: Saipem

Green feedstocks

Small scale urea plants per se can be part of a complex with a traditional scheme but, due to their reduced production capacity, they are best suited to valorise waste streams (e.g., of carbon dioxide), extra production (e.g., of ammonia) and/or the availability of renewable energy, thus becoming part of a complex with a sustainable scheme (see Fig. 4).

Fig. 4: **Possible scheme for sustainable urea production**



Source: Saipem

BLUENZYME™, the sustainable solution to capture CO_2

Post-combustion carbon capture technologies are going to be a key enabler for the effective application of green urea production. In this context, the carbon capture process technologies should yield low-cost, low-complexity operations, solving contemporary problems without creating new ones, while being sturdy under harsh post-combustion oxidising conditions.

Saipem has developed an enzymatic carbon capture technology, CO_2 Solutions, consisting of an innovative process that uses a non-toxic, non-volatile solvent, based on potassium carbonate, and promoted by enzymes. Contrary to conventional carbon-capture technologies, the CO_2 Solutions process neither requires nor produces toxic products. It is clean and harmless to human health and the environment, with fast absorption kinetics. Furthermore, the low-temperature regeneration allows residual heat to be used to drive the capture and reduce opex.

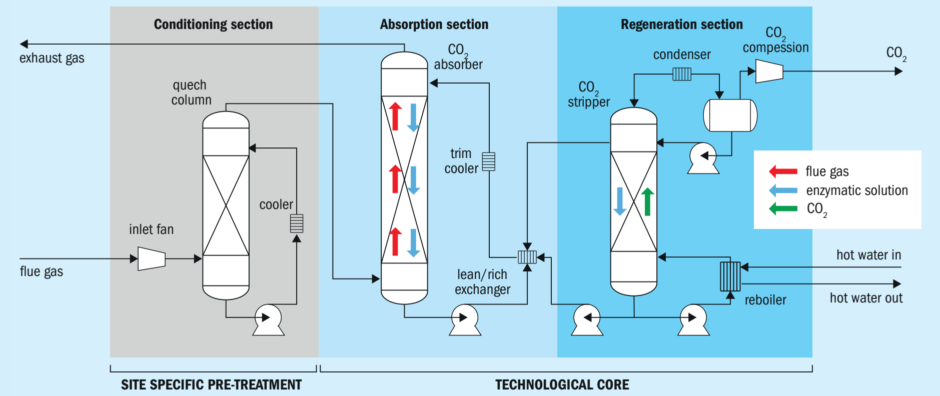
In addition, to further reduce the impacts related to carbon capture installations, Saipem has developed innovative solutions based on the application of rotating packing beds (RPB). These items boost the mass transfer thanks to the liquid-gas contact enhanced through the centrifugal effect. The RPB pilot plant has been successfully tested and prototypes are under development, targeting the commercialisation of the carbon capture scheme implementing RPBs instead of columns, hence drastically reducing the relevant cost and visual impact.

Thanks to its wide expertise as EPC contractor, Saipem developed BLUENZYME™, an industrialised solution line consisting of pre-engineered packages based on the application of the above-mentioned enzymatic proprietary carbon capture technology, and designed to be replicable and modular.

Capitalising the technological features of CO_2 Solutions, BLUENZYME™ can be effectively integrated into the host plant, even through the implementation of optimised energy balance. In particular, the capability of regenerating the solvent at low temperature allows the reuse of low-grade waste heat streams, the efficient application of heat pumps, as well as the exploitation of natural heat sources like geothermal, minimising the carbon footprint of related installations.

Developed as a plug-and-play concept unit, BLUENZYME™ is capable of capturing CO_2 from a post-combustion flue gas, with a reduced execution schedule, by relying on a dedicated and already engaged supply chain for long delivery items.

Fig. 5: **CO_2 Solutions by Saipem – Simplified PFD**



Source: Saipem

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The construction and installation scheme minimises site work with fast module hook-up and minimal underground work. The module design specifications are compatible with truck transportation for reduced installation costs and easier logistics.

Green urea from green hydrogen production

Urea production is not choosy when it comes to ammonia feed: ammonia could be from existing facilities where there could be extra production, from storage (e.g., in case of seasonal CO_2 availability), or from green ammonia plants.

Green ammonia plants are based on the conventional Haber-Bosch process which has been used for decades in the conventional ammonia industry. The main differentiators are the use of water electrolysis instead of hydrocarbon reforming/partial oxidation to generate hydrogen (while nitrogen is produced with standard air separation technologies such as cryogenic distillation or PSA) and the intermittency of renewable power production which implies solutions ensuring smooth operation of the ammonia plants: based on specific project needs, batteries or hydrogen storage are applied or alternatively the ammonia synthesis loop is designed to operate in dynamic mode, following the fluctuations of hydrogen production.

To meet green hydrogen market needs Saipem has developed a pre-engineered, modular, and scalable industrialised solution to be offered with defined and competitive time and costs, for power-to-gas hydrogen, based on the alkaline technology of a key electrolyser OEM, and using a replicable manufacturing approach, to achieve optimised capex/opex.

Fig. 6: BLUENZYME™ rendering (for a 200 t/d unit)

PHOTO: SAIPEM

The industrialised solution, called PtH2 Industrialisation Project, foresees the production of hydrogen using 1 to 5 electrolysis modules, 20 MW power each, according to the scheme as per Fig. 7. A model of the PtH2 Industrialisation Project is depicted in Fig. 8.

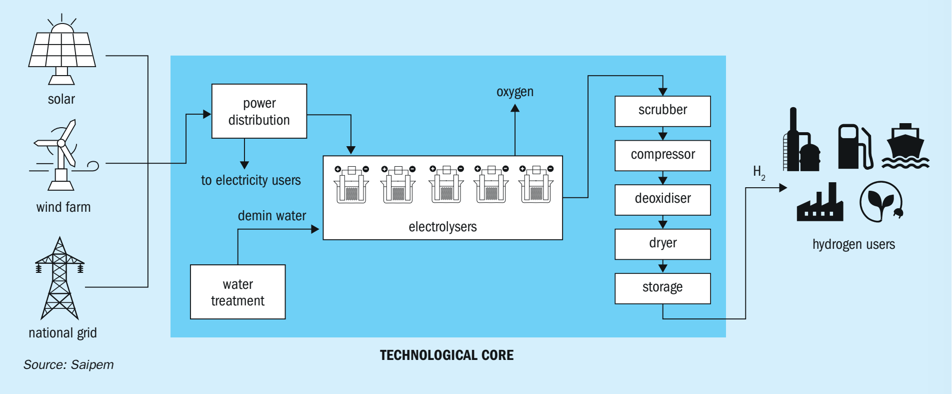
The power from renewable sources (or grid) prior to being fed to the modules is transformed and rectified. Transformers supply incoming AC voltage to the required input voltage for the rectifiers and rectifiers convert AC voltage to DC voltage using IGBT or Thyristor technology.

Each module consists of multiple stacks fed by power and water which is split into hydrogen and oxygen and separated from the electrolyte; the water consumed in the electrolyser is replenished to ensure continuous operation.

At the electrolyser outlet hydrogen is compressed and, since it contains impurities, is subject to a sequence of treatments for purification, mainly deoxidation and dehydration.

Hydrogen is finally sent to the network or to the downstream plant and part of it may be stored. Delivery pressure and storage facilities can be customised according to downstream requirements.

Fig. 7: **Green H_2 main blocks**



Source: Saipem

As an alternative to the scheme depicted in Fig. 4 for the small-scale fertilizer complex, PtH2 and BLUENZYME™ may also be used in existing ammonia-urea plants to debottleneck and/or decarbonise the production in different applications based on the desired targets and the natural gas availability and composition: for example, to increase ammonia production or reduce natural gas consumption in existing plants and/or to increase urea production in case of lack of CO_2 (Fig. 9).

Transportation and storage

Saipem can leverage on the EPC execution of more than 130,000 km of pipelines and the expertise gained in the development of engineering with supercritical CO_2, gaseous hydrogen and liquid ammonia.

In addition to the long experience in executing ammonia-urea complexes as EPC contractor, Saipem has proven in-house engineering capability to autonomously design and build ammonia storage tanks.

Fig. 8: PtH2 Industrialisation Project 3D model

PHOTO: SAIPEM

Conclusions

As the world moves towards tackling climate change, Saipem can provide technologies and expertise to boost and decarbonise existing facilities, to realise sustainable plants by recovering CO_2, by exploiting renewable energies to produce hydrogen and subsequently ammonia and urea at a suitable scale with time to market solutions.

A small scale urea plant has been developed by Saipem applying all its knowledge acquired so far to ensure flexibility of operation and limited cost of investment.

Saipem can also be the partner of choice for the set-up of the whole production chain from renewable energy, through CO_2 transportation, to product handling, storage and shipping. ■

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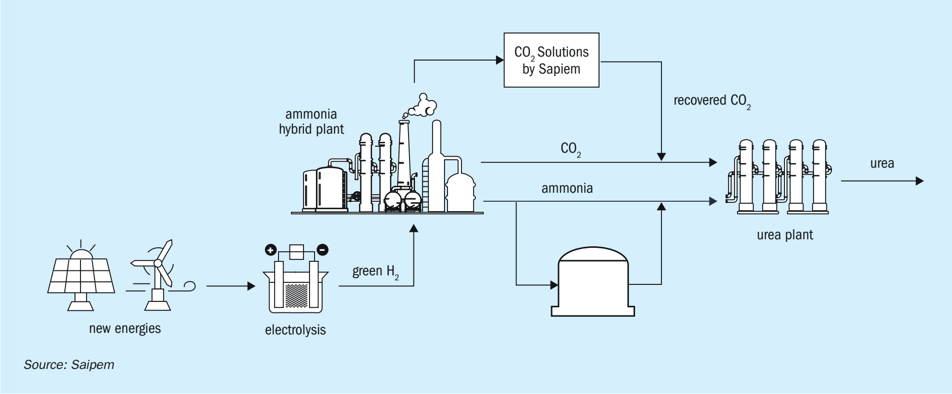
Fig 9: **Possible scheme for urea production increase in existing facility**



Source: Saipem

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Delivery of the first ULE pool reactor to Jiujiang Xinlianxin, China

PHOTO: STAMICARBON

STAMICARBON

Less steam, more urea

Rahul Patil, Veronica Rivas, Nikolay Ketov, Stamicarbon, the Netherlands

The global fertilizer industry is being reshaped by some of the most critical challenges of recent years. From global energy disruptions to the growing urgency of addressing climate change and transitioning to a lower-carbon economy, the nitrogen fertilizer market is one of the sectors most impacted. As the industry continuously works to reduce the environmental footprint associated with fertilizer production, the requirements for technological efficiency are growing faster than in the past.

