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Number 356

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nitrogen + syngas

www.nitrogenandsyngas.com

Waste to syngas

Latin America's syngas industries

Safety hazards in urea plants

CO₂ removal in ammonia plants



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Can methanol's rise continue?



The methanol industry has seen a remarkable rise over the past decade, virtually doubling in size from an annual consumption of just over 40 million t/a in 2008 to around 82 million t/a today. The comparable figures for ammonia are from about 146 million t/a to 168 million t/a, meaning that methanol production and consumption has actually grown almost twice as fast as ammonia, its larger cousin among syngas derivatives. The reason for this remarkable rise is almost entirely down to Chinese government policy – using domestic coal to produce methanol which was used first as fuel – directly blended into gasoline or converted to dimethyl ether or other ethers like MTBE – to reduce China's dependence on imported oil and refined products, and now more recently as a chemical feedstock to produce polyolefins like polyethylene and polypropylene via the country's rapidly expanding methanol to olefins (MTO) industry.

And now, even though China has moved to cap fertilizer use and forced a shakeout of polluting chemical plants near built-up areas, reducing domestic ammonia production and turning the country into a net importer of ammonia, its appetite for methanol appears to be undiminished. Indeed, several methanol plants are now under development in North America to convert cheap US shale gas into methanol which can be shipped across the Pacific to feed China's rapidly growing MTO production. While Northwest Innovation Works (NWIW) has had permitting trouble with its plans to build several huge methanol plants in Washington state and Oregon, its Kalama methanol plant, which if the second phase is completed would produce 3.6 million t/a of methanol, is still moving forward. The recently announced Nautical project in British Columbia, Canada (see Syngas News, this issue), would also produce 3 million t/a, and, while it would be on the east rather than west coast, Methanex's discussion of building a third plant at its Geismar site in Louisiana at the same time that it re-starts production at its Chile IV plant also indicates that it is looking to monetise more shale gas for the export methanol market. The US is already set to become a net methanol exporter in the next year or so, and these new plants could turn it into the largest exporter in the world.

Indeed, as our price graphs show on page 8, right now appears to be a very good time to be in methanol! While methanol and ammonia prices often fluctuate around the same kind of baseline, driven by a similar

bottom line in terms of feedstock costs, since 2016 methanol prices have been consistently higher than for ammonia, as China's fuels and plastics industries suck in any surplus production, in contrast to the over-capacity that has dogged nitrogen markets. Methanol prices tend to track oil, while production costs are determined by coal and natural gas prices, and over the past decade oil prices have run significantly ahead of other fossil fuels. With methanol consumption projected to reach 95 million t/a by 2021 as a new wave of Chinese MTO plants are completed and more methanol is blended into gasoline, IHS Markit has even suggested that there could be a significant shortage of methanol in the early years of the next decade unless more plants are completed quickly.

So the question is – how long can this go on for? The temptation with any trend line is to continue projecting it forward into the future, and assume that what is true today will also be true tomorrow. This is the bane of forecasting, as it often overlooks natural limits to growth; even the biggest markets become saturated, and feedstock costs are dragged up by product prices as the industry becomes a victim of its own success. We have seen this with China's over-building of capacity in so many industries, from coal to steel to fertilizer to property. In light of all that, my own natural inclination with any talk about China continuing to build new MTO capacity and accept more and more methanol from overseas is thus to dismiss it and assume that the trend will rapidly tail off. Methanol shortages lead to high prices which cut into margins (especially for those taking methanol from the merchant market), and choke off demand, as happened earlier this year for China's MTO producers. Even so, at the moment these seem to be just temporary blips, and the Chinese government still appears determined to make MTO a significant part of Chinese olefin production – 40% of it by 2020, according to IHS. For the medium term at least, there appears to be no end in sight for methanol's rise.

Richard Hands, Editor



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Price trends



MARKET INSIGHT

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

NITROGEN

Prices continued to increase throughout August and September, reaching a peak of \$340/t for granular urea at f.o.b. benchmarks in Egypt and the Arab Gulf in October. Prices have cooled somewhat since, as the market paused for breath and corrected downwards by \$10/t. However, little has changed fundamentally in the supply/demand dynamic, and uncertainty still surrounds Iran's ability to export urea and China's ability to provide much needed fourth-quarter liquidity. Despite the recent correction, we are still expecting prices to begin increasing again as northern hemisphere demand kicks off in November and US sanction on Iran tightens.

Chinese producers were forced to idle 2.1 million tonnes of gas-based, annual capacity in October as the government began to prioritise gas supplies away from urea production. This trend is expected to continue through Q4 2018, as was the experience of winter 2017. Our current expectation is for almost 14.0 million t/a of gas-based urea capacity to have been closed by the close of December 2018, significantly reducing China's ability to export more than 300,000 tonnes per month of urea in Q4 2018. If this comes to pass, then annual Chinese exports will

have dropped below 2.0 million t/a for the first time since 2006.

High gas pricing in the seaborne LNG market has been causing difficulties for urea producers in Bangladesh and Pakistan. In Bangladesh only two plants, Chittagong and KAFCO, appear to be operating, while Pakistan has had three plants idle for much of the year, as high gas prices have hurt production economics. This has also meant an increase in South Asian import buying as the region tries to avoid a urea shortfall in the current Rabi season. Integer is also expecting to see India issue another tender for 500-700,000 tonnes in late November, given that domestic stock levels have fallen to less than 500,000 tonnes.

That means around 1.5 million tonnes of import tender business for South Asia is still ahead of us for Q4 2018. And this increase in South Asian import business will combine with the kick-off of northern hemisphere buying and the need for Brazil to cover lost Petrobras production (from the closure of Laranjeiras and Camacari) is likely to tighten the market and lift prices in November and December. High gas pricing in the LNG market will also help to keep European gas prices elevated

(above \$8.00/MMBtu) and limit Ukraine's ability to increase production and provide liquidity f.o.b. Black Sea.

The main uncertainty around this outlook is whether or not Iran can cover any of this tender business. On the face of it, the answer to this is no. However, it is clearly in the region's interest for India, Pakistan and Bangladesh to find a way to circumvent the US sanctions and make the Iranian trade possible. Currently, Iranian spot sales are available at a significant, \$60-70/t discount to Arab Gulf f.o.b. values – an attractive proposition for the state-subsidised, South Asian urea markets. Our base assumption remains that the current

We are forecasting urea prices f.o.b. Egypt and Middle East to push above \$350/t by December.

round of sanctions will be more severe than the last round of sanctions implemented by the Obama administration. And that Iran's increased isolation will mean customs agencies in the UAE and China will not be amenable to changing, or in some fashion, masking source

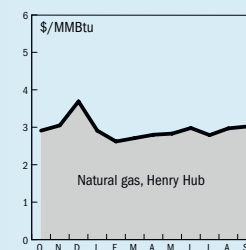
of origin documentation so as to weaken the impact of the sanctions.

We are forecasting urea prices f.o.b. Egypt and Middle East to push above \$350/t by December, before falling back towards \$300/t in the New Year as new capacity in Central Asia, Egypt and India commissions and begins commercial production from Q1 2019. Falling gas prices and the resumption of production from idle plants in China should allow prices to fall to \$275/t in Q2 2019 as the northern hemisphere seasons wind down.

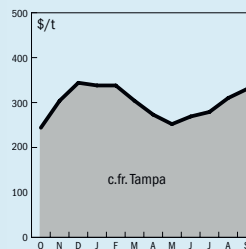
The ammonia market is also looking tight for the quarter ahead. High European gas prices have reduced merchant ammonia production from European and Ukrainian producers, and Trinidad's producers are facing a 25-35% reduction in gas availability in November. The US corn acreage for the season ahead looks likely to be 3-4 million acres higher, which should increase US ammonia applications in the Midwest corn belt. However, absolute corn prices have not significantly increased, so affordability will be tested if prices push much higher than \$370/t f.o.b. Middle East in November and December. But with urea markets looking firm and no new ammonia supply due online until Eurochem's Kingsepp commissions next year, ammonia values should be secure at current levels into Q1 2019.

END OF MONTH SPOT PRICES

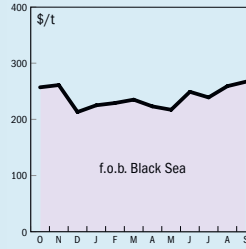
natural gas



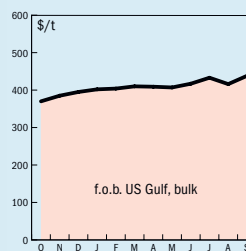
ammonia



urea



diammonium phosphate



MARKET INSIGHT

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

METHANOL

The official posted reference prices from the major producers for October are \$1.49/gal for Methanex (up 3 cents from last month) and \$1.48/gal for Southern Chemical (up 4 cents), equivalent to \$495/t and \$492/t respectively. Month-on-month weighted average spot prices in the US Gulf for September increased to \$1.17/gal (nominal \$389/t), as some deals conducted in August for September lifting were as low as \$1.12/gal. IHS Market Chemical's contract net transaction price for October is officially posted at \$1.4850/gal (nominal \$494/t), up 3.4 cents (\$12/t) on September.

The Americas average operating rate increased in September to 84% in spite of OCI Beaumont having issues relating to a compressor. Trinidad's overall operating rate fell in September, averaging around 78%. In Venezuela, the Supermetanol unit is believed to have re-started in late September after being offline after an issue in January this year. Methanex's Chilean unit is estimated to have run at 58% of nameplate capacity during September; operations have become constrained as they have in the past due to lower gas availability during winter in the southern hemisphere. Methanex says it plans to have the Chile IV plant up and running by the end of 2018. Americas demand remained healthy into all end-uses with very strong production numbers noted for biodiesel and formaldehyde.

In Europe, Methanex posted its 4Q 2018 West European Contract Price at €428/t f.o.b. Rotterdam T2, up €9/t from 3Q 2018. The ongoing suspension of duty on methanol arriving into the EU implemented by the European Commission is due to expire at the end of 2018. As yet, there is no guidance on whether the allowance will be extended or revert to previous levels. Demand into formaldehyde was generally stable at healthy rates, despite an impact from higher than expected temperatures in Europe in early September.

In Iran, Zagros restarted at the end of August following maintenance on one of its lines and ran at typical rates in September. Marjan Petrochemical Co. (1.75 million t/a) was inaugurated in late September and has produced trial methanol. In Russia, Tomsk

(1.0 million t/a) went down for a planned maintenance outage in late September.

Indian port prices averaged \$370/t in September, down \$14/t from August, due to regular imports from the Middle East and stable operating rates among Iranian producers. Regular imports from Iran, Saudi Arabia and even the US kept inventories at high levels at West Coast Indian ports even though heavy rainfall during September continued to put pressure on demand. The monsoon hampered demand into the construction sector, and by the end of the month Saudi Arabian producers preferred to ship methanol to Southeast Asia as the netbacks there were higher.

Asian prices in September traded up by \$5.50/t in a range of \$380-435/t c.f.r. with Chinese c.f.r. prices ranging from \$384-408/t. Methanex's posted APCP for October is \$495/t, up \$15/t from September. In Southeast Asia, Petronas's larger unit shut down in the second week of August for a 50-day planned maintenance outage, with a planned re-start at the end of September. Tight market supply should ease given the expected re-start of Petronas's large unit.

In China, overall capacity utilisation increased in September to 55% of nameplate capacity, or around 71% of effective capacity – lower for coking and natural gas-based producers and higher for coal. Inner Mongolia Jiutai came offline for a turnaround in mid-September, while Shaanxi Shenmu was offline after an industrial accident; the facility is expected to re-start in early October. On the demand side, all MTO units were operating to plan except for Fund Energy Changzhou, which has been offline since March 2017. MTO operating rates averaged 86% in September. The new Inner Mongolia Jiutai MTO plant (1.8 million t/a methanol consumption) began operating in early September and may run trial production soon.

The Korean market remained slightly tight, with delays to expected shipments from the US and the Middle East. There was some spot demand from the acetic acid sector, as well as buying interest from large international suppliers. Formaldehyde demand will increase when a new POMK unit comes on-stream in 4Q 2018.

