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nitrogen 60 YEARS ANNIVERSARY 1959-2019 syngas

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- Urea market trends
- Ammonia as an energy carrier
- Carbon pricing in the syngas industry
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JM

Making a difference to the world around us

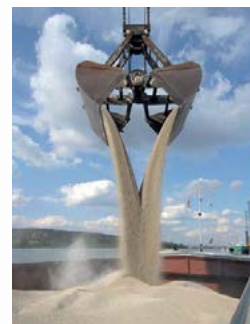
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Cover: Loading nitrogen fertilizers onto a barge, port of Rouen, France. Photoagriculture/Shutterstock.com



12 Energy carriers

Getting renewable energy to where it is needed.



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Controlled release and stabilised urea.

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10 Trends in the urea market

The urea market is currently still oversupplied and operating rates are low. In spite of Chinese plant closures and the potential impact of sanctions on Iran, continuing capacity expansions could keep prices depressed for some years to come.

12 Chemicals as energy carriers

Hydrogen, methanol and even ammonia have all been suggested as a way of transferring energy, perhaps renewable energy, produced or gathered in one place to a destination where the energy is required.

14 Carbon pricing and the siting of syngas capacity

This year, Canada is beginning to implement a federal carbon pricing scheme, while the EU's emissions trading scheme has finally moved out of the previous oversupply of permits via its Market Stability Reserve programme. Will these merely drive capacity to non-regulated environments ('carbon leakage'), or encourage innovation into lower carbon production of ammonia and methanol?

17 2019 AIChE Ammonia Safety Symposium

Venkat Pattabathula reports on the American Institute of Chemical Engineers' Safety in Ammonia Plants and Related Facilities Symposium, held 8-12 September in San Francisco, USA.

19 Nitrogen efficiency use and environmental sustainability

Enhanced efficiency fertilizers will be required to feed a growing population. Controlled release and stabilised urea products are capturing a greater share of the market. Innovative biodegradable polymer coatings are being developed to meet the requirements of new regulations in Europe.

25 Real time urea process analysis and control

A new powerful tool for on-line urea process analysis and control in real time is now available. L. Rugnone of Casale SA, C. Uerpmann of Kaiser Optical Systems and C. Minnich of S-PACT GmbH discuss the development of this breakthrough analyser which is designed to measure the full composition and the most important key performance indicators in urea synthesis.

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Ammonia for shipping



Ammonia's versatility as a chemical has been somewhat obscured by it being the only real way of building nitrogen-based fertilizers, primarily urea and ammonium nitrate. Because 75-80% of all ammonia finds its way into these uses, it is easy to forget that ammonia can be used for other purposes. One of these we discuss on pages 22-24 of this issue; the idea of ammonia being used as a way of transporting hydrogen over long distances. But another idea is also increasingly starting to take hold – that of ammonia as a fuel.

The use of ammonia as a fuel is not a new idea. In the 19th century, British inventor Goldsworthy Gurney, who had developed steam-powered cars, built an ammonia-powered engine. It was used in Belgium during the Second World War to power buses when no gasoline was available, and even fuelled the experimental US rocket plane X-15, the fastest aircraft ever built. However, the current interest centres around ammonia's potential as a marine fuel.

While the International Maritime Organisation's (IMO) regulations on sulphur content of marine fuels, due to come into force on January 1st 2020, have been causing headaches for refiners and ship owners alike, and leading to some vessel operators to turn to methanol as a low sulphur fuel, a target further down the line is also starting to cause concern. The IMO has set the target of reducing carbon emissions from shipping by 50% by 2050 (compared to a 2008 baseline), and the shipping industry is starting to look at how this might be achieved. It would mean, according to no less an authority than Maersk AS, the world's largest cargo carrier, that to convert sufficient ships to achieve this, the first "commercially viable carbon neutral vessels" would need to be in service by 2030.

Maersk says that it is looking at three main options to achieve this – alcohol, biogas, and ammonia. In a report published this month, it says that "other configurations such as batteries or fuel cells are much further behind in terms of development, and are not very likely to be part of the first generation of net zero configurations for deep sea shipping". The ammonia would of course be produced using hydrogen generated by renewable electricity. Maersk adds that: "as such it ties into an infinite resource and the sun to energy conversion rate of this system is higher than biomaterial-based systems. It is already produced in high volumes for other sectors which could be scaled given an indication from shipping."

With a 15% share of the world's container shipping market, the decisions that Maersk makes matter to the maritime industry. And there have been other straws in the wind recently. As reported by the Ammonia Energy Association, MAN and Alfa Laval have been working on converting marine diesel engines to burn ammonia. The Environmental Defence Fund Europe has also published a paper, 'Sailing on Solar', which puts the case for renewable ammonia as a marine fuel.

Bunker fuel consumption is around 200 million t/a, so even a small share of this market could be big news for the ammonia industry (ammonia's energy density is about half that of diesel, so it might also require more of it).

The drawbacks are also significant of course. There is a pretence that ammonia burns only to nitrogen and water, but in a high temperature/pressure combustion engine, volumes of NOx are also produced. Water injection can control this, but some kind of selective catalytic reduction system exhaust treatment would also be required. Ammonia's acute toxicity is also a handling and potential acceptance issue, although it is shipped and handled in large volumes today with only occasional accidental releases.

Finally, of course, there is the cost. Ammonia from natural gas might be competitive with diesel, but that would destroy the carbon neutral rationale for using ammonia. In order to be commercially viable, the costs of large-scale electrolysis to liberate hydrogen will need to come down further, although this is certainly dropping rapidly as research and development and economies of scale come into play. I have often remarked that on an energy basis, electrolysis is just about the most thermodynamically inefficient way of producing hydrogen, but I must admit that the prospect of large scale stranded and intermittent renewable power would seem to overcome most of these issues. With the backing of a major industry player like Maersk, we may only be a few years away from ammonia-powered ships. ■

Richard Hands, Editor



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Price trends

NITROGEN

US shale gas production continues to rise – the US now accounts for 22% of global gas production. In spite of increasing demand, US gas prices at the Henry Hub traded around \$2.25/MMBtu for most of October. With forecasts for a modestly cold winter ahead, futures prices on the NYMEX have tracked upwards to \$2.50/MMBtu, but this is still low by historical standards. Growing US exports of LNG – the US may be the world's largest LNG exporter by 2024 – are also starting to export lower US gas prices worldwide, at least where traded gas prices are paid for feedstock.

The ammonia outlook has changed for the final three months of the year as a reduction in global ammonia supply has finally offered ammonia prices some near-term support and carried upward price momentum into the fourth quarter. But concerns remain over how long the rally can last, with the threat of oversupply still looming over the market towards the end of 2019.

September saw the first meaningful upward price movement of 2019 and in turn, the spreads between the Caribbean, Russian and Middle Eastern pricing have narrowed and returned closer to previously established levels. Following the \$30/t hike in the contract price for Tampa October shipments, Trinidadian ammonia is now priced at a discount of \$15/t to Yuzhnyy and \$25/t to the Middle East.

With US import demand improving as

the market enters the autumn application period, US and Caribbean pricing is now expected to be firm until the end of the year. A recent month-long outage at one of Trinidad's largest ammonia plants has been restored, removing the chance of steep price increases in the region.

Outside of the Americas, the level at which Algerian production resumes is being closely monitored, as certain buyers in the region continue to have their options reduced, with Yuzhnyy supply directed towards more regional markets and Baltic exports largely contracted for the remainder of the year. The situation is exacerbated further as Europe is going through a period of steady demand. This is despite much lower European gas costs, which have kept many ammonia units in the region running close to full capacity.

Moroccan demand has also picked up in the third quarter and year-to-date imports are running about 5% higher than last year. Turkey has shown strong demand growth of around 7% this year, although this demand is tapering off, and may give more optionality from Yuzhnyy in the months ahead.

The trade balance reflects that further price increases are possible through October and into November. But once scheduled turnarounds and maintenance periods are completed at key production regions, there is unlikely to be enough demand to support higher pricing beyond this, unless more capacity is taken off line. But the potential for higher prices

remains, in line with the risk of further outages, particularly in the Middle East and North Africa.

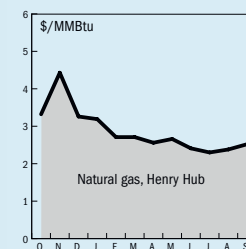
Despite the short-term firmness, few participants are expecting steep increases beyond the next few months, as the global market is still absorbing over 2.4 million t/a of new ammonia export capacity, which started up over the last 12-18 months, through new ammonia plants in Russia – the 1 million t/a Kingisepp ammonia plant – in Indonesia; the 600,000 t/a Panca Amara Utama plant – and in the US; Freeport's new 750,000 t/a plant.

Urea prices have fluctuated unusually little since August, Middle East and North African urea trading in a \$250-260/t f.o.b. range and showing little sign of breaking out in Q4. Outside India, demand has not met expectations. Buyers have deferred purchasing in Brazil and Europe, while dry conditions have reduced demand in other markets. Low gas prices have enabled the restart of exports from Ukraine, and Chinese exports are also up 2 million tonnes year-on-year.

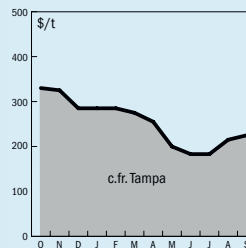
Prices are drifting lower and have to find a level at which marginal exporters are forced out to stabilise the market. Lack of demand is the main market driver in Q4. While India is enjoying a boom year due to a good monsoon, other Asian markets lack water to consume normal amounts of fertilizer. In the West, oversupply and cautious buyers will keep prices under pressure in Q4. A glut of gas and consequent low prices suggests no lasting upturn in prices will take place.

END OF MONTH SPOT PRICES

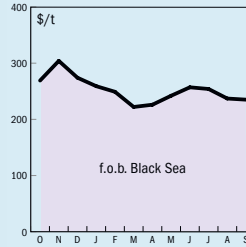
natural gas



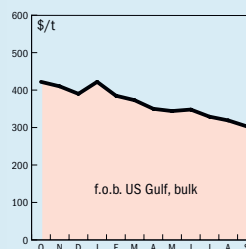
ammonia



urea



diammonium phosphate



METHANOL

Methanol prices are considerably down in 2019 on 2018, reflecting gloomier predictions for the global economy and the start-up of several large new methanol plants. In all major regions methanol prices for September 2019 were about \$150/t below their figures for September 2018. Methanex's US Gulf Coast non-discounted reference price (NDRP) was flat for October compared to September at \$1.03/gal (nominal \$342/tonne), which compares to a value of \$496/t for the same period in 2018. Southern Chemicals' October price was likewise flat from its September listing at \$1.00/gallon.

Celanese and Mitsui's 1.7 million t/a Fairway Methanol unit at its Clear Lake complex in Pasadena, Texas, restarted in early October after it and other units were idled when a fire damaged a carbon monoxide unit on September 21st. The company said that its downstream 300,000 t/a vinyl acetate monomer and 1.3 million t/a acetic acid units were expected to restart at reduced rates in October, with full operating rates for all production units expected in 4Q 2019.

In South America, Methanex announced it had reached a long-term gas supply agreement with Empresa Nacional de Petroleo for its Chile operations. The agreement should be sufficient to fulfil 25% of Methanex's gas needs out to 2025, according to Methanex. Added to existing commitments, this should take Methanex to 75% of its gas requirements in Chile overall, higher during the summer months in the southern hemisphere and lower during winter. Although the company has moved two of its Chilean plants to Geismar in Louisiana, it still has 1.7 million t/a of methanol capacity in Chile via its Chile I and Chile IV plants at Punta Arenas. The company says that the Chile I plant has now re-started following the first phase of its refurbishment. A shutdown for the second phase will occur in winter 2020.

Additional methanol was expected to begin coming from Trinidad with the start-up in October of the 1.0 million t/a Caribbean Gas Chemical methanol plant at La Brea. Although there is also some downstream DME capacity, it is only a small unit, and most of the plant's methanol output is slated for export. However, there has been speculation that given the current state of the methanol market the start-up may be delayed to the end of the year.

In China, falling prices led to some shutdowns and some switching to ammonia production where possible, and storage levels at coastal ports were fairly high into August. However, there has been some relief from extra demand. In September Ningxia Baofeng started up its new methanol-to-olefins (MTO) unit at Yinchuan in northwest China, with the operating rate soon rising to 80%. The MTO unit has 600,000 t/a of polyethylene and polypropylene capacity. It is intended to be fed by a 1.8 million t/a methanol plant, but start-up of the latter has been delayed to April 2020. As a result, Ningxia Baofeng needs to buy 150,000 tonnes/month of merchant methanol from the domestic market. This is added to the Nanjing Chengzi Clean Energy MTO plant which started operations in June and which also requires 1.8 million t/a of methanol at capacity. Yanchang Petroleum YanAn Energy & Chemical restarted its 600,000 t/a MTO plant on October 14th following a maintenance turnaround. The plant went down for maintenance on August 28th. Chinese imports of methanol to August were up 30% on last year at 6.3 million tonnes, with 1.1 million tonnes arriving in August alone, from Trinidad, Iran and Saudi Arabia. Total Chinese methanol imports in 2018 were 7.5 million tonnes, down on the 2017 figure of 8.1 million tonnes. The search for extra methanol has already contributed to an increase in methanol prices in northwest China, with prices rising from \$270/t to \$335/t from September into October, before falling back again to \$300/t c.f.r.

Southeast Asian prices rose slightly to \$265/tonne c.f.r. due to firmer demand from end-users. South Korea has seen additional demand from formaldehyde production which has also helped soak up excess supply.

European petrochemicals prices are affected by negative economic outlooks and poor performance in the automotive sector, as well as ample availability of methanol. Spot T-2 Rotterdam prices traded in the range of €220-230/tonne f.o.b. during September and October, after having dropped to a low point around €205/t f.o.b. Rotterdam. Even the Iranian drone attack on Saudi oil infrastructure or some high-profile outages have not made any significant impact on pricing, with the extra supply available from BioMCN's 450,000 t/a methanol plant in the Netherlands.

Table 1: Price indications

Cash equivalent	mid-Oct	mid-Aug	mid-June	mid-Apr
Ammonia (\$/t)				
f.o.b. Black Sea	225-233	195-215	200-210	242-250
f.o.b. Caribbean	193-210	170-190	175-190	223-228
f.o.b. Arab Gulf	230-250	190-205	200-215	245-255
c.f.r. N.W. Europe	250-285	225-265	230-265	275-290
Urea (\$/t)				
f.o.b. bulk Black Sea	225-240	245-260	250-266	224-230
f.o.b. bulk Arab Gulf*	244-260	256-270	285-295	247-272
f.o.b. NOLA barge (metric tonnes)	245	230	248	265
f.o.b. bagged China	263-280	277-295	285	300
DAP (\$/t)				
f.o.b. bulk US Gulf	294-303	313-326	346-349	353-369
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	200	197	205	235

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

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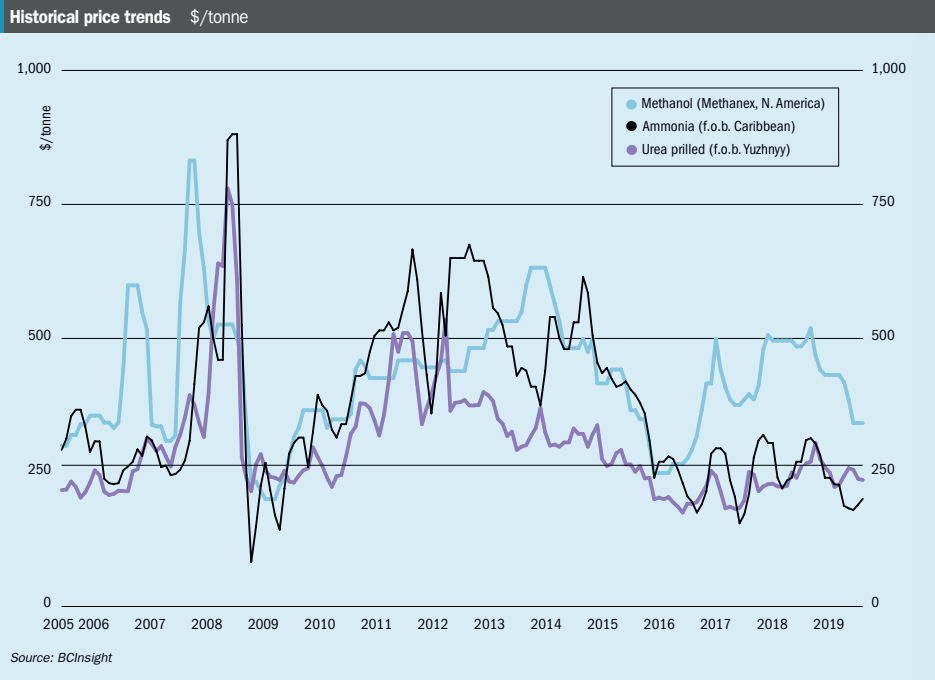
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Market Outlook



NITROGEN

- Global gas prices continue to run at historic lows, keeping price floors low, although increased gas demand for power and heating as the northern hemisphere moves into winter are beginning to push prices up. Nevertheless, with plenty of gas in storage in Europe and North America following last year's mild winter, the effects of this may be muted. European gas prices are 60% down on the same time last year.
- Ammonia outages have reduced availability and pushed prices back up again temporarily, but additional availability from Russia, Indonesia and the US has moved faster than demand and there seems little room for large price increases. US Fall ammonia applications look to be lower than usual, due to wet weather.
- Urea markets seem balanced. Delayed rains in Brazil have delayed applications of fertilizer, and urea demand from Brazil is expected to pick up over the coming months. Indian buying also continues to be fairly strong. However,

low gas prices are allowing increased availability from Ukraine, and there is also additional urea from China and Iran available. China has exported 2.7 million tonnes to September, 900,000 tonnes more than in 2018.

- US urea prices are trading at a discount to international prices, with NOLA November prices down to \$215/st f.o.b., \$35/st lower than for September, due to lower than usual application rates.
- However, Yara has said that it expects urea demand growth to pick up over the coming months as increased grain production is needed to keep pace with consumption growth. It also notes that global grain stocks are relatively low, particularly in China, and that supply growth outside of China is receding. Urea supply is only forecast to increase by 1.7 million tonnes in 2021, and further tightness is expected in 2021.

METHANOL

- Methanol Market Services Asia has predicted that global methanol demand will be up 5.9% in 2019 as compared

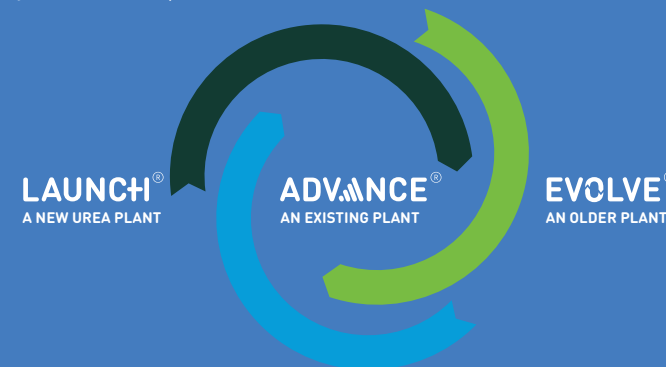
to 2018, at 96.6 million tonnes. Much of this rise in demand has come from Chinese MTO production, which is expected to be up 13.8% this year, providing over 3 million t/a of additional methanol requirement. However, new MTO production is starting to plateau in China, with rising competition from steam crackers and relatively expensive methanol leading to few additional new projects.

- The past few weeks have seen a flurry of new methanol plant announcements, including at Volgograd and Nakhodka in Russia. Coupled with construction work beginning in Malaysia and Methanex's decision to proceed with a third methanol plant at its Geismar facility, these represent an additional 6.3 million t/a of new capacity scheduled for 2023-24.
- For the next couple of years, however, the methanol project pipeline remains relatively light, leading to a tighter market, unless the slowing global economy and the continuing trade dispute between the US and China sees new demand begin to start falling off. ■



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AUSTRALIA

Topsoe to license technology for world's largest ammonia plant

Perdaman Chemicals and Fertilisers has signed a licensing and engineering contract with Haldor Topsoe for the latter's *SynCOR Ammonia™* technology for Perdaman's new A\$4 billion ammonia/urea plant in Karratha, Western Australia. Stamicarbon has been chosen as the urea technology licensor, and a gas supply has been secured. The next milestone for the project will be its financial closure, which is expected by the end of March 2020.

SynCOR Ammonia™ is Topsoe's solution for large-scale ammonia production, using a single step autothermal reformer and reducing steam throughput by 80%. The company claims that this enables significant economies of scale in large scale

grassroots ammonia plants, using proven technologies and catalysts. The Karratha ammonia plant will, at 3,500 t/d, be the largest single train unit in the world. Construction on the project is expected to begin next year.

"This is a significant step forward for the Karratha urea project. We are now full steam ahead on this important project that will use the latest and best technologies available. We expect Haldor Topsoe's innovative technology to deliver significant economies of scale that will contribute to making this world-scale plant exceptionally competitive," said Vikas Rambal, founding chairman and managing director, Perdaman Group. ■

RUSSIA

Tecnimont lined up for Kingisepp EPC contract

Maire Tecnimont says that it has signed a contract with fertilizer manufacturer EuroChem to carry out early works services with subsequent extension into engineering procurement and construction (EPC) activities on a new urea and ammonia production facility at Kingisepp in northwest Russia, subject to a final investment decision from EuroChem. The full value of the contract would be up to €1 billion, with plant capacities of 3,000 t/d of ammonia and 4,000 t/d of urea once the plant is in service. Under the terms of the early works agreement, Maire Tecnimont will carry out preliminary engineering and site surveying work at the brownfield site adjacent to EuroChem's existing production facilities at Kingisepp.

"We are pleased to take the next step toward building this world scale plant with Maire Tecnimont, a company that we have worked with closely for many years," said Petter Østbø, chief executive officer of EuroChem Group. "Expansion of production facilities is a strategic goal for us and reinforces our growing position in the fertilizer industry."

NORWAY

Renewable hydrogen for ammonia production

Yara has signed a deal with Nel Hydrogen with the 'shared ambition' of developing clean hydrogen technology to allow low carbon fertilizer production. The project is based on Nel's development of new water electrolyser technology which will be tested at Yara's existing ammonia plant in Porsgrunn, Norway. The goal is to

produce hydrogen from renewable sources to be fed into Yara's existing ammonia plant, which will either be used in fertilizer production or used as green ammonia. Nel is now developing their next generation electrolyser, and the prototype will be tested at Porsgrunn. The capacity of the electrolyser will be 5MW, corresponding to 1% of the hydrogen production at Porsgrunn. It is expected to be installed in 2022.

"We're excited to formally launch the partnership with Nel and work towards developing green ammonia and low carbon fertilizer," said Yara's Tove Andersen. "Yara's mission is to responsibly feed the world and protect the planet. We have already removed about half of our direct GHG emissions in the past few decades, and we're working towards carbon neutrality by 2050. Producing fertilizer with carbon free hydrogen will be a very important step towards that goal."

"We are very pleased with the partnership with Nel. Our ammonia plant will make the first small step towards carbon free fertilizer production," said Porsgrunn plant manager Jon Sletten. "When further developed, Yara Porsgrunn will be in a unique position due to the low carbon footprint from our nitric acid plants."

UKRAINE

Arbitration case settled against Togliatti

Ukrainian state-owned company Ukrkhimtransamiak has won an international arbitration dispute against Russian fertilizer producer Togliatti Azot. Togliatti produces a range of chemicals, including ammonia, which is piped into Ukraine and loaded onto ships via Ukrkhimtransamiak's pipeline infrastructure. The Ukrainian company charges the Russian producer for both transport

and loading. Ukrkhimtransamiak wanted to increase its loading fee by \$1/t, while Togliatti Azot demanded a reduction in the transit fee. The ensuing dispute has taken two years to resolve at the International Commercial Arbitration Court at the Ukrainian Chamber of Commerce and Industry in Kiev. Togliatti has said that it will appeal the decision. The pipeline, built in 1979-81 during the Soviet era, remains Togliatti's main means of exporting ammonia.