Improving the energy efficiency and sustainability of fertilizer production technology are essential tasks, and the technology provider's contribution can significantly impact the industry's environmental footprint using existing technology and materials. Recognising the urgency of these goals, Stamicarbon, the nitrogen technology licensor of MAIRE S.p.A, is dedicated to developing and bringing innovative and efficient technologies to market. As a global leader in urea technology, Stamicarbon has introduced its cutting-edge Ultra-Low Energy (ULE) design, a groundbreaking innovation that significantly enhances the energy efficiency of urea production.

The primary advantage of Stamicarbon's Ultra-Low Energy design lies in its efficient use of high-pressure steam, which is utilised three times instead of the standard two. This makes the process far more energy-efficient than traditional CO_2 stripping methods. This article will explore the technology's features and how it's setting new benchmarks for energy savings in the industry, demonstrating its potential to lead the way in more sustainable fertilizer production.

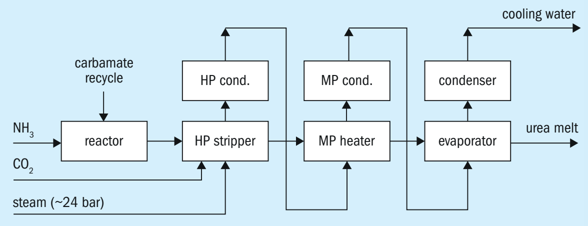
From one to three

The first conventional total recycle urea plants, designed in the 1950s and 1960s, had hardly any heat integration in the process flow scheme. These plants had a steam consumption of about 1.8 tonnes of steam per tonne of urea, which is very high by today's standards, and typically had high-pressure (HP), medium-pressure (MP), and low-pressure (LP) recirculation stages. Carbamate and ammonia were recycled separately to the urea reactor. The heat supplied to the urea synthesis solution was used only once in these first-generation urea plants. Therefore, these types of processes are referred to as N=1 processes.

In the 1960s, Stamicarbon introduced its CO_2 stripping process, which eventually became the industry standard. The main feature of this process was that CO_2 and heat were used to recycle most of the unconverted CO_2 and ammonia via the gas phase. The invention of the stripping process was a major milestone in the history of urea production process development. The stripping plants employed the idea of low-pressure steam generation by recovering heat through a high-pressure carbamate condenser. These stripping plants were more energy-efficient than the usual total recycle plants. This process was called the N=2 process because the heat supplied to the high-pressure stripper was recovered in the high-pressure carbamate condenser and utilised elsewhere in the urea plant, such as in the evaporation and wastewater treatment sections, effectively using the heat two times. The average energy consumption of the stripping process is 0.8-1.0 tonne of steam per tonne of urea.

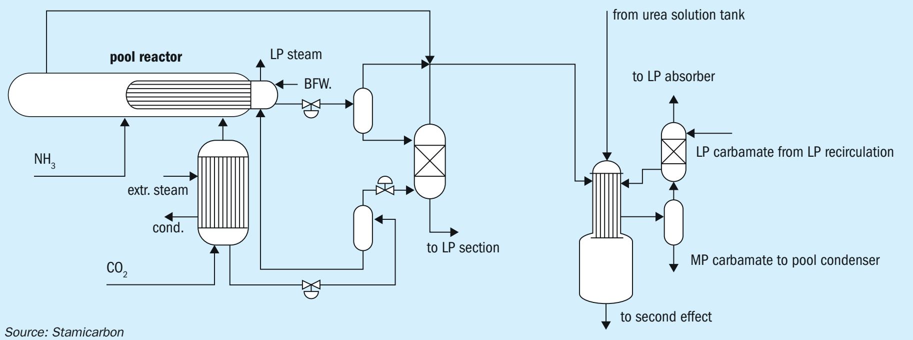
Stamicarbon's next revolutionary advancement in urea production was the invention of the pool condensation technology. For smaller capacities, the reactor and the HP carbamate condenser were combined into a single piece of equipment, called the pool reactor design. For large-capacity plants, a pool condenser is combined with a vertical reactor, offering a larger reaction volume. Since its introduction, this N=2 process design has been widely adopted by the industry, and Stamicarbon has been focusing on further reducing both operating and investment costs.

Fig 1: **N=3 concept**



Source: Stamicarbon

Fig 2: **Ultra-Low Energy process configuration**



Source: Stamicarbon

With the rising cost of energy, Stamicarbon took on the challenge of significantly reducing steam consumption. This effort led to the invention of the Ultra-Low Energy design, also part of the Launch Melt™ series, where the heat supplied in the form of steam is used three times. This advanced heat recovery scheme results in a reduction in steam consumption and a decrease in cooling water use, making the process far more energy-efficient than traditional CO_2 stripping methods.

New industry standard

The primary technological advancement of this process, which leads to significant energy savings, is the use of steam heat three times within the design. A medium-pressure recirculation section (MP section) is required to reuse this heat twice. This is achieved by arranging the carbamate to be flashed at medium pressure and reheated using the heat of reaction and condensation. The reheated carbamate is then used for heat recovery, specifically for evaporation, as shown in Fig. 1.

As a result, steam consumption can be reduced by up to 40%, and cooling water consumption can be reduced by about 16% compared to traditional CO_2 stripping processes. This process configuration achieves an impressively low steam consumption of less than 560 kg per tonne of urea, compared to approximately 870 kg per tonne in conventional urea processes.

The process configuration

The configuration of the process is shown in Fig. 2. The overall configuration of this design consists of a high-pressure stripper, an Ultra-Low Energy pool reactor or an Ultra-Low Energy pool condenser with a vertical reactor. The main change is that the Ultra-Low Energy pool reactor now contains two separate U-tube bundles in the shell. One bundle is for generating low-pressure steam as is commonly done in Stamicarbon's pool condenser and pool reactor plants. The second bundle is used for the heat integration with the MP recirculation section.

The first time the steam is used as a heating agent to obtain high stripping efficiencies in the high-pressure stripper. Subsequently, the heat is recovered by condensing the strip gas in the high-pressure carbamate condenser, pool condenser or pool reactor in the synthesis section to produce low-pressure steam that is used in the sections downstream.

As can be seen in Fig. 2, the urea/carbamate solution is flashed to a medium-pressure separator after leaving the stripper. The urea solution leaving the medium-pressure flash tank is heated inside the second tube bundle of the pool reactor, effectively reusing the heat inside the pool reactor the second time.

On the shell side of the carbamate bundle, condensation of strip gas releases heat (at about 144 bara and 175ºC), which is used to decompose carbamate into ammonia and carbon dioxide at the tube side. Consequently, the tube side of this tube bundle in the pool reactor functions as a medium-pressure rectifying heater. By integrating these two functions, without any intermediate heat transfer medium, the available temperature difference between both process sides allows the bundle to be relatively small.

As illustrated in Fig. 2, the synthesis of the technology includes only two high-pressure pieces of equipment: a high-pressure stripper and a high-pressure pool reactor. Since the gases from the synthesis section can be used in the MP section, the high-pressure scrubber is not needed. This allows for optimisation of the Ultra-Low Energy design's capex.

In Stamicarbon's pool reactor design, the total height of the high-pressure equipment structure is limited to about 20 m, where the heaviest piece of equipment, the pool reactor, is located. The stripper is located close to ground level. As the high-pressure scrubber is not part of the design, this results in the lower height of the structure. The vessel at the highest elevation in the plant is the first medium-pressure separator.

Additionally, milder stripper conditions extend the stripper's lifespan and reduce biuret formation, thereby enhancing the quality of the final product.

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More efficiency with Stami Digital

The ease of operation is another benefit of the Ultra-Low Energy design compared to traditional plants. The presence of the medium-pressure recirculation section with the carbamate bundle mitigates disturbances that typically occur in traditional CO_2 stripping plants, which arise from discharging liquid directly from the stripper operation to the low-pressure section. To improve the safety and efficiency of the plant's operation even further, operators should be trained and prepared for various scenarios.

Stamicarbon's high-fidelity training simulator, part of Stami Digital suite, offers significant advantages to any urea plant. Its unique thermodynamic and kinetic models enable personnel to receive comprehensive training on the urea process and its dynamic behaviour, including standard operating procedures like normal operation, start-up, blocking-in, restarting, and draining. As part of the training program, the model can simulate upsets in the plant, allowing operators to practice responding to upset conditions and bringing the plant back to normal operation.

The training simulator can be configured to replicate an Ultra-Low Energy urea plant precisely. This can include process equipment, control, and interlocking systems, with a corresponding DCS interface that mimics the look and feel of an actual operator's room. Additionally, it prepares operating staff to run the plant at maximum capacity while minimising specific steam consumption and ammonia losses and allows for testing new or modified operating procedures before implementation. This increased staff knowledge and experience leads to safer and more stable plant operations. It also helps to reduce startup time.

Start-up experience

The urea plant at Jinjiang Xinlianxin, with a capacity of 2,334 t/d, was the first facility to utilise Ultra-Low Energy technology. It successfully started up in February 2021. Prior to start-up, the plant staff was thoroughly trained by Stamicarbon using its operator training simulator to ensure a comprehensive understanding of the expected reactor and plant behaviour. The start-up went very smoothly without any issues from the first attempt. Initially, the plant operated at a turndown capacity. After securing the feedstocks, the plant's capacity was increased to over 100% within the first week of operation.

Table 1: **Actual plant performance parameters from the operation of the Jinjiang Xinlianxin Ultra-Low energy plant in China versus those of the standard pool reactor plant.**

Process concept	Steam consumption (23 bara, 330°C)	Cooling water consumption (ΔTCW as 10°C)
LAUNCH MELT™ Ultra-Low Energy plant in China	567 kg steam/t urea	61 t CW/t urea
LAUNCH MELT™ pool reactor designs	870 kg steam/t urea	73 t CW/t urea
Improvement	35%	16%

Source: Stamicarbon

The performance parameters at an average plant operation capacity of 102% demonstrate that the Ultra-Low Energy concept is a significant advancement in urea technology (Fig. 3). The actual high-pressure steam consumption (23 bara, 330 °C) is 567 kg/t urea, which is even lower than the initially expected value during design. This is anticipated to be further reduced by about 20 to 25 kg/t urea through optimisation of the ammonia feed temperature to the synthesis.