Table 1: Price indications

Cash equivalent	mid-Oct	mid-July	mid-May	mid-Mar
Ammonia (\$/t)				
f.o.b. Black Sea	335-360	244-250	280	250-255
f.o.b. Caribbean	305-316	270	220	270
f.o.b. Arab Gulf	340-365	260-280	263	265-275
c.f.r. N.W. Europe	380-387	300-310	280-305	290-300
Urea (\$/t)				
f.o.b. bulk Black Sea	280-300	245-260	215-220	232-238
f.o.b. bulk Arab Gulf*	320-340	270-280	215-223	253-263
f.o.b. NOLA barge (metric tonnes)	316	220-242	219-224	264-280
f.o.b. bagged China	320-338	270-290	257-262	305-315
DAP (\$/t)				
f.o.b. bulk US Gulf	458-461	427-430	408-410	413-415
UAN (£/tonne)				
f.o.t. ex-tank Rouen, 30%N	253	n.a.	153-158	158-161

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

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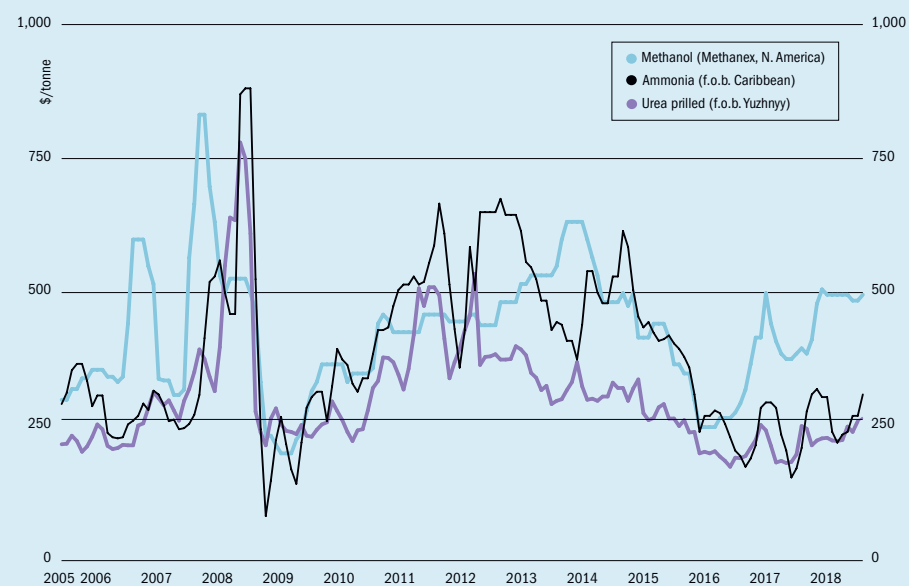
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Market outlook

Historical price trends \$/tonne



Source: BCInsight

AMMONIA

- Ammonia markets tightened through August, increasing prices to the \$350-360/t level. Values over September and October have been stable, the market looks relatively balanced.
- Restarts and ramp-ups of Asian capacity have helped balance demand from China and Europe where weak production economics have reduced output.
- A strong urea market looks like recovering momentum in Q4 2018, which will provide support for ammonia prices at current, or slightly elevated levels.
- Production curtailments from gas supply constraints in Trinidad should reduce Caribbean availability supporting higher Tampa prices and inland US values.
- Energy prices should increase this winter, meaning we should expect limited additional liquidity from European or Ukrainian producers.
- Iranian ammonia exports should be hit harder by US sanctions than urea exports, similar to what we saw in 2014/15.

- Kingisepp has the potential to push down on prices and force a significant downwards correction when it starts. Eurochem is expecting output from Kingisepp in Q1 2019.

UREA

- South Asian import buying looks strong in Q4 2018 as governments in Bangladesh and Pakistan compensate for poor production economics and lost output.
- India is also expected back in the seaborne urea market by late-November with another import tender for at least 500 kt to offset low inventory levels.
- US demand looks bullish given higher estimates for corn and wheat acres. However, worries around Turkish buying will likely offset any higher US import purchases.
- Chinese exports to remain muted despite high f.o.b. values. Gas likely to be rationed away from urea production, while coal-based producer should face usual air-quality restrictions this winter.
- Iran expected to be locked out of much of the seaborne urea market by

US sanctions. However, uncertainty remains over effectiveness of sanctions as countries seek to creatively circumvent, a price to hit an annual high.

METHANOL

- US methanol prices reached a four-year high in October on the back of supply outages in Trinidad and delays to some shipments.
- Conversely, European markets are affected by low water levels on the Rhine, preventing barge shipments moving inland and leading to a glut at Rotterdam.
- The impact of US sanctions on Iranian methanol supply still looks uncertain, but in general markets were braced for tighter supply.
- Demand for energy applications and a healthy methanol to olefins market in China still continue to set the tone for global prices. However, rising methanol prices tend to move MTO units into unprofitability and may choke off demand once more, as happened earlier in the year.

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GERMANY

thyssenkrupp to split

At an extraordinary board meeting on September 30th, thyssenkrupp AG agreed to split into two separate companies. The move comes after criticism by shareholders of poor returns, and in particular steadily increasing pressure from Swedish activist investor fund Cevian Capital, which acquired an 18% stake in the company, making it the largest single shareholding after the Krupp Foundation. Lars Förberg, Cevian's co-founder, called thyssenkrupp's corporate structure "too complex", and insisted that it simplify its operations.

In a statement following the meeting, Guido Kerkhoff, chairman of the Management Board of thyssenkrupp said that the split in operations "not only creates value for our shareholders, but also significantly improves the development prospects of our businesses". The split will see thyssenkrupp AG shareholders have two shares for every one of their current shares; one in the new thyssenkrupp Materials AG (formerly thyssenkrupp AG) and one in the new thyssenkrupp Industrials AG. Existing stockholders will continue to hold 100% of thyssenkrupp Materials AG and initially a clear majority of thyssenkrupp Industrials AG. The remaining stake will initially be held by thyssenkrupp Materials AG. Liabilities and pension obligations are allocated adequately to both companies.

thyssenkrupp Industrials will concentrate on capital goods manufacture, and will consist of three of the company's existing business units: elevators, automotive supplies and plant construction. The existing bearings and forging businesses will be spun off from the division. Industrials will also take the System Engineering division from Industrial Solutions.

thyssenkrupp Materials will consist of Materials Services, a 50% interest in the future steel joint venture, the bearings and forging businesses as well as the marine business, resulting in a materials group that combines steel and stainless steel production, materials trading and steel-related processing.

Based on figures for fiscal 2016/17, thyssenkrupp Industrials AG would have generated sales of around €16 billion with around 90,000 employees. thyssenkrupp Materials AG would have sales of around €18 billion with just under 40,000 employees. ■

UNITED STATES

Tax break agreed for ammonia plant

Texas City has agreed a decade long tax holiday on property taxes for the Gulf Coast Ammonia project, beginning in 2021. The \$800 million project, being developed by Agrifos and Borealis AG, would see the construction of a 750,000 t/a ammonia plant on brownfield land by the shipping channel. Rather than natural gas feedstock, the plant aims to buy in hydrogen from local suppliers to avoid a costly reformer. However, the plant has attracted local and environmental opposition in a city with long memories of the 1947 Texas City ammonium nitrate disaster which killed over 580 people in America's worst industrial accident. Current worries centre mainly around congestion in the shipping channel, disposal of waste water, and the risk of an accidental release of ammonia. The plant was first proposed in 2015, but has made slow progress so far through the permitting process.

Borealis meanwhile has split its struggling fertilizer operations into a separate Fertilizers and Melamine division, although the Austrian chemicals producer said it had no plans to sell the division. Borealis bought its way into the fertilizer industry in 2013 with the purchase of the fertilizer assets of French producer GPN, and last year bought Bulgaria's Feboran.

Cronus awards EPC contract for Illinois ammonia plant

Meanwhile, another ammonia plant, this time in the mid-West, has made more progress. Cronus Fertilizers has awarded a lump-sum turnkey engineering, procurement and construction (EPC) contract to thyssenkrupp Industrial Solutions (TKIS) for its proposed Tuscola, Illinois ammonia plant. Ground breaking is due in 2Q 2019 on the 2,300 t/d (760,000 t/a) facility, which aims to supply ammonia to farmers throughout Illinois and the mid-West.

"thyssenkrupp Industrial Solutions is honoured Cronus Chemicals has selected

us as the designated EPC contractor for their planned 2,300 t/d ammonia plant project in Illinois," said Dennis Lippmann, CEO thyssenkrupp Industrial Solutions, North America. "We look forward to continuing our partnership and supporting Cronus during the next phase of this exciting project... which will move forward once the financing is completed."

OSHA launches programme to reduce harmful AN, ammonia exposures

The Occupational Safety and Health Association (OSHA) has launched a 'regional emphasis programme' to address hazards stemming from exposure to fertilizer-grade ammonium nitrate and agricultural anhydrous ammonia. The Association says that employees in the fertilizer storage, mixing/blending, and distribution industries face fire and explosion risks, along with exposure to hazardous chemicals and toxic gases. The programme is being conducted in Arkansas, Kansas, Louisiana, Missouri, Nebraska, Oklahoma and Texas. The first 90 days will be education and prevention outreach by OSHA to promote compliance with existing standards. The agency also will be responding to fatalities, hospitalisations, complaints and referrals during that period. Enforcement will begin at the conclusion of the 90 days and continue until September 30th, 2019, unless the program is extended.

"The goal is to improve worker safety and reduce the potential for catastrophic incidents," said Eric Harbin, OSHA's acting regional administrator in Dallas. "At the end of the day, we want to ensure workers go home safely to their families."

AUSTRALIA

Trial on waste water in cattle feed

Yara is trialling the use of nitrogen-rich waste water from its Pilbara ammonia and ammonium nitrate facility on Western Australia's Burrup Peninsula as a fertilization aid in local pastures. The combination of fertilization and irrigation – fertigation – is ideal for the dry, sandy soil of the region. Local beef farming company the Pardoos Beef Corporation is partnering Yara in the six month trial, hoping to expand its rearing of Wagyu beef on local pasture land at Pardoos Station. The trial will look at whether the waste water fertilizer could be fully utilised by the plants, and not leach into the water table or other water sources.

The Burrup plant continues to face a threat from another source, however. The Western Australian government is pushing for the region to be given a World Heritage listing for its aboriginal rock art. There are fears that the 40,000 year old petroglyphs may be threatened by emissions from heavy industry on the Burrup Peninsula. The rock engravings were made by scraping a thin patina off the rocks to reveal a paler layer below, but the patina is strongly affected by the acidity of the rock surface, and if the acidity were to increase the carvings would disappear. The local Murujuga Aboriginal Corporation wants industry to be moved to the Maitland Industrial Area about 25km southwest. Woodside Petroleum, which operates the North West Shelf LNG plant on the Burrup Peninsula, says that it is investigating building a gas and solar power station backed by batteries on the Maitland Estate to either partially or entirely replace the power station at its North West Shelf LNG plant, which generates 70% of the LNG plant's emissions. There are also said to be particular concerns about nitrous oxide emissions from Yara's AN plant.

It could also threaten new developments, said to include a \$4.6 billion urea plant proposed by Perdaman, with development slated to begin in 2020, and a \$1.4 billion methanol and monoethylene glycol (MEG) plant being developed by a consortium of Wesfarmers, Coogee Chemicals and Mitsubishi. The latter three companies are currently conducting a pre-feasibility study, and are said to be not looking to start construction any time before 2021.

Coal-based ammonia proposal

Brisbane-based Australian Future Energy (AFE) has proposed a \$1 billion combined power and ammonia project based on gasified coal for the Queensland State Development Area at Gladstone, near Yarwun. Queensland state's Coordinator-General has given his go-ahead for the project and an environmental impact statement (EIS) is now being prepared. AFE proposes to convert 1.5 million t/a of coal from existing mines in the Gladstone region to produce up to 330,000 t/a of ammonia, six to eight petajoules of synthetic natural gas and up to 96 MW of electrical power generated from waste gas and heat. The ammonia and synthetic natural gas would be sold to "major industrial users, including those focusing on agriculture, the mining industry and

advanced manufacturing", according to the company.

The next step in the project is preparation of draft terms of reference by the Coordinator-General who will then invite community comment on the matters that must be addressed in the EIS. The project is estimated to commence construction mid-2020, with the first ammonia production proposed in mid-2022.

OMAN

Omifco considering \$1 billion expansion of Sur plant

The Oman India Fertiliser Co (Omifco) says that it is looking at expanding the capacity of its ammonia-urea complex at Sur by adding a third train with a capacity of 1.3 million t/a of urea, at an estimated cost of \$1.0 billion. Omifco is 50% owned by the Oman Oil Co, with two Indian fertilizer cooperatives; Indian Farmers Fertiliser Cooperative Ltd (IFFCO) and the Krishak Bharati Cooperative Ltd (Kribhco) each holding 25% and taking the offtake from the plant for use in India. Omifco told local press that it began a feasibility study on the expansion earlier in 2018, which it hopes to complete by the end of the year, but said that; "much would depend on availability of natural gas". The company says that it is also considering a debottlenecking option for the two existing 800,000 t/a ammonia-urea lines. Oman has additional gas availability following the start-up of its Khazzan project.

TURKMENISTAN

Urea plant commissioned

The Garabogazkarmabid urea plant was officially opened on September 17th by Turkmenistan's president Gurbanguly Berdimuhamedov. The plant, sited at Garabogaz on Turkmenistan's Caspian Sea coast, consists of a 2,000 t/d ammonia unit designed by Haldor Topsoe and 3,500 t/d urea plant designed by Saipem, with an Uhde Fertilizer Technology granulation section for product finishing. Mitsubishi was the EPC contractor, in cooperation with Turkey's Gap Insaat. The \$1.6 billion facility is owned by the state owned Turkmenhimiya State Concern. The complex includes seawater desalination and treatment and a gas turbine to produce its own electricity, as well as a loading dock with two Liebherr 80 tonne loaders, and worker housing near the plant.

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REPUBLIC OF CONGO

Feasibility study on nitrogen fertilizer plant

Haldor Topsoe is to assist the Republic of Congo with the development of a \$2.5 billion fertilizer plant near the port city of Pointe Noire, according to government sources in the country. Economy Minister Gilbert Ondongo said that Topsoe will work on the project with MGI Energy, a Pointe Noire-based company, which would supply gas feedstock to the project. While Topsoe would presumably provide its own ammonia technology, there was no detail given about downstream urea production, or proposed plant capacities. A feasibility study is currently under way, which if successful could see work begin in 2019 on the plant, for completion in 2022, according to Ondongo. Ondongo said three-quarters of the funding for the project would come from EKF, Denmark's export-credit agency, with the rest being provided by the Copenhagen-based Investment Fund for Developing Countries.

UKRAINE

OPZ signs new gas tolling arrangement

Oman-based ETEK UK Group has won a tender to supply gas to the troubled Odessa Port Plant (OPZ) on the Black Sea on a toll basis. The company would be paid \$34 per tonne of ammonia produced and \$46.50 per tonne of urea. OPZ said that it sees tolling as the only way of continuing operations at the plant following the failure of several attempts at privatisation and an accumulated debt for gas supplies from Naftogaz Ukrainy in excess of 1.5 billion hryvnia (\$53 million).