BANGLADESH

Tax on fertilizer imports withdrawn

Bangladesh's National Board of Revenue has withdrawn the imposition of a 5% advance on the import of all chemical fertilizers, in order to avoid any adverse impact on agriculture and keep the price of the products stable in the local market. The move from the NBR covers all types of chemical fertilizers, including triple superphosphate (TSP), diammonium phosphate (DAP), potassium sulphate (MOP) and monoammonium phosphate (MAP). The tax was imposed in April for the 2019-20 fiscal year on imports of fertilizer, but has been resisted by importers of non-urea based fertilizers. Importers argued that there should be no advance tax on import of fertilizers as the government paid a subsidy on the products to facilitate agricultural production and keep the prices of fertilizers affordable to farmers. Bangladesh's annual consumption of fertilizers is more than 5 million t/a, of which 2.4 million t/a is comprised of non-urea fertilizers, for which the country is almost completely dependent on imports – there is 75,000 t/a of TSP production domestically and 100,000 t/a of DAP. On urea, domestic production runs at around 800,000 t/a, leaving a further 2.4 million t/a to be imported.

CANADA

Urea and methanol project finally declared dead

The developers of an ammonia-urea and methanol project in Becancour, Quebec, have formally announced the abandonment of the project, after the joint development company, Entreprise IFFCO Canada Ltd, was unable to negotiate a fixed price for engineering services and construction. The project partners include La Coop federee, Investissement Quebec and Indian state owned fertilizer manufacturer IFFCO, who between them own 50% of the shares. The other 50% is held by Developpement Nauticol Quebec Ltd. Since the project first surfaced in 2012, costs have risen from an estimated C\$1.2 billion to C\$2 billion, which encouraged the original promoters to put the project on hold in 2015. It was then relaunched in a new form in 2017, adding the production of methanol to that of urea.

PAKISTAN

Fertilizer industry seeks government's support for urea export

Pakistan's fertilizer industry is seeking government's support for exploring urea export options to earn much needed foreign currency for the country, according to reports in local media. Pakistan operates about 7 million t/a of urea capacity, 90% of which is based on feedstock priced under the 2001 Fertilizer Policy rates for natural gas and imported LNG, and the remainder on gas priced under the 2012 Petroleum Policy, the cost of which is 56% higher than under the 2001 policy rates. Total domestic urea production runs at 5.9 million t/a, almost all of that produced from the 2001 policy plants, which is sufficient to meet domestic demand. However, the fertilizer industry argues that if were to produce and export the additional 700,000 t/a of urea in theory available, it could generate over \$200 million in foreign earnings.

EGYPT

EPC contract awarded for new ammonia plant

The Egypt Hydrocarbon Corporation, a subsidiary of Carbon Holdings, has awarded Tecnimont SpA a preliminary EPC contract for the construction of a new ammonia plant at Ain Sokhna, near Suez. The 1,320 t/d plant will license ammonia technology from KBR. The Egypt Hydrocarbon Corporation already produces ammonium nitrate at the site. The company is now working on completion of financing, with the support of the US EXIM Bank and SACE.

The project is expected to be completed in 36 months once it becomes effective. Pierroberto Folgiero, Maire Tecnimont Group CEO, commented: "We are very happy to expand our footprint in Egypt in our fertilizers core business, leveraging our long term relationships with the Egypt Hydrocarbon Corporation."

INDIA

Wuhuan to build Talcher urea plant

China's Wuhuan Engineering Co has been awarded a lump sum turnkey contract to build India's new coal-based urea plant at a cost of \$1.85 billion by September 2023. The project, at Talcher in Odisha state, will convert 2.5 million t/a of coal and 0.35 million t/a of petcoke into syngas to produce ammonia and 1.27 million t/a of urea. At the signing ceremony, Oil Minister Dharmendra Pradhan said:


"The Talcher fertilizer plant was shut down in 1999 due to financial losses. Twenty years later, we have handed over work order for revival of the same."

In order to augment domestic urea capacity, the government has placed a priority on the revival of the closed fertilizer units of Fertilizer Corporation of India Ltd (FCIL), and has mandated Talcher Fertilizers Ltd (TFL), a joint venture company of RCF, Coal India Ltd, FCIL and GAIL, to take charge of the project. TFL has been allotted northern part of North Arkhpal mine as a captive source of its coal requirements, and petcoke will be sourced from the IOCL Paradip refinery. It is hoped that successful implementation of the technology will open up the use of high ash Indian coal in areas other than conventional power production.

New plant at Namrup looking at 2023 start-up

The Brahmaputra Valley Fertilisers Corporation Ltd (BVFCL) fourth urea train at its Namrup site will be commissioned in 2023, according to India's Minister of Chemicals and Fertilisers D.V. Sadananda Gowda, who spoke to a meeting at BVFCL. He also reportedly asked BVFCL management to set out an action plan to revamp the existing Namrup-2 and Namrup-3 units and submit it to the ministry. BVFCL's first urea train was the oldest gas-based fertilizer plant in the country, dating back to 1969, although that unit closed in 1986. The second and third trains were built in 1976 and 1987 respectively, but have suffered from low production rates due to issues with ageing plant equipment and infrastructure and higher costs of production, and have averaged total production of 350,000 t/a of urea against a nameplate combined capacity of 555,000 t/a. ■

TENDER SALE & ONLINE AUCTION



SYNGAS MANUFACTURING PROCESSING PLANT (SMPP)
 of Falconara Marittima (AN) Italy

INCL. AIR SEPARATION UNIT incl. air compressor installation "Sulzer" (1997), cap 240.930 Nm³/hour; nitrogen installation "Borsig/Renk"; oxygen installation "Sulzer"; booster installation; **gasification area** incl. gasification plant; carbon extraction plant; gas cooling hydrolysis plant; **absorption area**; sulphur recovery area incl. sru plant, tail gas treatment plant; grey water treatment area incl. gwt plant; sour gas treatment plant;

ONLINE AUCTION - HIGH QUALITY, UNUSED UNIVERSAL AND REFINERY SPARE PARTS STOCK incl. thermo unit parts; reheater cooling tube bundles; single 6" gasifier process feed injectors; gas analyzer "Thermo"; turbines "Multisorb"; heavy pump "Flowserve" (2011);

CLOSING TENDER: 21 November
 CLOSING ONLINE AUCTION: 5 December
 VIEWING: November 14th by appointment

WWW.TROOSTWIJKAUCTIONS.COM

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UNITED STATES

Gas prices may fall to 1970s levels

A persistent oversupply of natural gas will drive the 2020 average price at the Henry Hub down (in real terms) to a level not seen in decades, according to new report from IHS Markit. The oversupply, to be reinforced by a new surge in associated gas production from the Permian basin, will push the average price down below \$2.00/MMBtu for the year, the lowest that prices have averaged in real terms since the 1970s (in nominal terms, the last time that prices fell below \$2 was 1995).

Prices are expected to fall despite robust domestic demand, which has increased by 14 billion cubic feet per day since 2017, as well as rising levels of exports. The US is expected to export an additional 3 bcf/d of liquefied natural gas (LNG) in 2020. However, this will not be enough to absorb production that has grown by more than 14 bcf/d since January 2018. IHS Markit expects production to average more than 90 bcf/d in 2019 and 2020.

"It is simply too much too fast," said Sam Andrus, executive director, IHS Markit who covers North American gas markets. "Drillers are now able to increase supply faster than domestic or global markets can consume it. Before market forces can correct the imbalance, here comes a fresh surge of supply from somewhere else."

That next surge of production is expected to come from the Permian basin in West Texas. Growth from the region will more than compensate for declines elsewhere, sustaining the oversupply and the downward pressure on prices that it creates. Two key factors will drive the Permian surge. Associated gas – the source for much of the region's production growth – is a by-product from oil production, meaning that it is less sensitive to natural gas price signals. Additional pipeline capacity is also expected to alleviate transportation constraints. The Gulf Coast Express pipeline, scheduled to come online in October, will allow for an additional 2 bcf/d production capacity. Overall, Permian gas takeaway capacity is expected to increase 6 bcf/d through 2022.

US gas prices fell by more than a \$0.60/MMBtu between March and August as inventories climbed towards their five-year rolling average despite record use of natural gas to generate electricity and growing LNG exports. Going forward IHS Markit predicts that the lower-48 storage inventory will come out of the winter at 2.1 tcf, or 263 bcf higher than the rolling five-year average.

Eventually the downward pressure on prices from rapid growth of associated gas will curtail drilling activity and bring the market back into balance. IHS Markit expects prices to rebound and average \$2.25/MMBtu for 2021, though that figure is still a downgrade from previous estimates.

Johnson Matthey technology selected for Louisiana methanol plant

Johnson Matthey (JM) says that it has been awarded the methanol plant licence for Methanex's new Geismar 3 plant in Louisiana, and that it will incorporate the largest standalone autothermal reformer (ATR) in the methanol industry. In mid-July, the Methanex board of directors reached a final investment decision to construct a 1.8 million t/a methanol plant at Geismar, adjacent to its existing Geismar 1 and 2 facilities. Johnson Matthey was awarded the contract to supply the licence for the ATR (autothermal reformer) methanol technology flowsheet, including associated basic engineering, proprietary equipment and catalyst supply. Construction on the \$1.3-1.4 billion plant will begin later this year with operations targeted for the second half of 2022.

JM says that when Geismar 3 starts up, it will become the eighth Methanex plant in operation to use JM-licensed methanol technology and the second to use a JM ATR. JM's world scale methanol generation technology has been licensed for more than four decades with over 90 plant licenses granted in that time.

"We are delighted to be selected as technology supplier by Methanex yet again, demonstrating our ability to deliver a bespoke flowsheet to suit our customers' requirements. We look forward to closely supporting the project through the engineering, construction, commissioning and start-up phases and into ongoing operation," said John Gordon, managing director, Johnson Matthey.

Air Liquide has been contracted to build the twin 2,500 t/d air separation units (ASUs) for the facility, at a cost of \$270 million. The ASUs will also provide oxygen

and other industrial gases to other customers in the vicinity. Production is expected to start in mid-2022 to support Methanex's production of methanol.

Environmental study secures permit

Northwest Innovation Works (NIW), which is seeking to build a \$1.8 billion methanol plant at the port of Kalama in Washington State, has had its permits for the project confirmed by local Cowlitz County, following the completion of an environmental impact study. The study argued that the proposed facility would help reduce global greenhouse gas emissions by at least 10 million t/a, as it would use far more efficient technology than the coal-based methanol plants currently in use in China – the plant would aim to export to the Chinese market. County officials said that they did not foresee any "significant unavoidable adverse impacts" with the project and reaffirmed their decision to grant shoreline permits for the proposed facility. The Washington State Department of Ecology has 30 days to approve or deny those permits, or request additional information from the company. Local environmentalists denounced the county's decision and reaffirmed their opposition to the study, arguing that it does not take into account the possibility that the methanol might be sold onto the fuels market in China. NIW meanwhile has agreed to develop a voluntary, in-state greenhouse gas mitigation program that exceeds the requirements of the county's shoreline permits.

New hydrogen plant for Las Vegas

Air Liquide says that it will build a new plant to produce renewable hydrogen in Las Vegas, Nevada, to serve the western US mobility market. Hydrogen will be produced in part from renewable natural gas upgraded from biogas using Air Liquide's separation membrane technology. The company said that the project will produce 30 t/d of liquid hydrogen, and represents the first step in expanding hydrogen supply to the region, enabling the market in neighbouring California to continue its growth to an expected 200 stations by 2025.

West Virginia approves CTL plant

The West Virginia Department of Environmental Protection has approved construction of a \$1.2 billion coal-to-liquids (CTL) plant in Mason County. The developer, Domestic Synthetic Fuels (DSF) says that its plant will convert a combination of coal and natural gas into low-sulphur diesel and jet fuel, gasoline and other by-products. It

will use roughly 23 million scf/d of natural gas and 2,500 t/d of coal to produce 10,750 bbl/d of fuel. The process uses the natural gas to generate hydrogen which is then used to reduce the coal to liquids. DSF plans to build the plant on a 200-acre industrial site north of Point Pleasant, West Virginia, along the Ohio River, with project completion set for early 2023.

CHINA

New catalyst improves plant performance

Clariant says that performance figures have improved at China Energy Corporation's Ningxia Coal Industry Company methanol plant at Yinchuan in Ningxia Province since the 1 million t/d plant switched to Clariant's next generation *MegaMax 800* methanol synthesis catalyst in August 2018. Following re-start, the plant achieved an anticipated operation load of 102% after just two months; the new catalyst's rapid start is due to its 40% higher activity compared to previous generations, according to Clariant. As well as higher yield at lower energy and feedstock costs, make-up gas consumption has dropped by 51 million cubic meters per year. These combined improvements will have a dramatic effect on the producer's cost savings, which are now expected to be approximately \$3 million annually. The facility is further reporting noticeably lower formation of by-products such as ethanol in the crude methanol product, which will undoubtedly add to its total profitability.

Start-up for new MTO unit

China's Ningxia Baofeng has started up the olefins section of its new methanol to olefins (MTO) unit at Yinchuan in north-west China's Ningxia province. The operating rate was said to have reached 80% in the first week. The MTO unit has 300,000 t/a of ethylene and 300,000 t/a of propylene capacity, which are integrated to downstream 300,000 t/a polyethylene and 300,000 t/a polypropylene capacities. However, the start-up of the accompanying upstream 1.8 million t/a coal-based methanol plant has been delayed, and may not now occur until April 2020. As a result, Ningxia Baofeng needs to buy 150,000 tonnes per month of merchant methanol from the domestic market until that time.

Ningxia Baofeng's first CTO plant, with a similar 1.8 million t/a of methanol and 600,000 t/a of olefins capacity, started up in November 2014.

RUSSIA

Topsoe wins license for Nakhodka methanol plant

The Nakhodka Mineral Fertilizer Plant has chosen Haldor Topsoe technology for a 5,400 t/d methanol plant near Vladivostok in the far east of Russia. Topsoe will provide the license, basic engineering, catalysts, and proprietary hardware for the methanol plant which will be based on Topsoe's two-step reforming technology. China Chengda Engineering Co., LTD, has been chosen for the engineering, procurement and construction (EPC) contract. The world-scale methanol plant will be located near the Russian port of Nakhodka in the Primorsky region, for ease of access to the Asia-Pacific region, where methanol demand continues to increase rapidly.

"We have chosen Topsoe for this very important project because they came to the table with proven and reliable technology, very competitive pricing and a long-standing presence in Russia," said Taras Ganaga, CEO Nakhodka Mineral Fertilizer Plant.

"We are pleased that Nakhodka Mineral Fertilizer Plant has selected Topsoe technology for their flagship project. This signals both confidence in our technology and our dedication to the Russian methanol industry. We look forward to deliver a world-scale methanol plant in partnership with China Chengda Engineering Co.," added Amy Hebert, deputy CEO of Haldor Topsoe.

And also for Volgograd methanol plant

GTM One has chosen Topsoe *SynCOR™* technology for its new 3,000 t/d methanol plant at the Khimprom site in Volgograd, southern Russia. Topsoe will provide the license, basic engineering, catalysts and proprietary hardware for methanol production, as well as, in the initial stage, basic engineering for the process unit, while Mitsubishi Heavy Industries Engineering will develop the front end engineering design (FEED) package for the site. At a later stage, the parties expect to sign an EPC contract. Construction is slated to begin in the second half of 2020.

The *SynCOR* reformer is used in large-scale methanol, ammonia and other processes. "We are very pleased to offer a solution that not only helps our customers comply with environmental regulations, but also stands out as the most cost-effective in large-scale methanol production. We see increasing demand for this technology

both in Russia and in other markets. We are also very content to continue our well-established cooperation with Mitsubishi Heavy Industries Engineering in Russia," said Peter Vang Christensen, managing director of Haldor Topsoe's Moscow office.

MALAYSIA

Ground broken on new methanol plant

Ground has been broken at Tanjung Kidurong in Sarawak State on a new 1.7 million t/a methanol plant. The plant is being developed by state-owned Petchem Sdn Bhd at a cost of 8.4 billion ringgits (\$2 billion), and is due to begin production in 2023. State oil and gas major Petronas will supply 160 million scf/d of natural gas for the project. Sarawak holds 54% of Malaysia's gas reserves, as well as 29% of the country's oil, and the state government is looking to monetise these resources. Sarawak Chief Minister Datuk Abang Johari Openg, who attended the ground breaking ceremony, said that he has high hopes for expansion of the state's downstream oil and gas industry, with Bintulu to become a petrochemical hub.

"We will be intensely involved in developing the high value downstream products of oil and gas industries such as specialised and fine chemicals," he said, adding that the state government will consider all feasible proposals to establish petrochemical industries and will facilitate them accordingly. Sarawak is also developing an ammonia and downstream products plant.

Samsung Engineering have the EPC contract for the new methanol plant, and say that they are aiming for mechanical completion in 4Q 2022. In December last year, Sarawak Petchem signed a sales and purchase agreement with Petronas Chemicals Marketing Labuan Ltd which guaranteed its product offtake.

SWEDEN

Partnership to develop methanol fuelled tankers

Swedish shipowner Stena Bulk has joined forces with Proman Shipping of Switzerland, launching Proman Stena Bulk Limited to jointly own and operate methanol-fuelled product tankers, dubbed 'IMOIMeMax' under long-term charters from Stena Bulk. Proman Shipping's chief executive David Cassidy said "In just eighteen months since Proman Shipping's foundation, we have made substantial advances and this joint venture with an industry leader is testament to that

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work. We are proud to be one of only three companies actively engaged in promoting methanol as a marine fuel, through this partnership with Stena Bulk. Proman Shipping is always seeking out new and innovative ways to use methanol, and to maximise our fully integrated, diversified platform across the whole value chain, from the production and conversion of natural gas, to the marketing and delivery of end products to customers."

Proman shipping's parent company Proman began producing gas-derived products in 1993 with the construction and start-up of the 500,000 t/a Caribbean Methanol Company (CMC, now known as M2) plant on the Point Lisas Industrial Estate in Trinidad and Tobago. The company's products include methanol, ammonia, urea ammonium nitrate and melamine. As well as Trinidad and Tobago, Proman has operations and offices in Switzerland, Germany, Italy, the United States, Portugal and Mexico which have a combined annual installed production capacity of more than 10 million t/a tonnes of bulk chemicals.

In November 2018, Proman Shipping and Mitsui OSK Lines (MOL) launched *Castara*, a 50,000 dwt new build methanol carrier for Proman Shipping at the Hyundai Mipo Drydock in South Korea. Methanol Holdings (Trinidad) Limited's chief executive Dennis Patrick said "Castara is Proman Shipping's first 50,000 dwt vessel and will become the largest vessel in the Proman Shipping fleet. This milestone is testament to our valued and long-term partnership with MOL."

UNITED KINGDOM

Ince plans 'plastic to hydrogen' plant

Peel Environmental has submitted plans to Cheshire West and Chester council for a £7 million 'waste plastic to hydrogen plant' near Ellesmere Port. The application forms part of a £130 million deal Peel has signed with technology firm PowerHouse Energy and energy from waste specialist Waste2Tricity to develop 1.1 plastic to hydrogen plants across the UK. The proposed plant would take up to 35 t/d of unrecyclable plastics and create a local source of hydrogen which could be used to power road vehicles, according to the developers. This could then be used as a clean and low-cost fuel for buses, heavy goods vehicles and cars, helping to reduce air pollution and improve air quality on local roads. The plant would use PowerHouse Energy's distributed modular gasification process. This involves passing plastic through a rotating reactor operating above 1,000°C,

converting it to syngas. In phase one the project will process 35 t/d of plastic using the syngas to produce 80 MWh of electricity, and in phase two will shift to producing 2 t/d of hydrogen and 35 MWh of electricity.

CANADA

Loan secured for GTL plant

Rocky Mountain GTL says it has secured a \$15 million loan from Roynat Capital, a division of Scotiabank, and has awarded a construction contract to the Midwest Construction Group for what would be Canada's first commercial gas-to-liquids plant, near Carseland, Alberta, east of Calgary. The project would tap into 5 million scf/d of natural gas from flare gas, natural gas and natural gas liquids and produce 500 bbl/d of synthetic diesel and naphtha using so-called Direct Fuel Production technology licensed from Greystone Energy. Preliminary plant construction began in May.

GERMANY

Leuna to produce methanol from renewable hydrogen

Total SA has signed a cooperation agreement with Sunfire for the latter to provide a megawatt-scale high temperature electrolyser. The HyLink 200 electrolyser, suitable for use in industrial environments, will generate hydrogen as part of the E-CO2MET research and development project. Sunfire will also be responsible for the integration at the site as well as the operation and maintenance of the electrolyser, which will be the first step for the industrial-scale production of synthetic methanol from renewables and recovered CO₂ from Total's Raffinerie Mitteldeutschland at Leuna.

The high-temperature electrolyser is able to directly use steam or waste heat from industrial and synthesis processes, reducing the need for more expensive 'green' electricity. Sunfire claim that it is the most efficient process on the market for converting electricity into hydrogen. The high efficiency of over 80% also significantly reduces the overall cost of the integrated process.

During the collaboration with Total, the electrolyser will be involved in various research and development projects to evaluate the performance of the system, including in relation to volatile renewable energy supplies.

"The use of our high-temperature electrolyser at one of the largest oil companies in the world confirms our years of hard work driving decarbonisation in large-scale industries.

This technology can become the core building block for energy sectors that cannot source electricity directly from renewables. With the transformation into renewable gases and fuels and the use of existing infrastructures, we can make the transport sector and the chemical industry climate-neutral," said Nils Aldag, Managing Director of Sunfire.

"Total is delighted to develop efficient technologies to re-use CO₂ to chemicals, materials and fuels. Carbon capture, utilisation and storage is going to play an essential role in achieving carbon neutrality without curbing economic and social growth," said Marie-Noelle Semeria, Senior Vice President, Group Chief Technology Officer at Total.

SOUTH AFRICA

Mossel Bay could run out of gas next year

South Africa's national oil company, PetroSA, says that it expects its flagship Mossel Bay gas-to-liquid (GTL) plant to run out of domestic natural gas supplies by the end of next year. In a presentation to the country's parliament, the company said that reserves are close to depletion there is still no sustainable long-term solution for the plant. The plant is currently operating well below its nameplate capacity of 36,000 bbl/d in spite of a \$1 billion offshore drilling campaign that was halted due to poor results in finding replacement reserves. In February, PetroSA said they had reached out to French oil major Total following the discovery of a huge offshore field containing gas condensate that could potentially be used as feedstock to Mossel Bay. Total announced the Brulpadda discovery at the beginning of the year, which is expected to have a substantial amount of gas. The find is fairly close to existing infrastructure, which would allow it to be brought onshore close to the Mossel Bay plant.

AUSTRALIA

Plans to build methanol plant in Darwin

Coogee Chemicals says that it is looking to build a 1,000 t/d methanol plant at the port of Darwin, in Australia's Northern Territory. The A\$500 million methanol plant could start operating by 2024, but will require 40 terajoules per day of natural gas. Coogee's chief executive indicated they would not be using any newly tapped reserves from the region's emerging shale gas industry, implying that the gas would come from offshore gas field developments. ■

People

Nassef Sawiris, chief executive officer of OCI, has also been named as CEO of OCI's new joint venture with the Abu Dhabi National Oil Co. (Adnoc) – Fertiglobe. The announcement came with the notification of the completion of the transaction to combine Adnoc's fertilizer business with OCI's Middle East and North Africa (MENA) nitrogen fertilizer platform. Fertiglobe, based in Abu Dhabi, will combine businesses with 2018 sales of more than \$1.7 billion. OCI holds a 58% stake in Fertiglobe and Adnoc the remaining 42%. The deal combined OCI's Egypt Basic Industries Corp., Egyptian Fertilizer Co., and Sorfert, with Adnoc's Fertel units. OCI says that Fertiglobe will be the largest export-focused nitrogen fertilizer platform globally, and the largest producer in the Middle East/North African region with a production capacity of 5 million t/a of urea and 1.5 million t/a of merchant ammonia. Fertiglobe, will now focus on the integration of the two businesses, which is expected to create significant value through the unlocking of commercial and technical synergies, the companies say.

To coincide with Global Fertilizer Day on October 13th, the International Fertilizer Industry Association (IFA) has announced that its 2019 Norman Borlaug Award has been given to **Dr Andrew Sharpley**, whose work has had a huge impact on helping farmers to better understand how to effectively manage phosphorus fertilizers to avoid losses.

Based at the University of Arkansas, Dr. Sharpley pioneered the development of new environmental risk assessment tools, based on his research findings, which have been used by farmers and agronomists, as well as regulatory and resource conservation agencies throughout the world, to develop cost-effective conservation strategies to protect water quality. By developing the P Index, a tool to identify which areas on a farm are most susceptible to phosphorus nutrient loss, Dr Sharpley has enabled farmers to more effectively target their fertilizer use, and helped reduce the amount of phosphorus lost to the environment in the US by an estimated 25,000 tonnes. The success of the P Index is highlighted by the fact that the US Department of Agriculture's National Resources Conservation Service (NRCS) has adopted it as the cornerstone of their nutrient management planning at Concentrated Animal Feeding Operations (CAFOs) in 49 states. The US Environmental Protection Agency and the NRCS also use the indexing approach to prioritize and target conservation measures across the country.