Compared to traditional pool condenser and pool reactor designs, this Ultra-Low Energy design plant has proven to reduce steam consumption by about 35% and cooling water consumption by about 16%.

The successful commissioning and stable operation of the plant also validated the mechanical design of the Ultra-Low Energy pool reactor. The design fully utilises the superior corrosion-resistant materials developed by Stamicarbon. The tube bundles and the internals of the distribution box are accessible through the manway by opening the internal covers, enabling non-destructive testing and inspection without restrictions and without the need to dismantle heavy parts.

Optimising conventional plant performance

Most of today's urea plants can be revamped using the Ultra-Low Energy design concept. Each project is unique, so a combination of these technology components can be selected to meet the specific goals of a plant, delivering distinct performance improvements and benefits.

The Ultra-Low Energy design can significantly increase urea production while keeping the flow rate of extraction steam unchanged. A possible revamp approach includes several steps. First, an existing HP carbamate condenser can be substituted with a double-bundle pool condenser or pool reactor, factoring in the additional reaction volume required for the increased capacity. Second, installing a modified Stamicarbon capacity add-on, which features an MP section with an MP stripper and a flash tank needed to recycle urea solution from the HP stripper to the second bundle of the pool reactor/condenser. Third, installing a modified first-stage evaporator with construction materials suitable to handle carbamate on the shell side. Finally, an economical MP CO_2 compressor can be installed to feed CO_2 at medium pressure to the MP stripper.

Combining these steps based on a plant's specifications can reduce steam consumption to levels close to those of the Ultra-Low Energy design while significantly increasing the plant's capacity.

Conclusion

The energy consumption of the Ultra-Low Energy plant is considered a benchmark performance worldwide. The Ultra-Low Energy design retains all the features of Stamicarbon's pool condenser and pool reactor designs, including reliability, operability, and corrosion resistance. It offers comparable capex while significantly lowering operating expenses.

With three plants already operational and six more in various stages of development, ranging from 1,640 t/d to 3,850 t/d, the ULE design has set new benchmarks for energy savings in the industry, demonstrating Stamicarbon's lead in efficient fertilizer production.

With Stamicarbon's extensive experience in full life cycle support to customers worldwide, these technological developments can be applied to new grassroots urea projects and to revamp existing urea plants, regardless of the original technology provider. ■

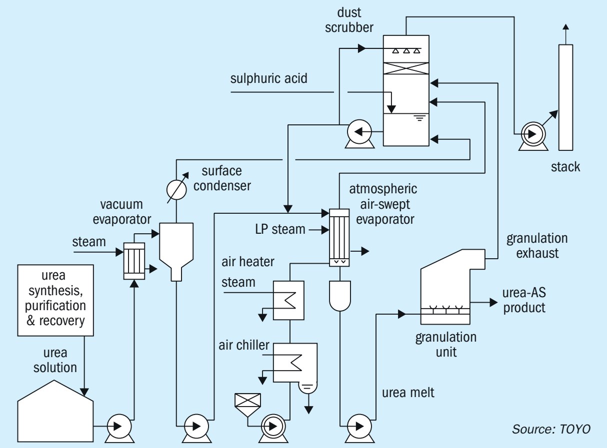
TOYO ENGINEERING CORPORATION

New process options for mixed fertilizers and green urea

Takahiro Kimura

Toyo Engineering Corporation (TOYO), a global leading engineering contractor and urea process licensor, has recently established new proprietary urea technologies. This article reports on two of these: a novel urea mixed fertilizer process and process options for smaller scale green urea plants. A third new technology, the first wet electrostatic precipitator integrated with a dust scrubbing system for ultimate cleanup of granulation/prilling exhaust air, will be featured in the September-October 2024 issue of *Nitrogen+Syngas*.

Fig. 1: **TOYO's Novel Urea Mixed Fertilizer Process**



Source: TOYO

Novel urea mixed fertilizer process

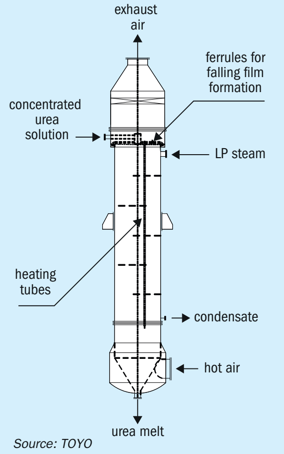
In addition to regulations on urea dust in the exhaust from granulation/prilling processes, regulations on ammonia emissions are also becoming stricter. Acid scrubbing is a viable method for ammonia emission abatement, but it results in ammonium salt by-products, which are sometimes not preferred due to their limited marketability and the necessity of additional facilities. Although various processes to avoid producing ammonium salt have been offered, these tend to be very complex. On another front, urea ammonium sulphate (UAS) demand is steadily increasing at a higher pace than single urea, aiming at better crop yields, higher N-efficiency (less N loss), to meet crop species requirements, soil conditions, and seasonal demands. To address these needs, TOYO offers a simpler and more energy-efficient solution, the Novel Urea Mixed Fertilizer Process, which provides multiple benefits and contributes to sustainability of the fertilizer industry.

Process description and features

A schematic process flow diagram for the Novel Urea Mixed Fertilizer Process is shown in Fig. 1.

The urea solution (approximately 70 wt-% urea) from the urea synthesis process, after passing through the urea solution tank, is concentrated in a two-stage process. First, the urea solution is concentrated by a vacuum evaporator. Subsequently, the concentrated urea solution is further concentrated by an atmospheric air-swept evaporator to obtain a highly concentrated urea solution. The highly concentrated urea solution or urea melt is fed to the product forming section (urea granulation and/or prilling). The exhaust air from the air-swept evaporator and granulation/prilling section is washed with aqueous urea solution and sulphuric acid in the dust scrubber, to less than 20 $mg\text{-}NH_3/Nm^3$ and 30 mg-urea/Nm³ respectively. The addition of a wet electrostatic precipitator (WESP) further decreases the urea emission to less than 5 mg-urea/Nm³ (WESP is not shown in Fig. 1). The urea and NH_3 contained in the exhaust air are recovered as a urea-ammonium salt aqueous solution (recovery solution after washing). The condensate in the first evaporator is used for make-up water in the scrubber cleaning solution, and urea and NH_3 contained in the condensate are recovered together with the recovery solution from the scrubber. The recovered solution is mixed with the

Fig. 2: **Schematic drawing of the atmospheric air-swept evaporator**



Source: TOYO

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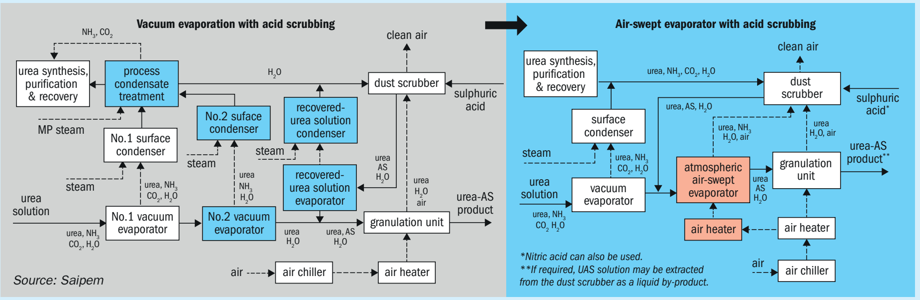
Fig. 3: **Conventional and Novel Urea Mixed Fertilizer Process**



Source: Saipem

*Nitric acid can also be used.
**If required, UAS solution may be extracted from the dust scrubber as a liquid by-product.

concentrated urea solution from the first evaporator to be further concentrated in the air-swept evaporator, then sent to the product forming section where urea-AS mixed granules or prills are produced.

Atmospheric air-swept evaporator

A schematic drawing of the atmospheric air-swept evaporator is shown in Fig. 2. The atmospheric air-swept evaporator is a liquid falling-film type vertical heat exchanger, heated by steam from the shell side. The urea solution flows down as a thin film on the internal wall of the tube and water rapidly evaporates by contacting counter-currently with dry hot air. This type of evaporator has been traditionally used in conventional urea plants including TOYO process plants, in the so-called "direct prilling process" instead of crystal separation. Although it has been dominated by vacuum evaporation due to several disadvantages, these can be overcome with the Novel Urea Mixed Fertilizer Process as follows:

- Loss of ammonia (derived from ammonia dissolved in feed, biuret formation and urea hydrolysis) and urea (vaporised urea derivatives) entrained with exhaust air – readily solved in combination with acid scrubbing.
- Necessity of additional equipment (air heater, chiller and blower) - common use with granulation unit resolves the problem.
- Relatively complex operation and maintenance (biuret control, deposition of urea derived polymers) – can be appropriately managed thanks to wealth of experience and knowhow in 60 years of operation of TOYO urea plants.

Cost and energy savings

Fig. 3 shows how the Novel Urea Mixed Fertilizer Process (block flow diagram on the right) simplifies the concentration and exhaust air acid-scrubbing system in comparison to the previous vacuum evaporation system (block flow diagram on the left). The units in blue boxes in the left diagram are eliminated, and the units in red boxes in the right diagram are added. Since the exhaust air from the atmospheric air-swept evaporator is treated directly in the dust scrubber, where it is nearly-saturated with water, it allows for water evaporation instead of condensation. All of the process condensate containing NH_3 and urea condensed in the surface condenser for the vacuum evaporator, except for the portion for make-up to the absorbent for the urea synthesis unit, can be used as make-up to the dust scrubber. Thus no excess process condensate containing NH_3 and urea is produced, making the whole process condensate treatment system unnecessary, and enabling the process condensate stripper, urea hydrolyser, associated heat exchangers and pumps to be eliminated.

Deletion of the whole process condensate treatment system and second vacuum evaporation system significantly improves the process performance as follows:

- elimination of medium-pressure (25-30 barg) steam for the urea hydrolyser, and low-pressure steam for the process condensate stripper and ejectors for vacuum generation;
- reduction of NH_3 and urea recycle from the concentration section to the synthesis section improves the H_2O/CO_2 ratio in the urea reactor, resulting in higher CO_2 conversion.

These improvements provide 5% steam saving in the overall urea process (from raw material supply to product forming) and a 20% capex saving in the concentration section (from 70 wt-% urea solution to melt).