LITHUANIA

Urea phosphate plant begins operation

EuroChem says that it has begun operations at its new \$16 urea phosphate plant at Kedainiai, Lithuania. The 25,000 t/a plant is operated by EuroChem subsidiary Lifosa, which also produces diammonium phosphate (DAP) and mono-ammonium phosphate (MAP).

"The new facility will further strengthen Lifosa's position in the global fertilizer market," Jonas Dastikas, general manager of AB Lifosa, said in a statement. "At the

same time, the construction of the plant is an investment in the sustainable development of the company. We constantly aim to protect our environment by rationing the use of natural resources."

INDIA

Foundation stone laid on new plant

Prime minister Narendra Modi has laid a foundation stone at the new coal gasification-based fertilizer plant at Talcher in Odisha state. The plant is being constructed by the joint venture Talcher Fertilizer Ltd, which combines four state-owned companies: Rashtriya Chemical and Fertilizers (RCF), the Gas Authority Of India Ltd (GAIL), Coal India Ltd (CIL) and Fertilizer Corporation of India Ltd (FCIL). FCIL has a 10.9% stake, and the other companies 29.7% each. The \$1.6 billion plant will have a capacity of 2,200 t/d of ammonia and 3,850 t/d of neem-coated urea when it is completed, scheduled for 2022. There will also be 100 t/d of by-product sulphur extracted from the gasified coal.

Go-ahead for Zuari expansion

India's Ministry of Environment and Forests' expert appraisal committee has approved the proposed expansion of the urea plant of Zuari Agro Chemicals at Sancoale, Goa. The expansion would see capacity rise from 1,500 t/d to 1,800 t/d, as well as the installation of new ammonia storage, a 25MW gas turbine and heat recovery steam generator. The cost of the debottlenecking is put at \$107 million.

Loan agreed for Gorakhpur urea plant

Hindustan Urvarak and Rasayan Ltd (HURL) has signed a loan agreement for the Gorakhpur fertilizer plant. The \$723 million loan was arranged with a consortium of banks led by the State Bank of India as lead, and also including the Punjab National Bank, Allahabad Bank, Union Bank of India, Indian Bank, Bank of India and Canara Bank. HURL is a joint venture between five state owned enterprises, including power company NTPC, the Indian Oil Co. and Coal India Ltd, as well as the Fertilizer Corporation of India Ltd and Hindustan Fertilizer and Corporation Ltd. HURL is implementing three urea projects at Gorakhpur, Sindri and Barauni in the eastern part of the country which aim to be producing 3,850 t/d of neem-coated urea from 2021. Total cost of the development is put at \$4.9 billion, including laying new gas pipelines,

with the three plants costing a total of \$2.8 billion.

PAKISTAN

Gas supplies restored to fertilizer plants

The government of Pakistan has restored gas supplies to three urea plants to try and generate sufficient urea to meet demand during the upcoming Rabi cropping season (October-March). The government will pay 50% of the cost of LNG imports which will provide one third of the gas required, the remainder coming from domestic sources. However, the arrangement will last only for four months. The previously idled plants include Fatima Fertilizers and Agritech, and are expected to produce 300,000 tonnes of urea over the four month period, against demand of 400,000 tonnes. The government will import the remaining 100,000 tonnes of urea required.

Longer term, however, Pakistan's fertilizer industry continues to face issues over gas supplies. Around 90% of gas feedstock for the country's urea plants comes from the Mari gas field, which is expected to start depleting in 6-8 years' time. Of the country's total urea capacity of 6.2 million t/a, Fauji Fertilizer Company, Fatima Fertilizers and Engro represent 5.2 million t/a, and all are dependent on Mari gas.

RUSSIA

Acron signs fertilizer supply agreements

Acron Group has signed fertilizer supply agreements with the Bryansk and Novgorod regional departments of agriculture for 2019. Under the agreements, Acron will supply over 100,000 tonnes of ammonium nitrate and NPK. In a press statement Acron said that it had supplied 630,000 tonnes of fertilizer to the Russian market in the first nine months of 2018, up 15% on the same period last year. Ammonium nitrate and NPKs remain the most popular fertilizers in Russia.

Acron chairman Alexander Popov commented: "supplying mineral fertilisers to Russian farmers is Acron Group's top priority. We sign agreements with regional subdivisions of Agro-Industrial Complex every year to map out our effective cooperation. The Group is ready to satisfy the needs of Russian farmers, and we are confident that it will help produce high yields".

SAUDI ARABIA

Ma'aden awards ammonia EPC contract

The Saudi Arabian Mining Company (Ma'aden) has awarded Daelim a \$892 million engineering, procurement and construction contract to build the first plant at the company's third large-scale phosphate complex - 'Phosphate 3'; Ma'aden is aiming to boost its processed phosphate capacity to 9 million t/a at a total cost of \$6.4 billion. The EPC contract was signed between Darren Davis, president and CEO of Ma'aden, and Heon Jae Yim, Daelim SEVP and CEO at Ma'aden's headquarters in Riyadh, and covers construction of a new 3,300 t/d (1.1 million t/a) ammonia plant at Ras Al-Khair on the east coast of Saudi Arabia. Technology for the plant is being provided by thyssenkrupp Industrial Solutions, who built Ma'aden's other ammonia plants and were previous awarded the front end engineering and design (FEED) contract. The plant will feed additional diammonium phosphate (DAP) production at Ras al Khair. Completion is set for the end of 2021.

"As a leader in global EPC, it is our pleasure to have another opportunity to work for Ma'aden," said Mr. Heon Jae Yim. "With Ma'aden's superb leadership and our accumulated expertise and know-how in project management, we recently successfully completed the ammonia plant for the Ma'aden Waad Al-Shamal Phosphate Company. We are very proud to once again serve Ma'aden and the Kingdom, and are committed to the success of this new project for Phosphate 3."

TANZANIA

No agreement yet on gas price

The development of an ammonia-urea plant in Tanzania continues to be held up by discussions over the cost of gas feedstock for the project. The Tanzania Petroleum Development Corporation (TPDC), which would supply the gas, has been unable to reach agreement with project developers Helm AG, Ferrostal Industries and Egypt's Capital DW Fertiliser Company. Back in 2016, the Tanzanian Energy and Water Utilities Regulatory Authority reportedly proposed an indicative price of \$2.60/MMBtu, but TPDC believes that this does not cover the cost of developing gas infrastructure for the \$1.9 billion project. The proposed plant would produce 2,200 t/d of ammonia and 3,850 t/d of urea.



Inspired by Peter Bruegel the Elder, *The Peasant Wedding*, 1567, oil on panel, 114x164 cm, Vienna, Kunsthistorisches Museum.

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CANADA

New mega-scale methanol project for Alberta

Calgary-based Nautical Energy says that it is aiming to construct a C\$2 billion methanol plant facility at Grande Prairie in northern Alberta, in the heart of the Montney shale gas basin. The company says that the planned facility has the support of the local Western Cree Tribal Council, which has signed an agreement to be an equity partner. The location chosen is a brownfield site near a pulp mill 6 km south of Grande Prairie, with a rail connection to Prince Rupert port in British Columbia.

The project envisages up to 3 million t/a of methanol production based on 300 million scf/d of locally produced shale gas – the Montney Basin, which extends into British Columbia, is Canada’s largest shale gas deposit and is estimated to have up to 450 trillion cubic feet of recoverable natural gas. While some of the methanol produced will supply local markets, most will be directed to Asian markets, which make up approximately 70% of current global demand, the company said, indicating that it is looking to China’s methanol to olefins market, and perhaps hoping to steam a march on the large methanol plants planned further south for the US Pacific Northwest in Washington State and Oregon, which are currently mired in permit disputes.

Nautical’s CEO Mark Tonner is a former president of GE Energy’s investment business in Canada, and the company’s board includes Tim Stauff, a former senior vice-president with Montney natural gas producer Seven Generations Energy. Nautical is chaired by Leo de Bever, former CEO of the Alberta Investment Management Corporation. Seven Generations Energy founder Pat Carlson is also on the board of directors.

Nautical says that it will be working over the coming months with all levels of government to obtain the required regulatory permits to successfully complete the project. Last year, Alberta launched a petrochemicals diversification program to encourage more natural gas petrochemical processing plants in the province with incentives of up to C\$500 million in royalty credits. The company has also started consultation and stakeholder engagement with the public, and has committed to continuing to do so throughout the project’s lifespan. The facility is currently planned to be complete in 2021. Nautical says it expects to start building in stages, using modules fabricated by PCL Construction elsewhere in the province. The company is also working on development plans for a methanol and urea project at Becanour in Quebec. ■

CHINA

Coal-based methanol plant to feed downstream MEG production

Chinese chemical producer Jiutai is planning to build a ‘coal-to-chemicals’ plant at the Togtoh Industrial Park in Inner Mongolia. The plant will ultimately produce mono-ethylene glycol (MEG) from coal, via intermediate gasification to syngas, methanol and formaldehyde production steps, using proprietary technology licensed from Johnson Matthey and the Eastman Chemical Company. The complex will have the capacity to produce 1.5 million t/a of formaldehyde and 1.0 million t/a of MEG. MEG, normally produced from ethylene, is used as a building block in the production of polyesters for fibre and packaging applications. The new process allows MEG to be produced from syngas feedstocks, thereby eliminating the need for ethylene. Johnson Matthey’s technology and catalysts will be used for the production of methanol and formaldehyde, and Eastman’s MEG process.

Cui Lianguo, chairman of Jiutai Group, said: “Jiutai is pleased to select Johnson Matthey and Eastman’s novel technology for the production of MEG. Jiutai’s aim is to utilise local coal and other precious resources, such as water, in a clean and sustainable manner to produce high value MEG at its new coal-to-chemicals complex.”

UNITED KINGDOM

UK to develop standards for hydrogen fuel

The Institution of Gas Engineers & Managers (IGEM) has been chosen to develop hydrogen standards for the government’s £25 million research and innovation programme. The ‘Hy4Heat’ programme is a feasibility study into the use of hydrogen for heating in UK homes and businesses, aimed at establishing whether it is technically possible, safe and convenient to replace methane with hydrogen in residential and commercial buildings. As part of this project, IGEM says that it will be “reviewing all relevant existing standards and bringing together a group of technical specialists to identify knowledge gaps, both in the UK and internationally”. This work will help the government to determine whether to proceed to a future community trial. A separate project will look at purity, odour and colourisation.

The Department for Business, Energy and Industrial Strategy (BEIS) has appointed Arup+ as the programme management contractor for the Hy4Heat programme to manage and co-ordinate the various work packages, including the standards work. Mark Neller, Director at Arup, said: “The UK has an opportunity to lead the way in using hydrogen as a domestic fuel, making a significant reduction in CO₂

emissions. This project will help establish the feasibility using hydrogen for cooking, hot water and heating our homes. It will also undertake the essential preparatory work for possible future community trials.”

IGEM is working on the project with industry partners DNV GL, Global Energy Associates, Health & Safety Laboratory, the Heating and Hot Water Industry Council (HHIC) and ICOM Energy Association.

UNITED STATES

Prototype modular hydrogen plant showcased

Albuquerque-based start-up company BayoTech Inc. has unveiled its first working prototype for modular hydrogen production. The company is looking to a time when modular, easily transportable production units might transform hydrogen and ammonia production. The company says that their technology, originally developed at Sandia National Laboratories, could allow chemical companies to produce fuel and fertilizer right where it’s used – at the doorsteps of farms, or next to future filling stations for hydrogen-powered vehicles, leading to lower costs for growing food, and for replacing carbon-emitting, gasoline-fuelled cars with cleaner ones that run on fuel cells.

The demonstrator unit has been funded by \$16 million in venture capital, includ-

ing a “substantial contribution” from a “global fertilizer producer” signed on as BayoTech’s strategic partner, although the company’s identity remains confidential. BayoTech CEO Justin Eisenach said that the partner was “one of the world’s largest fertilizer producers. They provide technology support, marketing, and help with strategic planning for system deployment. We’re very fortunate to have them.” That partner will be the first one to receive a hydrogen-production unit, when they become commercially available next year.

“We’ll begin building the first prototype system in November for delivery to our strategic partner in 2019,” Eisenach said. “The company will use it for fertilizer production, providing a much cheaper way for them to make the hydrogen they need for their manufacturing process. They’ll test it first, and then hopefully convert to commercial orders that we’ll fill under a supply agreement.”

With the hydrogen unit now developed, BayoTech says that it will build its first ammonia production unit next year, and then add a final unit to produce downstream nitrogen fertilizers such as urea. The modular units use steam methane reforming, with a “nested flow” containing the entire SMR process in a small space the size of a cargo container. The contained area makes better use of energy in the heating and cooling process, improving efficiency by about 25% compared with traditional plants, according to the company.

Sandia spent about \$50 million to develop the original technology, which BayoTech licensed from the laboratory. Some of the same scientists that worked on the project are now leading the commercial development at BayoTech.

Primus Green Energy to deliver its first US methanol plant

Another modular syngas technology developer, Primus Green Energy Inc., says that it plans to finalise development and delivery of a modular 160 t/d methanol plant to a location in the Marcellus shale region near New Martinsville, West Virginia. Primus will partner with EPC and oilfield technology provider Jeroh Oil and Gas Engineering Corporation to have the new plant up and running in 2020, according to the company.

“Primus has long-envisioned development of a methanol plant in the Marcellus region, but it is our relationship with Jeroh and other strategic partners that has resulted in substantially improved economics and will allow us to move the project for-

ward,” said Steven Murray, CEO of Primus Green Energy. “With gas supply and methanol offtake agreements from an integrated oil and gas company, assistance from Sumitomo Mitsui Banking Corporation to arrange project debt financing, and design work by Koch Modular Process Systems, the project economics are very strong.”