Dr Sharpley has also worked closely with farmers, crop consultants, state and federal agencies, and non-governmental stakeholders to develop and maintain an internationally recognised on-farm research and demonstration project, the Arkansas Discovery Farm Program. At the twelve discovery farms currently operating across Arkansas, researchers work to mini-

mize the potential runoff of nutrients from land to water by evaluating the role of conservation methods such as reduced tillage and cover crops, alongside nutrient stewardship, at protecting the soil and reducing nutrient run-off. The program results have reassured farmers that they are providing safe and affordable food supplies, while seeing the practices in action has empowered them to improve their nutrient management and water conservation.

Dr Sharpley has received a wide array of recognition for his research and outreach efforts, including Fellow of the American Society of Agronomy and Soil Science Society of America and those Society's Environmental Quality Research and Soil Science Applied Research Awards. He was inducted into the USDA-ARS Hall of Fame in 2008 and in 2010 received the International Plant Nutrition Institute Science Award.

"I am honoured and humbled to receive this award. We need to better manage phosphorus for future generations. Transferring scientific research on the subject to the field enables more sustainable farming that benefits the farmers, society and the environment," said Dr Sharpley.

"We are delighted to distinguish someone who has worked so tirelessly to ensure that farmers have the right tools and techniques to manage phosphorus properly to grow more crops while minimizing their environmental footprint," observed Charlotte Hebebrand, IFA's Director-General. ■

Calendar 2019/2020

DECEMBER 2019

4-5

European Mineral Fertilizer Summit, BRUSSELS, Belgium
Contact: Mado Lampropoulou, ACI
Tel: +44 (0)20 3141 0607
Email: mlampropoulou@acieu.net

JANUARY 2020

20-22

Fertilizer Latino Americano, SAO PAULO, Brazil
Contact: Argus Media
Tel: +44 (0)20 7780 4340
Email: fertconferences@argusmedia.com

FEBRUARY

11-13

AFA Annual Forum & Exhibition, SHARM EL SHEIKH, Egypt

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

17-19

Nitrogen+Syngas 2020, THE HAGUE, Netherlands
Contact: CRU Events
Tel: +44 (0) 20 7903 2444
Fax: +44 (0) 20 7903 2172
Email: conferences@crugroup.com

19-21

Argus Africa Fertilizer 2020, CAPE TOWN, South Africa
Contact: Argus Media
Tel: +44 (0)20 7780 4340
Email: fertconferences@argusmedia.com

MARCH

3-5

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

9-11

Syngas 2020, MEMPHIS, Tennessee, USA
Contact: Betty Helm, Syngas Association, Baton Rouge, Louisiana
Tel: +1 225 706 8403
Web: www.syngasassociation.com

APRIL

20-22

IFA 88th Annual Conference, NEW DELHI, India
Contact: IFA Conference Service
Tel: +33 1 53 93 05 00
Email: ifa@fertilizer.org

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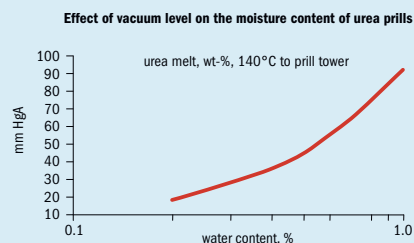
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Plant Manager+

Problem No. 57 Higher moisture content in urea melt due to vacuum pressure issues

To illustrate the direct effect of vacuum level on the moisture content of urea prills please refer to the wt-% urea melt graph for aqueous urea at 140°C. As the absolute pressure increases (lower vacuum) the urea melt declines in concentration (water content % increases). With this illustrative graph, one can quickly see the effect of suction pressure on the moisture content of the urea melt. A non-optimum vacuum pressure is one cause of high moisture content in the urea melt, but there are also other possible causes as you will read in the round table discussion below. Sharing troubleshooting cases leads to a much wider view on the possible causes and helps to solve problems more quickly.



Mohammed Munir of Pakarab Fertilizer in Pakistan starts the Round Table discussion: We have a 300 t/d Snamprogetti urea plant (ammonia stripping process) on site. The vacuum system design has two vacuum separators: V-6 at 0.3 atm and V-7 at 0.03 atm. Recently, we experienced higher moisture content in the product due to V-6 and V-7 pressure fluctuations to 0.4 and 0.07 atm respectively. I am interested in the relationship between the variation of the pressure in V-6 and V-7 and the moisture content.

Muhammad Kashif Naseem of SAFCO in Saudi Arabia replies: The vacuum of the evaporators is dependent on the performance of the cooling system and the ejectors. There is a relationship between temperature and vacuum pressure which is directly proportional to the moisture. Please check if the vacuum condensers have urea polymers depositions. In that case flush the condensers and ejectors.

Ancaza of Igsas in Turkey shares his experience: Please also consider the following possible causes of a higher moisture content in the urea melt:

- Upstream of the separator a tube in the heat exchanger may be punctured (possibly due to vibrations and baffle hammering).
- A leak may be present in the steam jacket which forms part of the urea melt lines.
- The seal water of the urea melt feed pump may be leaking into the urea melt.

Prem Baboo of Dangote Fertilizers Projects in Nigeria contributes to the discussion: Please also refer to two other round table discussions "Vacuum problem in ACES TEC urea plant" and "Low vacuum pressure problem in final concentrator", which contains interesting related information, like the following post from Al Cadena of Graham Corporation:

The ejector performance is a critical factor, meaning it creates a shockwave within the diffuser. This is where compression is created; the high velocity suction load/motive is converted into high pressure, designed to overcome the discharge pressure at the diffuser outlet. Decreasing the motive pressure to below the design pressure set by the manufacturer, will lead to the shockwave not establishing; thus, the ejector fails to operate.

As the capacity of the plant increases or decreases it will have an impact on the ejector's suction pressure. The ejector operates on a curve, this performance curve is available from the ejector manufacturer. Lower load leads to a higher vacuum, and higher loads lead to a loss of vacuum.

The intercondenser removes condensable vapour and steam, thus reducing the load on downstream equipment. It also controls the discharge pressure of the upstream ejector. If there is fouling, higher cooling water temperatures are experienced and the heat transfer capabilities of the intercondenser will be diminished. The pressure within the intercondenser will increase, affecting the upstream ejector. If the discharge pressure is greater than what the ejector was designed for, it will disrupt operation of the upstream ejector.

Moisture droplets in steam lines are accelerated to high velocities, causing eroded nozzle internals. The diffuser inlet may also be damaged. Good practice would be to have a steam separator and trap installed before the ejector's motive steam connection.

Mohammed replies: Thanks a lot, that helped!

I am also interested in the relationship between the differential pressure of the two vacuum stages (V-6 and V-7) of the Snamprogetti plant and the moisture content in the product. At the time of our incident, our V-6 operating pressure was 0.4 atm (design 0.3 atm) and V-7 was 0.05-0.07 atm (design 0.03 atm).

Prem responds: The vacuum conditions seem ok to me: 0.4 ata and 0.05 ata are not so bad. The design condition of the temperatures are also an important factor: At a design condition of 0.33 ata the temperature outlet is 128°C and at 0.03 ata the outlet temperature is 140°C.

If your vacuum condition is more than 0.3 ata, for example 0.4 ata, then the temperature must be higher than 128°C and also similar for the 2nd stage vacuum. However, I think your vacuum conditions are ok. The following problems may be occurring:

- water or steam ingress in urea solution;
- flushing water quantity not optimum at that time;
- separator flushing conditions;
- erratic pressure transmitter (1st and 2nd stage);

- sometimes flushing water goes towards the process side while its direction should be towards the condenser side. It can happen due to perforated coil disturbance (this is a shutdown job), in this case the flushing water must be closed;
- flushing water injection or low pressure steam injection condition.

Jim Lines of Graham Corporation in the United States shares his expertise: Increased operating pressure for both V-06 and V-07 is unusual. There are certain initial considerations.

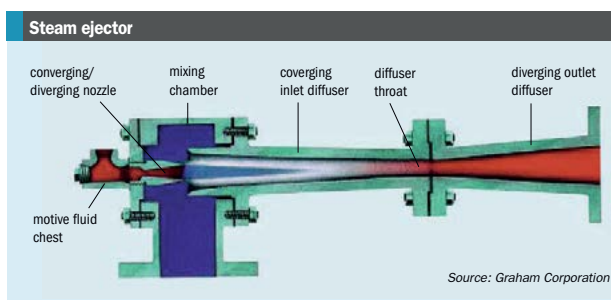
- Is there solids build-up in the booster ejector of V-07 and precondenser of V-06 removed via daily flushing? Most plants have flushing nozzles in the booster ejector and precondenser that are operated once per shift or daily at a minimum for 10-15 minutes to reduce solids that build up. Solids formation will hinder booster ejector performance dramatically and will act as fouling in the precondenser, thus reducing its condensing efficiency.

- Is your plant operating well above nameplate capacity (although for V-07 it is appears that the booster is operating in a "broken" condition)?

- Is the steam generated by the high pressure carbamate condenser at a pressure below the minimum for proper ejector operation? The ejector performance curves will provide minimum steam pressure requirement for satisfactory ejector performance.

- When was the last maintenance inspection of ejector motive nozzles and internals? Is there corrosion or erosion damage of the ejectors resulting in poor operating capability?

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



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Unloading urea at Namhae, Korea.



Trends in the urea market

The urea market is currently still oversupplied and operating rates are low. In spite of Chinese plant closures and the potential impact of sanctions on Iran, continuing capacity expansions could keep prices depressed for some years to come.

Indian demand and Chinese exports have been the major story of the global urea market for the past few years, but a Chinese environmental crackdown and an Indian push for self-sufficiency are changing these old certainties. Elsewhere, demand is rising in Africa and South America, while new capacity is expected in Russia and Africa.

China

China is the world's largest producer and consumer of urea, and the balance between the two and the consequent volume of imports or exports that the country experiences has long been one of the key factors driving global urea markets.

China has long pursued a policy of self-sufficiency in domestic nitrogen production, which expanded aggressively during China's period of rapid industrialisation over the past two decades, reaching a peak capacity of 86 million t/a in 2015, outstripping domestic demand of 60 million t/a, and leading to 13.7 million t/a of imports by that year.

Since then however, there has been a change of policy direction, with a greater focus on environmental concerns, and especially industrial pollution in the Yangtze river, and winter air pollution in Beijing, Tianjin and 26 other cities in the east of the country. This in turn led to a crackdown on coal-based chemical production

in those regions. Along the Yangtze river, 47 chemical plants are being relocated or closed down, including 900,000 t/a of urea capacity, and air and water emissions standards have been tightened nationally. Some new emissions licenses mean plants can only operate at reduced rates or shorter run times.

Feedstock prices are also rising. Most of China's ammonia production is based on coal gasification, and Chinese government attempts to rein in coal mining overcapacity and push electricity generation towards less carbon intensive sources like natural gas and renewables have driven up both coal and natural gas prices, and hence the cost of urea production. Chinese coal production peaked in 2013 and 700 million t/a of capacity closed between 2016 and 2018. The government's target is for 800 million t/a of closures during the current Five Year Plan (2016-2020). Coal prices have risen, particularly affecting urea plants with older, less advanced gasification systems which require more expensive anthracite coal to operate. Meanwhile, as China moves towards more gas-based power production, prices have risen for natural gas and lack of availability has meant many gas-based urea plants having to run at low rates or close completely during the peak winter demand season.

The effect of these pressures has been the closure of older, less efficient and especially anthracite-based plants. Peak

urea production in China was 68 million t/a in 2015. This fell to 65.7 million t/a in 2016, and just 54.3 million t/a in 2017. In spite of some new capacity being built, Chinese information service BAIINFO forecasts Chinese urea capacity to fall to 65 million t/a by 2020, although actual production is nevertheless likely to rise as relocations are completed and more plants meet the new pollution requirements. CRU predicted earlier this year that 12 million t/a of Chinese urea capacity would close between 2019 and 2023.

On the consumption side, China over-applies urea, leading to leaching into water courses and attendant pollution issues. To tackle this the Chinese government has set a target that there be zero growth in nitrogen fertilizer demand in China from 2020, and agricultural consumption has actually been falling for four years, although industrial urea consumption for e.g. diesel exhaust treatment, and urea-formaldehyde and urea-melamine resins continues to rise. Overall Chinese urea consumption fell from 61 million t/a in 2015 to 52 million t/a in 2018. With fertilizer consumption likely to remain fairly constant going forward, incremental increases in industrial demand for urea could see this rise to 53.5 million t/a by 2022.

The combined effect of stagnant demand and rapidly falling capacity has been to rapidly remove China from its position as the world's largest urea exporter. Imports fell from 13.7 million t/a in 2015 to 8.9 million tonnes in 2016, 4.7 million tonnes in 2017, and 2.4 million tonnes in 2018. This is expected to be slightly higher for 2019 at 3.0 million t/a. Going forward, new, more efficient capacity will increase production by up to 4 million t/a by 2023. Some of this will be absorbed by additional domestic demand, but overall Chinese exports may rise to 3.7 million t/a over that period.

US-China trade dispute

Another wrinkle in the story of China's impact on urea markets has come from the ongoing trade dispute between the US and China, which has seen numerous types of goods facing additional tariffs. US tariffs on imports of Chinese urea were raised to 30% in October 2019, although the US imports very little urea from China (340,000 tonnes in 2017), and so this has had limited market impact. However, another key commodity affected has been deliveries of US LNG – China placed a 10%

tariff on imports of US LNG in 2018, rising to 25% in June 2019, which has effectively ended US LNG deliveries, helping push up Chinese domestic gas prices and force gas-based urea producers to idle capacity. Similarly, Chinese tariffs on imports of US soybeans have led soybean producers in America to switch to corn cultivation, which is more nitrogen intensive.

India

India is the second largest consumer of urea in the world, reaching 32 million t/a in 2018-19. While prices for most fertilizers have been decontrolled to a greater or lesser extent, urea represents half of India's fertilizer consumption, and governments have not dared to fully decontrol urea pricing. India, like China, had a policy of self-sufficiency in urea production, dating back to the 'Green Revolution' of the 1970s and 80s, but this lapsed in the mid-90s as naphtha and natural gas prices rose and availability tightened. Indian urea production plateaued at 20-22 million t/a, and since 1995 India progressively became an increasing urea importer, rising to become the world's largest.

The Modi government has decided to set a return to urea self-sufficiency as one of its major targets, and in 2017, the government announced an ambitious \$8.7 billion plan to end imports of urea within five years. This would be achieved by reviving five mothballed urea plants and setting up new facilities, bringing 6.4 million t/a of new urea capacity on-stream. Gas import and pipeline schemes to feed the plants also form part of the plan, which involves the revamp and re-start of five idled urea plants previously operated by the Fertilizer Corporation of India Ltd (FCIL) and Hindustan Fertilizer Co. Ltd (HFCL). The plants are at Barauni in Bihar state, Sindri in Jharkhand, Talcher in Odisha, Ramagundam in Telangana and Gorakhpur in Uttar Pradesh. Major state utility companies such as Gas Association of India Ltd (GAIL) and Coal India Ltd (CIL) are involved in financing and providing feedstock for the units, which will be operated by existing fertilizer firms. At Sindri, Gorakhpur and Barauni, CIL and the Indian Oil Company (IOC) are the lead investors, together with the National Thermal Power Corporation (NTPC), via a special purpose investment vehicle – Hindustan Urvurak and Raysan Ltd (HURL). Each of the three plants is to be a 1.27 million t/a unit, and all three are looking to mechanical completion of construction in early 2021,

with production later in the year. All three will be fed by LNG imported on the east coast at Haldia and supplied along the Jagdishpur-Haldia pipeline.

Ramagundam will be another 1.27 million t/a plant, at the site of an old FCIL coal gasification plant, although the new plant will be gas-based. It is the furthest advanced of the government-backed projects, and is expected to be commissioned early in 2020, once a gas pipeline spur to supply it has been completed.

The final plant of the five government developments is at Talcher in Odisha State. Like the other projects, it is to have a final capacity of 1.27 million t/a of urea, although unlike the others the plan is to run it on coal as a feedstock. This is something of a radical development for India, which had an unhappy history with its first two coal-based urea plants, built at Ramagundam and Talcher in the 1970s, which suffered from all manner of production issues and which were finally closed down. The high ash content (35-45%) of Indian coal also means that certain types of gasifier are not suitable. However, the success of China in developing coal-based urea capacity has led to a re-think, and India, with its large coal reserves, is now looking seriously at coal gasification once more. Talcher Fertilizers Ltd is a joint venture between GAIL, Rashtriya Chemicals & Fertilizers, FCIL and Coal India Ltd. The project has made slow progress, but is now looking towards completion in 2023.

As well as the five government-backed projects, there are a number of privately funded projects under development, but the only one that has made any significant progress has been the revival by Chambal Fertilizers and Chemicals of its old urea plant at Kota near Gadepan in Rajasthan state, which closed in 2015 due to unfavourable economics. A new 1.27 million t/a replacement plant was completed late last year and commissioned in January 2019.

In addition to this, another government project is under development – the establishment of a new brownfield ammonia/urea complex at the Brahmaputra Valley Fertilizer Corp (BVFCL) site at Namrup in Assam, so-called Namrup-IV – was approved in October 2018. A new 860,000 t/a ammonia-urea plant will replace the two older 220,000 t/a and 270,000 t/a units currently at the site, adding a net 370,000 t/a. All of these projects taken together will add 8 million t/a of new urea capacity in India by about 2023.

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Iowa Fertilizer Company's new plant at Wever.

North America

North America is a net importer of nitrogen fertilizer, and indeed had become so to quite a significant extent as capacity closed during the 1990s due to high natural gas prices. However, this turned around from the mid-2000s as US shale gas drilling began to rapidly expand domestic natural gas production.

A wave of new nitrogen fertilizer capacity based on cheap shale gas began to come on-stream from the early years of this decade, mainly affecting the ammonia industry and US ammonia imports from Trinidad and Venezuela. But there has also been a considerable amount of new urea capacity, including CF Industries at Donaldsonville and Port Neal, Agrium at Borger, Texas, Koch at Enid, Dakota Gasification at Beulah, and Iowa Fertilizer at Wever, adding 5 million t/a of urea capacity in total. While some of this urea goes into UAN production, it has begun to displace imports. US demand for urea is relatively stable at around 11 million t/a, but the share of this represented by domestic production has risen steadily, and US urea imports fell from 8.1 million t/a in 2015 to 5.4 million t/a in 2018. Most of the additional new capacity is now operational, and although several other projects have been mooted or are under development, there are no new plants currently under construction, and one project (at Becanour in Canada) was recently abandoned.

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Iran

Iran remains another wild card in the international urea market. Iran has long sought to monetise its huge natural gas reserves via downstream chemical production, with urea and methanol among the major products. Global sanctions on Iran over its nuclear programme slowed and

Urea capacity in Russia has been rising steadily over the past decade.

in some cases suspended the development of this capacity. However, in 2015 the 'Joint Comprehensive Plan of Action' (JCPOA) deal between Iran and the 'P5+1' countries – the five permanent UN Security Council members plus the European Union – paved the way for a relaxation of sanctions, and an acceleration of the completion of ammonia-urea and methanol plants. Since the election of the Trump Administration in the US, however, the US has withdrawn from the JCPOA in 2018, and in November 2018 it re-imposed sanctions on Iran.

Iran exported 4 million tonnes of urea in 2018, and under normal circumstances this would have been expected to rise this year with the completion of the 1.3 million t/a Lordegan urea plant. However, Lordegan has been pushed back to next year, and in spite of some re-export of Iranian urea sent via Chinese ports, Iranian exports of urea are expected to fall this year to 2.6 million t/a. Iran has begun looking to markets further afield, including in Africa, but the volumes involved are much smaller than its main customers in South Asia.

Russia and the CIS

Blessed with the largest gas reserves in the world and a favourable dollar exchange rate, Russia has been taking steps to monetise this via downstream chemical and petrochemical projects. Russia is already the fourth largest urea producer in the world, after India, China and the USA, and urea capacity in Russia has been rising steadily over the past decade, via revamps and several new units, at Novomoskovsk, Cherepovets, Mendeleevsk and two units at Acron's Veliky Novgorod site, totalling 2.6 million t/a in total. More plants are on their way. In 2017 methanol producer Metafrax signed a contract with Casale to build a new 570,000 t/a urea plant at the company's Gubakha site, using CO₂ from the methanol plant as part of the feed. TogliattiAzot has likewise commissioned Casale to supply technology for a new 726,000 t/a third urea plant at Perm. Both facilities are expected to be commissioned in 2021, as is KuibyshevAzot's 540,000 t/a urea plant at Togliatti. More recently, EuroChem announced plans for a huge 1.32 million t/a urea plant at Kingisepp near St Petersburg, and Shchekinoazot is building a new 660,000 t/a plant in the Tula region. These five will add another 3.8 million t/a of urea capacity by 2023.

Most of these plants are aimed at export markets. Russia's domestic fertilizer consumption fell drastically in the wake of the collapse of the USSR, and has only recovered slowly. However, the weak rouble has also boosted grain production and exports, and fertilizer consumption has increased. However, most nitrogen in

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Russia is applied as ammonium nitrate. Urea consumption is also now increasing as well, for industrial uses as well as agricultural, although from relatively low levels, and certainly not sufficient to significantly affect the large new volumes of urea that will be seeking a market outside of Russia.

Elsewhere in the CIS, the gas-rich countries in Central Asia are also looking to monetise gas via petrochemicals, especially where gas export pipeline options are limited, or subject to Gasprom tariffs. Uzbekistan's new 580,000 t/a urea plant at Navoi is due on-stream in 2020, and the country is now looking at another new fertilizer complex at Samarkand, while Azerbaijan's SOCAR is planning to build a second 660,000 t/a urea train at its existing site. Turkmenistan commissioned its new 1.2 million t/a Garabogazkarbamid urea plant in late 2018.

Africa

Africa has been a region under-served by fertilizer production and under developed in terms of fertilizer consumption. For the moment 70% of Africa's fertilizer consumption is accounted for by Egypt, South Africa and Nigeria. However, this is changing – consumption is rising at 5% year on year in sub-Saharan Africa as more fertilizer is applied, and consumption is expected to almost double from 2018 to 2030, with east and west Africa the major growth areas.

On the production side, Nigeria is becoming a major production hub, with capacity set to almost triple to 4.1 million t/a by 2023 as new plants are completed



Unloading granular urea.

for Dangote and Indorama (1.2 million t/a and 1.3 million t/a respectively), although both projects continue to see major delays. Elsewhere, new gas discoveries in east and west Africa have generated a large number of potential downstream ammonia-urea projects, but so far no concrete proposals, and the only firm new urea capacity elsewhere in Africa is likely to be in Egypt.

Elsewhere

The Arab Gulf continues to be the major source of urea exports, as a great deal of capacity was built in the 1990s and early 2000s due to cheap and widely available gas. Gas availability is falling though, and there is no real new capacity being built in the region outside of Iran, which, as noted, is hampered by sanctions. Mexico has plans to restart some of its capacity at Cosoleacaque, potentially up to 1 million t/a.

On the demand side, Brazil remains one of the fastest growing countries, and there have been plant closures at Camaçari and Laranjeiras, taking the country's deficit up still further.

World situation

Overall, global urea capacity is projected to rise from 210 million t/a in 2018 to 226 million t/a in 2023. Most of the additional capacity will be in India and Russia, as well as Egypt and potentially Nigeria, unless the projects in the latter slip further. Net capacity in China will fall, although not by as much as it has in recent years, as closures are balanced by new projects.

Demand is expected to rise by 12 million t/a over the same period, from 172 million t/a to 184 million t/a. Africa and South America (especially Brazil) are projected to be the fastest growing areas. Demand additions are expected to start exceeding new supply next year, but there are potentially large new increases in supply towards 2023, and overall demand may not exceed supply my much. This means, unless some of the plants are delayed – and this is a significant possibility for several of the projects – prices are unlikely to rise very high. For the past four or five years, demand growth in the urea industry has run behind new capacity additions, even with the huge reductions in Chinese capacity that have been seen. Chinese production costs are at the higher end of the cost curve, and with China having been so dominant on the export market, Chinese costs have tended to set a price floor, although capacity expansions outside China have decreased the need for Chinese urea, and there have been periods over the past two years when pricing has fallen below the Chinese floor price. As the cost curve continues to flatten as new capacity enters the market, we may be seeing relatively low urea prices for several more years to come.