Quality and application of urea-AS mixed fertilizer

Urea fertilizers containing a moderate amount of ammonium salts, especially UAS (from a few percent up to 50% ammonium sulphate), are widely used in Europe and North America. In addition, farmlands of other important regions in the rest of the world, for example, India and South East Asia have also been lacking in sulphate. In these scenarios, the supply of urea-AS fertilizers should be increased, and TOYO's Novel Urea Mixed Fertilizer Process will contribute to more crop yields by better N-efficiency and by addressing the problem of sulphur-deficient soils. Table 1 shows a typical composition of the urea-AS product produced by TOYO's Novel Urea Mixed Fertilizer Process.

Table 1: **Typical composition of urea-AS product (dry basis)**

Urea, wt-%	95 to 99.9
AS*, wt-%	0.1 to 5
N, wt-%	45.1 to 46.4
S, wt-%	0.02 to 1.2
Biuret, wt-%	<1.0

*Higher AS (=S) content is possible by adding sulphuric acid and ammonia to the process.

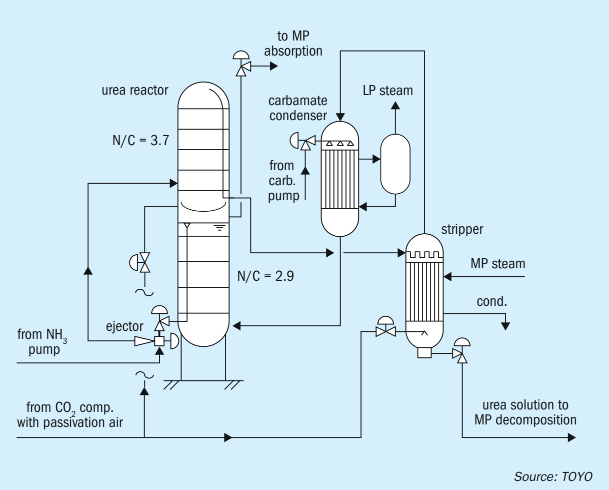
Source: TOYO

Advantages and benefits

As discussed above, "good chemistry" of the atmospheric air-swept evaporator and acid scrubbing provides the following advantages and benefits while achieving NH_3 and urea in the scrubber exhaust air of less than 20 mg/Nm³ and 30 mg/Nm³ (5 mg/Nm³ with WESP) respectively:

- no ammonium salt (liquid) by-product because all of the recovered urea-AS solution from the scrubber is concentrated together with the urea solution from the vacuum evaporator in the atmospheric air-swept evaporator, producing urea-AS mixed granules or prills;
- elimination of the entire process condensate treatment section since no excess process condensate is produced in the water-saturated environment of the dust scrubber;
- no ammonium salt contamination to urea synthesis because all ammonium sulphate recovered in the dust scrubber is shipped as urea-AS fertilizer after concentration in the air-swept evaporator;
- flexible urea/AS ratio by adding sulphuric acid and ammonia to the feed stream of the product forming section before the air-swept evaporator;
- acid consumption can be reduced by stripping NH_3 in the process condensate from the first evaporator with a condensate stripper (not shown in Fig. 1);
- easy application to existing plants by replacing the existing vacuum evaporator with an atmospheric air-swept evaporator or by adding it downstream of the existing vacuum evaporator;
- better N-efficiency of urea-AS mixed fertilizer;
- all proven process components including air-swept evaporator;
- less capex and opex.

Fig. 4: **Conceptual flow diagram for scaled-down ACES21®**

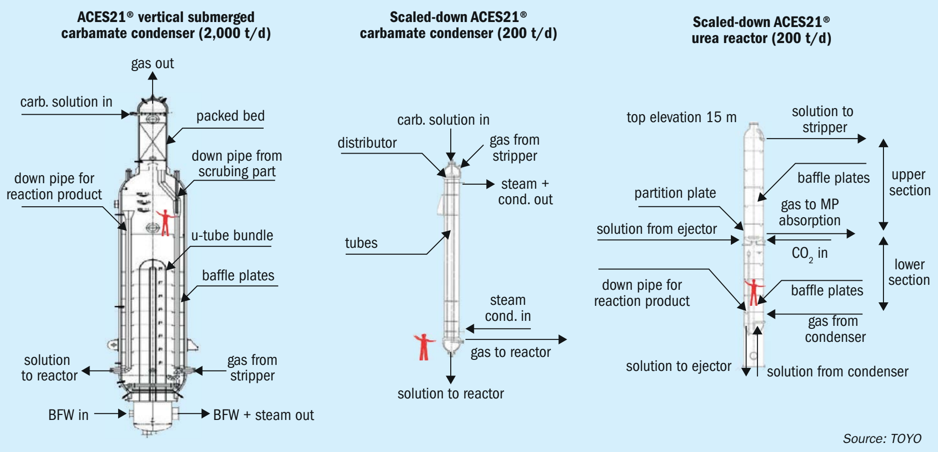


Source: TOYO

Smaller scale urea plants

In pursuit of a carbon-neutral society, demand for sustainable urea production utilising renewable resources and non-fossil resources, such as green ammonia, CO_2 captured from industrial plant flue gases or DAC (direct air capture), biomass, and municipal solid waste (MSW), is increasing. Green urea plants will be,

Fig. 5: **Size Comparison of synthesis equipment – 2,000 t/d ACES21® vs. 200 t/d scaled-down ACES21®**



Source: TOYO

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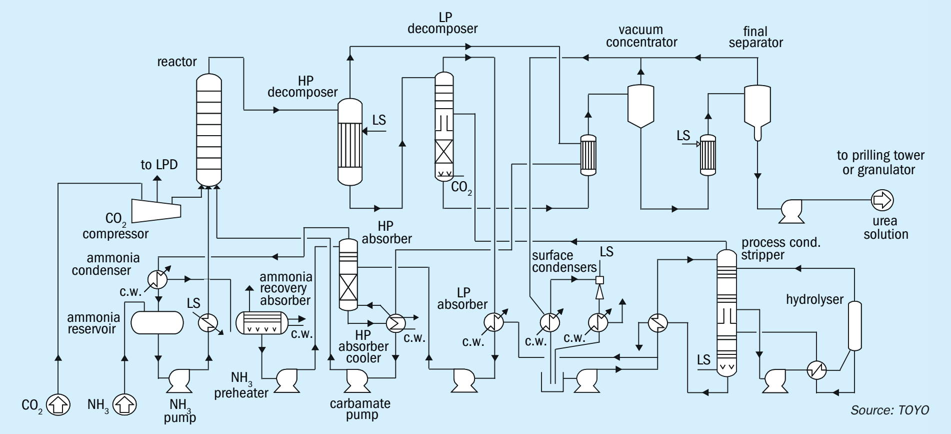
Fig. 6: **The Advanced Total Recycle Process**



Source: TOYO

in many cases, small scale (50-500 t/d) due to constraints in renewable resources and energy. Two process options for green urea are available from TOYO; the scaled-down ACES21® process as an energy saving option and the Advanced Total Recycle Process as a capex saving option.

Scaled-down ACES21® process

The conceptual flow diagram of a scaled-down ACES21® plant is shown in Fig. 4.

The scaled-down ACES21® process is designed to be suited to small to medium scale plants (200 to 2,000+ t/d), adopting a conventional fixed tubesheet vertical heat exchanger to carbamate condenser and a reactor consisting of two partitioned sections. Fig. 5 shows a size comparison of the vertical submerged carbamate condenser (VSCC), carbamate condenser and urea reactor of a 2,000 t/d ACES21® plant compared to a 200 t/d scaled-down ACES21® plant with the following HP equipment features:

- Urea reactor:
  - ❍ Self-supporting tower without U-tube bundle enables inspection and maintenance inside the reactor even for 200 t/d plant.
  - ❍ Partition to upper and lower sections for specific N/C ratios realises low-pressure synthesis at 152 barg at high NH_3/CO_2 3.7 (same as ACES21®)
  - ❍ Forced circulation with HP ejector connecting the two sections enables ground level installation.
- Carbamate condenser:
  - ❍ Fixed tubesheet vertical heat exchanger without internal bore welding (IBW) requires only conventional welding technique for fabrication and maintenance.
  - ❍ Natural circulation of boiling water in shell side eliminates circulation pumps.
  - ❍ Application of DP28W™ (super duplex SS by TOYO) to the whole synthesis section eliminates the HP scrubber thanks to a drastic reduction of passivation air requirement.

Advanced Total Recycle Process

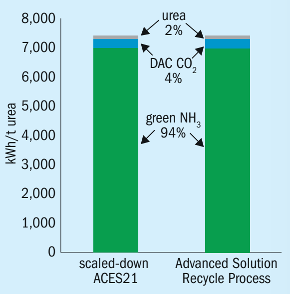
The Advanced Total Recycle Process is designed to be suited to small scale plants (200 to 500 t/d) that meet the latest product quality and environmental requirements by applying advanced modern technologies. The DP28W™ urea reactor equipped with TOYO proprietary baffle plates achieves high CO_2 conversion (70% at N/C 4.0) at milder conditions (196 barg, 192 °C) than conventional total recycle processes. Fig. 6 shows the overall process flow diagram.

Either vacuum evaporation or crystal separation can be selected for the concentration process. A Vibropriller, which produces excellent uniform prilled urea, can be applied for product forming. Since there is only one item of high-pressure critical equipment (the urea reactor), maintenance is easier than for stripping processes. Electrification is easier in a full-green environment with green ammonia and captured CO_2 thanks to the requirement for only low-pressure steam as heat source compared to stripping processes which require medium-pressure steam.

Process performance and economics

Full green urea production (g-Urea®) from green ammonia and CO_2 from flue gas or DAC, consumes significantly more energy (renewable electricity) than that from natural gas. As shown in Table 2, while a urea plant consumes only 117 to 131 kWh/tonne of urea, green ammonia production consumes 7 MWh/tonne of urea (including hydrogen production by water electrolysis), and CO_2 capture from flue gas or DAC consumes 25-300 kWh/tonne of urea, i.e. electricity consumption for production of green ammonia and CO_2 from DAC accounts for 94% and 4% respectively, and the rest (only) 2% is for the urea plant (see Fig. 7). Energy and the cost for green hydrogen (to ammonia) production dominate the economics (opex and capex) of nitrogen fertilizers (urea and ammonium nitrate).

Fig. 7: **Electric power break-down for g-Urea®**



Source: TOYO

As discussed in the box to the right, the weight of urea capex, opex and energy requirement will be significantly smaller in a "full-green environment" than a fossil-based environment and, for small-scale urea plants, it would be hard to justify devoting the same amount of resources (workforce and fixed expenses) to O&M activities as for large scale plants. The Advanced Total Recycle Process would be a promising solution for g-Urea® as it has only one item of critical high pressure equipment (urea reactor) and is easier to operate owing to the solution recycle system without HP synthesis loop. The g-Urea® concept will also be advantageous in realising an autonomous and maintenance-free urea plant in the near future.