The plant will use Primus’s STG+™ technology, which was developed to be able to use a wide range of natural gas feedstocks, including wellhead and pipeline gas, dry or wet associated gas, “stranded” ethane, excess syngas from underutilised reformers, or mixed natural gas liquids. Production areas with stranded and associated gas are an ideal potential market because many areas lack traditional natural gas pipeline infrastructure, especially in remote locations, enabling the monetisation of gas that would otherwise be stranded or flared.

GTL plant to be shut down

Velocys says that its joint venture partner company Envia Energy is suspending operations at the companies’ Oklahoma City plant due to financial circumstances. The gas-to-liquids (GTL) facility, which features Velocys’ Fischer-Tropsch technology, began producing finished products in mid-2017. The Envia plant experienced a leak in May due to an ancillary coolant system, but on September 10th, Velocys announced Envia’s board has elected to suspend operations at the plant and to undertake a review of strategic alternatives to preserve value inherent at the facility.

According to Velocys, the decision was driven by financial circumstances following the May leak. Envia had been operating the plant at reduced capacity using a single reactor to generate products since May. However, that configuration of the plant does not meet the specific process energy requirements applicable under its Renewable Fuel Standard pathway to generate renewable fuel credits (RINs). Velocys said its board fully supports Envia’s decision to suspend operations at the Oklahoma City plant given the likely capital requirements of the plant. Velocys also said it believes that its capital is better invested in progressing its proposed UK waste-to-jet fuel project and Mississippi ‘bio-refinery’, which reached an environmental milestone in August.

“The decision to suspend plant operations was taken after careful consideration by the boards of Envia and Velocys and with our Envia JV partners,” said David

Pummell, CEO of Velocys. We are working with Envia to find a strategic alternative that will realize the maximum value potential inherent in the facility.” He added that, “nonetheless, the Oklahoma City plant has demonstrated the scalability and commerciality of our technology, providing a strong strategic foundation for Velocys to deliver our UK and US bio-refinery projects.”

INDIA

CIL pushing coalbed methane-based methanol plant

Coal India Ltd (CIL), the world’s largest coal miner, is pushing ahead with development of a coalbed methane-based methanol plant in India, according to chairman Anil Kumar Jha said. As we noted in our previous issue (*Nitrogen+Syngas 355*, Sept/Oct 2018, p22), India has high hopes in developing domestic methanol capacity to produce alternative fuels in much the same way that China has done. The central government has assisted by easing restrictions on the licensing process that CIL needed to go through to extract coalbed methane from coal seams. The company says that it is now planning a 680,000 t/a methanol plant at the Dankuni Coal Complex of CIL subsidiary South-Eastern Coalfields Ltd.

CHILE

Methanex restarts Chile IV

Methanex says that it has successfully restarted production at its 800,000 t/a Chile IV methanol plant at Punta Arenas. The company announced in July 2017 plans to spend \$55 million to restart the Chile IV facility. Methanex will spend an additional \$50 million to refurbish its Chile I plant, adding an additional 800,000 t/a to its current capacity, the company said. The Chile IV plant has been idle since 2007, due to lack of natural gas to operate the facility after cross-border arrangements with Argentina broke down.



Methanex’s Chile site.

PHOTO: METHANEX

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Argentina's government recently granted permits to allow the export of natural gas from Argentina to Chile, and Methanex has begun to receive natural gas from Argentine suppliers.

"We expect that our current gas agreements will allow for a two-plant operation in Chile during the southern hemisphere summer months and up to a maximum of 75% of a two-plant operation annually until mid-2020," the company said. Argentina restricts gas supplies during the southern hemisphere winter when they are needed for domestic heating and power production.

GERMANY

Pilot biomass gasification-based SNG plant completes initial tests

The Karlsruhe Institute of Technology says that it has completed field tests on a biomass-based synthetic natural gas (SNG) plant at a site in the city of Köping, Sweden. KIT's researchers succeeded in producing methane from a biomass-based syngas gas mixture using "honeycomb methanation". KIT says that the quality of the resulting SNG is comparable to that of fossil natural gas and can be used as fuel in co-generation and heating plants as well as in cars or trucks. The pilot plant was designed and tested by researchers of Karlsruhe Institute of Technology (KIT) and the Research Centre of the German Technical and Scientific Association for Gas and Water (DVGW).

While existing 'biogas' facilities produce methane mainly by fermenting biological waste, KIT believes that in countries with a large forestry sector, such as Finland or Sweden, there is a high potential for the production of SNG from waste wood by means of biomass gasification. The resulting syngas can then be converted into methane by methanation. Researchers of KIT's Engler-Bunte Institute and the DVGW Research Centre have now successfully tested a highly efficient methanation process over a period of several weeks. The synthetic methane produced was then applied as fuel in the natural gas vehicles of Swedish project partner Cortus AB.

The core components of the plant are honeycomb catalysts developed and optimised for use by the Catalytic Fuel Conversion group of the EBI Division of Fuel Chemistry and Technology (EBI ceb). In a single-stage process, metallic nickel catalysts convert hydrogen and carbon monoxide and, in case of sufficient hydrogen

supply, also carbon dioxide into methane and water.

After its successful operation in Sweden, the pilot plant is now on its way back to Karlsruhe, where it will be integrated into the infrastructure of the Energy Lab 2.0 on KIT's Campus North, where KIT wants to further improve the honeycomb methanation process and optimise the catalysts for use in much larger facilities.

AUSTRALIA

First syngas from Leigh Creek UCG

Leigh Creek Energy says that it has produced its first synthesis gas from underground coal gasification at the Leigh Creek coalfield in South Australia. The syngas production was the final step of Leigh Creek's pre-commercial demonstration, following the construction of an above ground plant and the drilling of three process wells. Leigh Creek chairman Justyn Peters said that it was a milestone for the company.

UCG has had an unhappy history in Australia, with Link Energy's Queensland project shut down in 2013 over environmental concerns, resulting in a court case and an A\$4.5 million fine earlier this year. The South Australian Supreme Court dismissed an injunction from the New South Wales Environmental Defenders Office to delay the operational start-up of the Leigh Creek UCG facility in September, but Greens in the state parliament continue to try and stop the project. The pre-commercial demonstration is expected to last between two and three months, with regulators and Leigh Creek Energy staff undertaking around-the-clock environmental monitoring.

ZIMBABWE

MoU signed on coal to chemicals plants

The government of Zimbabwe has signed memoranda of understanding and non-disclosure agreements with FEED and EPC contractors for the development of a \$5 billion package including a coal to chemicals plant in Lusulu in the Zambezi basin and a coal to fertilizer plant at Mkwesine. The projects are being developed by Vectol Zimbabwe, a joint venture between state owned Verify Engineering and Nkosikhona Holdings, owned by the Canadian Magcor Consortium Group. The work is being funded by China with two as yet unnamed Chinese firms providing the technology and engineering expertise. There are still some

issues over money transfers due to restrictions imposed by US sanctions on Zimbabwe, but it was hoped that these would be overcome soon. The government hopes to launch the projects officially before the end of the year.

TRINIDAD AND TOBAGO

Questions over troubled GTL plant

NiQuan Energy Ltd, the company that has bought Petrotrin's ill-fated gas to liquids (GTL) plant, says that it still needs to find more than \$100 million in order to get the plant up and running. According to local media sources, NiQuan Energy says that it will find the money from private sources and will not seek any government funding. The company dismissed as "media speculation" reports that NiQuan struggled to repay a \$1 million loan earlier this year, and eventually did so late and with considerable interest accrued.

NiQuan bought the 2,400 t/d World Gas to Liquids (WGTL) plant at Pointe a Pierre in 2016 for \$10 million down and \$25 million in equity. The WGTL plant – a joint venture with a 49% minority stake for state oil company Petrotrin – had been in receivership since 2009 after spiralling construction costs and technical difficulties forced WGTL to sell up to the government. Although plant construction was 90% complete as of 2009, the project had already cost \$3.3 billion by that time. Subsequent court cases and investigations meant that a final sales and purchase agreement was not signed with the official receiver, price-Waterhousecoopers, until July 2018.

JAPAN

Construction begins on renewable hydrogen-based power plant

Japan has started building a 10MW hydrogen-based power plant. Officially named the Fukushima Hydrogen Energy Research Field (FH2R), the facility is being developed by a consortium comprising the New Energy and Industrial Technology Development Organisation, Toshiba, Tohoku Electric Power and Iwatani, as well as Japan's Ministry of Economy, Trade and Industry. The consortium is building a 900 t/a hydrogen production plant in Fukushima Prefecture to produce renewable gas to be used to power fuel cell vehicles, support clean factory operations, store surplus renewable energy and balance the grid. The facility is due to be operational by 2020. ■

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People

Clariant has announced the appointment of Hans Bohnen as the newest member of its Executive Committee as of October 12th. Bohnen has been with the company for almost 10 years and was previously Clariant's Head of Global Business Services. He will assume responsibility for the business areas Plastics & Coatings, Global Business Services, Group Information Technology, Digital4Clariant, and the Latin American and North American regions. Bohnen has also served as Senior Vice President and Head of Clariant Masterbatches. Prior to joining Clariant, he held several senior positions across Europe and North America for the SGL Group, Celanese and Hoechst AG, and worked in strategic management consultancy with Booz Allen Hamilton. He studied Chemistry at the University of Duisburg-Essen, obtained a PhD in Chemistry from the University of Tübingen and holds an MBA from the Aston Business School.

At the same time, **Britta Fuenfstueck** has decided to leave Clariant as of 31st October 2018 to become CEO of the Hartmann Group, a leading international supplier of medical and hygiene products based in Heidenheim, Germany. Harioif Kottmann, CEO of Clariant, said: "We are very pleased



Hans Bohnen.

that Hans Bohnen will join the Executive Committee. With his extensive knowledge of Clariant as well as the wider chemical industry, he will be a valued contributor to the management team and will further enhance the long-term development of Clariant's value creation capabilities for all stakeholders. We regret losing Britta Fuenfstueck and want to especially express our gratitude for her role in Clariant's successful strategic developments over the past years. We wish her all the best in her new role."

Notore Chemical Industries Plc has appointed **Ohis Ohiwere** as its new executive director, following the retirement of **Femi Agbaje**. The company said in a statement that Agbaje's retirement would take effect

from September 30th. Agbaje, who joined the organisation in January 2007, had served as a member of the board of directors since February 2011, and will remain on the board as a non-executive director.

Methanex has announced the appointment of **James Bertram** to its board of directors from October 1st, 2018. Bertram served as the Chief Executive Officer of Keyera Corporation, one of the largest independent midstream energy companies in Canada, from its inception in 1998 until 2014 and is currently the Chair of the Board for that company. Prior to working at Keyera, Mr. Bertram held senior marketing roles with other energy companies: Gulf Canada and Amerada Hess Canada (now Hess Corporation). He holds a Bachelor of Commerce degree from the University of Calgary and also serves as a director of Emera Inc.

John Floren, President and CEO of Methanex, commented, "We are pleased to welcome Jim to Methanex's board. He brings to Methanex a wealth of senior management experience in both the North American and global energy markets. His experience as a former CEO of a public company is a significant asset and will complement our current Board's skills and experience." ■



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For general information about the Ammonia Symposium, please contact Iliia F. Killeen at 646-495-1316 or iliak@aiiche.org.

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4-7

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6-7

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11-13

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8-11

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IFA 87th Annual Conference, MONTREAL, Canada. Contact: IFA Conference Service, 28 rue Marbeuf, 75008 Paris, France.
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NOVEMBER-DECEMBER 2018

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Plant Manager+

Problem No. 51 Restriction orifices in VOP exchangers

Vertical one pass (VOP) heat exchangers are commonly applied in urea plants. As the residence time in these heat exchangers is small, unwanted side reactions like biuret formation and hydrolysis of urea are limited. Liquid enters the tubes of the heat exchanger at the bottom side via a control valve. Due to the pressure drop over this control valve some flashing will occur. Furthermore the heat input from the shell side will also result in gas formation. The gas causes a turbulent environment at the tube side increasing the heat exchange coefficient.

Some phenomena, however, can limit or reduce the performance of these heat exchangers, for example, bad distribution of the inlet liquid/gas mixture over the tubes. Uneven feed distribution of the tubes and recirculation from the outlet to the inlet can occur limiting the performance. Another problem can be fouling on the tube side, which causes limitations of the heat exchanger.

The more turbulence on the tube side of VOP heat exchangers, the higher the heat transfer coefficient, the better the performance of the heat exchanger and the lower the risk that fouling can settle on the tube side. It is common knowledge that orifices



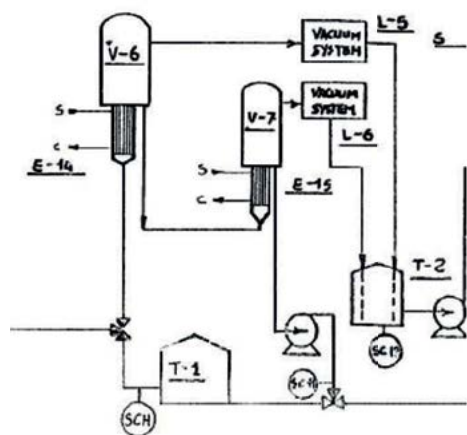
at the inlet of the tubes improve the distribution over all the tubes, increase the turbulence on the tube side, reduce the fouling on the tube side and thus increase the performance.