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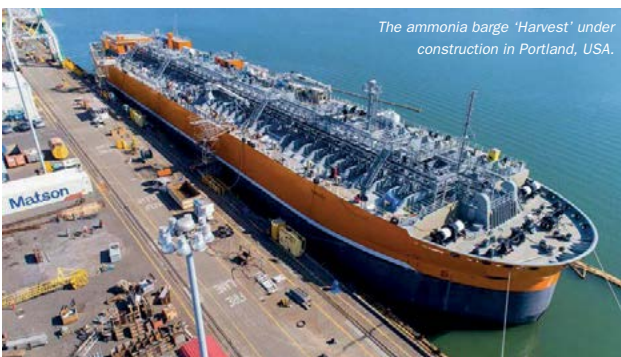
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The ammonia barge 'Harvest' under construction in Portland, USA.

PHOTO: BARD MARI TIME

Chemicals as energy carriers

Hydrogen, methanol and even ammonia have all been suggested as a way of transferring energy, perhaps renewable energy, produced or gathered in one place to a destination where the energy is required.

One of the major issues with the widespread uptake of renewable electricity generation is that places most suitable for wind or solar energy production are not necessarily those which most require electricity. Furthermore, the fluctuating nature of solar or wind energy means that power generation can itself be patchy, and not necessarily available in the quantity required at the time of day required, or perhaps over-abundant at times when demand is low.

Converting electrical energy into chemicals which can then be stored and used to generate chemical energy at the time and place required is therefore looking like a potentially attractive option to assist with large-scale uptake of renewables. The ammonia and methanol industries could potentially have a significant part to play in that process.

Hydrogen

The purest way of converting electrical energy into chemical energy is via water electrolysis to produce hydrogen. Hydrogen

can then be stored and, if necessary moved to where it is needed, where it can be used in a fuel cell to generate electricity back, or if necessary burnt cleanly with air to generate heat, steam (and thus potentially electricity), producing only water as a by-product.

The problem with the use of hydrogen as an energy carrier is that hydrogen is a very difficult material to handle. It resists being liquefied until cooled to very low temperatures, and so therefore is more usually stored in compressed form. However, the energy used in compression or liquefaction of hydrogen actually removes 10-40% of the energy released from combustion of hydrogen.

Its extremely low density, even when compressed, also means that its energy density on a volumetric basis remains markedly inferior to most liquid fuels (see Table 1)¹. As the table shows, hydrogen also has a much wider range of concentrations over which it remains potentially explosive. A series of recent incidents at hydrogen vehicle filling stations have illustrated that hydrogen may be cleaner than conventional fuels, but it is not necessarily safer.

For this reason, there is increasing interest in using other hydrogen-containing molecules to 'carry' hydrogen from the point of manufacture to the point of use.

Methanol

The idea of using methanol as an energy carrier started to gather interest in the first decade of the 21st century, and was given a major boost in 2005 when Nobel laureate George Olah published his paper *Beyond Oil and Gas: The Methanol Economy*. The argument was and is that methanol can be produced from a wide variety of sources, from coal and natural gas to biomass and of course renewable hydrogen and atmospheric carbon dioxide. It is a liquid at room temperature, and therefore easily transportable, and indeed a large transport infrastructure for its carriage already exists. And it can be used in a wide variety of potential end-uses, as well as being easily blendable into existing gasoline. It therefore offers, it was argued, a bridge from the old fossil fuel economy to a new renewable-based economy.

The place where the idea has been most widely taken up is of course China, which has used methanol as a fuel blendstock in road vehicles, as a way of producing dimethyl ether, which in turn has been used to substitute for liquefied petroleum gas (LPG), and as a way of producing polyethylene and polypropylene via various methanol to olefins (MTO) processes. China has driven the huge upsurge in methanol consumption over the past two decades, taking the methanol industry to over 90 million t/a of annual production and consumption.

Outside China, though, which has looked for a way to monetise its coal reserves, the take-up for methanol as a fuel has not been as significant, although India has also recently seriously looked at the concept, with a report by government policy think tank NITI Aayog in 2016 advocating that India move to a similar 'methanol economy'. Actual practical effects of this remain hard to discern so far, however. Elsewhere, there has been some interest in methanol as a clean marine fuel to comply with new International Maritime Organisation low sulphur fuel standards, and it has been successfully tested as a power plant fuel. Levels of uptake remain low however.

One issue is that, while methanol is much cleaner burning than most fossil fuels, it still generates CO₂ when used as a fuel. Methanol can be used in fuel cells to

generate electricity, and it can be reformed back to syngas to liberate hydrogen and effectively be used as a hydrogen carrier, but again at the price of liberating CO₂. The Methanol Institute has argued² that while this is the case, methanol produced from renewable hydrogen nevertheless is responsible for 95% fewer CO₂ emissions than that produced from fossil fuels. However, it has nevertheless driven some of the attention towards ammonia, which does not emit CO₂ when combusted.

Another potential way forward for methanol is the direct conversion of CO₂ to methanol – actually reducing CO₂ from the atmosphere rather than generating it. Since 2012, Carbon Recycling International has operated a 4,000 t/a methanol plant in Iceland using captured CO₂ and renewable hydrogen generated from geothermal electricity. Thyssenkrupp announced in June this year that it was entering a partnership with Swiss Liquid Fuels to offer small-scale (10-200 t/d) modular methanol plants based on hydrogen from electrolysis and captured CO₂ recovered from flue gas or waste gas streams. A number of other companies have also announced that they are working on direct conversion of captured CO₂ to methanol. These technologies are still in their early days, but could offer a way for the use of methanol as an energy carrier, and there will be an article in *Nitrogen+Syngas* covering the subject in greater depth next year.

Ammonia

Although ammonia is mostly nitrogen, it is still 18% hydrogen by weight, which means that in terms of hydrogen density it is 50% higher than compressed or liquefied hydrogen (as shown in Table 1). The relative ease of conversion of hydrogen to ammonia on a large scale has encouraged people to look at ammonia's potential as an energy or hydrogen carrier. One major advantage is that, as

with methanol, there is also an already existing infrastructure for production, transport and distribution of ammonia at a bulk level. Ammonia can also, in theory, be combusted to produce only nitrogen and water as emissions, although in practice nitrous oxides (NO_x) are often also generated, especially if the combustion happens at higher temperatures and/or under pressure, such as in a vehicle engine. Like methanol, ammonia can be blended in gasoline, or used on its own, including in gas turbines – it has even been used as a rocket fuel. It can also be used directly in fuel cells.

Ammonia also has its drawbacks, however, most notable of which is its toxicity when released in air. The efficiency of conversion of energy to hydrogen to ammonia also only runs at about 54%, lower than the 66% for reformer-based ammonia. However, it is theoretically possible to improve the efficiency of the process. Solar energy could be used to heat an ammonia reactor, for example. Furthermore, over long distances (>2,000 km), the energy lost in transporting ammonia is far lower than for transporting electricity. As an energy storage medium, it is also far denser and occupies a much lower footprint than the equivalent in batteries or compressed hydrogen, and offers the lowest potential cost of storage compared to other media.

According to the Ammonia Energy Association³, Equinor, Saudi Aramco, Woodside Petroleum, Shenhua Group, Shell, and Total are all now invested in demonstrating or developing new technologies or business cases for ammonia energy in a low-carbon economy.

Japan

One of the drivers for chemicals to carry hydrogen has been Japan's ambition to become a hydrogen-based economy. The initial impetus for this has been the plan to run the 2020 Tokyo Olympics completely on

hydrogen, including a fleet of fuel cell buses for the Olympic Village. However, it has grown to become "the world's first hydrogen-based society", including a Basic Hydrogen Strategy which has identified short, medium and long-term goals, with the aim of making as complete a transition as possible by 2050⁴. One milestone is the objective of increasing renewable hydrogen consumption in fuel cells and the like from 200 t/a today to 300,000 t/a by 2030, driving a fleet of 800,000 fuel cell cars, 12,000 buses and 10,000 forklifts by that time. On the ammonia side, Japan's Strategic Innovation Programme (SIP), under the auspices of the Council for Science, Technology and Innovation, has established the Green Ammonia Consortium to help develop an ammonia supply chain using ammonia made from renewable hydrogen⁵.

Other East Asian economies are following suit. South Korea's Hydrogen Economy Act is looking towards building a hydrogen production and distribution system using 70% renewable hydrogen, and reducing greenhouse gas emissions by 27 million tonnes by 2040. By this time Korea hopes to have 6.2 million hydrogen fuel cell passenger vehicles in service, 40,000 buses and 1,200 hydrogen refuelling stations, as well as generating 17 GW of electricity from fuel cells; 15 GW of public electricity and 2.1 GW for individual households.

China's Hydrogen Fuel Cell Vehicle Technology Roadmap anticipates hydrogen's widespread production and use by 2030, with a 50% increase in hydrogen production from clean energies, and deployment of 1 million passenger and commercial fuel cell vehicles by that year. It is also targeting a 95% reduction in fuel cell stack cost by 2025 compared to 2015.

Finally, Singapore is now also engaged in a study as to how hydrogen can be used to reduce emissions from electricity generation by 60%, replacing imported liquefied natural gas (LNG).

Australia

Another country that is looking seriously at the potential for ammonia as an energy or hydrogen carrier is Australia – in part because of the opportunities afforded by the planned uptake in hydrogen consumption in the Far East, and the abundance of solar energy across Australia. Indeed, Japan's Green Ammonia Consortium is specifically looking to Australia as a potential source of renewable hydrogen, and ammonia as a hydrogen carrier forms one part of this strategy⁶.

Table 1: Key properties of potential hydrogen carriers

Storage method	Hydrogen density (kgH ₂ /m ³)	Explosive limits (%vol in air)	Permitted exposure limit 8hr (ppmv)
Compressed H ₂ , 70MPa	42	4-75	n/a
Liquid H ₂ , 20.2 Kelvin	70	4-75	n/a
Liquid NH ₃ , 239K, 0.1Mpa	121	15-28	50
Liquid NH ₃ , 298K, 1 MPa	107	15-28	50
Methanol, ambient liquid	100	6.7-36	200

Source: Makepeace et al¹

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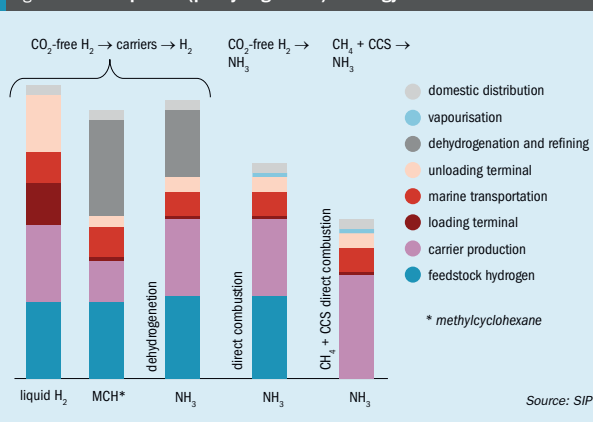
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Fig. 1: Cost comparison (per hydrogen unit) of energy carriers



This has generated several pilot projects across Australia. The Australian Renewable Energy Agency (ARENA) is helping to fund 40% of an A\$2.7 million study in conjunction with Dyno Nobel Moranbah, a subsidiary of Australian fertilizer producer IncitecPivot Ltd on the feasibility of building a renewable ammonia facility at Dyno's existing Moranbah site in Queensland. The study is considering a 160 MW electrolyser connected to a 210 MW solar farm at the site, which would then electrolyse water to produce hydrogen for ammonia production. The current facility operates a 150,000 t/a ammonia plant which feeds downstream nitric acid and 360,000 t/a of ammonium nitrate production, and the project, if it were to proceed, would envisage expanding ammonia and downstream capacity at the site.

ARENA is also funding a feasibility study with Queensland Nitrates for the construction of a renewable hydrogen-based ammonia plant at the company's existing site at Moura, Queensland. Queensland Nitrates is leading a consortium including France's Neoen and Australian energy consultant Worley, who are investigating the possibility of using wind, solar and energy storage capacity owned by Neoen to produce sufficient hydrogen to produce 20,000 t/a of ammonia, roughly 20% of Moura's current output.

Meanwhile, in South Australia, Hydrogen Utility (H2U) is developing a hydrogen and ammonia supply chain demonstrator project at Port Lincoln near Adelaide as part of the state's Hydrogen Action Plan to help scale-up renewable hydrogen production for export and domestic consumption. H2U's facility would

use wind and solar power generation to produce 32 MW of electricity and 18,000 t/a of renewable hydrogen-based ammonia capacity.

In Western Australia, Yara is also actively looking at integrating renewable solar hydrogen into ammonia production at Pilbara.

Dehydrogenation

If ammonia is to be used as a hydrogen 'carrier' rather than simply as a fuel at the other end of the transportation chain, then thought needs to be given as to how the hydrogen is separated back from the ammonia at the end of the journey – dehydrogenation. This has been a topic of research for Australia's Commonwealth Scientific and Industrial Research Organization (CSIRO), which in August 2018 presented its newly developed ammonia to hydrogen fuelling technology. The system takes ammonia vapour from the storage tank to a conversion module where it is 'cracked' over a ruthenium-based catalyst. A second set of tubes that incorporate a vanadium membrane separates the hydrogen from nitrogen. The hydrogen is then bubbled through a water bath to remove residual ammonia, and can be fed directly to a fuel cell vehicle. CSIRO is now working on commercialisation of the technology, via a A\$10 million commercial scale unit, which can produce 200 kg H_2 per day, as compared to the 15 kg/day of the current system.

In Japan, the Sawafuji Electric Company is working on its own ammonia to hydrogen conversion technology in conjunction with Gifu University. The bench-scale demonstrator used an ammonia decomposition

catalyst and a non-thermal plasma to facilitate electrolytic dissociation of ammonia at atmospheric temperature and pressure. A palladium membrane helps separate hydrogen from the process stream at very high purity. Scale-up is of course always an issue, but has already proceeded from 3.6 litres/hour to 2.4 kg/hour of hydrogen, and is now moving to 8 kg/hour. Sawafuji says it anticipates commercialisation in 2020.

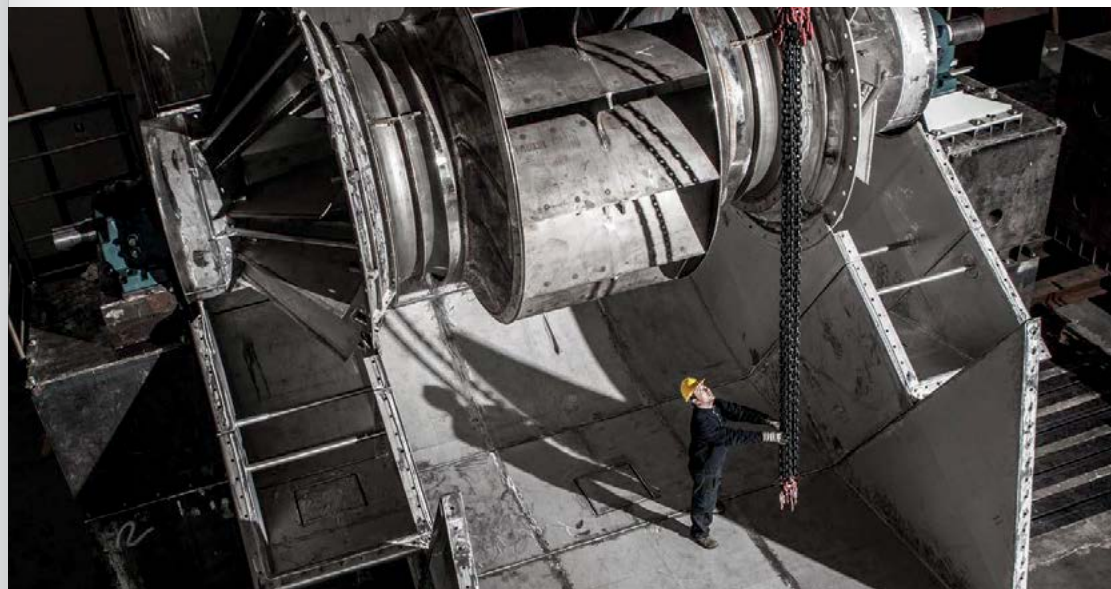
There are other programmes under way in the UK, Denmark, and the USA. RenCat, in Denmark, uses a nickel-iron rather than ruthenium catalyst, at a temperature of 300°C.

Cost

At the end of the day, any long distance energy transmission medium must be able to compete on a cost-effective basis. The relative costs of various approaches has been calculated by Japan's SIP as part of a feasibility study on chemical carriers for hydrogen⁵. In any region globally where renewable electricity costs are \$30/MWh or less, solar or wind electrolysis would be competitive with natural gas-based ammonia production. Figure 2 show's SIP's calculations for various methods of transmission. It concludes that conversion to ammonia and back is cheaper than conveying liquid hydrogen even at current costs (which could come down if there are advances in dehydrogenation techniques), while direct combustion of ammonia is cheaper still. Cheapest in the study is, perhaps unsurprisingly, conventional production of ammonia from natural gas with carbon capture and storage (CCS). However, this would depend upon the large-scale adoption of CCS, a technology which has not lived up to the high expectations that were once placed upon it.

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Carbon pricing and the siting of syngas capacity

This year, Canada is beginning to implement a federal carbon pricing scheme, while the EU's emissions trading scheme has finally moved out of the previous oversupply of permits via its Market Stability Reserve programme. Will these merely drive capacity to non-regulated environments ('carbon leakage'), or encourage innovation into lower carbon production of ammonia and methanol?

It is becoming increasingly acknowledged that climate change is one of the greatest challenges facing the world in the 21st century. The most recent report from the Intergovernmental Panel on Climate Change (IPCC) warns of dangerous effects on agriculture, water resources, ecosystems, and human health if countries do not take action. If the world warms by more than 2°C, which may be reached in less than 30 years, there could be food shortages, unprecedented heat-waves, and more intense storms. To stay below this 2°C target, the IPCC says the world will need to reach zero net carbon dioxide (CO₂) and equivalent gases emissions before the end of this century.

The ammonia industry is a carbon intensive one; ammonia and downstream nitrogen fertilizer production represent an estimated 1% of global carbon dioxide emis-

sions. The methanol industry is only about half the size of the ammonia industry, but it is growing rapidly, especially as methanol is used increasingly as a chemical intermediate for the production of olefins in China.

Methods of achieving the anticipated reduction in carbon emissions from all sources could include government regulation to encourage renewable energy development but the 1997 Kyoto Protocol also tried to introduce market mechanisms to encourage development of less carbon intensive technologies, and the concept of 'carbon pricing' was born, attempting to capture the additional societal costs of CO₂ emissions via a tax on those carbon emissions, putting the cost back onto the generator of the emissions, who are best able to reduce it. The International Monetary Fund has described carbon pricing mechanisms as "the single most effective mitigation instrument" that

governments can use to reduce their carbon emissions to the 1990 Kyoto baseline.

There are two main types of carbon pricing: emissions trading systems (ETS) and carbon taxes. An ETS, also referred to as a 'cap-and-trade system' caps the total level of greenhouse gas emissions and allows those industries with lower emissions to sell their extra allowances to larger emitters. By creating supply and demand for emissions allowances, an ETS establishes a market price for greenhouse gas emissions. The cap helps ensure that the required emission reductions will take place to keep the emitters (in aggregate) within their pre-allocated carbon budget.

A carbon tax directly sets a price on carbon by defining a tax rate on greenhouse gas emissions or – more commonly – on the carbon content of fossil fuels. It differs from an ETS in that the emission reduction

Above: Berwick Solar Park in the UK produces enough energy to power 2,540 households per annum.

outcome of a carbon tax is not pre-defined, whereas the carbon price is.

Carbon pricing mechanisms are now present to some extent in over 40 countries as well as various individual cities, states and provinces, and cover about 50% of the emissions from those regions, representing about 13% of global greenhouse gas emissions. As carbon pricing schemes spread, they are likely to play an increasing part in the operating costs of large scale carbon emitters like the global ammonia and methanol industries.

Current status of carbon pricing

Every year the World Bank publishes a Status and Trends of Carbon Pricing report, assessing how far carbon pricing mechanisms have spread and likely moves in the future. This year's report, published in June, notes that

"a growing number of jurisdictions are implementing or planning to implement a carbon tax or an emission trading system – a total of 57 initiatives compared to 51 in 2018 and this number is set to grow, according to countries' climate pledges. Most of this action has taken place in the Americas, and particularly in Canada, where the federal carbon pricing approach has prompted new initiatives at the provincial level. Important developments have also occurred in other parts of the world with new carbon taxes in Singapore and South Africa, the first carbon pricing instrument implemented in Africa, and new initiatives explored in Colombia, Mexico, the Netherlands, Senegal, Ukraine, and Vietnam."

The report also surveyed for the first time what it called 'implicit carbon taxes', i.e. government initiatives which were designed to lower fossil fuel use, such as fuel taxes or reforms to fuel subsidies, without necessarily being branded as carbon taxes. Its overall picture of current carbon pricing regimes currently adopted worldwide is reproduced in Figure 1.

However, the report also notes that only 5% of the emissions covered by carbon pricing schemes currently falls in or above the \$40-80/t range that is regarded by the IPCC as driving meaningful change in behaviour, and 50% are priced below \$10/t.

Europe

As well as a number of individual carbon pricing schemes in member states, the European Union as a whole has the world's most developed carbon trading system, the EU Emissions Trading Scheme, which began operating in 2005. However, it has attracted considerable criticism by pricing its carbon credits too low to drive meaningful behaviour change, especially after the 2009 recession meant too many credits were available. By late 2012, the price for a tonne of CO₂e had fallen to less than €7. However, as experience grows with managing the system, so the scheme has become tighter. This year carbon prices rose to €29/t CO₂e in July 2019, the highest level since July 2008, as the number of 'free' credits available to industry has been cut back, and it remains above €25/t at time of writing.

Canada

While there have been initiatives at a provincial level, from January 1st this year, Canada introduced a carbon pricing scheme on a federal level. This began on

January 1st with a carbon pricing "backstop" scheme, intended to cover jurisdictions within Canada which do not already have a local or regional carbon pricing scheme. The federal carbon pricing system has two components: a charge on fossil fuels to be paid by fuel producers or distributors, and the output-based pricing scheme (OBPS), a separate pricing system for industrial facilities that are emissions-intensive (>50,000 tonnes CO₂e/year) and trade-exposed. This sets a carbon price of C\$20/tonne CO₂e in 2019, rising by C\$10/tonne each year to C\$50/t in 2022. The tax only applies to emissions above a benchmark set for each industry, however. That benchmark is set at 80% for most industries, but it was recognised that some sectors faced a higher competitive risk, with the possibility that the carbon tax could lead to so-called 'carbon leakage' – see below – and their threshold was raised to 90% of the benchmark emissions level. The four industries were cement, lime, iron and steel manufacture, and the nitrogen fertilizer industry.

In addition to this 'backstop', the provinces of British Columbia, Alberta and Québec had carbon pricing systems in place before the backstop, and Manitoba and the Northwest Territories implemented a carbon tax in 2019, while Nova Scotia will implement its own cap-and-trade system. New Brunswick has decided to shift part of its gasoline tax to a climate fund, Prince Edward Island has said it will reduce the amount of sales tax payable on electricity, and Newfoundland & Labrador has not yet announced carbon pricing plans. However, both Ontario and Saskatchewan have mounted legal challenges to the federal government's ability to impose a carbon price on the provinces, and Alberta has said it may pull out of the scheme. Ontario also pulled out of the common cap and trade system it was in with Quebec and California last year after the election of conservative premier Doug Ford.

China

Perhaps the most anticipated scheme will cover China. This is an emissions trading scheme, and was officially launched in December 2017, although regional pilot schemes and development of the legal and technical infrastructure of the system has meant that no credits have been traded across China yet – this is expected to begin next year. Coal fired power

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generation will be the first industry covered in the initial phase, representing 3 billion t/a of CO₂ emissions. However, once it is fully operational, perhaps by the end of the next five year plan (2025), the scheme is expected to cover around 8 billion t/a of emissions – more than twice the size of the EU scheme. At present prices for carbon credits are low by international standards,

less than \$7/tonne, but this is expected to rise as the system develops.