Conclusion

TOYO's Novel Urea-AS Mixed Fertilizer Process, which combines an atmospheric air-swept evaporator and acid scrubbing, offers multiple solutions and benefits with regard to pollution abatement and high-value added products.

TOYO also offers two new process options to meet the needs for smaller scale urea plants for its g-Urea® concept: scaled-down ACES21® for energy saving and easier maintenance, and the Advanced Solution Recycle Process for capex saving and easier O&M, as well as for autonomous and maintenance-free urea plants in the near future. ■

Table 2: **Raw material and utility consumptions for g-Urea®**

	Scaled-down ACES21®	Advanced Solution Recycle Process
NH_3 (100%), tonne	0.567	0.567
CO_2 (100%), tonne	0.744	0.744
Steam, tonne	0.67 (20 barg)	1.27 (8 barg)
Electricity, kWh	117	131
Electricity for green NH_3 production (incl. electrolysis), MWh	7 (12 MWh/t NH_3)[2]	
Electricity for CO_2 capture, kWh	25-300 40 kWh/t CO_2 (flue gas) 400 kWh/t CO_2 (DAC)[3]	

Source: TOYO

Cost for g-Urea®

The cost for g-Urea® can be estimated assuming costs of green ammonia and green CO_2 as follows referring to published literature[2,3,4,5]

Table 3: **Provisional cost estimate of ammonia and CO_2**

	Ammonia[4]	CO_2 [5]	
	(Year 2030)	Flue gas	DAC
$/t	900 (600-1,200)	85	225

Source: TOYO

In this case, the raw material costs for g-Urea® can be calculated as:

$$900 \times 0.567 + 85 \times 0.744 = 574 \text{ \$/t urea } (CO_2 \text{ from flue gas})$$

$$900 \times 0.567 + 225 \times 0.744 = 678 \text{ \$/t urea } (CO_2 \text{ from DAC})$$

Since the urea production process is essentially the same for a full-green environment, the urea production cost (capex+opex) can be estimated from current market prices as follows:

Ammonia = 295 $/t (fob Arab Gulf, mid-Apr)

Urea = 285 $/t (fob bulk Arab Gulf, mid-Apr)

Production cost attributable to urea plant:

$$285 - 295 \times 0.574 = 116 \text{ \$/t urea}$$

Based on the above, the weight of g-Urea® production will be 15 to 17% of the total cost as follows:

$$116/(116+574) \times 100\% = 17\%,$$

$$116/(116+678) \times 100\% = 15\%$$

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Reliability of reformer outlet systems

The reliability of primary reformers is a key issue for syngas plants. In this article **O. Chung**, **N. Goodman** and **C. Thomas** of Quest Integrity describe the damage mechanisms and material limitations that impact the reliability of reformer outlet systems and the improvements that may be implemented.

The primary reformer in petrochemical plants is a critical asset that enables the conversion of hydrocarbons (e.g. natural gas or methane) into hydrogen-rich synthesis gas (syngas). The main chemical reactions to generate syngas occur within a reformer furnace, which contains spun cast HP50 tubes filled with a catalyst. The main damage mechanism for these catalyst tubes is creep from internal pressure. Literature is available to describe the metallurgical changes that occur for HP50 catalyst tubes, the effect this has on HP50 creep properties and the life assessment methodology based on this understanding[1,2].

Downstream of the reformer furnace is the hot collection system. This outlet system typically consists of the following equipment:

- outlet pigtails – small diameter tubing, known as pigtails due to their often convoluted geometry, is used to accommodate for thermal expansion between the large catalyst tubes and manifolds during start-up and shutdown;
- manifolds;
- bull-tees.

A schematic showing an example of a hot collector system and materials of construction is shown in Fig. 1.

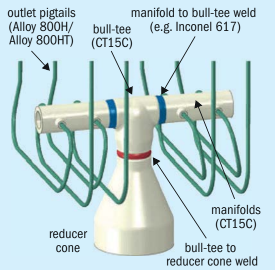
The hot collector system is equally as important as the catalyst tubes because the equipment operates at a sufficiently elevated temperature for creep to occur and complex stresses are generated during operation. Methods used to assess fitness for service and remaining life of high temperature components are well-established and are embodied in codes such as API 579-1/ASME FFS-1 "Fitness-For-Service" (API 579)[3]. However, metallurgical factors such as in-service changes to the materials used for the hot collector equipment and other damage mechanisms not accounted for in the design of the hot collector system present additional aspects to incorporate into the assessment. There is a need to understand the useful remaining life of these components to ensure continued safe operation and reliability, especially for an aging plant.

This article discusses other damage mechanisms and metallurgical factors not accounted for in the design of reformer hot collector systems and the material limitations that affect a fitness for service assessment.

Outlet pigtails

Outlet pigtails are predominantly fabricated from Alloy 800H, Alloy 800HT or their proprietary variants. The nominal material properties for Alloy 800, Alloy 800H and Alloy 800HT, as specified in ASTM B407, are summarised in Table 1[4]. The outlet pigtails may also be dual specified as Alloy 800H/800HT due to the similarities in the nominal specifications.

Fig. 1: **Example of a hot collector system and representative materials of construction**



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Alloy 800 was developed from high value but scrap Nimonic (nickel-chromium) alloys with additions of aluminium and/or titanium and diluted with iron[5]. The Nimonic alloy contained significant levels of aluminium and titanium, which effectively became contaminants in the resulting Alloy 800. Nonetheless, these elements are reported to generate benefits despite a drop in ductility between 650 °C and 750 °C[6]. The 800H and 800HT variants are modifications that offer improved material properties over Alloy 800. These are as follows[6]:

- 800H: a more restricted carbon concentration and grain size than Alloy 800. An average ASTM grain size specification of size 5 or coarser is specified. Introduced as a variant after improvements in the creep and rupture properties were obtained with higher-carbon versions of Alloy 800.
- 800HT: A subsequent variant with further restrictions on carbon, aluminium, and titanium concentrations. Further improvement of creep and rupture properties due to the higher carbon content and higher aluminium and titanium content to enable higher levels of precipitation in the relevant temperature range. An average ASTM grain size specification of size 5 or coarser is also specified.

Alloy 800 and its variants are solid solution alloys. The microstructure of these alloys consists of wrought equiaxed austenitic grains with annealing twins, see Fig. 2. Grain boundary and cuboidal orange/pink intragranular precipitates (e.g. Ti(C,N)) are also present in the microstructure.

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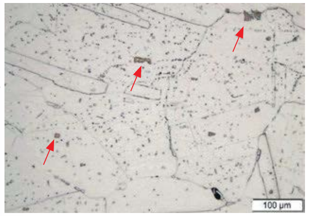

Fig. 2: Representative microstructure - examples of Ti(C,N) precipitates are shown by the red arrows.

Damage that occurs in outlet pigtails can be grouped as creep, creep fatigue, environmental attack and relaxation cracking[7]. The main damage mechanism for pigtails covered in design codes and standards such as API 530[8] is creep. Classical creep damage accumulates in a pigtail as a change in diameter from internal pressure (i.e. hoop stress). Using standardised material properties, conservative design temperatures and pressures, a minimum wall thickness can be determined to obtain a nominal design life of 100,000 hours. In-service creep damage from hoop stress can be monitored by measurement of diametral expansion of the pigtail tube at nominally the hottest part of the outlet tube, see Fig. 3. An example of diametral expansion of pigtails due to creep was presented by M. J. Smillie et al[9]. For a case study presented, diametral expansions of up to 13% were measured on the pup-pieces welded to the end of the main pigtail tubes after seven years of service, whereas the pigtail tubes had significantly lower diametral expansions (e.g. 1.5% compared to 13 % for the pup-piece expansion). The difference in diametral growth was attributed to a variation in grain size between the different pigtail tube sections examined even though both sections conformed to the specification.

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Fig. 3: Observed diametral expansion of a pigtail

Table 1: **Specified properties of ASTM B407 Alloys 800, 800H and 800HT[4].**

<table>
<tr><th colspan="2">Material property</th><th>UNS N08800
Alloy 800</th><th>UNS N08810
Alloy 800H</th><th colspan="2">UNS N08811
Alloy 800HT</th></tr>
<tr><td rowspan="10">Chemical composition (weight %)</td><td>C</td><td>0.10 max.</td><td>0.05 - 0.10</td><td colspan="2">0.06 - 0.10</td></tr>
<tr><td>Al</td><td>0.15 - 0.60</td><td>0.15 - 0.60</td><td>0.15 - 0.60</td><td rowspan="2">Al + Ti = 0.85 - 1.20</td></tr>
<tr><td>Ti</td><td>0.15 - 0.60</td><td>0.15 - 0.60</td><td>0.15 - 0.60</td></tr>
<tr><td>Si</td><td>1.0</td><td>1.0</td><td colspan="2">1.0</td></tr>
<tr><td>S</td><td>0.015 max.</td><td>0.015 max</td><td colspan="2">0.015 max</td></tr>
<tr><td>Cr</td><td>19.0 -23.0</td><td>19.0 - 23.0</td><td colspan="2">19.0 - 23.0</td></tr>
<tr><td>Mn</td><td>1.50 max.</td><td>1.50 max</td><td colspan="2">1.50 max</td></tr>
<tr><td>Fe</td><td>balance</td><td>balance</td><td colspan="2">balance</td></tr>
<tr><td>Ni</td><td>30.0 - 35.0</td><td>30.0 - 35.0</td><td colspan="2">30.0 - 35.0</td></tr>
<tr><td>Cu</td><td>0.75 max.</td><td>0.75 max</td><td colspan="2">0.75 max</td></tr>
<tr><td colspan="2">Average grain size</td><td>-</td><td>ASTM 5 or coarser</td><td colspan="2">ASTM 5 or coarser</td></tr>
<tr><td colspan="2">Tensile strength</td><td>520 MPa (cold-worked annealed)
450 MPa (hot-finished annealed)</td><td>450 MPa (all conditions)</td><td colspan="2">450 MPa (all conditions)</td></tr>
<tr><td colspan="2">Yield strength</td><td>205 MPa (cold-worked annealed)
170 MPa (hot-finished annealed)</td><td>170 MPa (all conditions)</td><td colspan="2">170 MPa (all conditions)</td></tr>
<tr><td colspan="2">Elongation</td><td colspan="4">30 % (all conditions)</td></tr>
</table>

Source: Quest Integrity

Creep damage in the circumferential direction can also occur in pigtail tubes, where axial stresses are greater than hoop stress. Axial stresses can be from transient thermal stresses experienced during start-up/shutdown, bending loads and/or other system loads. Additional factors from fabrication (e.g. ovality) may also contribute to locally higher axial stresses. Creep damage from axial stresses can be difficult to monitor between plant shutdowns and will likely involve on-line monitoring methods.