Munirm Munir of Pakarab Fertilizer in Pakistan initiates the discussion: Can anyone share their experience of installation of restriction orifices in the vertical one pass (VOP) evaporation heaters (E-14, E-15 or other) in a Saipem urea plant and the reduction in biuret as a result?

Please see the sketch of the vacuum and evaporation section of the plant at our site below.

Will the installation of restriction orifices in VOP heaters E-14 and E-15 on the process side help us in reducing the biuret in our final product?

At this time, the biuret content in our final product is 1.1 wt-%.



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Prem Baboo of National Fertilizers Ltd in India replies: In our plant a control valve is provided in the steam supply to E-14 and E-15 for controlling the desired temperature of urea solution to control the biuret. In VOP heat exchangers there is a problem of flashing because the control valve is located at grade level. Afterwards a pressure drop occurs due to the two phases (gas and liquid) sometimes causing hammering in the vertical line.

The orifices can provide the following advantages:

- increased logarithmic mean temperature difference (LMTD) across vertical heat exchanger;
- no flashing problem;
- regular and constant flow;
- two-phase (gas-liquid) problem will be solved;
- biuret can be controlled at constant plant load;
- unwanted side reaction can be controlled.

I have some more suggestions: The control valve can be relocated to a position closer to the vertical heat exchanger. Orifices have a fixed diameter and are suitable for constant load. For variable loads the control valve can be relocated near the vertical one pass heat exchanger.

Munirm responds: Actually, our plant mostly runs at constant load i.e. (120% of 300 t/d capacity). If the restriction orifices can help us to reduce the biuret content in the product then we can go for it. Do you know of any reference where restriction orifices have been installed? Maybe we could get some data from them regarding their performance. The control valve (LV-22) is located down L-3 (LP decomposer holder) and it is about 100 m distance between the LV-22 and E-14 inlet. I believe you mean relocating this control valve. Will it help us to decrease biuret in our final product?

Prem replies again: If you installed the orifices before E-14 what would the function be of the upstream control valve (LV-22)? The

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control valve can be relocated near E-14 as shown in the figure and there is no need of an orifice. This will help to rectify the problem.

Munirm continues: Relocation of LV-22 is probably an optimal solution. At this point, the biuret in our final product is ~1.15 wt-%. Will we be able to achieve < 1 wt-% target with this modification? Do you know of any references?

Prem responds again: Yes, the relocation of the control valve is proven, but I don't know about the orifice. We have also relocated this control valve to the vacuum section area from the LP holder.

Munirm continues: Ok, thank you. We'll be looking to implement this at our site. In case of further queries, we'll contact you.

Majid Mohammadian of OCI Nitrogen in the Netherlands contributes to the discussion: Restriction orifices (plugs) are installed mostly in the second stage of evaporation in the inlet of each tube which will result in an increase of the velocity, to minimise the residence time and therefore to reduce the biuret formation at high temperature and high concentration of urea melt.

In Stamicarbon plants the tube diameter of the evaporator will typically be reduced to 7 mm. Please check with your licensor to decide on the diameter of the plugs.

Munirm replies: The outside diameter (OD) of the tubes of our VOPs is 3/8". The size of the orifice is clear, but how much the biuret content will be reduced as a result of orifices in a Snamprogetti urea plant is still unclear. Can you share the performance improvement achieved at your plant after orifice installation?

Majid replies: If the OD is 3/8" = 9.5 mm, I don't think the restriction orifice will be effective in your case. In our case the OD was 20 mm therefore installation of orifices could increase the velocity and reduce the biuret.

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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Latin America's syngas industries

Trinidad and Brazil's gas constraints, Venezuela's social and economic ferment, and new plants in Bolivia and Mexico are all contributing to the changing dynamics of this region.

The AUM plant at Point Lisas, Trinidad.

Initially based on 'stranded' natural gas or associated gas from oil production, considerable volumes of ammonia and methanol production were built in Latin America from the 1970s to 1990s, much of it export-oriented. However, rising demand for natural gas for power production has changed the economics of producing in the region, while domestic demand for nitrogen fertilizer continues to rise, especially in Brazil. Much of the new capacity appeared in Trinidad and Venezuela, aimed at the North American market, but the change in the US gas market has likewise led to a revival in capacity there and shut Caribbean producers out.

Trinidad

Trinidad has seen its fortunes take a major swing over the past three decades, from virtually no syngas-based industries to becoming one of the world's largest exporters of ammonia and methanol, but

now that leading position is steadily eroding. In a way Trinidad has been a victim of its own success. Large offshore natural gas discoveries during the 1980s and 90s prompted the rapid development of ammonia and methanol capacity as well as the Atlantic LNG export project, which helped balance falling revenues from the country's older oil fields, which were depleting. Table 1 shows Trinidad's nitrogen and methanol plants. The success of Trinidad's ammonia and methanol industries was predicated on rising natural gas prices in the US, and Trinidad became an offshore adjunct to the US market. However, the rise of shale gas in the US and the re-start and new building of domestic ammonia and methanol capacity in the US has come at a time when Trinidad finds itself short of gas and having to operate capacity at lower production rates.

Trinidad's proved natural gas reserves peaked in 2004 at 20.7 trillion cubic feet (tcf). According to BP estimates, last year that had more than halved to 9.7 tcf –

simply speaking, Trinidad has not been finding enough gas to replace that being used by its petrochemical and LNG industries. Part of this has been a pricing issue – gas pricing and sale is controlled by the Natural Gas Company of Trinidad and Tobago (NGC), and operates at a base price plus escalator for ammonia and methanol companies depending on product prices, with a cap. As the cost of new gas development in more difficult fields increased, so there was less incentive for producers to develop it. The requirement for NGC to act as middleman and take a cut of profits – producers, with a few exceptions (like BP's tie-up with Methanex) are not allowed to sell directly to end users – also became a bone of contention for ammonia and methanol producers.

Proman Group, one of the partners in Methanol Holdings Trinidad Ltd (MHTL), took matters into its own hands and invested directly in upstream production. DeNovo Energy – owned by Proman – is looking to supply another 70-90 million

scf/d of gas to MHTL via a T&T\$200 million pipeline under construction from the Phoenix Park Valve Station to DeNovo's gas processing station at Point Lisas, with another 3.4 km spur to the MHTL facilities. The decision has taken some wrangling however, and required Proman to reach a compromise with NGC. In the meantime MHTL was operating without gas contracts for four of its plants after previous contracts expired from 2013-15, meaning that NGC was only offering gas to those plants after supplying its other contracted customers. The result was that MHTL was forced to mothball two of its plants and lay off workers and talked about doing similar for a third.

The gas shortage became acute during 2011-12, pushing Trinidad to more gas licensing rounds and belatedly gas output began to rebound in November 2017 on the back of two projects led by the country's gas producer BP – Juniper and TOCP – which have added 790 million cfd of gas. Trinidad's gas production was up 12.5% for the first half of 2018 compared to 2017, according to its Energy Ministry. Long-standing talks with Venezuela about supplying gas across the small strait that separates Trinidad from the mainland of South America have also finally borne fruit. Agreement was finally reached in June 2018, and Shell will begin receiving 150 million cfd from Venezuela's Dragon field in 2020 at its Hibiscus platform, rising ultimately to 300 million cfd, although the continuing chaos in Venezuela puts some question marks over this. Overall, Trinidad plans to expand domestic gas production to 4.14 billion cfd by the end of 2021, according to the government, 22% above 2017 output.

The new gas has led to production increases. In Q1-Q3 2018, Trinidad produced 3.99 million tonnes of methanol, up from 3.41 million tonnes for the same period in 2017, the first production increase since 2014, according to Energy Ministry figures. However, one of MHTL's plants remains idled for lack of gas, and whether the new Mitsubishi Chemicals planned methanol and DME plant will have sufficient gas remains open to question – Mitsubishi is hoping to build a 1.0 million t/a methanol and 20,000 t/a DME plant, but requires 150 million scf/d of gas to operate it. Ammonia production also fell 1.5% over the same period to 3.68 million tonnes, with CNC's plant down for some months in early 2018 due to wrangling

Fig. 1: Ammonia and methanol plants in Latin America



over a new gas supply contract with NGC.

Finally, mention should be made of the 2,400 t/d World GTL plant, developed by trouble state petrochemicals company Petrotrin. This was built during the early 2000s, but massive cost overruns and issues during start-up led to creditors calling in loans and the plant went into receivership in 2009. After several years of legal wrangling and the potential scrapping of

the plant, it was bought by NiQuan Energy Ltd, who are refurbishing the plant with the hope of start-up in 2019.

Venezuela

Venezuela's petrochemical industry grew, like Trinidad's, in the 1980s and 90s. Venezuela had large quantities of associated gas available from oil production which led

Table 1: Nitrogen and methanol plants on Trinidad

Company	Product	Capacity (t/a)
Yara	Ammonia	310,000
Tringen*	Ammonia	465,000
	Ammonia	550,000
Nutrien	Ammonia	450,000
	Ammonia	450,000
	Ammonia	270,000
	Ammonia	650,000
	Urea	600,000
PLNL**	Ammonia	650,000
CNC***	Ammonia	650,000
Nitrogen 2000***	Ammonia	650,000
MHTL†:		
TTMC I	Methanol	460,000
TTMC II	Methanol	550,000
Caribbean Methanol Co	Methanol	500,000
Methanol IV	Methanol	550,000
M5000	Methanol	1,780,000
AUM	Ammonia	650,000
	UAN	1,420,000
Methanex:		
Titan	Methanol	850,000
Atlas	Methanol	1,700,000

Notes: *Government of Trinidad and Tobago 51%, Yara 49%.

**Koch Nitrogen 50%, CF Industries 50%.

***Ownership includes Proman Group, EOG Resources, Koch Nitrogen.

†MHTL is now 50:50 owned by Helm AG and Proman Group.

to the development of three nitrogen complexes on the country's northern coast – Nitroven at Zulia in the west, Fertinitro at Jose in the east, and Pequiven's Puerto Moron in between the two. There were also two methanol plants at the Jose complex, owned by Metor and Supermetanol. Altogether, Venezuela's production capacity totalled 2 million t/a of urea and 1.5 million t/a of methanol. Most of the plants were state-owned, but Fertinitro, completed in 2002, was a joint venture between state petrochemical major Pequiven (35%), Koch Nitrogen (35%), Snamprogetti (20%) and Empriseas Polar (10%). Koch became involved after PCS Nitrogen pulled out of the project in the late 1990s.

However, things began to turn for Venezuela as it entered the 21st century. The government of Hugo Chavez, elected president in 1999, began a rolling programme of nationalisation of foreign-owned companies and appointing members of his own party to senior positions in Pequiven,

state oil and gas company PDVSA, and other entities, especially after a general strike and coup attempt in 2002. His government moved from a kind of democratic socialism to a more autocratic, Marxist strain. Plans for expansions and new plants in Venezuela foundered as foreign investment dried up, and repairs and maintenance of existing facilities became more difficult. Fertinitro was nationalised in 2010 and Koch's involvement ended – an international tribunal ruled in Koch's favour earlier this year that its interest was unlawfully expropriated and ordered Venezuela to pay \$300 million in compensation, although Venezuela has appealed the decision. A plan to develop two plants jointly with Iran, one in each country, failed to materialise in Venezuela (although work did begin on the Iranian plant). There was only one new plant development during this time, for Pequiven at Moron. Ferrostaal built the 1,800 t/d ammonia plant using KBR technology, while Toyo devel-

oped the 2,200 t/d urea plant. The project's gestation was protracted, with initial contracts awarded in 2007, but operations did not finally begin until 2014, with financial support provided by China.

Venezuela's economy stumbled along, propped up by high oil prices which represented 98% of export earnings, although oil exports declined from 3 million bbl/d in 2000 to 1.7 million bbl/d in 2010 due to depleting oil fields, lack of maintenance and the suspension of various projects to exploit the Orinoco oil sands belt. Chavez died in 2013 but his replacement Nicolas Maduro continued the same policies. When oil prices collapsed in 2014 the country was hit particularly hard, and the economy imploded. Lack of foreign earnings meant that Venezuela could no longer afford to import goods. The government printed money to try and pay salaries, but this led to hyperinflation, and this, coupled with rising unemployment has led to an ongoing social crisis. Around 7% of the country's 32 million people have left.

The country's nitrogen and methanol producers now face intermittent power blackouts and natural gas feedstock shortages. The El Tablazo complex at Zulia, with twin 600,000 t/a urea plants, has not produced since 2012 due to gas shortages and technical issues. Fertinitro at Jose has reportedly struggled with staff shortages and maintenance issues. Only the more modern Moron plant, finished in 2014, is still operating regularly, although operating rates are said to be down to 30-40% due to gas availability.

Brazil

Brazil was to have been the great success stories of the early 21st century, identified in 2001 as one of the countries to watch as a 'BRIC' (Brazil, Russia, India and China). Currently the world's 8th largest economy, Brazil boomed in the first decade of the century, with living standards rising, the wild inflation of the 1990s falling to reasonable rates, and new oil discoveries underpinning economic success. In spite of a hit from the financial crash in 2009, the economy rebounded in 2010 to grow by 7.5%. However, the past few years has been a sorry story of falling commodity prices, increasing government debt and unemployment, the huge 'Operation Car Wash' corruption scandal which saw the impeachment of president Dilma Rousseff and former president Lula da Silva, and

a hard recession from 2014-2017 – the worst in the country's history. GDP grew by only 1% in 2017 and is forecast to be little better in 2018. The election of right wing strongman Jair Bolsonaro has also highlighted the country's out of control crime and public disorder issues.