United States

The United States remains the most notable holdout on carbon pricing, although some states have introduced their own schemes, including Washington State and

Massachusetts. The largest and most comprehensive scheme is of course in California, which covers around 85% of emissions. However, given the stance of the Trump administration on climate change, and its withdrawal from the 2016 Paris Agreement, while a few more states are considering emissions trading schemes, including Virginia, Oregon and

New Jersey, no federal scheme is likely in the next few years.

India

India is now the world's third largest emitter of greenhouse gases. The country has pledged a 33-35% reduction in the "emissions intensity" of its economy by 2030, compared to 2005 levels – a comparable, though lower pledge to China's move to cut carbon intensity by 45% between 2005 and 2020 (a target it has already achieved). By this time it is aiming for 40% of its installed electricity capacity, currently highly coal dependent, to be renewable or nuclear by 2030 (the actual figure was 18% in 2017). However, while there are numerous schemes to promote lower carbon use via subsidies, there is no carbon pricing scheme in view at present.

an indicator of where international scientific sentiment is leaning. Of course, widespread carbon pricing on such a level could have a major impact upon the syngas-based industries, which typically produce large amounts of CO₂.

Carbon leakage

Carbon leakage generally refers to the risk that economic activity and its associated carbon pollution are displaced to another jurisdiction with a lower or no price on carbon pollution and/or less stringent GHG regulations, which will ultimately not result in a net decrease in pollution.

The cost of producing ammonia or methanol is essentially determined by four main sub-costs; the cost of capital if the plant is a new/recent build; operating expenditures such as maintenance, power, salaries etc; feedstock costs; and the cost of transporting the product to market. Of these, the largest slice is usually taken by feedstock costs. Every \$1.00/MMBtu increase in natural gas costs adds approximately another \$35/t onto production costs, for a reasonably efficient plant. In Europe, producers typically pay higher natural gas feedstock costs compared to other regions of the world, where gas prices may be low due to abundant supply (e.g. the United States) or held at lower levels due to government subsidies or price caps. This can lead to feedstock costs for ammonia production being up to \$150-200/t higher in for example India or Europe than in the US, Russia or the Arabian Gulf. However, higher feedstock costs can be offset for older, written-down plants close to the centre of demand by not having to pay off the high capital cost of a new plant, nor the cost of transport and handling to take the product from the overseas producer. This, and the fact that many European ammonia plants are integrated into larger complexes which produce a variety of products, allowing costs to be amortised across several different outputs, has served to keep the European nitrogen fertilizer industry operating in spite of overseas competition, although arguments continue to run over so-called 'anti-dumping' actions, where product is allowed to be sold below cost price to gain market share.

However, adding carbon costs onto the cost of production threatens to upend

the present delicate balance. An energy efficient ammonia plant emits around 2.1 tonnes CO₂e per tonne of ammonia produced. This can vary quite widely – a Chinese coal-based plant for example may emit up to 4.4 tonnes CO₂e/tonne of ammonia. European plants tend to be among the most energy-efficient in the world. Even so, 2.1 tonnes of CO₂ emissions, if priced at the recommended \$40-80/t figure above, with no rebate or other allowances, could thus incur an additional production cost of \$84-168/tonne of ammonia – a level unsustainably high to permit continued operation of most ammonia plants, when set against the cost of importing ammonia, or urea/ammonium nitrate derived from ammonia, from a cheaper region of the world.

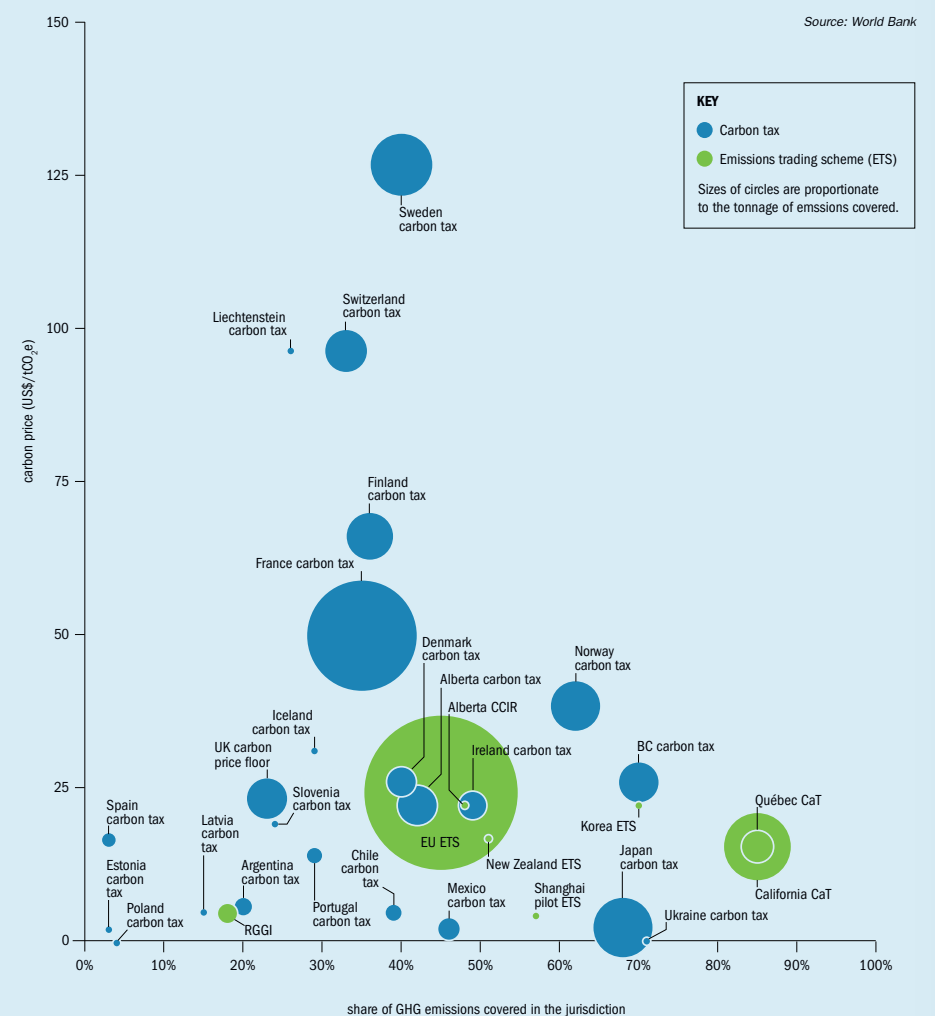
The argument of Fertilizers Europe is that, if carbon pricing meant that that production were closed down in Europe, and urea was imported instead from, e.g. China, far from lowering global CO₂ emissions, there would be a net increase, while putting European producers out of business. This is the essence of so-called 'carbon leakage'.

Nitric acid

It is not just the ammonia industry which is under consideration. The nitric acid (and by extension ammonium nitrate) industry has also been at risk from carbon pricing, not from carbon dioxide emissions this time, but from nitrous oxide (N₂O) emissions. Nitrous oxide has a greenhouse gas equivalent rating of 350 times that of CO₂, so while nitric acid manufacture typically produces only around 6kg N₂O per tonne of nitric acid, this represents a similar 2.1 tonnes CO₂ equivalent to ammonia manufacture. For this reason the nitric acid industry has invested significantly in N₂O abatement technologies over the past decade and a half, and brought emissions down to less than 1kg N₂O per tonne nitric acid. However, it remains vulnerable to increases in carbon pricing.

Another factor in the argument is that nitric acid is used to make ammonium nitrate, which is taken up by plants more quickly than urea – one reason it is preferred in Europe, which has a shorter growing season. This makes it less subject

Fig. 1: Carbon price and share of emissions covered of current carbon price initiatives



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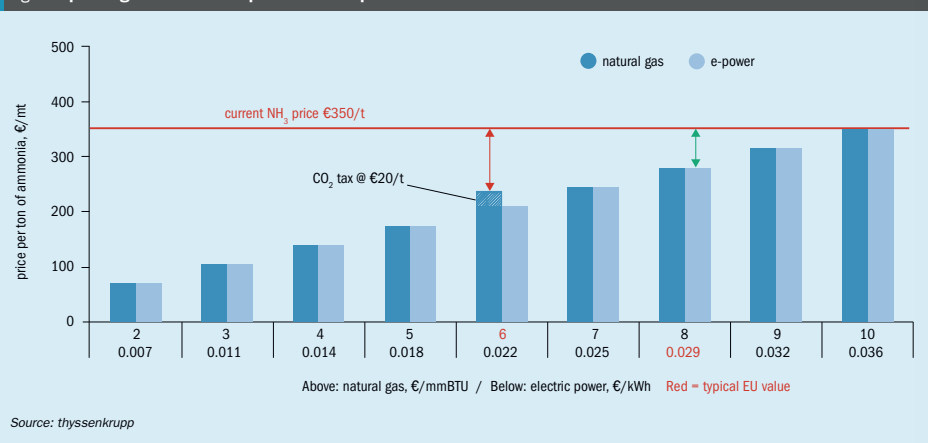
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Fig. 2: Operating costs for a European ammonia plant



to N₂O emissions in the field, so the argument of the fertilizer industry is that the lifecycle greenhouse gas emissions of AN are lower than urea, even though the emissions during production are lower for urea than AN. However, the EU ETS, for one, does not take lifecycle costs into account – it taxes CO₂ and equivalents purely at the point of production.

Shifting capacity

The difficulty for producers of ammonia, urea and nitric acid is thus not that there could be carbon taxes on their products, but that there will be a disparity in carbon taxes between different countries and regions. This means that there will not be a level global playing field for production in an industry which is global – ammonia trade works essentially in two hemispheres, eastern and western, but urea, the end use for most ammonia production, is a truly global product.

This has led to some considerations for energy-intensive industries at risk of carbon leakage, such as the 10% additional hike in baseline value for Canada's fertilizer industry mentioned above. However, this still means that the producers will pay carbon tax. In the European Union, industries which are subject to the risk of carbon leakage receive free credits under the emissions trading scheme up to a benchmark based on the most efficient 10% of plants. The net effect is that the average EU ammonia/urea plant

receives free credits covering up to 75% of emissions. However, if carbon prices were to rise to the recommended \$40-80/tCO₂e range, this would still mean an additional cost of \$20-40/tonne of ammonia; potentially enough to tip a plant from profit into loss.

Low carbon alternatives

The alternative that policymakers would clearly like is for syngas producers to switch to lower carbon feedstocks. In one sense this is already happening, though not necessarily due to carbon pricing – the closure of Chinese coal-based ammonia capacity is helping swing a global balance back towards lower carbon gas-based production, for example, and is driven by government policy to reduce overall carbon emissions by reducing consumption of coal, although it is not being achieved by carbon pricing but rather via more stringent enforcement of environmental standards.

However, for countries which are introducing carbon prices or emissions trading schemes, the question then becomes whether the cost of renewable electricity is low enough to justify a switch away from natural gas or coal-based syngas generation to renewables, biomass or other low carbon sources. We will look at this in more detail in an article next year, but briefly, in a paper presented in March this year at the Nitrogen+Syngas conference in Berlin, Tobias Birwe of thyssenkrupp

examined the potential costs for renewable ammonia production. He concluded that capital costs are already comparable for small-scale plants, although he admitted that there was still some way to go in terms of economies of scale. On operating costs, he presented Figure 2, which shows a current cost comparison, using typical European natural gas and electricity prices. These figures are based on \$6.00/MMBtu natural gas, a figure which has actually fallen this year in European markets to around \$4.50/MMBtu, but which has not been untypical of European prices in recent years. Clearly, even with the cost of a €20/tonne carbon tax, this is not enough to make renewable ammonia competitive. However, if electrolysis continues to become more efficient, bringing electricity costs down, carbon prices continue to rise, and natural gas becomes more expensive, then the situation in a few years may look quite different. ■

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2019 AIChE Ammonia Safety Symposium



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Venkat Pattabathula reports on the American Institute of Chemical Engineers' Safety in Ammonia Plants and Related Facilities Symposium, held 8-12 September in San Francisco, USA.

strategies for improving plant safety, maintenance, and management. Ammonia industry leaders and practitioners describe how their organisations avoid or manage potential plant accidents, and present solutions to safety engineering problems.

“**Safety culture is how the organisation behaves when no one is watching**”

The annual Ammonia Safety Symposium is organised by AIChE's Ammonia Safety Committee and is dedicated to improving the safety of plants that manufacture ammonia and related chemicals, such as urea, nitric acid, ammonium nitrate, and methanol. Attendees, which include plant safety personnel, plant managers, and process engineers representing a spectrum of nitrogen fertilizer based industries, amongst others, participate in the symposium, where they share technological advances and discuss

From 8 to 12 September 2019, about 350 engineers from more than 30 countries and 100 companies attended the AIChE's 64th Ammonia Safety Symposium at the Hyatt Regency hotel in San Francisco, California in USA. The San Francisco weather was ideal for outside activities and encouraged many people to visit the Golden Gate Bridge, Fisherman Wharf etc. Johnson Matthey's outing included a tour of the city via a Hornblower cable car to see the highlights of San Francisco, followed by dinner at Bistro Boudin, site of the bakery

for San Francisco's famous sourdough bread. Haldor Topsoe's outing included a cruise to Angel Island on San Francisco Bay, which gave people the opportunity to view the San Francisco skyline.

This year's keynote speech "Cultures Influence on Safety" was presented by Manny Ehrlich, member of the US Chemical Safety Board (CSB), and focused on process safety. Manny's speech grabbed the attention of the audience as he recounted major incidents that have taken place in the chemical industry over a number of decades.

Normalisation of deviance

In his presentation Manny stressed that most root causes don't involve rocket science issues and that there are many repeat or repetitive causes. In many cases the issue becomes one of repetitive findings related to deviation from basic fundamentals of acceptable safety practices when there is full understanding of what deviation from them could mean.

For example, typical repetitive issues for confined space violations include:

- Hot work practice violations

- Improper handling hazardous materials:
 - Flammables
 - Combustibles
 - Toxins
 - Corrosives
 - Explosives (or substances capable of exploding)
 - Poor utilisation or lack of proper PPE
 - Poor utilisation or lack of proper RPE
- management blames individuals for an accident.

Manny stated that we have to stop behaving like an ostrich, sticking our heads in the sand and believing it will improve if we do nothing. We need to start talking, start doing and by believing together we can move toward zero fatalities.

Safety incidents

The key safety related papers were:

Fire due to oil tank rupture

A power outage tripped the ammonia plant and 30 minutes later the syngas compressor oil tank exploded. They had all the components needed for an explosion in the tank. Oil vapour likely containing hydrogen degassed from oil to a limited extent ignited as oxygen enriched ambient air entered the oil tank. The missing pressure switch trip on the nitrogen compressor and the leaking end lid contributed to the incident. It is very unlikely to identify such a scenario through a HAZOP, where double jeopardy isn't usually considered. All unwanted incidents, like a nitrogen compressor not stopping when it should, must have two independent technical barriers. In this case the water mist system limited the damage. Another fact is that during the 30 minutes between the plant trip by the power outage and the fire, the control room operator got 900 alarms from the DCS.

Process gas cooler (PGC) tubesheet thermal disintegration

This paper highlighted the complexity of designing and operating a process gas cooler. The fibre materials used (high SiO₂ content) were not resistant to the reducing gas atmosphere and started to dissolve over time, opening gaps. The inliner of the central bypass was restricted in axial movement and pushed the refractory away from the tubesheet. The gap between the ferrules and the tubesheet holes was not closed with resistant material and allowed the gas to flow through.

The learnings were as follows:

- Damage along the tubesheet (gas side) cannot be detected during regular inspections without having the refractory removed.
- If the gas bypasses the refractory it may cause overheating of the metal shell, leading to coking and material loss. Also, the risk of high temperature hydrogen attack arises.

These issues occur over and over again. But why are we seeing repeat "violations" involving issues that we know to be problematic? Is it:

- a competence issue?
- a personnel issue?
- an individual/organisational issue?
- attitudinal in nature?
- behavioural in nature?
- related to risk?
- an ownership problem?
- a lack of commitment issue?
- a normalisation issue?
- a matter of beliefs?

It is believed that the intersection of all of these issues in aggregate constitute "the culture", or in this case, safety culture. Safety culture is important because management systems and their associated policies and procedures depend upon the actions of individuals and groups for their successful implementation.

It is the product of the individual/group values, attitudes, competencies and patterns of behaviour that determine the commitment to, and the style and proficiency of, an organisation's health and safety programs. A more succinct definition has been suggested: "Safety culture is how the organisation behaves when no one is watching."

Human beings take shortcuts for a variety of reasons and may do so without unacceptable consequences. Over time this can result in normalisation of deviance and lead to a poor safety culture, for example:

- little or no safety planning;
- no balance between safety and profitability;
- lack of training;
- no reporting of hazards;
- general lack of awareness of consequences of actions which could lead to a catastrophic disaster;
- inevitable consequences of actions led to catastrophic disaster;
- no commitment from workforce;
- feedback loop is not closed after an accident;



Manny Ehrlich, CSB Board Member, 2014-2019

A basic safety philosophy for success

- All accidents are preventable.
- No job is worth getting hurt for.
- Every job will be done safely.
- Incidents can be managed.
- Safety is everyone's responsibility.
- Continuous improvement.
- Safety as a "way of life" 24/7.
- All individuals have the responsibility and accountability to identify, eliminate or manage risks associated with their workplace.
- Legal obligations will be the minimum requirements for health and safety standards.
- Individuals will be trained and equipped to have the skills and facilities to ensure an accident-free workplace.

Ways to improve safety culture

- Establish safety as a core value.
- Provide strong leadership.
- Establish and enforce high standards of performance.
- Formalise the safety culture emphasis/approach.
- Maintain a sense of vulnerability.
- Empower individuals to successfully fulfil their safety responsibilities.
- Defer to expertise.
- Ensure open and effective communications.
- Establish a questioning/learning environment.
- Foster mutual trust.
- Provide timely response to safety issues and concerns.
- Provide continuous monitoring of performance.

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- Fitness for service analysis can determine whether a PGC with a damaged tubeshet is further usable.
- During equipment design an exchange of all operating parameters including start-up and shutdown conditions is extremely important as design parameters are easily compromised during those operational stages.
- During manufacturing and repair a high focus must be put on refractory design and execution as well as details regarding ferrule tolerances and the bypass in liner.

HP scrubber undetected carbamate corrosion

In February 2018, a leak was noticed in the spherical dome part of a HP scrubber in a urea plant. The plant was stopped immediately to attend to the leak. Upon opening of the HP scrubber sphere, it became clear that severe corrosion had occurred on the liners. The liner was covered with a huge amount of corrosive products and many cracks were observed which resulted in leaks.

The severe corrosion of the pressure bearing part of the sphere was due to the fact that the liner leakage preceding this corrosion could not be noticed as leak detection holes got plugged. This demonstrates the importance of a reliable and robust leak detection system. Nowadays the technology licensor recommends using a state of the art leak detection system, which is based on continuous forced air flow fed to an ammonia analyser (so-called pressurise system), which can be connected to the DCS system.

The leakage in the liner occurred due to so-called strain induced intergranular corrosion (SIIC). This was the result of condensation of reactor off gases in combination with plastic deformation of the 316L UG liner.

The plastic deformation was mainly the result of bending the liner plates during manufacturing. However frequent temperature and pressure cycles may play a role as well.

Condensation of the hot reactor off gases cannot be avoided completely in the HP scrubber sphere, despite the presence of a steam tracing. Plastic deformation of the 316L UG liner material cannot be completely avoided either.

Due to the liner leak, ammonia-carbamate started to corrode the carbon-steel pressure shell. Besides wall thinning,

hydrogen induced cracks (HIC) were also developed in the carbon-steel. Unfortunately, the selected steel (20MnMoNi45 DIN 17201) for the HP Scrubber sphere is prone to this failure mode (HIC) due to the high strength properties. Corrosion of the carbon-steel pressure retaining part should be avoided always. This is managed by having a reliable leak detection system in place. Furthermore, the risk of hydrogen induced cracking can be reduced by applying so-called low strength steels instead of high strength steels.

Damage of combustion air ducting

Severe damage to the parent material and structural integrity of the combustion air ducting (CAD) arrangement was experienced in an ammonia plant primary reformer. The root cause of the damage was the reverse flow of excessively hot combustion air/flue gas from within the radiant section of the primary reformer through the CAD. Investigation into the cause of the severe damage was performed in conjunction with the furnace designer.

During a controlled plant shutdown of the primary reformer, the FD fan was taken offline. Control logic causes both the cold and hot air doors to open. The ID fan would then remain online to assist in cool down of the entire reformer train. It was noted on May 2016 that the FD fan was taken offline followed by an ID fan trip within a few minutes.

With the cold and the hot air doors opened and no forced or induced draft, hot flue gases have travelled from the convection section to the radiant section, up through the CADs to the hot air doors, and towards the atmosphere.

All six CADs in the primary reformer penthouse have experienced flue gas temperatures in excess of 980°C (1,800°F). Due to lack of temperature indicators within the ducting, it was not possible to determine the actual temperature that the CADs were exposed to. To prevent a recurrence, the following recommendations were made:

- Adjust the cold and hot air doors logic: In the event the ID fan trips during a plant shutdown, control logic should automatically close the hot and cold air doors to mitigate against the potential for reverse flow through the CADs.
- Amend standard operating procedures (SOPs): Restart of the ID fan is now included in the SOP if the ID fan trips

during a plant shutdown. This would allow for controlled cooling of the primary reformer train from the radiant section through the convection section. In the event the ID fan cannot be restarted, ensure that the hot and cold air doors are closed until restart of the ID fan.

- Install temperature indicators (TIs) on all six CADs within the primary reformer penthouse: Due to the absence of TIs within the CADs, the plant operators were unaware of the fact that the CADs were experiencing temperature excursion during the plant shutdown. TIs were subsequently installed on the CADs with high temperature alarms of 400°C (750°F) set to assist with operator intervention in the event of temperature excursions.

The consequence associated with temperature excursions within the primary reformer CADs can be significant and the importance of continuous operator monitoring during plant shutdowns and start-ups would be crucial in identifying and addressing deviations in a timely manner. Evaluation of installed instrumentation on the primary reformer train as well as a review of SOPs for primary reformer shutdown should be considered.

Secondary reformer burner tip failure

A loss of containment scenario occurred on the secondary reformer in an ammonia plant resulting in an emergency shutdown and a fire emitting from the top head of the vessel. The root cause of failure was a cracked weld joint on the internal air distribution pipe. This caused a flammable mixture to leak internally in the secondary reformer and flame impingement on the internal components eventually deteriorated the liner, refractory, and outer wall. Further analysis indicated that cracking on the air distribution pipe was caused by thermal fatigue.

Strict quality control (QA/QC) is required for repairs on a system like this. Every practical effort should be made to reduce the number of start-ups/shutdowns to limit thermal cycling.

Rupture and fire in synthesis loop

There was a localised cracking/rupture which led to fire in ammonia synthesis loop in a spool piece of 1.3-m length of the vertical leg of pipe between two exchangers at the downstream of synthesis converter.



As part of the plant upgrade activities, the synthesis loop boiler feed water exchanger of Ammonia Unit II was replaced in February 2012 due to its tube plugging history. The elevation of the inlet nozzle of the new BFW exchanger was higher than the previous one. To accommodate the change in inlet nozzle elevation of the old BFW exchanger, a pipe spool piece of 1.3-m (4-ft) length was inserted into the vertical leg of piping from a new exchanger installed in 1993 plant revamp at the exit of old BFW exchanger.

The fire incident happened due to localised cracking/rupture at the weld joint of this inserted spool piece which was carrying synthesis gas at a temperature of 285°C (545°F) and pressure of 179.5 bar (2603.5 psig). The incident took place on 5th November 2017 at 10:08 am and the fire was controlled within 15 minutes. The plant was operating normally prior to this incident.

The fire caused damage to the equipment, pipelines, instrument and electrical cables, insulation etc. in the vicinity, which were assessed and restored. The plant operations were fully normalised by 30th November 2017.

Positive material identification (PMI) of the inserted 1.3-m spool piece revealed that low temperature carbon steel A333 Grade 6 (incorrect material of construction for this service) was inserted. Since the existing material was ASTM A335

Grade P22, the 1.3-m spool piece added should also have been of same material. LTCS (A333 Grade 6) is not recommended as per API 941 and discontinued since 1991 for such service as synthesis gas at the operating temperature being handled by pipe.

Methanator vessel overheating

Several Yara ammonia plants have recently experienced overheating of their methanator vessels leading to complete catalyst unloading for internal inspection.