The extent of observed creep damage is affected by the grain size distribution within the pigtail tube's microstructure. For Alloy 800H and Alloy 800HT, an average grain size of ASTM #5 or coarser is routinely specified. The material's creep performance is dependent on the grain size distribution to achieve this specification and the relative uniformity of the grains. In particular, coarse-grained regions have better creep strength but have lower creep ductility (i.e. "creep brittle" behaviour) and are unable to deform without voiding and/or cracking. Fine-grained regions have better creep ductility and can deform with less voiding. An example of a mixed grain size distribution in an Alloy 800H/800HT pigtail cross section that meets the ASTM average grain size specification and the corresponding circumferential creep damage observed is shown in Fig. 4. This wide variation in grain size frequently leads to cracking either due to the poor ductility of coarse grains or the concentration of strain into fine grained zones. In addition to the requirement to maintain grain size coarser than ASTM grain size #5, it is recommended that there be a requirement to limit grain size variability.

The variation in grain size is best managed during fabrication. Grain boundary response during heat treatment is strongly influenced by the extent of prior cold work. Cold bending will automatically generate variable degrees of cold work and hence variable response to subsequent solution annealing. Fabrication methodologies should be developed to minimise grain size variation.

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The presence of creep voids and cracking can also provide a path for nitridation to occur in Alloy 800H and Alloy 800HT pigtails. Nitridation is the formation of nitrogen-rich precipitates and two main forms of nitrides are formed in Alloy 800H and Alloy 800HT materials, see Fig. 5:

- Titanium carbo-nitrides (Ti(C,N)), which are stable precipitates formed during fabrication.
- Aluminium nitrides (AIN), which are typically formed in-service and are generally fine, acicular needle-like precipitates near the external surface. The primary source of nitrogen for in-service pigtail tubes is from the external atmosphere.

The formation of nitride-rich acicular precipitates in-service have been observed around creep cracks and have contributed to pigtail failures[7,9,10]. Nitridation can reduce ductility and cause embrittlement, although it is acknowledged that published literature validating the effect of in-service nitridation on mechanical and creep properties of Alloy 800H and 800HT is very limited. The rate of formation is a function of the exposure of the pigtail material to air at elevated temperatures. An initial model of the kinetics that enable nitridation to occur in-service for Alloy 800H has been provided by Young et al[11].

Stress relaxation cracking can occur in Alloy 800H and Alloy 800HT at temperatures between 500°C and 750°C due to grain boundary strain[7]. This is generally associated with thick-walled components but can also occur in pigtails. This damage is observed as an intergranular crack morphology with a Fe-Ni rich layer sandwiched between chromium/oxide layers (see Fig. 6). Susceptibility to stress relaxation cracking is also increased for outlet pigtail tubes due to the use of Inconel 617 weld filler material. This filler material has relatively better creep properties than Alloy 800H/ Alloy 800HT and therefore result in a mismatch in material performance as observed by a band of creep voids near the weld fusion line in the parent material (see Fig. 7). The risk of stress relaxation cracking can be reduced by using a matching filler material. In addition, procurement of material in a thermally stabilised condition and heat treatment and stress relieving/post-weld heat treatment of welds and cold-worked sections can further reduce risk. For Alloy 800H, the risk of in-service cracking can be further reduced by using a base metal and weld filler material with a combined aluminium and titanium content less than 0.7%.

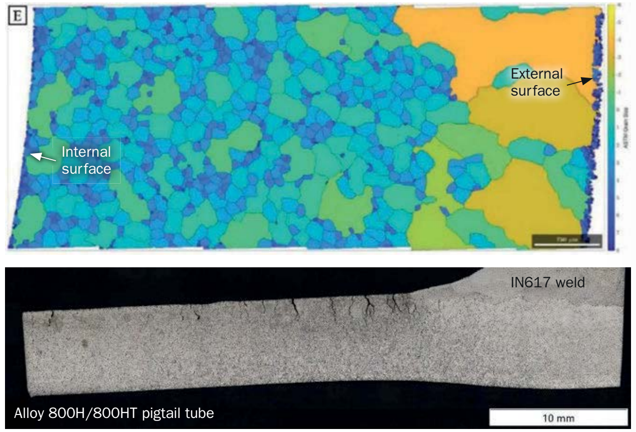

Fig. 4: Example of a mixed grain size distribution and the corresponding circumferential creep damage observed. Average ASTM grain size = 2.99. Evidence of bending is also shown in the pigtail cross section.

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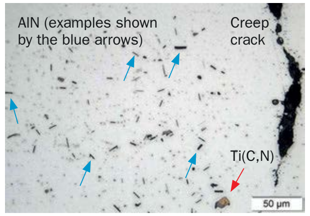

Fig. 5: Representative microstructure showing nitride-rich precipitates. A creep crack is also shown.

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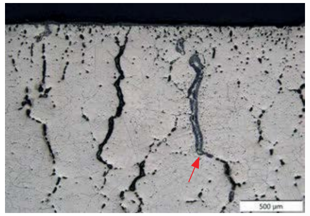

Fig. 6: Example of stress relaxation cracking in an Alloy 800H/ Alloy 800HT pigtail, highlighted by the red arrow. Creep voiding and cracking is also shown.

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Manifolds and bull-tees

By far the most common material of construction for steam reformer outlet manifolds and bull-tees is CT15C as described in ASME SA-351/SA-351M[12]. (SA-351/351M is identical to ASTM specification A351/A351M). It is marketed by a range of suppliers typically using their own proprietary trade designations. This alloy was developed as a cast version of Alloy 800H/ Alloy 800HT and followed catalyst tube developments in being further strengthened by the addition of niobium.

The material is often considered to be a cast version of Alloy 800 and its variants based on its similarity in chemical composition. The adoption of a cast variant saw the use of similar levels of the prime alloying elements, chromium and nickel. Titanium and aluminium were not used in the cast variant. However, in parallel with the development of spun cast reformer tube alloys involving alloying with small amounts of niobium, CT15C similarly was alloyed with approximately 1% of niobium to improve creep properties by encouraging the formation of a fine distribution of niobium carbide particles. The similarities in the compositions of CT15C and Alloy 800HT, as listed in Table 2, are obvious.

As for pigtails, the design of manifolds is typically based on API 530[8] which allows the calculation of required material thickness based on material creep properties at the design pressure and temperature. However, there are no standardised creep properties for alloy CT15C and design is based on creep data provided by the relevant manufacturer. Fig. 8 shows a comparison of published stress rupture data for the CT15C cast material (based on a typical manufacturer's data) and the wrought Alloy 800HT (based on WRC/API 579 data[3]). According to this data, the expected life of the cast material is an order of magnitude higher than that of the wrought material at typical design stress levels around 10 MPa.

Given this improvement in strength and the lower cost of manufacture of the cast material, the benefits of CT15C are clear. This alloy however is not without its problems. Even after relatively short periods in service, routine inspection at scheduled plant outages frequently leads to the discovery of cracking at the weldments connecting the main manifold arms to the bull-tee (see Fig. 9).

Fig. 9 shows a typical bull-tee, and the cracking that may occur. Such cracking has been attributed to bending of the manifold arms relative to the bull-tee[13,15]. Under such circumstances, the weldments act as a fulcrum point concentrating bending loads at the bull-tee to manifold arm welds. The external bending loads leading to this damage are due to thermal movement of the system caused by both start up and shut down cycles and day to day temperature variations.

This cracking has led to a need to ensure fitness for service or repair. Both of these options are potentially problematic. Fitness for service using codes such as API 579[3] requires knowledge of material properties including creep strength, creep crack growth rate and fracture toughness. These data are not readily available for alloy CT15C. Furthermore, experience has shown that ex-service material properties of CT15C may vary significantly from those provided to enable initial design. Fig. 10 shows creep and toughness data obtained following laboratory testing of ex-service manifold material from an ammonia plant that had operated at 760 °C. Testing of this material revealed that the creep properties had degraded significantly and the material toughness was extremely low[14]. Subsequent experience has shown that the material properties shown in Fig. 10 were at the extreme low end of the range, highlighting the uncertainty associated with selecting data for use in fitness for service assessments.

Repair of cracking has shown itself to be equally problematic. Information regarding repair of manifolds is available in API 942-A[16]. The difficulty lies in the low temperature toughness experienced in ex-service CT15C (Fig. 10) with Charpy impact energies below 10 joules. This has led to serious welding problems. Repair welds typically result in further cracking. The data in Fig. 10 shows that some toughness can be restored by solution annealing, which demonstrates that solution annealing can restore weldability. This is not trivial requiring temperatures in excess of 1,100°C.

The loss of ductility is due to the in-service formation of G-phase[15]. Analogous to the more familiar sigma phase in stainless steel, G-phase is an intermetallic formed between niobium and silicon. In wrought niobium containing stainless steels, it has been shown that G phase forms most rapidly at approximately 750°C to 800°C[17], which is very close to the outlet temperature of many steam reformers.

Given the significant impact of G-phase in modifying toughness and possibly creep properties by the absorption of niobium and the resulting uncertainty around the resulting material properties, it is suggested that alloying with niobium could be usefully avoided. A niobium-free alloy would in principle at least, not embrittle in service due to G-phase. Alloying with niobium has become standard due to the improvement it offers in creep strength as

Fig. 7: Creep voiding observed along the fusion line of a pigtail weld joint

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Fig. 8: **Comparison of rupture life for Alloy 800HT And CT15C**

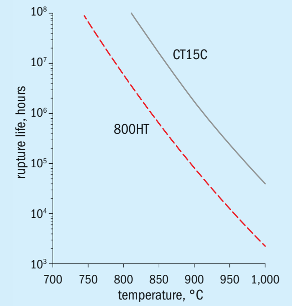

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Table 2: **Nominal chemical compositions of CT15C and Alloy 800HT.**

Material specification	**Element (weight %)**										
	C	Cr	Ni	Si	Mn	S	P	Nb	Ti	Al	Fe
UNS N08151 (CT15C)[12]	0.05-0.15	19.0 - 21.0	31.0 - 34.0	0.50 - 1.50	0.15 -1.50	0.03 max.	0.03 max.	0.50 - 1.50	-	-	bal.
UNS N08811 (Alloy 800HT)[4]	0.10 max.	19.0 -23.0	30.0 -35.0	1.0	1.50 max	0.015 max.	-	-	0.15 -0.60	0.15 -0.60	bal.