As far as the syngas industries go, Brazil is of course one of the world's largest agricultural producers, and the world's fourth largest consumer of fertilizers. Brazil's relatively poor soils need extra application of fertilizers to achieve sufficient agricultural productivity. Overall Brazilian nitrogen demand represents about 60% of that for the whole of Latin America, and this is serviced particularly in the form of urea – Brazil's demand for urea reached 6.3 million t/a in 2016, according to IFA figures. Domestic production, however, remains relatively low, because of lack of natural gas feedstock. Brazil's gas reserves are mostly (90%) in the hands of state owned oil and gas giant Petrobras. The company was heavily implicated in the Operation Car Wash scandal, but over the past couple of years it has reduced costs and its huge debt and improved safety performance, and increased divestment and partnerships with oil majors such as BP, ExxonMobil, Total and Statoil. There are ongoing licensing rounds both onshore and offshore. Brazil is known to have considerable gas deposits in offshore pre-salt layers, although exploitation of these remains at an early stage. At the moment, as most gas is associated with oil production, much of Brazil's gas production is reinjected. As a consequence, Brazil remains a net gas consumer, using 38.3 bcm of gas in 2017, and producing only 27.5 bcm, according to BP. To make up the shortfall Brazil imports natural gas, mainly via the Gasbol pipeline from Bolivia (8.6 bcm in 2017), with some (1.9 bcm) LNG deliveries also arriving from Nigeria, the US and Angola at the country's In three regasification terminals at Pecem in the northeast, TRB in Bahia and Guanabara Bay in the southeast.

Lack of gas has in turn cramped Brazil's development of a domestic nitrogen industry in spite of its huge need for fertilizer and dependence on agricultural export commodities. Brazil's nitrogen industry has always run at a deficit, but a few

years ago Brazil had developed four nitrogen plants – two producing urea, owned by Petrobras, at Camacari and Laranjeiras, and two built by Fosfertil at Cubatao and Araucaria – the latter produced urea, but Cubatao was an ammonium nitrate plant, mainly producing industrial grade AN for the mining industry. The Fosfertil plants were bought first by mining company Vale and then in 2017 Vale Fertilizantes division was bought by North American producer Mosaic.

Petrobras meanwhile had ambitious plans to develop three new fertilizer complexes, at Linhares, Uberaba and Tres Lagoas, at a total cost of \$6.5 billion, with the strategic goal of reducing or ending Brazil's dependence on nitrogen fertilizer imports. However, the lack of additional natural gas availability, and the downturn in the economy

led to Linhares being cancelled, Uberaba being postponed and work at Tres Lagoas, where a 720,000 t/a ammonia plant and 1.2 million t/a urea were reportedly 80% complete, being halted in 2014. Petrobras further added to Brazil's nitrogen deficit in March 2018 when it closed down the Camacari and Laranjeiras plants, with a combined total of just over 1 million t/a of urea capacity. Petrobras is reportedly looking to divest its nitrogen operations, and has been in negotiations with Russian fertilizer producer Acron, who have looked at buying and refurbishing the plants, running them of gas imported across the border from Brazil.

In the meantime, however, this leaves Araucaria, with a capacity of 660,000 t/a of urea, as the only nitrogen fertilizer plant operating in Brazil. Brazil consumes about 6.0-6.5 million t/a of urea, and will now be forced to import 90% of that – 2017 imports totalled 5.4 million t/a.

Argentina

Argentina until recently had two ammonia-urea plants. The first, Bunge's Campana unit, was a small, domestic-focused plant producing 120,000 t/a of ammonia and 200,000 t/a of urea, as well as 500,000 t/a of UAN. The other, Profertil at Bahia Blanca, is a much larger plant, co-owned by Argentinian oil and gas firm YPF and North American fertilizer producer Nutrien,

and has 780,000 t/a of ammonia and 1.3 million t/a of urea capacity. The Bunge plant closed in December 2017, however, leaving Profertil as the only remaining nitrogen producer in Argentina. Around 96% of Profertil's output went to the domestic market in 2017, with the rest sold to Brazil and Uruguay. Even so, Argentina required an additional 290,000 tonnes of urea and 470,000 tonnes of UAN as imports last year. Since the Argentine government removed export taxes on cereals and other crops (except soybean) in 2015, farmers have planted more corn and wheat, increasing the demand for nitrogen fertilizers.

Argentina has been experimenting with shale gas production and has a huge shale gas deposit at Vaca Muerta in Neuquen province. Profertil is reportedly interested in this as a potential feedstock for a second nitrogen plant in the country, possibly building a second 1.3 million t/a ammonia-urea plant at its Bahia Blanca site fed from Vaca Muerta gas. So far this proposal is only a feasibility study, with Haldor Topsoe and Saipem said to be involved on the technology side. The study is reportedly due for completion by the end of the year.

Bolivia

Large natural gas fields were discovered in Bolivia in the 1980s and 90s, increasing the country's proved natural gas reserves tenfold and making it the second largest natural gas reserves in South America after Venezuela. Monetisation of these reserves was initially via a gas pipeline to Brazil, which as noted above remains critically short of gas. However, lags in developing new fields in Bolivia caused by president Evo Morales' nationalisation of the country's oil and gas industry meant that the country's gas reserves gradually shrank again as gas was piped east to Brazil and Argentina. Bolivia has reportedly begun to tackle this and is now offering licensing and partnership deals to attract more foreign investment into its oil and gas sector, currently controlled by the state-owned Yacimientos Petroliferos Fiscales Bolivianos (YPFB) company.

Developing a downstream industry took longer. A fertilizer plant was in development in Bolivia for several years before the YPFB plant at Bulu Bulu finally began construction. The plant became operational last year, producing 1,200 t/d of ammonia and 2,200 t/d of urea, although

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it has had teething troubles and several shutdowns for maintenance work. Once fully operational, surplus from the domestic market will be exported mainly to Brazil. Acron, which as noted above is looking at buying Petrobras' urea plants in Brazil and running them off Bolivian natural gas, is also looking at an offtake agreement with YFPB for urea sales into Brazil.

Chile

Chile has no nitrogen fertilizer company, but explosives producer Enaex operates 850,000 t/a of ammonium nitrate production at Mejillones for explosives production. The site began operating in 1983, and has grown to four AN trains over the succeeding decades, the most recent capacity increase being in 2010. There is no domestic ammonia production, however – ammonia is bought in to feed downstream nitric acid and ammonium nitrate production. The site's ageing ammonia plant was sold, dismantled and transported to be rebuilt in China in 2013.

The country has a more significant role in the methanol industry. It was where Methanex selected Punta Arenas in the far south of the country as a site for one of its global methanol complexes, the first plant coming on-stream in 1988. Gas was bought from across the border in Argentina, and when the first plant became operational there was plenty of local gas available. Three more methanol plants followed, of increasing size, until Methanex had 2.7 million t/a of capacity there. Unfortunately Argentina's increasing need for gas for power production and depletion from the gas fields there meant that by the early 2000s Methanex was forced to start idling plants during winter when Argentina was unable to supply gas. Methanex sought to assist local firms with offshore exploration for gas to try and help resolve this, and even considered switching to coal gasification as a feedstock for a while. However, the US shale gas boom eventually led to the company relocating two of the Punta Arenas plants to Louisiana, where they both are now operating. Methanex has considered bringing a third plant across, but for now gas exploration in Tierra del Fuego has started to pay off and the company has been able to sign a long-term gas supply arrangement that will keep at least one and possible both of the remaining plants in Punta Arenas operational.

Peru

Peru operated a small ammonia-urea plant at Callao from 1959-1992, and a small electrolysis based plant at Cusco, but by and large has had to rely upon imports for its fertilizer needs. However, ever since the development of the huge Camisea natural gas field in the 1990s, plans have been drawn up for a large-scale ammonia-urea plant to be built in Peru, with Oswal and CF Industries both developing projects in the 2000s. In 2013 another proposal crystallised into the Nitratos del Peru project, to be situated either in the northern region of Piura or the southern region of Pisco, with a capacity of 1.1 million t/a of ammonia and 1.2 million t/a of urea, only 30% of this going to domestic use and the remainder being exported. This project was put in hold in 2014, however, and has not been heard of since.

Mexico

Finally, Mexico, via state-owned Petroleos Mexicanos (Pemex), operated several ammonia and urea plants at Cosoleacaque, Veracruz state, Chihuahua and Salamanca, and two methanol plants at Independencia, Texmelucan, in the central Mexican state of Puebla. The earliest of the ammonia plants dated back to 1950, and most of the plants were of 1960s and 70s vintage. By the 1990s, however, Mexico was suffering much the same gas price rises as its northern neighbour, and the ammonia plants were forced to close due to high feedstock prices. In 1996 Mexico produced 2.5 million t/a of ammonia and 1 million t/a of urea, but by 2000 ammonia production had fallen to 920,000 t/a, and by 2005 just 500,000 t/a. Methanol production was finally stopped in 2007, and Mexico became an increasingly larger importer of ammonia, urea and methanol. In 2017 Mexico imported 1.89 million tonnes of urea.

The government has tried to refurbish plants and restart production at Cosoleacaque, but Mexico is hampered by its gas pipeline network, which does not connect southeastern Mexico to the more extensive pipeline network in the north of the country, which is able to import cheaper natural gas from the United States. Consequently, Proman AG, via its Mexican subsidiary, has proposed a new urea plant to be built at Topolobambo, Sinaloa state, on Mexico's west coast. The 770,000 t/a

ammonia and 700,000 t/a urea facility was blocked in 2015 by environmental concerns about the lagoons in the area, a World Heritage site. However, last year Mexico's environmental regulator PROFEPA had a change of heart, and in January this year Proman signed a 15 year gas supply contract and work has begun again, with start-up expected in 2021.

The elephant in the room

The US is something of the "elephant in the room" for Latin America's nitrogen and methanol producers. As natural gas prices in the US during the 1990s, so Latin American countries – especially around the Caribbean – were able to build up a domestic industry servicing the US market and monetising domestic gas reserves. However, as US gas prices fell with the spread of shale gas production, and US natural gas production rose by 50% over a decade, so mothballed plants have come back to production and new capacity has been and is being built. On the methanol side, two entire plants have been relocated by Methanex from their Punta Arenas site at the tip of Chile to Geismar, Louisiana. The US is now an exporter of LNG. Becoming a net exporter of ammonia, urea and nitrates may take longer, but construction continues. The US has added 2.5 million t/a of ammonia, 2.7 million t/a of urea and 2.8 million t/a of UAN capacity over the past few years.

On the methanol side, US production, which fell from 6.6 million t/a in 1998 to 1.0 million t/a in 2005, has risen back to 5.6 million t/a last year, while capacity has reached 7.5 million t/a. This is set against US methanol demand of around 7.0-7.2 million t/a. Completion of some new plants under construction will take the US into surplus, with several plants being built with the specific aim of exporting methanol to China's burgeoning methanol to olefins (MTO) market. This in turn puts pressure on Latin American producers, especially Venezuela and Trinidad, who have been traditional exporters to the US.

For the future, outside of isolated potential developments like Proman's plant in Mexico, refurbishment and re-start of ammonia and methanol plants in Latin America depends upon gas availability, and in Brazil, Chile, Venezuela and Trinidad this remains open to question. At the same time, demand in the region keeps on growing, making it an attractive target for exporters. ■



Ammonia safety symposium

Venkat Pattabathula reports on the 63rd American Institute of Chemical Engineers' Safety in Ammonia Plants and Related Facilities Symposium, held in September in Toronto, Canada.

This 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, ammonia nitrate, and methanol. Attendees, including plant safety personnel, plant managers, and process engineers representing a spectrum of nitrogen fertilizer based industries, all participate in the symposium, where they share technological advances and discuss 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 a variety of safety engineering problems.

This year, from September 16th to 20th, 400 delegates from more than 30 countries and 120 companies attended

the 63rd Ammonia Safety Symposium at the Sheraton Centre in Toronto, Canada. The Toronto weather was ideal for outside activities and encouraged many people to visit Niagara Falls, 120 kilometres away. Haldor Topsoe's outing also included a boat ride on Lake Ontario, which gave people a close-up view of the Canadian National (CN) Tower and views of the Toronto skyline.

The alchemy of air

The keynote speaker, Thomas Hager of the University of Oregon and the author of a book called *The Alchemy of Air*, described how, in his words, "three men turned a table top prototype into a city-sized factory in just four years". The speech attracted lot of interest among the audience as it recapped the history of the invention of synthetic ammonia production. Tom

described how Fritz Haber and Carl Bosch were the two chemists who invented the ammonia process, a way "to turn air into bread", built factories the size of small cities, made enormous fortunes, helped engineer the deaths of millions of people, and saved the lives of billions more. The third of the trio was Alvin Mittasch, who helped to develop the catalysts for the reaction.

Tom – and the global ammonia industry – believe this was the most important discovery ever made. One can't think of another that ranks with it in terms of life and death importance for the largest number of people. In the simplest terms, their discovery keeps alive nearly half the people on Earth. Most people do not know the names of either the men or their invention, but we should thank them every time we take a bite of food. Their work lives today in the form of giant factories, usually located in remote areas, that drink rivers

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2018 AIChE Ammonia Safety Committee



Front (L-R): John Brightling (Johnson Matthey), Ian Welch (PCS Nitrogen), Ahmed Esmael Rahimi (QAFCO), John Mason (Agrium), Dorothy Shaffer (Baker Risk), Scott Rodrigue (CF Industries), AK Singh (IFFCO), Venkat Pattabathula (Incitec Pivot), Eugene Britton (CF Industries). **Back (L-R):** Harrie Duisters (OCI Fertilizers), Taylor Archer (Clariant), Klaus Noelker (thyssenkrupp Industrial Solutions), Robert Collins (KBR), Neal Barkley (Coffeeyville Resources Nitrogen), Scott Rodrigue (CF Industries), Michel Warzee (Yara). **Not present:** Svend Erik Nielsen (Haldor Topsoe).

of water, inhale oceans of air, and burn about 2% of all the world's energy. If all the machines these men invented were shut down today, more than two billion people would starve to death. Think of it this way: Inside your body, every protein molecule, every cell, and every stitch of DNA includes atoms that are there because of this invention. Half of the nitrogen in your body is synthetic, the product of a Haber-Bosch factory.