What went wrong? The four incidents described showed how overheating could occur very quickly when key operational, control and safety measures fail. The causes of each described incident were different; however, the human factor was predominant in all of the four, in particular with respect to the override of the safety instrumented system (SIS) and the management of change of the SIS logics.

Recommendations:

- Ensure that the CO₂ removal and methanator trip systems are properly working.
- Verify that the trip thermocouples are correctly located.
- Verify that proper maintenance and inspection routines are correctly executed on trip systems, trip valves, solenoids, relays, thermocouples.
- Verify that the loop testing of trip

circuits are properly carried out during turnarounds.

- The override of the safety functions shall not be allowed unless a complete risk assessment is done, and all the required mitigating actions are in place.
- In almost all the cases, one should question if the metal wall temperature of the vessel has gone up at the same temperature of the bulk catalyst. The only way to answer to this interrogation would be to install metal temperature measurements on the vessel which will record the real metal temperature of it. This cannot be considered as an active prevention for the methanator overheating event, but it could eventually reduce the economic impact of it, immediately indicating if the integrity of the vessel was threatened or not by the event itself.
- In case of overheating methanator vessel event, do not restart the plant without having executed a proper integrity assessment of the vessel.

Roundtable Session

On the fourth day of the symposium, a roundtable session covered industry incidents, risks of leaks in urea plants, and ammonia and flammable gas leak detection systems.

The 2020 Symposium will take place in Munich, Germany, August 30 to September 2 at the Westin Grand Munich hotel.

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Nitrogen efficiency use and environmental sustainability

Enhanced efficiency fertilizers will have a role to play in the sustainable increases in crop reduction that will be required to feed a growing population. Controlled release and stabilised urea products are capturing a greater share of the market. Innovative biodegradable polymer coatings are being developed to meet the requirements of new regulations in Europe.

With the world's population expected to exceed nine billion by 2050, feeding everyone will require worldwide food production to increase by an estimated 70% over the next 30 years. Maintaining global food security in the face of population growth and limited land resources – and doing so sustainably – is one of humankind's greatest challenges. Consequently, there is a clear agronomic, economic and environmental need for innovative technologies capable of boosting crop production while achieving this in the most sustainable way.

Nitrogen fertilizers are vital for crop production – this primary nutrient being essential for plant growth and development. This has made the application of nitrogen in large amounts common practice in agriculture.

Due to its availability and high N content (46%), urea is the most widely-applied nitrogen fertilizer worldwide, representing approximately 67% of worldwide nitrogen fertilizer consumption. However, the use of conventional nitrogen fertilizers such as urea, while greatly increasing crop yields, can cause environmental pollution and soil nutrient imbalances. Indeed, the overuse of nitrogen in some parts of the world damages both crops and the wider environment.

An estimated 120 million tonnes of urea fertilizer is utilised by the agricultural industry worldwide, but has considerable risk of nitrogen loss if not adequately incorporated into the soil. Adequate incorporation means more than 1.2 cm of rain or irrigation or mechanical incorporation into the soil of more than 5 cm deep within a day or two after application.

Some calculations suggest that, on average, only 50% of the nitrogen applied to the soil as urea is taken up by growing crops. The unused nitrogen can remain in the soil, be removed by leaching or through runoff, or be lost to the atmosphere by volatilisation. Despite improvements in agronomic practices, nitrogen use efficiency (NUE) is still unsatisfactory with the proportion of N recovered by crops generally remaining below 60%.

The nitrogen loss problem

Soil applied nitrogen can be lost to the environment by a number of processes, including:

- Ammonia volatilisation
- Nitrification/nitrate leaching
- Denitrification/nitrous oxide emissions.

In volatilisation, the urease enzyme present in the soil rapidly hydrolyses urea to plant-available ammonium. If it is not incorporated into the soil, either by irrigation or rain, then a major proportion (up to 40%) of applied urea can be lost to the atmosphere as ammonia. Volatilisation can take place in every soil type. The risk of nitrogen loss through volatilisation or leaching depends on the weather and soil conditions and is severe under dry and alkaline conditions, thus reducing the nitrogen available for absorption by the plant.

Nitrification/nitrate leaching is the biological process in which the ammonium form of nitrogen is transformed to the nitrate form by soil bacteria. Nitrate is plant-available but also very susceptible to leaching as it is highly mobile in the soil

and it can move into deeper soil, below the plant's root zone, where it is no longer accessible to plants. It can contaminate nearby waterways and cause soil acidification. Leaching typically happens in permeable, sandy or low CEC soils and under excessive precipitation.

Applied nitrogen can also be lost through denitrification. This microbial process biologically reduces nitrate – ultimately to molecular nitrogen (N₂) – via a series of intermediate nitrogen oxide gases. These include nitric oxide (NO) and nitrous oxide (N₂O), a greenhouse gas. The denitrification process is favoured under anaerobic soil conditions and is most prevalent in soils that are poorly drained or become waterlogged.

It is important to develop and employ management practices that use nitrogen fertilizers both effectively and efficiently. This can be achieved by combining the 4R nutrient management principles (right source, right rate, right time, right place) with the use of modern fertilizer technologies¹.

Enhanced efficiency fertilizers

Slow- and controlled-release and stabilised fertilizers (SCRFS), also termed enhanced efficiency fertilizers (EEFs), have come under the spotlight in recent times.

The adoption of these speciality products provides growers with an invaluable tool for improving NUE and reducing the negative environmental impacts associated with commodity nitrogen fertilizers such as urea.

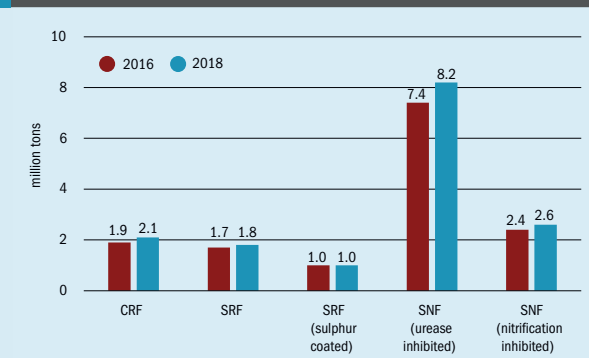
Table 1 shows the main types of SCRFS, their mode of action and relative costs.

Table 1: Main types of SCRFS: mode of action, technology and cost

Types	Mode of action	Technology	Cost in use
Slow release fertilizer (SRF)	Microbial	Urea-aldehyde	\$\$\$\$
	Physical	Sulphur coated urea (SCU)	\$\$\$
Controlled release fertilizer (CRF)	Physical	Polymer coated urea	\$\$\$\$\$
Stabilised nitrogen fertilizer (SNF)	Biological	Treated with urease and nitrification inhibitors	\$\$

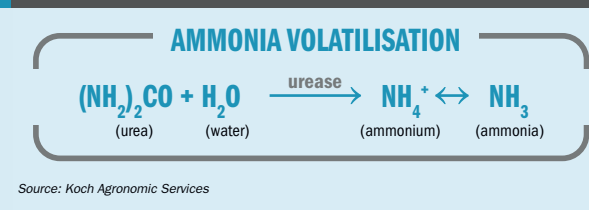
Source: Solvay

Fig. 1: World consumption of SCRFS: 2018 vs 2016



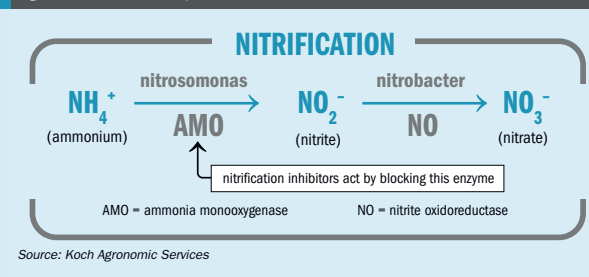
Source: Rams & Co presentation, IFA conference, Dublin, April 2019.

Fig. 2: The ammonia volatilisation process



Source: Koch Agronomic Services

Fig. 3: The nitrification process



Source: Koch Agronomic Services

The value of the global SCRFS market was estimated at \$4.7 billion in 2018, and looks set to grow at 9% per annum to exceed \$10 billion by 2028. The consumption of SCRFS reached 15.7 million tonnes in 2018, up from 14.4 million tonnes in 2016. Market growth was mainly due to the rising popularity of SNFs, particularly urea stabilised with urease inhibitors (Fig. 1).

Tools to prevent nitrogen loss

By definition, EEFs provide increased nutrient availability while reducing potential nutrient loss. How EEFs achieve those benefits, varies by technology. Knowing how these technologies work can better help a fertilizer producer understand the value these solutions provide to the end-user².

Stabilised nitrogen fertilizers (SNFs)

Two different types of stabilised urea fertilizers have been developed, namely stabilised urea with urease and/or nitrification inhibitors and urea coated with a polymer leading to slower and controlled release of the nutrients (CRF-controlled release fertilizer).

Urease and/or nitrification inhibitors

SNFs typically combine urea with urease and/or nitrification inhibitors. They work by delaying the conversion of nitrogen into forms that are readily lost to the environment through leaching, denitrification and volatilisation.

Urease inhibitors delay the hydrolysis of urea while nitrification inhibitors delay the biological conversion of ammonium to nitrite and nitrate. These delays allow time for rainfall to move the urea into the soil where it is less prone to volatilisation. The use of inhibitors also keeps nitrogen within the plant/soil system for longer. Broad acre crops are the major application for these stabilised nitrogen products.

The most common commercial urease inhibitor in the market is N-(n-butyl) thiophosphoric triamide (NBPT). This technology works more effectively when the granule or prill is on the soil surface by slowing the conversion of urea to ammonium gas that can then be lost to the atmosphere through volatilisation (Fig. 2).

Nitrification inhibitors provide protection from losses of nitrogen once the fertilizer is incorporated into the soil. The most commonly used nitrification inhibitors are dicyandiamide (DCD), nitrapyrin and dimethylpyrazole phosphate (DMPP). Ammonia rapidly converts to ammonium when it combines with water in the soil. Nitrification is the conver-

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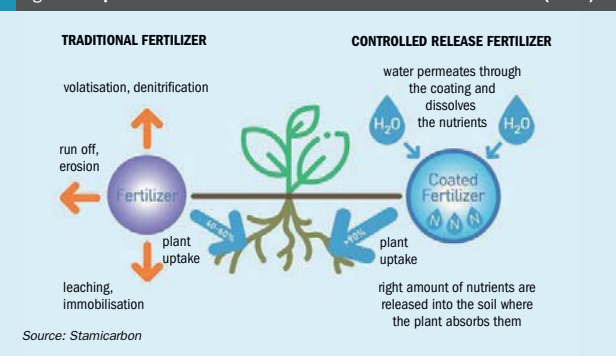
Urea stabilised fertilizers

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Fig. 4: Comparison between traditional and controlled-release fertilizers (CRFs)



sion of ammonium to nitrate by the soil bacteria *Nitrosomonas* and *Nitrobacter* (Fig. 3) Ammonium is held by the soil, compared to nitrates which move freely through soil water.

If growers face saturated soils, nitrates can also convert to nitrogen gas which is then lost to the air, a process called denitrification.

By inhibiting the AMO enzyme which is found within the *Nitrosomonas* bacteria, nitrification inhibitors can reduce leaching and denitrification loss potential.

By incorporating two types of stabilisers, dual inhibitors are designed to protect against all three forms of nitrogen loss.

Controlled-release fertilizers (CRF)

Conventional fertilization with urea requires multiple applications. The use of controlled release fertilizers can reduce the number of applications per growing season (Fig. 4). Controlled-release fertilizers (CRFs) are also known as polymer-coated fertilizers (PCFs).

The manufacturing process involves coating a readily available fertilizer substrate such as urea with a polymer coating. PCFs release nutrients based on osmosis and diffusion through the coating. Water passes through the polymer outer layer and dissolves nutrients inside. Release rate and longevity are controlled by coating thickness and soil temperature. By using different coating materials and thicknesses, as well as blending different coated fertilizers with different nutrient release characteristics, it is possible to match the needs of the plant. Because controlled-release fertilizers follow a known temperature response, CRFs provide a predictable, controlled release of nutrients over a desired timeframe. Release times of up to a year or even longer are possible.

The main market for CRFs has until recently been the turf and ornamental sector.

Products suitable for mass application in broad-acre agriculture have only recently become available. The full potential of CRFs is only starting to be recognised too³.

The World Economic Forum, for example, in its 2019 report on *Top 10 Emerging Technologies*, states:

"Controlled-release fertilizers are part of a sustainable approach to agriculture known as precision farming. This approach improves crop yield and minimises excessive nutrient release by combining data analytics, AI and various sensor systems to determine exactly how much fertilizer and water plants need at any given time and by deploying autonomous vehicles to deliver nutrients in prescribed amounts and locations."

Slow-release fertilizers

Slow-release nitrogen sources provide greater longevities of available nitrogen rather than quick-release sources, and are safer to use on turf grasses, for example, because of their lower burn potential. There are several types of slow-release fertilizers available for use e.g. sulphur-coated urea (SCU), polymer-coated SCU (PSCU) and reacted urea products such as urea-formaldehyde or methylene urea.

Solvay's nitrogen stabiliser solutions for EEF

Solvay has developed nitrogen stabilisers namely the AgRho[®] N Protect™ range of eco-friendly formulations based on NBPT and DCD. The AgRho[®] N Protect™ family has gone through Solvay's Sustainable Portfolio Management (SPM) methodology, which

explores potential risks and opportunities in both the manufacturing process and the market place. The methodology identifies key features of the footprint of a product, including CO₂ emissions, consumption of non-renewable resources, impact on human health and ecosystem quality, as well as the water footprint, and concludes with recommendations to make the solution more environmentally friendly. AgRho[®] N Protect™ thus leverages Solvay's expertise in green solvent technology and agrochemical formulations, delivering a load capacity of up to 50% of active ingredients in a non-toxic solvent formulation.

Commercial benefits

Nitrogen stabilisers result in more nitrogen available for the plant absorption thus increasing the yield and optimising the farmer's investment. Solvay has carried out extensive field trials with its AgRho[®] N Protect™ range of urease (NBPT) and nitrification inhibitors (DCD) on various crops in different regions resulting in the increased yield of up to 20% or nitrogen fertilizer savings of up to 20%.

Tillage is important to consider when choosing a urease inhibiting product. AgRho[®] N Protect™ works even better under no-till situation as in no-till situation if the surface applied nitrogen is left on the surface then much of the nitrogen applied will be lost as ammonia into the atmosphere due to high enzyme activity breaking down the urea. AgRho[®] N Protect™ stops the activity of the enzyme for up to two weeks.

Also, the use of urease and nitrification inhibitors allows for increased options for the timing as well as number of nitrogen applications potentially helping the growers to save on the cost and labour of split nitrogen applications.

Environmental benefits

Nitrogen stabilisers are an important part of grower's environmental stewardship efforts; they have helped growers to improve their environmental impact by reducing air and water pollution, keeping the nitrates out of the water and decreasing greenhouse gas emissions.

30% or more of the applied nitrogen is lost as ammonia into the atmosphere. Ammonia is one of the major pollutants of the atmosphere and also reported as one of the reasons for the atmospheric haze. One of the most effective management tools for preventing ammonia loss from surface applications of urea or UAN is through the use

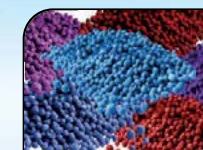
Bringing Life To Your Fertilizer With Colours



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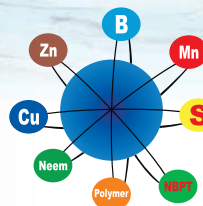
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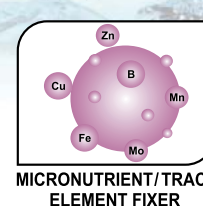
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DIATOMACEOUS EARTH / REACTIVE SILICA



Micronutrient Coating Technology



MICRONUTRIENT/TRACE ELEMENT FIXER



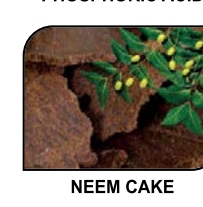
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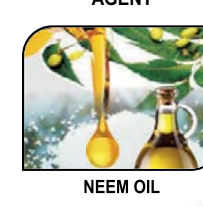
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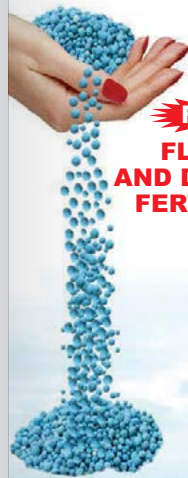
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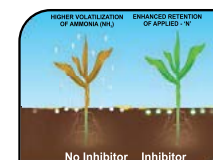
NEEM CAKE



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FREE FLOWING AND DUST FREE FERTILIZERS



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of urease inhibitor such as NBPT. With the use of NBPT over 80% reduction in ammonia volatilisation has been observed.

Nitrate leaching is of a major concern for contamination of water ways and algae bloom. Preventing water pollution is a win-win for growers, as it's critical that growers keep nitrogen in the root zone and available for crop uptake, and out of the tile lines and waterways. The environmental benefit of keeping nitrogen out of the waterways is that it's typically a limiting factor for algae blooms. Nitrate leaching is reduced by over 60% by using nitrification inhibitor

Through denitrification process nitrogen can be released in the form of nitrogen oxides into the atmosphere. Two main nitrogen oxides that are released during the denitrification process are nitric oxide (NO) and nitrous oxide (N₂O). N₂O is a greenhouse gas with nearly 300 times more global warming potential than that of CO₂. Up to 2% of the applied nitrogen is lost as N₂O into the atmosphere. The atmospheric concentration of N₂O has increased at an average rate of 0.75 ppb/year rising 20% since 1,750 to 324 ppb. Emissions associated with nitrogen application to agricultural soils comprise 60% of global N₂O emissions and are projected to cross over 7 Tg N₂O-N/year by 2030. The use of mineral fertilizers has been one of the principal drivers of this increase in emissions. Excess nitrogen fertilizer application has resulted in enhanced nitrogen losses to the environment. With the use of nitrogen stabiliser formulation Solvay has shown over 50% reduction of N₂O emission when compared to untreated fertilizer.

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One size does not fit all

The risk of nitrogen losses through ammonia volatilisation or nitrate leaching depends on many parameters such as:

- weather and soil conditions (environmental factors);
- types of fertilizer(s) used;
- targeted number of fertilizer applications (nitrogen program).

Nitrogen fertilizers don't all require the same nitrogen stabilisers. Therefore it is important to choose the tailored nitrogen stabiliser formulation targeting grower's specific environmental factors and nitrogen program.

To help find the right nitrogen stabiliser Solvay has developed a web-based tool (nprotect-solvay.com) that allows the grower to select the best nitrogen stabiliser formulation that fits his needs.

Koch Agronomic Services EEF technologies

Koch Agronomic Services (Koch) works with leading universities and third-party researchers to conduct trials to study the efficacy and benefits of enhanced efficiency fertilizers (EEF) technologies for growers. Research results indicate the technologies utilised by EEFs can be more effective in optimising plant nutrient uptake when compared to non-EEF sources. Additional studies have shown EEFs reduce the potential of nutrient losses to the environmental (i.e. volatilisation, denitrification, or leaching). Effective solutions provide greater protection of nitrogen which can translate to greater yield.

While there are many options a grower can select from to protect their urea nitrogen, SUPERU® fertilizer and AGROTAIN® nitrogen stabiliser are two solutions that can be produced using a technology that can be easily implemented and is designed to work seamlessly in the urea manufacturing process.

AGROTAIN® nitrogen stabiliser is a urease inhibitor. The active ingredient in AGROTAIN® is NBPT.

SUPERU® fertilizer incorporates two types of stabilisers, NBPT and DCD, to deliver protection, productivity and efficiency in one homogenous urea granule. The dual inhibitor protects fertilizer from all three forms of nitrogen loss – volatilisation, denitrification and leaching.

The production of EEFs can be done at many levels, including at the manufacturer, distributor, retailer or at the farm gate. Each of these options vary in cost, and ease of use which contribute to the value to a grower.

A proven, consistent quality, and cost-effective method of EEF value creation can be produced by the urea manufacturer at their plant. The incorporation of inhibitors through technology such as the Koch's N-TEGRATION™ Technology can be a simple, cost effective, and reliable method for a manufacturer to create both value for the end user and capture some of that value for themselves.

N-TEGRATION Technology is currently in use at a fertilizer production facility in Enid, Oklahoma, US, and Brandon, Manitoba, Canada, where it is used to produce SUPERU® fertilizer. N-TEGRATION Technology offers benefits including the following:

- Minimal scope/impact: Can be "bolted on" to existing or new urea plants.
- Short installation schedule: Estimated 10 months from beginning of design process to plant start up.

- Operational flexibility: N-TEGRATION Technology can be switched "On" or "Off" easily – allowing campaign runs or 100% EEF production.
- Minimal capex investment: Approximately \$3-\$12 million.
- Ability to capture higher margins: Premium margins vs. commodity urea.
- Differentiation = liquidity: Differentiated product enables urea plant liquidity and/or net-back improvement in a long commodity urea market.
- Sustainability: Differentiated products that can meet growing regulations and help achieve corporate sustainability goals.

Other manufactured products at a plant can be costlier and involve more complicated equipment, causing additional difficulties to overall plant support operations.

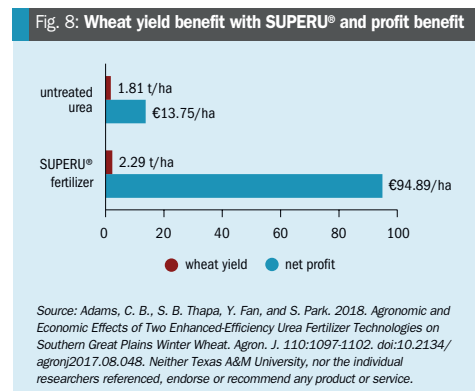
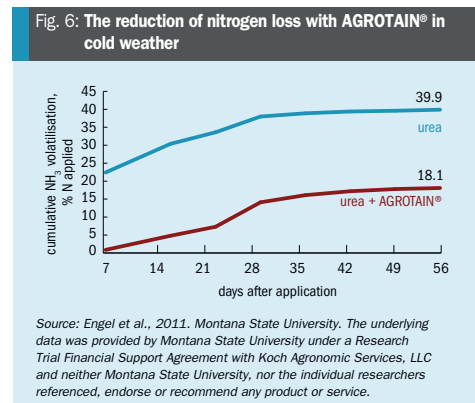
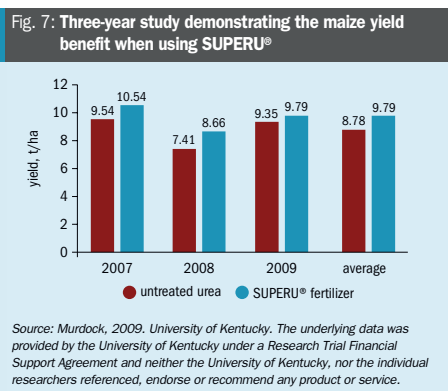
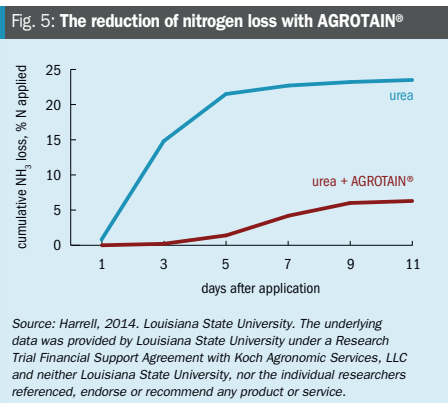
University research results for AGROTAIN® and SUPERU® which include varying climatic and crop specific challenges are shown in Figs 5, 6, 7 and 8.

Fig. 5 shows reduced ammonia volatilisation losses with AGROTAIN® in a rice field study. Untreated urea was applied to dry soil ten days prior to flooding where approximately 24% of the nitrogen was lost to ammonia volatilisation. When urea was treated with AGROTAIN® stabiliser, nitrogen loss to ammonia volatilisation was less than 7%.

Fig. 6 shows the results of a trial conducted by Dr Rick Engel at Montana State University, US. The study found reduced ammonia volatilisation losses with AGROTAIN® in cold weather. Even in cold weather, nitrogen is at risk of loss. The high soil moisture at fertilisation time explains the high loss for untreated urea in the first week. Eight weeks after application, approximately 40% of the nitrogen in untreated urea was lost to ammonia volatilisation. When urea was treated with AGROTAIN® stabiliser, nitrogen loss to ammonia volatilisation was less than 19%.