Source: Quest Integrity

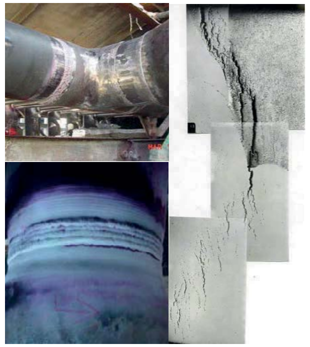

Fig. 9: A typical manifold bull-tee weldment, cracking revealed by dye penetrant and an extreme example of that cracking in cross-section[13,14]

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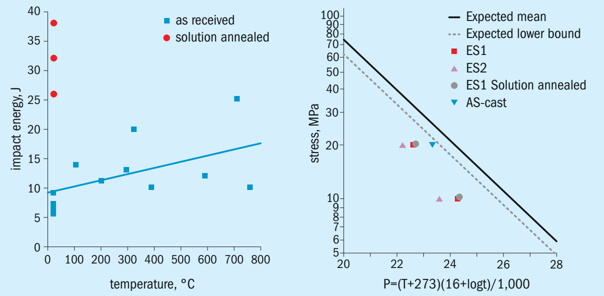
Fig. 10: **Charpy impact and creep data for ex-service CT15C before and after solution anneal heat treatments (ES=Ex-service)**[14]



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measured on as-cast material. Manifolds are not restricted to a particular thickness and adequate strength while using a niobium free alloy could be obtained by design. It is significant that failure due to pressure generated creep damage is not unknown but is very rare compared to cracking at bull-tee to manifold welds. Creep data for a niobium-free material has not been found. Nor has information relating to embrittlement processes in such an alloy. Nonetheless, it is considered that the improvement in embrittlement resistance and the variability of ex-service properties may offset the reduction of initial creep strength.

The choice of weld consumable may also affect the performance of these welds. A description of the weld consumables that are used in manifold welds is provided in API Technical Report 942-A[16]. Inconel 82 has been used extensively in the past. This weld metal has relatively low creep strength and creep failures within the weld metal have seen a migration to the high strength alloys such as 617. Inconel 617 has significantly higher creep strength than the parent CT15C material. The consequence of this appears to be relaxation of weld residual stress concentrated into a narrow zone of parent material adjacent to the weld fusion line. Inconel 617 has the potential to lead to a form of stress relaxation cracking that will exacerbate damage from any bending loads caused by thermal movement of the manifold. This damage is also noted for outlet pigtail joints, as described above. While the objective of using a high strength weld metal would appear to have merit, it is considered more beneficial to use a weld consumable of matching strength to the parent material thereby more evenly distributing welding residual stress.

Discussion

The choice of material of fabrication for both pigtails and manifolds has become firmly entrenched. In the case of pigtails, Alloy 800H and/or 800HT and in the case of manifolds and bull-tees CT15C and its proprietary variants are dominant choices of material. Both alloys have performed well in their respective roles but each has its own unique problems.

In the case of Alloy 800H/Alloy 800HT and its application in outlet pigtails, the aluminium and titanium content has led to long term nitridation damage, ductility drop issues and consequently an increased risk of stress relaxation cracking. Given the spurious origin of these alloying elements in Alloy 800 and its subsequent variants, alternative alloys are considered worthy of consideration. This includes Alloy 330, which is effectively Alloy 800 without the aluminium and titanium additions and hence may avoid some of the deleterious aging characteristics. It is normally used for high temperature corrosion resistance. However, its creep properties without the benefit of grain size control are similar to those of the basic Alloy 800 (Fig. 11)[5]. If similarly processed to generate a coarse grain size, similar or superior creep properties are likely to be obtained.

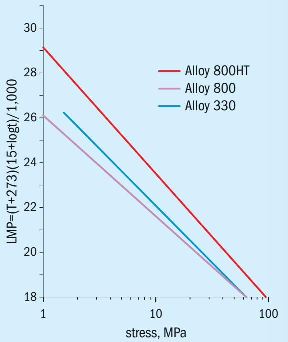
Control of grain size in Alloy 800H and 800HT is of prime importance in order to obtain the expected properties. This is normally managed by specifying grain size to ASTM grain size #5 or coarser. This limitation has been found to be oversimplified given that grain size variation within this range can lead to low ductility cracking issues. This grain size variability is mainly caused by fabrication methods since the grain growth during heat treatment is strongly affected by the degree of cold work prior to the solution anneal heat treatment. It is considered that fabrication approaches need to be modified to control this affect. An example would be to hot bend pigtails, in addition to quality checks of the product during fabrication.

In the case of manifold materials, the use of CT15C as the material of choice has merit due to its good creep performance. However, its propensity to aging leading to variable material properties and embrittlement has led to problems. The prime reason for this is believed to be the formation of G-phase in service. It absorbs niobium removing it from its prime role of improving creep strength and leads to low temperature embrittlement leading to weld repair difficulties. Eliminating the source of G-phase i.e. niobium would likely require compensation by design to increase wall thickness but has the potential to at least reduce in service degradation of material properties.

Choice of weld metal is also important. Inconel 617 has found favour to counteract creep failures encountered in weaker weld metal. It is suggested however that stronger is not necessarily better and results in high residual stress and consequential relaxation cracking in the adjacent parent metal. It is considered that a matching weld metal is more likely to provide long time reliable performance.

The materials issues highlighted here have their roots in attempts to improve high temperature performance by alloying i.e., aluminium and titanium in Alloy 800(H/HT) and niobium in alloy CT15C. These alloying additions however result in long term instability of material properties. In selecting alloys for stability, unless absolutely necessary to maximise strength, keeping the material as simple as possible would appear to have merit. ■

Fig. 11: **Comparison of Alloy 800HT, Alloy 800 and Alloy 330 creep properties**[5]



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Methods to mitigate metal dusting in syngas production

Industrial plants using synthesis gas at elevated temperatures risk metal dusting attack on the equipment, which are typically made of steels or Ni-based alloys. Parameters which impact the metal dusting risk are discussed and factors affecting the material selection and processing are described. One important focus is surface preparation, showing that grinding (40 grit) improves the metal dusting resistance compared to glass bead blasting and brushing. The surface treatment outweighs the impact of welds or the manufacturing route.

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Process plants handling carbon-containing gases at high temperatures often face a corrosive attack termed "metal dusting". This occurs at 450 to 750°C in gases with a high carbon activity and is catalysed by iron, nickel and cobalt[1–3]. Among other industries, synthesis gas production is highly affected by metal dusting which is known to occur in the downstream sections of these plants. A common solution is cooling the gas very quickly in the critical metal dusting temperature regime. However, the losses of process heat are immense, and were estimated at $220 to 290 million per year in 2000 in US hydrogen production alone[4]. With the increasing demand for hydrogen and CO_2 neutral syngas, optimisation of steam reformers and development of new syngas production technologies become even more important. Independent of the technology used, losses in process efficiency are less acceptable than ever, driving a strong need for effective and efficient mitigation of metal dusting.

Components prone to metal dusting are commonly made of steels or Ni-based alloys. Alloying additions of Cr, Al, and/or Si can result in the formation of an oxide scale under process conditions. The oxide scale acts as a barrier between the process gas and metal substrate. In carbon-rich gases, carbon may deposit on the surface of the oxide by CO or CH_4 dissociation. However, if the oxide scale fails to provide a protective barrier after an initiation period, the corrosive attack will start locally. Carbon accesses the metal through the oxide, dissolves and supersaturates. Cementite (Fe_3C) forms in most steels. Both cementite in steels and nickel in Ni-base alloys catalyse graphite formation along grain boundaries from the supersaturated carbon. This breaks up the integrity of the material, resulting in the corrosion product "coke". Coke is a mixture of metallic particles, graphite, amorphous carbon, and oxides[1,5].

Due to the initiation of the attack at local failures within the oxide scale, the attack grows into the material in the form of pits. Once metal dusting attack starts, it proceeds very rapidly. Therefore, most effective mitigation strategies aim to stop the attack from the beginning, that is before carbon ingress occurs in the metal.

Experimental methods

The results were obtained using quasi-isothermal laboratory exposure experiments. If not stated otherwise, samples of sheet materials were wire eroded (electro-discharge machined) and ground to P1200 grit with SiC paper. Samples were then cleaned ultrasonically with ethanol and placed in separate slitted alumina crucibles. Tests were performed in a horizontal tube furnace at elevated pressure. Details of the apparatuses are given in[6]. The samples were heated up in Ar, then pressurised with the test gas. After a given exposure time, the system was de-pressurised and cooled down simultaneously. The samples were cleaned after each exposure period.

Results and discussion

The following discussion is divided in two sections: 1) the process conditions, and 2) the material selection. In both sections, the main parameters are discussed first, followed by an overview of mitigation strategies.

Process conditions

Impact of the process conditions

Low or stagnant gas velocities were shown to enhance localised attack and allow transformation of the gas to a more (or less) aggressive composition[7]. On the other hand, a high gas flow can remove the already formed coke from the surface, which promotes access of the process gas to the damaged oxide/metal surface and results in a faster and more uniform attack[7,8]. In addition, hard particle erosion can enhance the corrosive attack[8]. Depending on the gas and metal temperature, the gas velocity can also make a difference in reaching or avoiding the critical metal dusting temperature range[7,8].

Several studies showed that the incubation time of the metal dusting attack is significantly shorter at elevated pressures when compared to ambient pressure for the same gas composition and temperature[4,6,9]. Other parameters affecting the metal dusting attack are gas impurities[10] and surface stresses from temperature and pressure gradients[8].