Tom dived deeply into the history, and said that 80% of the atmosphere around us is nitrogen, but we cannot use a single atom of it. We breathe it in and out all day long without incorporating any of it. Atmospheric nitrogen is inert, a dead molecule, because it exists in the form of two N atoms very tightly bound to each other with triple covalent bonds. In this form, the nitrogen is unavailable for use by living organisms (with the exception of a few groups

of bacteria). To get into our bodies, to nourish us – and nitrogen is essential for nutrition; it is the fourth most common element in our bodies; proteins and nucleic acids depend on it – the atmospheric nitrogen must be “fixed,” the two N atoms torn apart and reforged into new molecules with other elements, mostly oxygen, carbon or hydrogen. Nitrogen fixation is a difficult, energy-intensive, and critical process. Haber and Bosch figured out how to do it at an industrial level in 1913. The same basic process they discovered 105 years ago is used today in scores of huge ammonia plants around the world that produce a flood of synthetic nitrogen fertilizer. That fertilizer feeds the crops that feed the animals that feed you. Thanks to Haber-Bosch factories, a bit of the almost limitless supply of natural nitrogen from the air is purified, processed, chemically

“The same basic process they discovered 105 years ago is used today in scores of huge ammonia plants around the world that produce a flood of synthetic nitrogen fertilizer.”

altered, made into fertilizer, and eventually ends up on your plate. That's why half the nitrogen in your body is synthetic.

The work of Haber and Bosch changed the chemical industry. Haber-Bosch turned Malthus on his head. Haber-Bosch is the reason our grocery shelves (in the US, at least) are groaning, more people aren't starving, and we are able to have a population explosion at the same time as an obesity epidemic.

Safety

The key safety related papers were:

Failure of HP boiler feed water pump

A catastrophic failure occurred in the main high-pressure boiler feed water pump train in an ammonia plant. The direct cause of the failure was flow reversal from the boiler feed water system and/or the steam drum, to the turbine driven high pressure boiler feed water pump. The paper presented the sequence of events and associated root causes that resulted in the failure of the pump as well as recommendations to

prevent a re-occurrence. The consequence of failure of a high-pressure BFW pump train can be significant in certain situations. Safeguards for existing systems and procedures governing pump operations should be evaluated in light of this incident.

Hot spots in refractory lined equipment

Refractory lined equipment is typically used in high temperature processes in the chemical processing industry. Degradation of refractory over time commonly leads to the development of hot spots at the pressure boundary, which may present a serious risk to the structural integrity of the equipment and can even lead to a catastrophic failure. Significant hot spots were detected on the refractory lined outlet piping system of a steam methane reformer (SMR) plant. Extensive fitness for service analyses were performed to study the impact of hot spots on the structural integrity of the piping system and to establish the safe operating limits. External cooling was applied to control the piping temperature. Rigorous temperature monitoring and inspection procedures were implemented to ensure the plant was operated within the safe limits established by above analysis. The SMR plant was successfully operated over a year with the presence of hot spots on the outlet piping system until the refractory lined piping was replaced. The successful experience demonstrated that the state of the art engineering analysis, robust monitoring and inspection procedures and a strong culture of operational discipline are essential components for safe plant operation in case an unexpected situation arises.

Rupture in high pressure drain line

This paper highlighted a critical leak incident that occurred in one of the high pressure pipes of the urea plant during an emergency shutdown, and how the situation was analysed to prevent the re-occurrence of similar incidents in urea plant. Lessons learned were:

- i. Inspecting and monitoring operating conditions of the high pressure lines periodically are critical to ensuring safe operation.
- ii. Periodically inspect insulation on high pressure pipes to ensure it is in good condition and has good sealing.
- iii. Avoid any source of chloride in urea high pressure lines to avoid stress corrosion cracking.

- iv. Time and money spent in inspection and maintaining the vessel in healthy condition will always be paid back and achieve the goal of preventing accidents and improving safety at the plant.
- v. Emergency preparedness – an emergency response team (ERT) should be available.

Urea reactor top head and diaphragm failure

During the process of urea production, multiple compounds will form that are highly corrosive to standard metals under existing process conditions. Thus, it is imperative to use the correct materials when constructing piping and vessels. When a leak developed on the head of a high pressure urea reactor in a urea plant, the cause was the failure of the diaphragm that protected the pressure containing reactor bolted head cover. The diaphragm was found to have been constructed with 316 stainless steel, rather than the correct 317L.

The diaphragm corroded and developed a pinhole leak after extended exposure to active corrosion from the top of the reactor. The failure of the diaphragm allowed the carbon steel bolted head cover to be exposed to carbamate, resulting in significant corrosion to the cover. The MTR (material test requirements) from the OEM shop that had repaired the head after the 2010 incident indicated that the diaphragm was the correct grade of stainless steel. Checking the diaphragm with a PMI tester before installation could have prevented the most recent incident.

Over-firing of primary reformer

In early 2015, when an ammonia plant was performing a hot restart, an uncontrolled and rapid increase in flue gas temperature was noticed in the primary reformer. After natural gas feed was introduced to the primary reformer, it was observed that a rupture of several catalyst tubes had occurred and the plant was tripped immediately. The company requested Haldor Topsoe A/S to take the lead technical advisor role in a thorough root cause analysis, performed to identify the reason(s) for the tube rupture incident.

The incident with ruptured tubes not only impaired plant capacity utilization until the re-tubing of the furnace, but more importantly, the leaked gas from the ruptured tube could have resulted in unsafe conditions. Following this incident, an auto-

mated over-firing protection (OFF) management system which provides four elements of protection against over-firing of primary reformer tubes was developed.

The over-firing protection management system (OFF) addresses both 'local' and 'global' causes of primary reformer catalyst tube over-heating. The current system does not allow fuel header pressure increase during start-up and enforces a symmetric burner ignition pattern. During startup, these two protection elements not only help avoiding catalyst tube over-heating but also ensures better heat distribution inside the furnace.

Moreover, double protection elements of duty and bridge wall temperatures (BWT) limitation ensure parity in duty input and duty uptake by adjusting fuel flow to the burners based on maximum estimated duty for the primary reformer at a particular capacity.

Reformer post combustion problem

After a plant revamp, poor combustion in the radiant section of the primary reformer was observed largely as indicated by measured carbon monoxide (CO). Flame patterns were irregular, including flickering with visible flame impingement on the reformer catalyst tubes. Apart from low methane conversion, poor combustion in the radiant section was also causing post combustion in the convection section where the oxygen was in excess. The post combustion was raising the convection coils' temperature too high, close to their operating limits, and thus limiting plant load.

After fabrication and installation of new burners as per the original revamped design, post combustion issues were resolved and provided significant safe operating margins. The reliability and life of the reformer has been improved in terms of lower tube metal temperatures, and elimination of post combustion which could lead to severe failures. A significant gain was also observed in furnace thermal efficiency and methane conversion.

Round table session

On the fourth day of the symposium, a roundtable session covered industry incidents, safety related systems and the Fertiliser Industry Safety Information Analysis and Sharing Program.

The 2019 Symposium will be in San Francisco, USA, from September 8th to 12th.

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ANNA 2018



Peace Bridge, Calgary, is a pedestrian bridge, designed by Spanish architect Santiago Calatrava.

A report on papers presented at the Ammonium Nitrate and Nitric Acid Producers' meeting (ANNA) in Calgary in September.

The Ammonium Nitrate – Nitric Acid producers' meeting continues to attract strong support from the industry. This year, hosted by Orica Carseland and taking place in Calgary, Alberta, just 25 km from the plant site itself, it attracted 400 delegates from 34 countries. Although the meeting had a strong North American bias, considerable numbers of delegates from Europe, Russia and Australia, and increasingly also Asia, were also present.

Precious metals

The nitric acid half of the meeting began with a series of papers on precious metals – the raw material for nitric acid catalyst gauzes and one of the major expenses in plant operation. Regine Albrecht flew the flag for the International Precious Metals Institute (IPMI), an organisation of both producers and consumers of precious metals. Her husband Bodo Albrecht, long of Degussa and now running his own consultancy company, then spoke on precious metals management within the nitric acid plant. He noted that frequent shutdowns were not just an issue of production loss, but also thermal cycling of the catalyst, shortening its lifespan, and longer campaigns were better. Precious metals also face far more restrictions on their sale and purchase these days to combat money laundering, and anyone buying more than

\$150,000 per year is now considered a 'dealer'. As a result, metal tracking balance sheets are essential, and can also help monitor trends. As for the distribution of catalyst within the plant – with 40-60% of catalyst lost over a campaign, the metal ends up nearly everywhere, but waste heat boilers are a particular concentration point for platinum. Getters, he said, were almost always worthwhile, even when palladium prices are, as now, higher than platinum (as the 40% loss ratio means that losing 0.4 oz of Pd can still gain 1 oz of Pt). Almost 20% of platinum can be retained for easy recovery, extending cleaning cycles.

Nitric acid technology

As well as tips on how best to manage a nitric acid plant revamp, Casale's Jean Francois Granger presented a nitric acid revamping scheme which added a new bleacher and 3MW air compressor parallel to the existing cooler-condenser which can increase capacity in a typical plant from 900 t/d to 1,100 t/d, and increase burner capacity with no effect on efficiency or modifications to critical equipment items.

One of those critical equipment items is the compressor train. MAN Germany have developed a new complete compressor train package for nitric acid plants which they call NAMAX (nitric acid max), as described by Stefan Ubben. This incorpo-

rates MAN's MAX1 axial blade technology which significantly increases power density, and eliminates the need for intermediate gearing between the steam turbine and NO compressor section and the axial flow compressor and tail gas expander section – these components can now be placed in modular format in any order required, with a significantly (35%) smaller footprint.

Other papers discussed chilling of inlet air to increase density and O₂ availability, especially during warmer summer months when plants often run at lower capacities, and Dan Schuler of Nutrien reviewed the optimal use of acidified water to pickle nitric acid gauzes and remove contaminants – a paper which was given the best presentation award.

NOx emissions

The perennial topic of NOx emissions from nitric acid plants as usual generated several papers. Krastvetmet, Russia's largest precious metals refiner, presented its new SKSplus catalyst gauze pack coated with rare earth oxides for primary N₂O emission reduction without decreasing NO yield. Test data presented showed N₂O concentrations reduced below 1,000 ppm for all test conditions.

Jan van Hoorn of Intertek examined the validation of automatic measurement systems for N₂O and NOx, to prove that

a plant is operating below its emissions limits. Those N₂O emissions limits are tight enough in some countries, especially in North America, that high N₂O concentrations can now often lead to plant trips, leading to a focus on how to prevent such situations. Two paper from Orica looked at their discovery of N₂O leaks at the Carseland site which had been causing plant trips, and then steps they had taken to identify the cause and redesign their reactor basket to allow a better seal of the reactor to reduce N₂O emissions.

AN markets

On the ammonium nitrate side of the conference, Luke Hutson of Fertecon gave an overview of the ammonium nitrate market. AN and AN-derived fertilizers (CAN, UAN) represent 1.6% of global nitrogen demand. Overall, 45 million tonnes of AN are produced annually, both solid and liquid, with the explosives market now accounting for up to one third of this, he said. The fertilizer market is concentrated in Europe, North America and Eurasia (especially Russia), which collectively represent about 75% of that market, while explosives are strongest in the mining areas of East Asia, Australia and the Americas. Trade, at 18% of production, is largely flat, although Russia exports significant amounts to Latin America (>2 million t/a), especially Brazil. AN prices closely track urea prices on a tonnes nitrogen basis, with gas feedstock costs providing the baseline. The industry is coming to the end of a period of rapid capacity growth, although more new capacity is scheduled for 2021-2, in China, Malaysia and the US. Consumption is growing only at around 1.1% per year, slightly higher for explosives (1.4%) over the next few years.

AN operations

There were fewer papers on the technology side this year, with most focusing on operations, especially product finishing. Borealis presented an incident in a granulation drum at Grand-Quevilly in France caused by improper sealing creating a blockage for material caught in the back shield, resulting in a re-think of drum design. NIIK presented their high speed drum granulator for ammonium sulphate nitrate forming. Stefan Kelly of Surface Chemists described work that had been undertaken to try and develop better early warning of caking in

solid ammonium nitrate, and the effect of different coatings. Jenike and Johanson expanded on the importance of flow characteristics in bulk solids handling and how flow problems can be avoided. Solex Thermal Solutions looked at the impact of additives to AN or CAN on flow characteristics and hence the design of a plate heat exchanger for product cooling. Grupa Azoty/Suez introduced a methodology for total organic carbon (TOC) determination in AN production, and AWS Corporation showcased the use of wet electrostatic precipitation to reduce dust emissions at

Lovochemie's new ammonium sulphate nitrate/CAN plant in the Czech Republic.

Next year

The meeting has for some time experimented with moving to Europe every third year, and next year will take place in Vienna in early September. Unfortunately, it has managed to clash with the Ammonia Safety Symposium once again, but I am assured by the organisers that they will be taking steps to make sure that doesn't happen again!