Fig. 7 shows the maize yield benefit of using SUPERU®. In a three-year study SUPERU® averaged 1 tonne/hectare yield increase compared to untreated urea. Treatments were broadcast at one to two weeks after planting at a rate of 84 kg N/hectare.

Fig. 8 shows wheat yield benefit and profit benefit with SUPERU®. In this study SUPERU® fertilizer was compared to untreated urea at different application rates, timing and two soil types on dryland winter wheat. The results indicated



SUPERU® has the potential to improve wheat grain yield and protein concentration relative to untreated urea.

Wheat fertilized with SUPERU® at 70.6 kg N/hectare at planting achieved 26% greater yield than untreated urea. The economic analysis of net profit for each treatment was at the wheat price points of €129.36, €194.04 and €258.35/tonne, which represents the low, average and high prices in the Southern Great Plains over the past eight years.

Broadcasting SUPERU® resulted in higher net profits than untreated urea at all price points. As wheat price increased, the crop treated with SUPERU® saw more economic benefit. By protecting the nitrogen investment with SUPERU®, the study showed an increase in yield, resulting in an increase in net profit by €81.32 per hectare compared to untreated urea.

The DUROMIDE™ advantage

As urea is the largest nitrogen source used in agriculture, KAS sought to improve on one of the most recognised urease inhibitor active ingredients, NBPT, with the patented active ingredient in ANVOL™ nitrogen stabiliser DUROMIDE™.

Earlier this year KAS announced that its ANVOL™ nitrogen stabiliser is now available to growers in the US. When compared to other urease inhibitor technologies, this next-generation stabiliser provides the longest-lasting protection against ammonia volatilisation, thanks to an optimal amount of dual active ingredients – DUROMIDE™ and NBPT.

DUROMIDE offers:

- patented chemical structure;
- more stable over a wider range of soil environments;

- slows down urea hydrolysis of free urea in the soil over longer window;
- more effective than NBPT alone;
- buys more time for rainfall incorporation;
- reduces ammonia loss.

Better farm economics

Improving environmental protection and increasing food production are both vital and necessary objectives for world agriculture. But, for individual farms and farmers, financial returns usually provide the best incentive when it comes to changing fertilizer purchasing and application decisions.

Numerous field studies over the last decade have compared the performance of controlled-release fertilizers with conventional split-application fertilizers. The analysis shown in (Fig. 9) is based on US field trials with corn in 2017 and 2018. It compares

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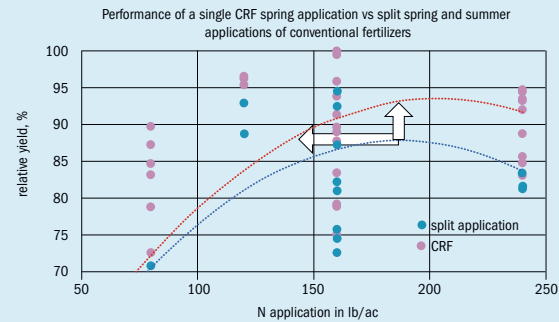
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Fig. 9: US corn trials, 2017-2018



a single spring application of a controlled-release fertilizer (CRF) to split applications with conventional fertilizers in spring and early summer. For each individual test site and test year, the highest yield obtained is recorded as 100% and used as a yardstick. All other results were then measured against this maximum reference point.

Although not every crop yield result for CRFs is higher than the corresponding yield result for a split application with conventional fertilizers, the statistical analysis does reveal a clear and unambiguous trend: CRFs in general offer a steady yield improvement over conventional split applications. Results also confirm that nutrient use efficiency improves with CRFs resulting in higher yields, or lower application rates, due to a reduction in volatility and leaching losses.

Based on these field trial results, the following observations on cost have been made for a single CRF application versus split applications of conventional fertilizers, assuming \$400/t for the urea price and \$4/bushel for the corn price:

- At similar application rates: the 6-7% yield improvement achieved means CRFs are still cost competitive with conventional fertilizers even when sold at a premium of more than \$200/t.
- At 25% lower application rates: the similar yield achieved by a lower amount of CRF allows for a price premium of \$130/t.

The above calculations are conservative estimates as they do not include additional savings to the farmer such as the fuel saved from the single application of CRFs. In general, the business case for CRFs is always positive, providing a sound financial incentive for their increased adoption and use.

For broad-acre agriculture in North America, targeting a \$100/t price premium over urea for CRFs could provide significant financial incentives for farmers to switch from commodity to coated fertilizers.

New EU regulations

From 2020, urea can only be used in the stabilised form. In Germany it has to be incorporated into the soil immediately after the application. Stabilised form here means improved physical and chemical stability leading to improved and prolonged availability of the fertilizer.

The new European Fertilizer Regulation, a replacement for the previous 2003 regulation, will require all fertilizer polymer coatings to be biodegradable in the near future. The regulation requires 90% polymer degradation within 48 months after the fertilizer is applied. The regulation comes with a transition period of five years, after which all products on the market will have to comply.

However, the test method for compliance with the new biodegradation requirements has yet to be defined, although it will need to be decided on within the next five years. Fulfilling the normal requirements of a controlled-release coating, while at the same time satisfying the EU's conditions for soil and water biodegradability, will be quite a challenge for CRF producers. Nevertheless, companies such as Pursell Agri-Tech in partnership with Stamicarbon and thyssenkrupp Industrial Solutions are actively developing innovative but practical coating solutions that meet the requirements of the European CRF market.

Stamicarbon/Pursell Agri-Tech complete CRF production package

Stamicarbon in cooperation with Pursell Agri-Tech is offering a complete package for controlled-release fertilizer production – one that is based on a novel coating technology exclusively developed for this purpose. This production package, based on a batch coating process in a high intensity mixer, is able to encapsulate a wide variety of different fertilizer products with a new kind of polymer coating. This coats fertilizer granules within an extremely thin and durable membrane. The controlled release of nutrients can be adjusted over a time span of between one and 12 months, depending on the weight of the applied coating.

The novel polymer used in the production process is exclusively supplied by a major global polymer producer. The equipment manufacturer, also working in exclusive cooperation, is able to supply customers with complete production installations on a lump sum, turnkey basis.

The guarantees provided by these exclusive arrangements eliminate investment risks in new plant capacity, and provide a solid foundation for a major expansion in controlled-release fertilizer production. This production package makes it possible for fertilizer producers, importers and distributors to access CRF production technology and manufacture products for their domestic customers. The production units are designed to be located close to the end-user (farmers) so as to avoid the unnecessary handling of the coated product.

The first CRF demonstration plant, operated by Pursell Agri-Tech in Sylacauga, Alabama (pictured below), has been performing successfully since spring 2018. The plant is currently running 24 hours a day, in five days a week operation, providing just under 100,000 t/a of coated product capacity. The current coating line can coat nearly all fertilizer grades, including granular and prilled urea, DAP, MAP, NPK, etc.



Pursell Agri-Tech's Sylacauga CRF demonstration plant.

PHOTO: PURSELL AGRITECH

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Fig. 10: The first step of synthesis of PLA: dimerization to lactide

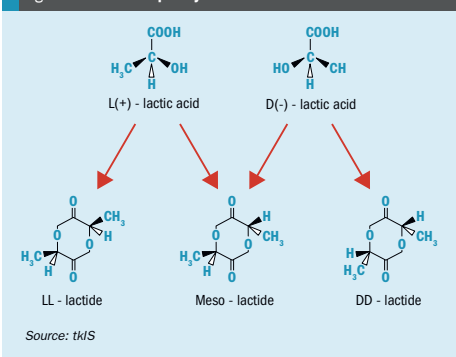


Fig. 11: Available PLA product portfolio

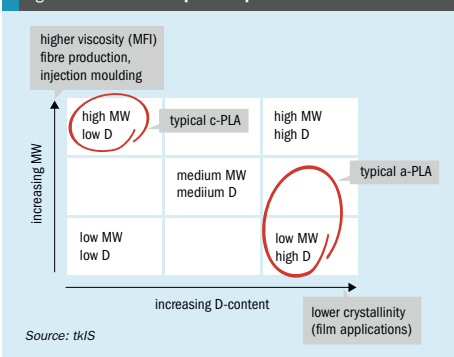
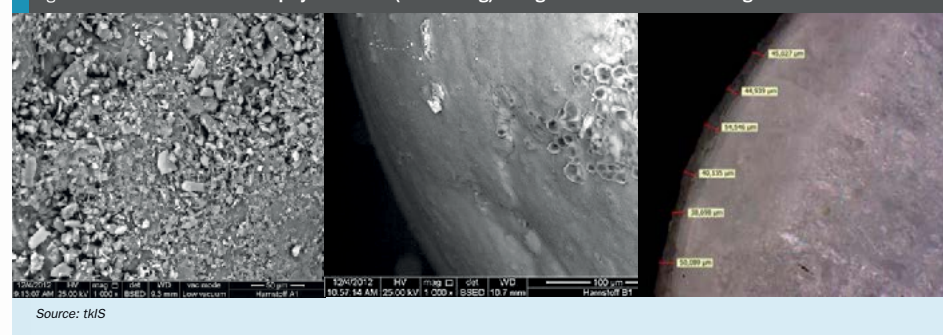


Fig. 12: Surface of untreated and polymer-coated (PLA-coating) urea granules with uniform coating thickness



tkIS biodegradable and sustainable SCRFs

thyssenkrupp Industrial Solutions (tkIS), one of the leading EPC contractors for ammonia and urea plants, has been working on the development of stabilised and controlled release fertilizers (SCRFs) and their production process.

Experiments for production and application of polymer coated fertilizers to crops have been made from characterisation of their physical properties to release properties and agricultural effect. The key message from all experiments is that fertilizers with controlled release of nutrients demonstrably result in less nitrogen losses, both in the form of nitrate and by volatilisation. Efficient availability and distribution of nutrients lead to increase of crop yield or decrease of nutrient consumption. Special attention has been given to the application of biologically degradable polymers.

These polymers decompose in the soil without producing any environmentally harmful substances and can even be produced from renewable resources, using a process owned by tkIS. This ensures sustainability for the whole production and application process.

In addition to being biologically safe, biodegradable and non-bactericidal, the coating materials should have sufficient stability for prolonged storage or when used in the soil to be able to ensure the designed nutrient release even over longer growing seasons. Last but not least, the coating processes to be developed should be as simple as possible, so that they can be integrated into the operation of a fertilizer plants with their very large throughputs.

Coating medium / Polylactic acid (PLA)

Polylactic acid or polylactide is a biodegradable and sustainable thermoplastic aliphatic polyester which can be derived from renewable resources. The feedstock for the Polycondensation Technologies PLAneo® by tkIS/UIF (thyssenkrupp Industrial Solutions / Uhde Inventa Fischer) is lactic acid. The lactic acid (LA) required for polymerisation is fermented from glucose or sucrose, thus it can be produced from renewable resources. PLA has properties similar to PET, PP and PS and can be used as a substitute for these materials, helping to save fossil resources, such as petroleum. In the first polymerisation step, lactic acid is concentrated to remove any residual water. An oligomer of limited molecular weight is then produced in the subsequent polycondensation stage. This prepolymer is thermally depolymerised to form lactide, the cyclic dimer of lactic acid (Fig. 10).

In the subsequent ring-opening polymerisation the high molecular weight PLA is obtained but commonly PLA can be produced in many different grades. The two main parameters distinguishing the grades are molecular weight and crystallinity of PLA. In general, the following rule can be applied: the lower the D-lactide content, the higher the crystallinity. Fast-crystallising types are e.g. required for fibre applications or injection moulding, whereas medium or high-D-content grades are used for thermoforming or film applications.

Meso-lactide, which is a side-product of the PLA process, usually has to be separated and hydrolysed back to lactic acid, thus reducing the overall efficiency and

increasing the feedstock conversion cost. In the PLAneo® process, meso-lactide is polymerised and blended with standard, crystalline PLA, without adversely affecting the properties of the PLA produced in the PLAneo® process. The PLAneo® process from UIF Polycondensation Technologies is able to produce all PLA grades available on the market: from fast crystallising types to nearly amorphous ones (Fig. 11).

PLA is well-known for its biodegradability as well as for its very good recycling properties. These polymers have to decompose in soil without producing any environmentally harmful substances. This ensures sustainability for the whole production and application process. Since the polymer is compostable, this process is well described and characterised in the literature. Much less is known about the speed and degradation steps of the polymer in the soil. It is even suspected, that such biodegradable polymers will decompose in the natural environment very slowly and will accumulate resulting in an increased microplastics problem.

In this context we can refer to the literature⁴, in which the degradability of the PLA films of 300 µm in thickness was investigated under wastewater treatment, landfill and composter conditions. PLA polymer samples lost about 50% of the molecular weight under wastewater treatment conditions in 15 months, and under the landfill conditions, weight loss was as high as 80-85%. These results mean that films with a lower film thickness will most likely disappear completely within 2-2.5 years. The exact duration of degradation may vary depending on the weather conditions and biological activity of the soil.

Since the polymer is rather inert and intermediates of degradation are harmless, it is assumed that even if swallowed no damage to humans and animals occurs from the polymer. Relevant coating thicknesses for agriculture are on average in the range of 10-100 µm with a particle size of approximately 2-4 mm (see also Fig. 12).

Coating process

Dense coatings are required to effectively control the release of the nutrients over time. The fluidised bed technique has merits for large scale applications with PLA solutions, although its equipment is somewhat more expensive than the drum coating processes. Recommendation of the fluidised bed process was made on the basis of the quality of the coating, depending on the process used. Probably the best results would be achieved by combining the advantages of both coating processes. This combined process has been developed by tkIS, the patent application is pending. In the process, the first layer or shell is applied with a drum coater and the outermost layer is applied by the fluidised bed coater, provided primarily to address any defects that have arisen from the first coating step. The combination of these two methods is particularly advantageous when the surface of the granules is highly irregular.

During the extended test series a wide spectrum of polymer-coated granules of different fertilizers (PLA, PBS and other polyesters) was studied and different layer properties were analysed in more detail:

- Coating thickness – from 15 µm to 120 µm, (a coating thickness in the range 25 µm to 45 µm seems to be most efficient for agricultural purposes).
- Coating structure – both convoluted, rich on voids and tight, “plastered”, poor on

defects structures were examined. The best results from an economical point of view were achieved through the combination of the both structure types.

- Abrasion – for every coating type the essential reduction of abrasion was achieved. In the best cases reduction from the typical values of 0.1% down to almost 0% was achieved.
- Crucial strength – even in case of relatively little coating the crucial strength increased considerably, typically by 10 to 50%. Significantly higher values of 100% and more, compared to uncoated material, can be produced if desired. Additionally, the coated granules with higher polymer load typical for controlled-release fertilizers (CRF) retain their shape even if they are crushed. The polymer shell keeps the nutrient together even if the core is destroyed.

Examination of coating stability

Tests have been made to quantify the stability of the coated fertilizers and to allow for a rough comparison of the differently coated samples. For this purpose, the coated granules were each subjected to release tests in a water bath while continuously measuring the density and the refractive index. A wide range of qualities was obtained, ranging from rather unstable (quick release) to very stable (slow release) or even encapsulated samples (very little release) (Fig. 13).

Soil tests

Several series of soil tests were carried out under controlled and defined conditions. For this purpose, defined amounts of different fertilizer samples were introduced into uniform planters and the growth

behaviour of the plants was observed over each complete period of vegetation. Ryegrass, spring barley and winter wheat have been used as plant species. For all of the plants tested the conditions resulting in the crop surplus were identified.

It is reasonable to assume, that the dissolution behaviour in soil corresponds to the dissolution behaviour in the water bath with some proportion coefficient.

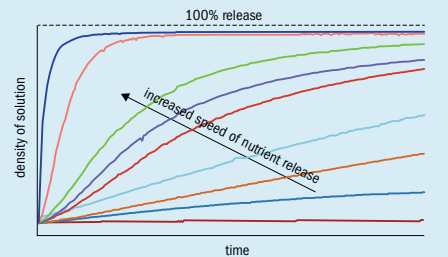
Determination of the release properties in the soil

The setup of the experiments carried out at an agricultural test institute consisted of a number of vertically arranged tubes, which were filled with soil and each charged with a defined amount of coated fertilizers. The tubes had a defined amount of water, which corresponds to the average amount of rainfall in Western Europe. The effluent was collected and analysed to determine the amount of released urea, ammonium and nitrate and to gain information about the release behaviour of different samples of urea and the time frame of the reaction of urea to ammonium and then to nitrate. A total of four sample types were used: untreated urea and the coated samples with quick, average and slow release (see Fig. 13).

In the evaluation of the results, the following interesting results were found:

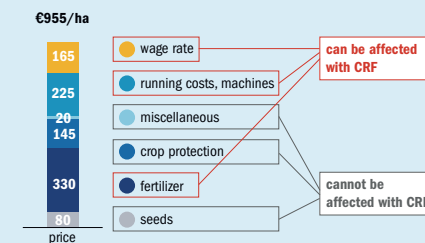
- The total amount of ammoniacal nitrogen in the eluate was max. 1.2% of the amount of nitrogen used, urea was not detected in the eluate.
- The only major product in the eluate was the nitrate ion. In the best case, about 65% of the nitrogen used was recovered as nitrate in the eluate.
- In conventional urea, only about 30% of the nitrogen was recovered as nitrate. It

Fig. 13: Release properties of coated samples in water bath



Source: tkIS

Fig. 14: Structure of variable production costs for winter wheat, typical for Western Europe



Source: tkIS

is believed that the remaining nitrogen is volatilised either as gaseous ammonia or as a nitrous oxide.

- There was no noticeable delay in release (maximum two weeks) but improved transformation into nitrate in all coated samples.

The results indicate that the ammonium ion, and most likely urea, has limited mobility in the soil. It appears that urea is rapidly converted into ammonia/ammonium ion. This ammonium ion remains adsorbed on the soil until it is converted into nitrate by soil flora. The nitrate ion is sufficiently mobile and is transported away quickly with the eluate. The limiting step seems to be the biological transformation of ammonium ions into highly mobile nitrate ions. If the ammonium concentrations are too high, the soil organisms probably will not be able to carry out the conversion to the nitrate quickly and completely. The nitrogen is lost as ammonia and a part as a nitrous oxide. It can also be concluded that because double the amount of nitrate is produced due to reduced losses, less (up to 50% less) fertilizer may be needed (due to more efficient fertilizer use). These results have also been confirmed experimentally⁶.

Economics of coated urea fertilizer

The specific costs of the coating medium are of central importance to the overall economics of the process. Due to its relatively high price, the polymer cost is a major part of the overall costs. Therefore, an economical solution for urea with PLA only appears possible if sufficiently sealed and stable coatings with a specific PLA consumption of not more than 10 wt-%, based on the amount of coated fertilizer produced, can

be realised. This corresponds well with known commercial products which usually have coating agent consumptions of 4 to 10 wt-% depending on application⁶.

Basically, the market will determine the price of the new coated fertilizer. On the other hand, the manufacturing costs per tonne are added to the desired margins of the distributors, which must be lower than the market price. The market price will cover the increased yields of farmers with reduced quantities of fertilizer giving rise to profit, defined as:
Profit = Revenue (crop) - Variable production costs

Higher profit can be reached by increased crop yield and/or decreased production costs, ideally combining both, more crops with less fertilizer, and less work effort during critical periods.

In the structure of variable production costs, some costs cannot be influenced by the use of CRF (see Fig. 14⁷). These costs include for example seeds or crop protection. Other costs, such as the cost of fertilizers are directly influenced by the use of CRF and can be calculated exactly. There remains a set of other parameters, such as the cost of machinery and wage rates, which are indirectly influenced and can only be calculated approximately. Finally, parameters such as the increased availability of personnel and machines during the very labour-intensive periods through the use of CRF cannot be quantified numerically but also contribute positively to the entire result.

The case study performed by tkIS, considering different scenarios, such as higher crop yield with the same amount of fertilizer or less fertilizer used for the same crop yield, showed that the use of CRF solely

or in combination with uncoated fertilizer is in all cases more profitable compared to the base case – the use of solely uncoated fertilizer – but to different degrees. Results are strongly dependent on fertilizer type, polymer load, crops and their prices. Some scenarios seem to be more attractive but generally it is valid: the more expensive the fertilizer, the lower the price increase in percent and the higher the acceptance of the modified fertilizer by the customers.

The case study was performed solely with urea (uncoated and coated). The price of urea is currently quite low and the coating might almost double its price, but still remain economical. For more expensive products, such as NPK fertilizer, this price increase has less impact, making the fertilizer stabilisation procedure more attractive. ■

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Real time urea process analysis and control

A new powerful tool for on-line urea process analysis and control in real time is now available.

L. Rugnone of Casale SA, **C. Uermann** of Kaiser Optical Systems and **C. Minnich** of S-PACT GmbH discuss the development of this breakthrough analyser which is designed to measure the full composition and the most important key performance indicators in urea synthesis.

The on-line Raman urea process analyser is a new powerful tool for on-line urea process analysis and control developed by Casale in cooperation with Kaiser Optical Systems Inc, a company of Endress + Hauser, world leader in spectrographic instrumentation, and SPACT, service contractor to Kaiser for quantitative spectral analysis and chemometric software.

The new analyser is a breakthrough in the on-line analysis applied to high-pressure urea synthesis. It is much more than a simple analyser since it is designed to measure the full composition and the most important key performance indicators of the urea synthesis.

In 2013 Casale and Kaiser Optical Systems tested the concept in the urea plant of a leading European producer of chemicals and fertilizers in Pulawy, Poland, who actively contributed to the success of this development.

Real samples withdrawn from the urea plant were tested off-line and compared to standard solutions containing urea and ammonium carbonate, bicarbonate and carbamate salts.

In view of the promising results, Casale and Kaiser Optical Systems jointly developed a special probe for high pressure urea service. This step made it possible to install the analyser directly into the urea reactor outlet pipe, to collect on-line data and develop a model of the urea chemistry.

In 2018, after five years of development activities and modelling, Casale, Kaiser Optical Systems and S-PACT announced that the development had been successfully completed and the Raman urea process analyser was ready to market.

Raman spectroscopy

In Raman spectroscopy, a sample is illuminated with a monochromatic laser light and the scattered photons are collected and analysed.

The principle is based on the interaction between the light and the sample resulting in a selective energy exchange. The energy is transferred dynamically from the laser light to the sample to excite molecular vibrations and from the sample back to the light.

The major part of the scattered photons has the same exact wavelength of the incident laser light (Rayleigh effect) while only a minor portion (about 1 out of 10⁷) is shifted to a different wavelength. The phenomenon of wavelength shift is called the Raman effect.

Depending on the chemistry the shift of the Raman photons may change hence the principle can be used for molecular identification and quantification.

Most of the Raman scattered photons are shifted to a longer wavelength (Stokes shift) while a part is shifted to shorter wavelengths (Anti-stokes shift). The Raman Stokes region is more intense and for this reason is normally preferred in Raman spectroscopy.

A Raman spectrum is a plot of the Raman intensity as a function of the frequency difference between the incident laser and the scattered radiation. Fig. 1 is an example of a Raman spectrum including Stokes, Rayleigh and anti-Stokes regions.

The information contained in the Raman spectrum can be translated into composition by means of advanced modelling techniques.

Fig. 1: Raman spectrum including Rayleigh, Stokes and anti-Stokes scattering

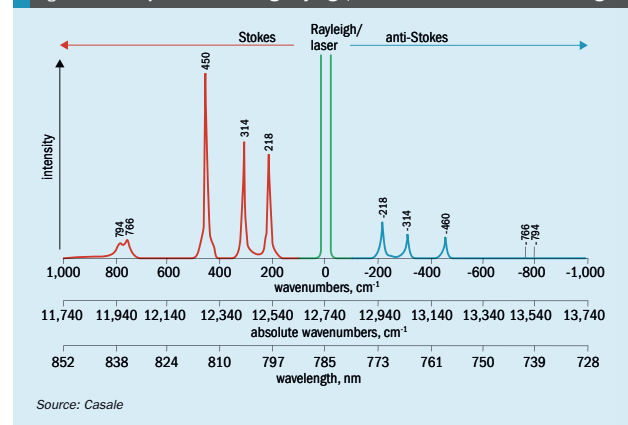
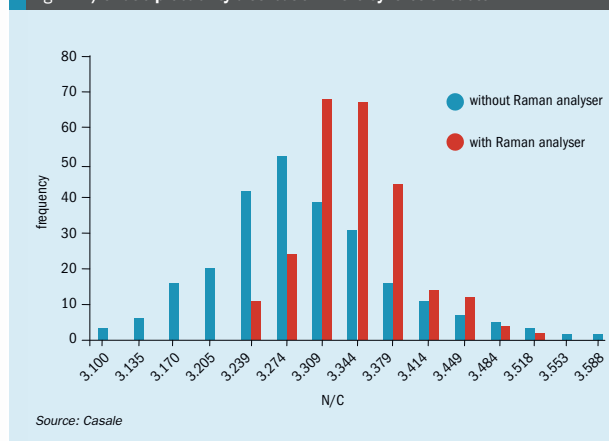


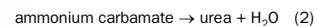
Fig. 2: N/C ratio probability distribution in the synthesis reactor



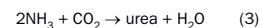
On-line Raman urea process analyser

The urea synthesis section is the heart of every urea process where carbon dioxide and ammonia are converted into urea through a complex scheme of reactions.