The gas composition is decisive for the metal dusting risk. Process gases with a low driving force for carbon deposition have a low metal dusting risk as this reduces the supersaturation potential. However, the driving force for carbon deposition currently cannot be determined precisely. In the literature, various methods to estimate the driving force for carbon deposition, and thus the risk for metal dusting have been discussed. These chemical reactions for carbon deposition have been considered:

$$CO + H_2 \rightleftharpoons C + H_2O \quad \text{syngas reaction}$$

$$2CO \rightleftharpoons C + CO_2 \quad \text{Boudouard reaction}$$

$$CH_4 \rightleftharpoons C + 2H_2 \quad \text{methane cracking}$$

However, at 650°C methane formation is more likely than methane cracking[11]. Thus, often only the syngas reaction and the Boudouard reactions are considered. One way to estimate the driving force for carbon deposition is the CO/H_2 ratio in the gas[12]. A second option is to calculate the carbon activity in the syngas reaction:

$$a_{C,syn} \rightleftharpoons K_{syn}\,(p_{H2} \cdot p_{CO}) \,/\, p_{H2O}$$

And the Boudouard reaction:

$$a_{C,Boud} \rightleftharpoons K_{Boud}\,(p_{CO}{}^{2}) \,/\, p_{CO2}$$

where K_{syn} and K_{Boud} are the equilibrium constants of the reactions and pi is the partial pressure of the components. For the purpose of this calculation, carbon activities greater than one are interpreted as a high driving force for carbon deposition.

Hermse et al.[7] pointed out that in addition to the carbon deposition reactions, the water gas shift reaction may also take place.

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

water gas shift reaction (WGS)

These local changes in the gas composition may occur near the surface or in areas with low gas exchange rates. Hermse et al. suggested to assume that the water gas shift reaction proceeds until thermodynamic equilibrium is reached[7]. The changed gas composition can then be calculated. The carbon activity of the changed gas is labelled $a_{C,synWGS}$. Hermse et al. reported a positive correlation between these parameters and the aggressivity of the attack observed in laboratory tests[7].

The gas composition at equilibrium, now considering all possible reactions between the species, can be calculated with the CALPHAD approach. In order to obtain the driving force for carbon deposition similar to those above, graphite formation is suppressed in the calculation. The result gives the carbon activity in metastable equilibrium ($a_{C,metast}$). It is metastable because in full thermodynamic equilibrium, graphite may form. Comparison of all of the described parameters against experimentally observed attack have been reported in detail in[13].

Further work is necessary to extend the model with kinetics and surface reactions.

Mitigation strategies through adapting process conditions

Within the design limits of the process and plant, adaptations can be implemented to lower the metal dusting risk. Mitigation strategies by changing process conditions and their drawbacks are summarised in Table 1.

Material selection

Impact of the material and surface

Two approaches in alloy design can improve the resistance of the materials against metal dusting. One is alloying with stable oxide-forming elements such as chromium, aluminium and silicon. The other is adding elements which inhibit the catalytic dissociation of CO and formation of graphite, such as copper or tin[18–20]. The more recently developed alloy HR-235 and alloy 696 combine both strategies by alloying with oxide-forming elements and copper. However, the currently most used alloy systems are steels or Ni-based alloys with high additions of oxide formers. The following discussion is therefore focused on these alloys.

The oxide scale acts as a barrier between the gas and the metal. A protective barrier is expected to form under process

Table 1: **Metal dusting mitigation strategies through changing process conditions**

Method	Background	Drawbacks	See also
Rapid cooling from 875 to 340°C	Avoid the critical temperature regime of slow oxide scale formation and high carbon activity. Below 400°C the MD reaction is too sluggish.	High inefficiencies through loss of process heat.	Refs 4, 8
Lower pressure	Later onset of attack at atmospheric pressure compared to higher pressures.	Process efficiency losses.	Refs 4, 6, 9
Higher H_2O content	H_2O additions shift the syngas reaction. Also, preferred adsorption of H_2O mitigates CO dissociation. In addition, a higher resistance of stainless steel over Ni-based alloys in high H_2O-containing gases was reported.	Feasability with the desired process gas composition, increased costs, lower efficiency, condensation issues.	Refs 14, 15
H_2S addition	Adsorbed sulphur blocks the CO adsorption sites and thus inhibits CO dissociation at the surface. It also mitigates the nucleation and growth of graphite.	Likely to block catalyst sites, risk of material sulfidation from too high H_2S content, additional safety hazard from using H_2S.	Ref 16
Intermediate oxidation step in a carbon-free gas	Supports the formation and maintainance of a protective oxide scale (before the start of pit formation).	Not feasible in all plants, time consuming (plant downtime), additional cost.	Ref 17

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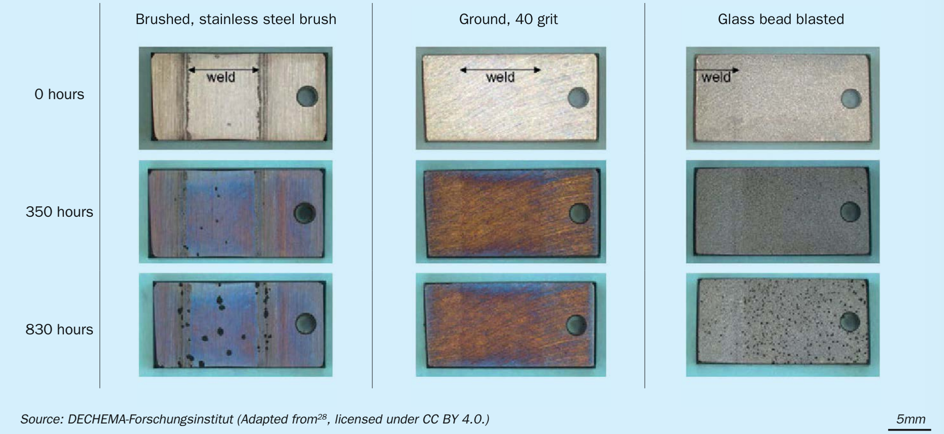
Fig 1: **Weld beads of alloy 602 CA with three industrially applied surface treatments: brushed, ground, or glass bead blasted exposed in harsh laboratory metal dusting environments.**



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conditions, regrow in case of damage and should, of course, be impermeable to carbon. The pure oxides chromia, alumina and silica offer excellent protection, but mixed oxide layers and spinels which grow under process conditions may be infiltrated by carbon after long times and/or in very aggressive environments[21–24]. Oxide scale formation can be optimised by tailored alloying and surface preparation.

Several studies showed that a high alloying content of chromium and aluminium reduces the metal dusting attack[25–27]. Thus, commercial alloys with very high chromium and relatively high aluminium contents were developed for these applications (e.g. alloy 699 XA, alloy 693). Alternatively, coatings can be used to establish a protective barrier between the process gas and metal, for example by applying a diffusion coating enriched in oxide-forming elements.

Surface treatments are often applied to remove impurities, such as oxides formed during welding. In most industrially used surface treatments, the surface roughness is generally lowered and the near-surface zone is deformed. In the deformed zone, more diffusion paths are available for the oxide forming elements like chromium, aluminium and silicon. This may be decisive in the formation and maintenance of an oxide scale during operation. Samples of weld beads on alloy 602 CA with different surface treatments, before and after metal dusting exposure experiments in a harsh laboratory environment are displayed in Fig.1.

The surface treatments were performed industrially. After the metal dusting exposure experiment, no attack or carbon deposition was observed on the ground sample (40 grit zircon corundum paper). Some carbon deposition resulted on the glass bead blasted sample and the strongest attack occurred on the brushed sample (stainless steel brush). During brushing, iron impurities contaminate the alloy and act as nucleation sites for the metal dusting attack[29]. In general, all working media used in the last step of the surface treatment should be free of any steel to prevent this effect.

Fig. 1 also shows that with a suitable surface treatment, a weld can be as resistant against metal dusting as the base alloy. Here, it is important that the filler material has a similar composition to the base material. Also, the removal of impurities from the weld, achieved in the shown example by fully flattening the weld bead while grinding, can prolong the metal dusting resistance.

Additive manufacturing (AM) enables a faster exchange of attacked parts through just-in-time on-site production of components. A study was carried out to evaluate whether the manufacturing route changes the metal dusting susceptibility. Samples of hot rolled and AM alloy 699 XA, with and without heat treatment (solution annealing), were exposed to industrially relevant process conditions.

First results showed that no metal dusting pits were observed on any of the samples. On the ground AM samples (P1200 grit SiC paper), no carbon deposition was visible independent of the heat treatment. The same is true for the hot rolled and mill ground sample. However, carbon deposition was clearly visible on the heat-treated AM sample with as-built surface. Carbon was also present on the AM as-built sample (without heat treatment) due to the higher surface roughness. In conclusion of this first study, the surface state of the samples is more decisive for the metal dusting resistance than the manufacturing route.

Mitigation by material selection and coatings

Careful choice of materials, coatings, surface treatment and equipment design are vital to reduce the risk of metal dusting attack. Table 2 summarises approaches to mitigate metal dusting from the component side.

Conclusions

Overcoming the problems resulting from metal dusting attack is a key element in reaching a low CO_2 footprint in syngas production. As the gas compositions differ between old and new technologies, it is important to understand the impact of the gas composition on the metal dusting risk.

If altering the gas composition or process conditions are possible, this is a powerful tool to mitigate the metal dusting attack. Alternatively, the component material and surface finish must be selected carefully. Initial results of additively manufactured parts show limited impact of the manufacturing route. The surface treatment (and surface area) has a stronger impact on the metal dusting resistance for highly alloyed Ni-based materials, such as alloy 699XA. Choice of highly alloyed materials or suitable coating strategies are recommended to mitigate metal dusting. ■

Table 2: **Metal dusting mitigation strategies using materials, coatings, and design**

Method	Background	Drawbacks	See also
Suitable design of equipment	Adaptations in the design of the parts in the most critical regions, replacement with ceramic parts, if possible.	Design, manufacturing and process limitations.	Ref 14
Alloys with relatively high chromium, aluminum, and silicon content	Improved formation of a protective oxide scale by high availability of the oxide forming elements.	Weldability, processability and cost of the alloys.	Refs 27, 30
Grinding the surface of oxide forming alloys	Deformation of the top surface zone to enhance oxide scale formation, removal of impurities.	Difficult for hard-to-access parts and complex geometries.	Refs 28, 31
Alloys with copper additions	Copper lowers the solubility of carbon in the metal and mitigates graphite formation.	Lower mechanical properties of high copper alloys, weldability issues and higher cost.	Refs 19, 20
Coatings with highly resistant alloys	Coatings of higher alloyed materials may be used in critical areas, e.g. as claddings or via plasma spraying.	Increased costs, application of coatings on complex parts and interior geometries can be difficult. Loss of protection if the coating fails.	Ref 32
Aluminizing or chromizing (diffusion coating with aluminium or chromium)	Diffusion coatings are known to be adherent and provide an increased reservoir of oxide formers. Possible during post-weld treatment.	Increased cost, coating parameters need to be adjusted to the base material. Degradation by interdiffusion with the base material especially at high temperatures.	Refs 28, 33

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