To simplify, the urea synthesis can be described by the following main steps:



while the overall reaction can be written as:



Reaction (1) is fast and exothermic, while reaction (2) is slow and slightly endothermic.

The overall synthesis reaction (3) is an equilibrium reaction. This means that at the outlet of every urea reactor the conversion to urea is incomplete and strictly depends on pressure, temperature and especially composition. The unconverted ammonium carbamate needs to be recovered and reprocessed requiring some effort in terms of energy.

Keeping the optimum conditions for the urea synthesis is the everyday challenge and the correction of deviations in composition is of great importance. Depending on environmental conditions and specific constraints of the plant, the optimum conditions for the synthesis may change requiring additional efforts to lower the energy consumption and ammonia emissions while at the same time improving throughput and plant stability.

The modern urea process is designed to be reliable and efficient and achieve such goals, but it is nevertheless essential that plant operators have the ability to correct deviations.

For this, the instrumentation and analytics are of paramount importance. Presently only limited options are possible. For example, the market already offers N/C monitoring systems for installation at the outlet of the urea reactor. The available methods are based on physical parameters such as the density which are used to infer the molar ratio N/C. These methods normally work in a limited range of conditions and only for the on-line measurement of the N/C molar ratio at the reactor outlet.

For the aforementioned reasons, in most urea plants worldwide people still sample the outlet solution from the urea reactor for its NH₃, CO₂, urea and H₂O content. This is the only way to measure the composition while monitoring the reactor conversion and critical parameters such as the molar ratio N/C and H/C. Other samples are normally required, for instance at the outlet of the HP stripper, HP condenser, HP scrubber, etc.

The sampling operation from the high-pressure synthesis has several drawbacks. The reactor analysis takes some hours to be completed by which time the urea process may have evolved with fast dynamics. For this reason, the lab analysis doesn't allow to take action in real time. Moreover, sampling from high pressure equipment requires some expertise

because of safety concerns and because volatile components such as NH₃ can be easily lost during the sampling operation affecting the quality of the analysis.

The Raman urea process analyser is therefore a breakthrough in on-line analysis applied to high-pressure urea synthesis. It overcomes the limitation of existing on-line analytics. Furthermore, it allows measurement of the full composition at the reactor outlet and in several HP process streams (% NH₃, % CO₂, % urea) as well as providing the most important key performance indicators of the reactor such as, N/C molar ratio, H/C molar ratio and Conversion % in the urea reactor and the efficiency in the urea stripper.

In this respect the Raman urea process analyser is a "real time performance meter" and it can be used with any urea reactor and any process technology.

The output of the Raman urea process analyser can be used by plant personnel as real-time guidance for process optimisation. For instance, the operators can correct deviations in the N/C molar ratio in the urea reactor avoiding the lower performance region (Fig. 2).

The distinctive features of the analyser also aid in the configuration of smart model predictive control (MPC) with extremely promising results in terms of benefits.

Expected benefits

The Raman urea process analyser can be installed in every stream of the urea process and especially in the HP urea synthesis where it is of major importance to monitor the composition.

A typical installation is at the outlet of the urea reactor. The analyser is configured to support up to four sampling points such as the urea stripper, carbamate condenser, urea reactor and recycle carbamate.

In terms of monitoring and control, the Raman urea process analyser allows surveillance of the most critical locations in the urea process and enables intervention in real time to correct deviations.

The resulting profit for the urea plant provides a fast return of investment which could be expected to be less than one year.

Urea plants are often kept running in a "comfort zone" and the operating parameters are relaxed to avoid hitting constraints.

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For instance, it is well known that NH_3 has a positive effect on the equilibrium of the urea synthesis but it can also impact pressure control and emissions.

Conversely, H_2O has a negative effect on the synthesis performance and should be controlled in the recycle streams to keep the emissions within limits and to avoid the risk of crystallisation in the recycle condensers.

On average, taking worldwide urea production into account, it is found that the reactor is often operated with less than optimum NH_3 resulting in the N/C molar ratio being 0.05 to 0.12 lower than optimum. At the same time, the H_2O in the recycle is kept higher than required resulting in a H/C molar ratio that exceeds the optimum by 0.05 to 0.1.

By on-line monitoring and performance optimisation it is possible to run the reactor closer to the optimum and to gain up to 3% conversion. The results are even more promising if the Raman urea process analyser is coupled with model predictive control software.

The benefits of the Raman urea process analyser can be translated into:

- **Specific energy consumption reduction**
Depending on the urea process technology, the stripper steam demand can be reduced by 2-5%.

In terms of specific consumption the expected saving is within the range 20-40 kg/t of superheated steam.

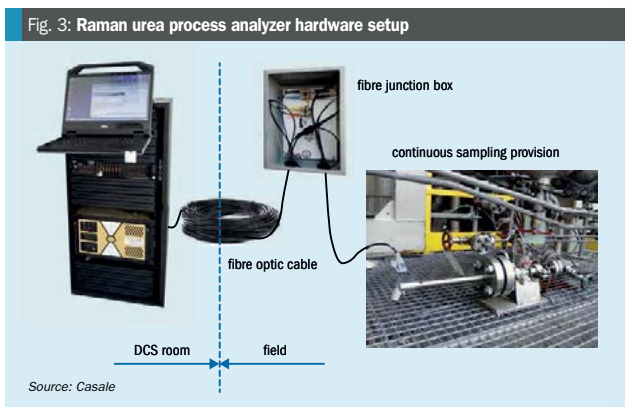
- **Reduced NH_3 emissions**
The N/C ratio in the urea reactor is always kept at its optimum according to the season, the day and night dynamics and the limit of the existing equipment to process and recover excess ammonia. Depending on the plant background and process equipment, the on-line process control reduces the ammonia loss, saving up to 5 kg NH_3 /tonne.

- **Higher throughput**
The plant is debottlenecked by improving the reactor performance.

Depending on the plant background and operating conditions, the expected production gain is up to 3% on yearly average basis.

If we consider a urea plant of average size this translates into an additional 5,000 to 10,000 t/a of product.

- **Better product quality**
In urea plants the NH_3 is controlled to achieve the best product quality. If the NH_3 excess cannot be handled correctly then the operation of the downstream



Source: Casale

plant sections may be affected. Even the evaporation section vacuum can be compromised. The consequence is that water and ammonia cannot be efficiently removed from the urea melt going to the prilling tower or the urea solution going to the granulation plant, resulting in a fragile, powdery and sticky product.

On-line process control helps to keep NH_3 at its optimum minimising the quality issues in the finishing section.

- **Improves safety by reducing the need for sampling from HP equipment**

Taking samples from the HP urea synthesis section is intrinsically unsafe. The synthesis environment is under pressure and temperature. Furthermore, ammonia is a volatile toxic component and can be easily lost, also leading to erroneous analysis results. The sampling operation should be carried out by skilled and trained personnel and proper personal protective equipment must be used.

The new on-line Raman urea process analyser drastically reduces the need for lab analysis.

- **Minimises unscheduled shutdowns, speeds up start-ups and smoother plant operation**

During plant transitory conditions, during upsets or start-up, deviations need to be corrected to bring the system back into the "safe zone".

For instance, in case of NH_3 excess the pressure can build up in the urea synthesis section leading to shutdown for very high pressure.

The on-line analysis helps to minimise the risk of composition deviations and

the shutdown probability is drastically reduced by consequence.

Raman urea process analyser hardware setup

The Raman urea process analyser consists of a sophisticated Raman spectrometer and a special high pressure urea service probe. The field is provided with special provision for continuous sampling and analysis which is completely engineered with the piping materials in compliance with the high-pressure urea service piping class.

The analyser system is connected to the field via a special fibre optic cable. A fibre optic junction box is installed in close proximity to the probe to create the connectivity (Fig. 3).

The analyser is installed in a robust rack enclosure (Fig 4). The rack is also provided with a human machine interface (HMI) controlling the analyser and including the urea model to translate the field signals into concentration. The analyser cabinet is typically placed in the control room or the auxiliary DCS room.

The analytical components are embedded in the analyser module (Fig 5) which includes the laser source, spectrograph and detector. The laser is used to generate the Raman scattering. The Raman scattered photons entering the analyser are fed directly to the spectrograph. A transmission grating separates the photons by wavelength and send them to the detector which records the intensity of the Raman signals. The data are then processed by the analyser software and plotted as a Raman spectrum.



PHOTO: CASALE

The laser light emitted by the analyser is driven to the measuring point by a special fibre optic cable.

Fibre optic cables are frequently used to allow the analyser base unit to be located remotely from the sampling point. In the process industry it is common to locate the electronics in a protected environment (i.e. DCS room) to safeguard the integrity of the components.

In urea process applications a typical cable routing ranges from 50 to 500 m.

The laser light is delivered to a special focusing device which has the purpose to inject photons into the high-pressure urea process.

Casale and Kaiser Optical Systems have developed a special HP urea service probe. The probe is suitable for installation in all urea processes and is designed to withstand up to 260 bar and 220°C. The wetted components are made of 25Cr.22Ni.2Mo according to the strict requirements as per Casale's material specification. The probe is equipped with special flange and lens gasket seating to be connected to the process through a special continuous flow cell designed with piping elements.

Light passes through the probe and is directed into the high-pressure solution

by means of a high strength sapphire window located in the tip. The sapphire is sealed into the stainless steel by means of Kaiser's proprietary technology. The sapphire window provides excellent resistance to the pressure and thermal shocks.

The photons entering the process solution are recovered back by the same probe which is designed to collect the scattered photons, filter out the Rayleigh and background signals and send back the Raman photons to the fibre optical cable connectors (Fig. 6).

In case of installation of the probe at the outlet of the urea reactor, the provision for sampling can be easily arranged as a by-pass of the reactor level control valve provided that there is a positive delta pressure of at least a few bars. This is enough to by-pass about 200 l/h of solution to the sampling system.

Double block and bleed isolation valve groups (typical size ¼" or ½" size depending on the conditions) are arranged including a flushing system.

The sampling system can be easily isolated and safely depressurised if required. The probe can be installed or removed without affecting the plant operation.

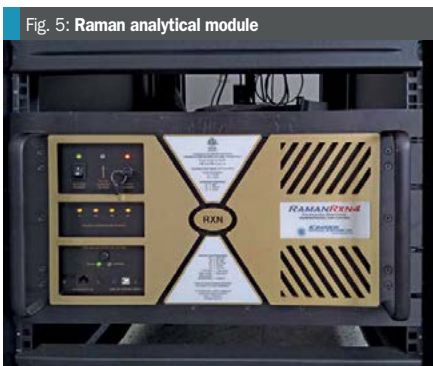


PHOTO: CASALE



PHOTO: CASALE

The sampling system lines are insulated and electrically traced to avoid the risk of choking especially during the winter time and in case of a sudden plant shutdown. A temperature transmitter is installed in the outer skin of the sampling system pipes to monitor the process temperature. If the line is blocked it will lose temperature activating an alarm.

In other process technology the delta pressure across the reactor outlet valve is not enough to ensure a steady and positive flow through the sampling system. This is the case for CO_2 stripping urea plants.

In this case the bypass design may not be effective, therefore in this case the system is installed as a by-pass of the HP stripper and is equipped with a HP let down valve from the high-pressure side to the downstream urea recovery stage working at medium or low pressure.

Fig. 7 shows a typical sampling system.

Raman urea process analyser software and connectivity

The Raman probe irradiates the reactor outlet solution with the laser light generated by the analyser.

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As per the Raman spectroscopy principle, when the laser light passes through the solution some radiation undergoes a change in the incident wavelength.

The light returns to the analyser through the fibre optic cable. The shift in the laser light wavelength (Raman effect) generates a spectrum (Fig 8) which is registered by the analyser software and it is translated by a predictive model into composition and information on the reactor KPIs.

The on-line analysis output can then be transferred to the DCS where it can be monitored by the panel operators and connected to the model predictive control (MPC) software.

The connectivity between the analyser and DCS can be established via OPC, Modbus or Profibus.

Fig. 9 shows a simplified sketch of the analyser connectivity and Fig. 10 shows a reactor outlet composition trend (DCS).

Raman urea process spectra modelling

As previously described, the Raman spectra from the process stream at the reactor outlet are acquired by the instrument software and are translated into composition by an embedded chemometric model.

An effective Raman model for on-line analysis in industrial urea plants should be able to simplify the chemistry and provide the composition information which is typically provided by laboratory analysis as per international standards.

For instance, a good Raman model should be able to reliably translate the spectra into $\text{NH}_3\%$, $\text{CO}_2\%$, urea % and thus to predict the reactor key performance indicators such as the N/C and H/C molar ratios, as well as % CO_2 conversion.

In urea synthesis ammonia, carbon dioxide and urea are just basic components of the process chemistry but depending on the process conditions (P, T, composition) different molecules and salts can be found.

For instance, unconverted carbon (i.e. percentage CO_2) in the presence of excess ammonia under pressure and temperature is found in the form of ammonium salts such as carbonate, bicarbonate and carbamate.

Depending on the plant conditions the equilibrium shifts towards one particular molecular form over another. All of the molecular forms are visible with the Raman spectroscopy, but the scope of the model-



Fig. 7: Typical sampling provision

PHOTO: CASALE

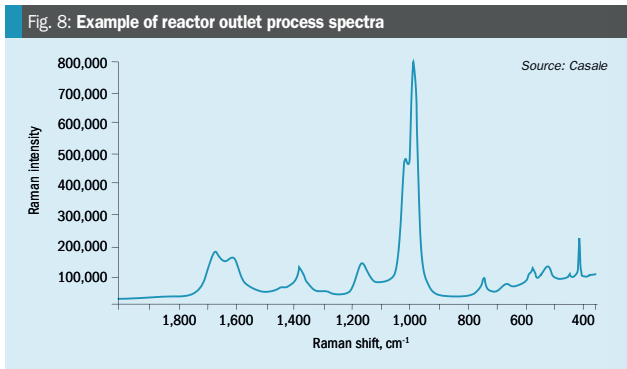


Fig. 8: Example of reactor outlet process spectra

Source: Casale

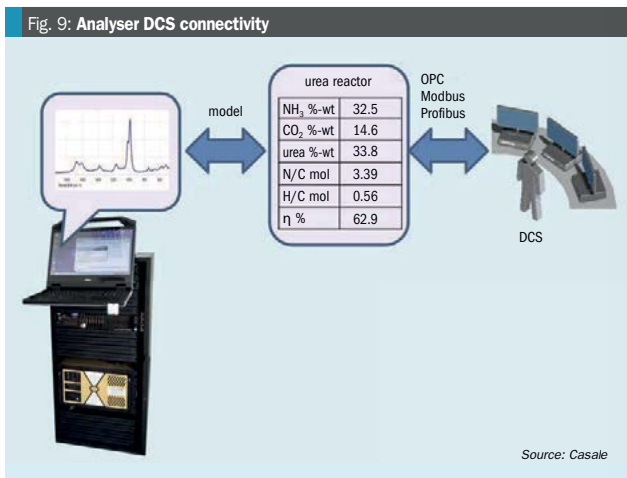


Fig. 9: Analyser DCS connectivity

Source: Casale

ling should be to cope with the results of a typical laboratory analysis which is the current basis for process control.

As mentioned, the relevant control parameters for urea synthesis are not molecular constituents, hence indirect determination from the spectra is required. Comparison of the spectra from the process with lab spectra of samples at ambient conditions confirms that the molecular forms of the basic chemical components changes importantly, which means that bottom-up modelling is not promising (see Fig. 11).

Using spectra from the industrial reactor, acquired continuously for several months,

and advanced chemometric methods, correlations have been found with the results of the laboratory analysis.

Samples have been withdrawn from the reactor outlet with the frequency of one per shift (3 samples per day).

Process spectra show reproducible correlations with the parameters (i.e. % NH_3 , % CO_2 , % urea...).

Fig. 12 shows the correlation found among the spectra and the % urea in the process stream.

The correlations are exploitable in quantitative modelling. The model, developed with the help of S-PACT was implemented

in the instrument software and tested for several months to predict the parameters in real time. The testing period allowed the model to be improved and finalised in readiness for its transferability to new conditions.

The model is now available for application in any urea process stream according to any urea process technology. Model prediction results are excellent. (see Fig. 13)

A setting up period of a number of weeks is needed in order to perform fine tuning depending on the specific conditions of each plant.

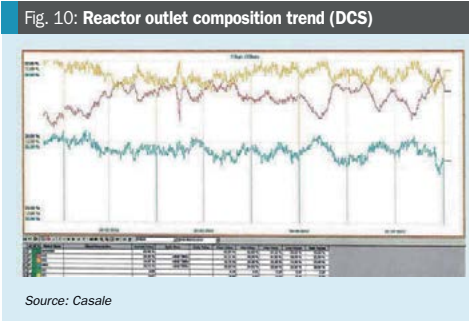


Fig. 10: Reactor outlet composition trend (DCS)

Source: Casale

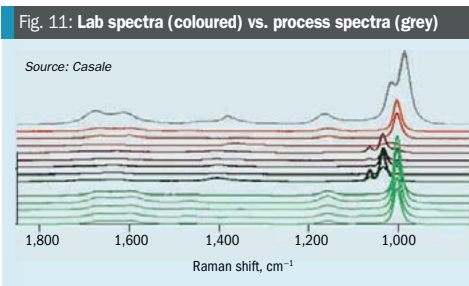


Fig. 11: Lab spectra (coloured) vs. process spectra (grey)

Source: Casale

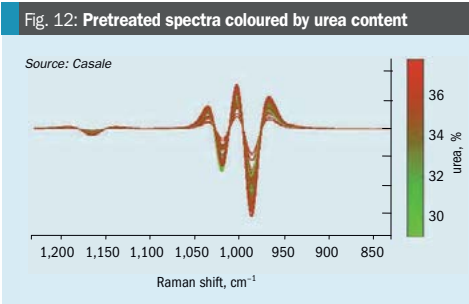


Fig. 12: Pretreated spectra coloured by urea content

Source: Casale

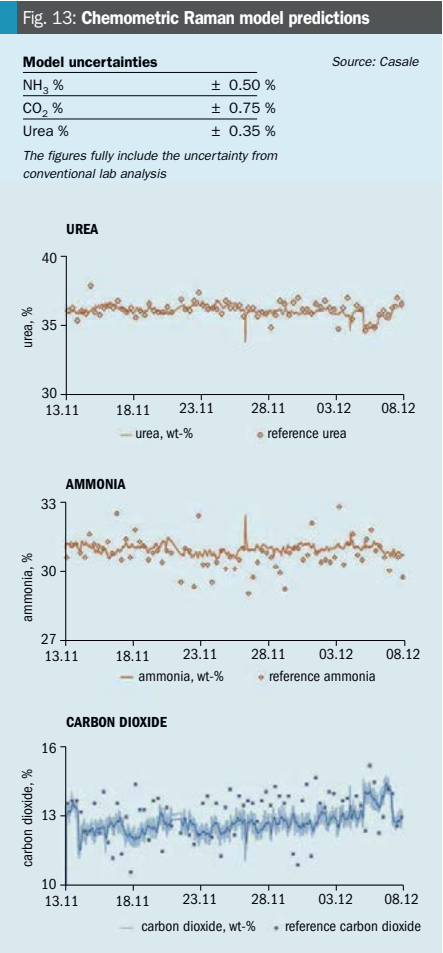
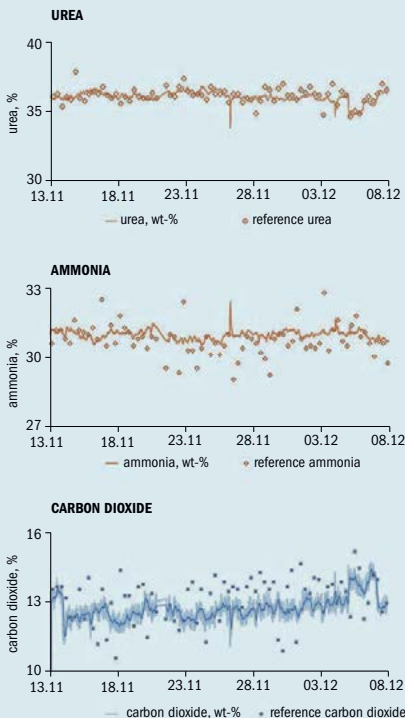


Fig. 13: Chemometric Raman model predictions

Model uncertainties		Source: Casale
NH_3 %	± 0.50 %	
CO_2 %	± 0.75 %	
Urea %	± 0.35 %	

The figures fully include the uncertainty from conventional lab analysis



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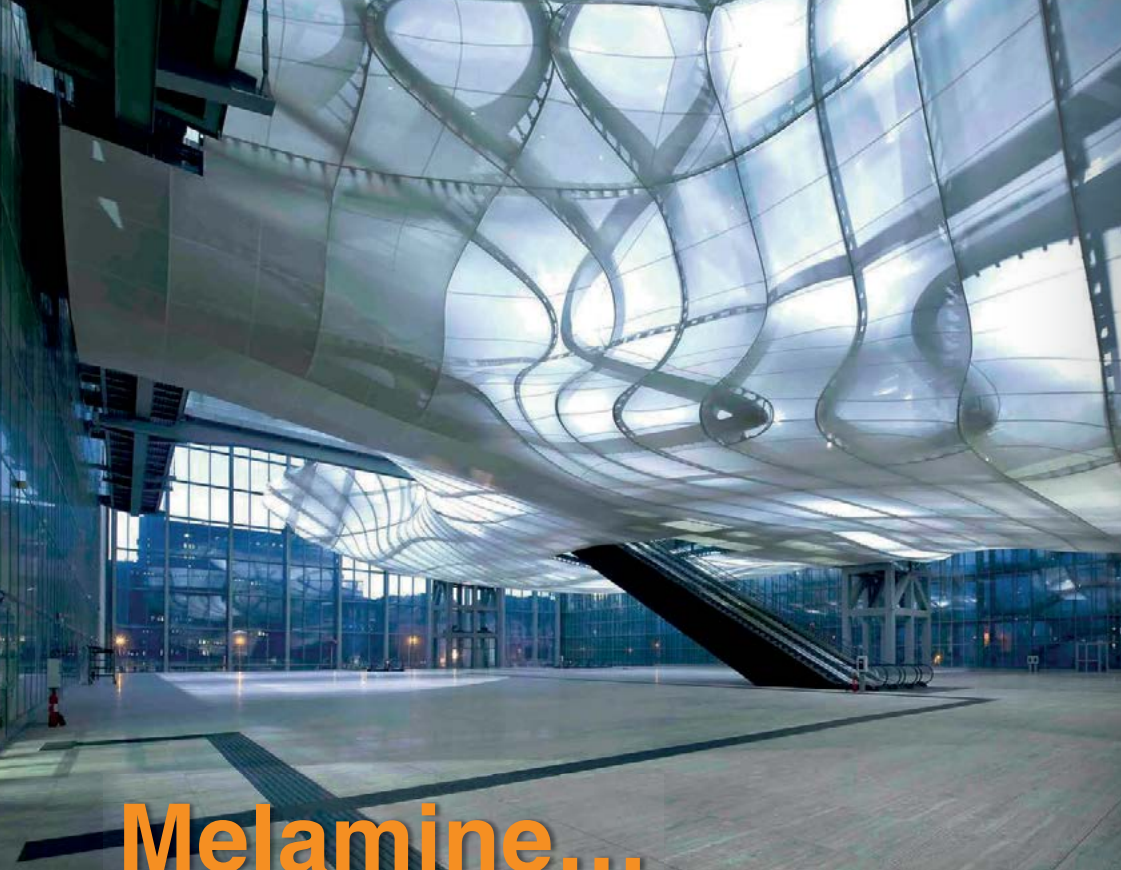
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