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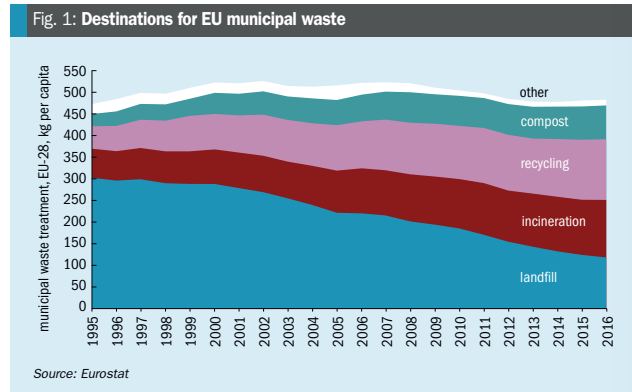
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The growing lack of landfill space in developed countries is leading to increased interest in the gasification of municipal waste to produce power, and even fuels, chemicals and fertilizer.

Waste to syngas

Above: Buckhead Mesa landfill site, Arizona.



According to the World Bank, 1.3 billion tonnes of municipal solid waste (MSW) was generated in 2010, and that figure is projected to reach 2.2 billion t/a by 2025. While recycling rates are improving in the developed world, as Figure 1 shows, even in the environmentally-conscious European Union, the average citizen generated 480 kg of waste in 2016, and only 29% of this was recycled. While Figure 1 shows that rates of disposal to landfill are falling, in some cases this has been of necessity, as suitable sites for disposal are filling up and permits to develop new sites are becoming harder to come by. In the EU, the United Kingdom, for example has begun to become a major net exporter of solid waste, exporting 3 million t/a of MSW overseas for disposal. The EU Landfill Directive has tried to divert biological/biodegradable waste into composting, recycling or incineration, with some success, but even in Europe a core of solid waste remains to be dealt with. Japan is also rapidly running out of the country's limited landfill space.

The International Solid Waste Association (ISWA) reckons that overall, some 40% of the world's waste ends up in open dump sites, which have often been prone to collapses, and more than 750 deaths at such sites were recorded in 2016 alone, including 115 at one incident in Ethiopia. Methane emissions from landfill sites can be collected to form 'biogas', but otherwise are lost to the atmosphere and contribute to climate change. Waste incineration has become an increasingly popular option for

solid waste, with the option of using the heat generated to drive combined cycle turbines to produce electricity or to heat water or steam for local district heating. However, the wide variety of waste that finds its way into MSW means that there are concerns about emissions, including dioxins and furans, sulphur dioxide and nitrous oxides, heavy metals such as mercury, and of course it contributes to carbon dioxide emissions. As a result, there has been increasing interest in the use of gasi-

fication to deal with such waste, allowing for easier clean-up of waste streams, and the generation of power or production of chemicals via syngas.

Enerkem

So far the largest and most successful installation has been at the city of Edmonton in Canada's province of Alberta. Development was via Montreal-based Enerkem, founded in 2000, which has worked up its own fluidised bed gasification process from laboratory, through pilot plant and up to commercial scale. In 2003, Enerkem began operations at a waste to fuels gasification pilot plant at Sherbrooke in Quebec, and a commercial-scale demonstrator plant followed at Westbury, also in Quebec. In 2010, the company began construction of its largest facility at Edmonton, Alberta, via its wholly owned subsidiary Enerkem Alberta Biofuels (EAB). Enerkem designed and built the plant using a modular system. Construction was complete in early 2014, at a cost of C\$80 million (US\$61 million), with 40% of the funding coming from the City of Edmonton. EAB owns and operates the plant.

The plant takes 100,000 t/a of Edmonton's MSW under a 25-year supply agreement, amounting to about 30% of the solid waste that the city generates. The non-compostable and non-recyclable solid wastes come from households and are sorted in the city's Integrated Processing and Transport Facility (IPTF), which divides the city's waste into three streams – one suitable for recycling or composting, most of the rest to going to the EAB gasification plant, and the remainder (about 10% of the total) sent to landfill.

The waste fraction heading to the gasification plant is now pre-treated (shredded) into a homogenised form suitable for the bubbling fluidised bed gasifier. The syngas stream from the top of the gasifier passes via a heat recovery step to a scrubbing and cleaning section which removes metals, sulphur compounds and other undesirable components before the cleaned syngas is sent to downstream processing sections. The Edmonton site mainly converts the syngas into methanol and ethanol, producing a total of 33,000 t/a of these products, with other side streams sent to a much smaller research facility which generates synthetic diesel via Fischer-Tropsch conversion. Some of the methanol is also converted in the research facility to dime-



Enerkem's waste to methanol facility, Edmonton, Alberta.

thyl ether (DME) and methanol to gasoline (MTG). Enerkem says that the plant will decrease the carbon dioxide footprint in Alberta by about six million tonnes during the 25 years of its operation.

Future projects

Enerkem is now working on several other projects based on the company's experience with the Edmonton plant. The first is likely to be Enerkem Varennes in Quebec, which will produce methanol and ethanol from non-recyclable residual materials from the institutional, commercial and industrial sectors, as well as construction and demolition debris. The facility will be built in two phases; first a methanol plant followed in the second phase by a plant converting methanol to ethanol. Construction is scheduled to start this year, with a total project cost of C\$280 million (US\$207 million).

In Rotterdam, Enerkem is partnering Air Liquide, AkzoNobel Specialty Chemicals and the Port of Rotterdam in waste-to-methanol facility. The partners agreed an initial €200 million funding in February 2018. The plant will be able to process 360,000 tonnes of waste per year into 220,000 t/a of methanol for use in the local chemical cluster at Rotterdam.

Finally, earlier this year Enerkem signed an agreement with China's Sinobioway Group worth over C\$125 million (US\$290 million) in equity investment in Enerkem Inc., future licenses, equipment manufacturing and sales, as well as for the creation of "a major joint venture to accelerate Enerkem's global expansion and create a joint venture to build over 100 Enerkem state-of-the-art facilities in China by 2035", according to the company.

United Kingdom

The UK is facing a shortage of landfill sites, as noted above, and so has become very interested in waste to syngas projects as a potential way of dealing with its solid waste problem; the UK Department for the Environment, Food and Rural Affairs estimates that the UK generates 40 million t/a of solid waste, and in spite of a recycling rate higher than the EU average at 45%, it still sends 15.7 million t/a to landfill (2016 figures). This has led to considerable interest in developing waste to syngas projects. However, while various proposals have been put forward, the development history has been somewhat chequered to say the least.

The largest project was Tees Valley (TV) 1 and 2 at Billingham, twin waste gasifiers in a project proposed by Air Products, with a combined throughput capacity of 700,000 t/a of waste from the northeast of England, generating 100 MW of power from syngas. However, Air Products was aiming to use AlterNRG's plasma gasification for the project, and although construction began in 2013, by 2015 as operations began at TV1, the company realised that it was going to face "significant operational challenges" in making the process work as intended. In November 2015 construction work was suspended on TV 2, which was at that stage 75% complete, and in 2016 first one and then the other trains were abandoned. Air Products tried to sell the TV 1 site but failed to find a buyer, and the company walked away from the affair with a \$1 billion write-down on the project. AlterNRG is at pains to point out that although flaws were identified, corrective action was taken, and none were "critical" flaws with the plasma gasification technology. Rather, it argues Air Products had taken a strategic decision to abandon gasification and focus on its industrial gases business as part of a reorganisation. Nevertheless, the plants remain idled.

New Earth Solutions designed, built and commissioned a 120,000 t/a waste to syngas to energy facility at Avonmouth near Bristol in 2013, designed to produce 12 MW of electricity to be sold to the UK national grid, with waste coming from the West of England waste partnership, Bath and North East Somerset and South Gloucestershire councils, as well as Blaenau Gwent and Torfaen in Wales. But technical performance issues limited output to 9-10 MW of power, and the facility ran at a loss. There were uncertainties over government commitment to renewable subsidies,

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Meeting the challenges of coal-based methanol

The challenging operating conditions of coal-based methanol plants and the economic need in recent years to build them on an ever larger scale has necessitated a technological breakthrough in methanol synthesis loop design. Casale has more than a decade of experience of coal-based methanol plants in China and shares some of its experiences.



Xinneng Energy Ltd, Xin'ao Group converter structure with steam drum on top level.

PHOTO: CASALE

Methanol synthesis loop technology heavily depends on several crucial process variables: synthesis gas composition, catalyst activity and quality, synthesis loop recycle ratio and converter operating pressure.

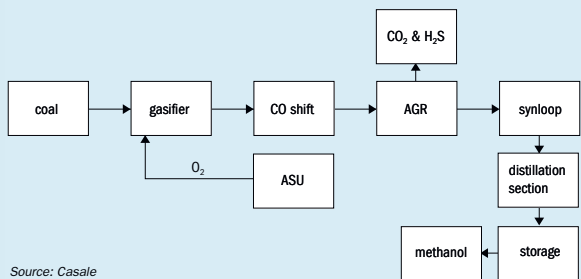
Synthesis gas composition

Natural gas is the most widely used feedstock in most of the world but, in the last decade, a sizeable methanol industry has grown up in China using coal as its source of carbon. The composition of the synthesis gas produced by steam reforming of natural gas is sufficiently different from that produced by gasification of coal to give rise to differences in the process flowsheet and engineering of the methanol synthesis loop.

Synthesis gas obtained through pure steam reforming is rich in hydrogen, giving it a stoichiometric number (SN) of about 3. This can be adjusted to approximate to the optimal value of 2 for methanol make-up gas by using combined steam reforming technology (a primary steam reforming furnace followed by an autothermal reformer).

Synthesis gas from coal gasification is too rich in carbon monoxide (CO) and carbon dioxide (CO₂); therefore, before entering the synthesis loop, it has to pass through a CO shift unit and an acid gas removal unit (see Fig. 1). In the first section, the CO is converted into CO₂ and hydrogen and then, in the second section, the surplus CO₂ and all poisoning sulphur compounds are extracted from the main stream. After these units the SN is still low (below 2), so a hydrogen recovery unit is strictly necessary to recover hydrogen from purge gases withdrawn from the synthesis loop.

Fig. 1: Coal-based methanol plant block flow diagram



Source: Casale

Table 1: Typical make-up gas composition for natural gas-based and coal-based plants

	NG-base plant loop feed composition	Coal-based plant loop feed composition
CO, mol-%	15.78	29.77
H ₂ , mol-%	73.17	66.48
CO ₂ , mol-%	6.66	3.13
CH ₄ , mol-%	3.66	0.12
Ar, mol-%	0.00	0.16
N ₂ , mol-%	0.53	0.34
SN	2.93	1.93

Source: Casale

Table 2: Comparison of typical loop performances – various feeds and processes

Syngas generation process	Steam reforming	Combined reforming	Coal gasification
Feedstock	NG	NG	coal
Specific production, MTD/m ³ cat	~15	~20	~30
Converter outlet pressure, bar g	80-100	80-100	70-90
CH ₃ OH at converter outlet, mol-%	4-8	8-12	12-17
MUG H ₂ /CO _x , mol/mol	~3.3	~2.4	~2
Circulation/MUG, mol/mol	4.5-7.5	3.0-4.0	2.5-3.5

Source: Casale

Table 3: IMC design options

	Gas-gas IMC	Steam raising IMC	Axial catalyst bed	Axial-radial catalyst bed
Steam reforming	✓	✓	✓	✓
Combined reforming	✓*	✓	✓	✓
Coal gasification		✓	✓	✓

*combined with a steam raising bed

Source: Casale

A comparison between the typical synthesis gas composition for natural gas (pure steam reforming) and coal-based plants is given in Table 1.

In natural gas-based plants the inerts content depends on the nitrogen content in the natural gas and on the methane slip at the outlet of the reforming section: it ranges from 5% to less than 1% for front-ends equipped with an autothermal reformer. For a coal-based plant it is typically less than 1% of the total gas composition. On account of its low inert gas content and low SN, coal-derived synthesis gas is more reactive than synthesis gas produced by natural gas reforming.

Catalyst activity and quality

Casale has developed considerable experience with methanol synthesis catalysts from a number of vendors, including first-class manufacturers in China, and has the versatility to be able to tailor its synthesis loop technology to whichever catalyst is to be used.

This design approach is supported by proven test procedures in an experienced laboratory. Catalysts have to comply with minimum technical requirements to assure high quality results. Casale generally reserves the right to analyse a sample of a catalyst batch either before delivery to the site or before loading in the methanol converter.

Synthesis loop performance

The synthesis loop in a plant based on coal gasification is, in principle, similar to that of a natural gas-based plant, but it has to be designed to take into account the challenges (reactivity and impurities) and opportunities (favourable composition) of the coal gasification synthesis gas.

Table 2 clearly shows the higher reactivity of the coal gasification synthesis gas in comparison with the natural gas-based synthesis gas. The coal gasification synthesis gas has a more favourable composition, which allows higher methanol production per m³ of catalyst, lower recycle ratios, less compressor power consumption and smaller-size loop equipment.

Casale process design has been focused on defining optimised conditions to reach the best compromise between investment cost and operating cost in each scenario.

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IMC (Isothermal Methanol Converter)

Converter design is very important in coal-based methanol plants. The fact that the make-up gas of coal-based methanol plants normally has a low inert content and is rich in carbon makes it possible to achieve high production rates with low recycle ratios and low catalyst volumes, however, as the gas is very reactive, it can easily create problems with catalyst overheating and hot spots in the converter.

The technical basis of Casale's methanol converter development is governed by the characteristics not just of methanol formation reactions but also of undesired side-reactions. These reactions need a high temperature to take place but are significantly exothermic and, if uncontrolled, could raise the temperature to the point where the catalyst is damaged. Therefore the heat of reaction has to be efficiently removed to optimise methanol generation and avoid unstable process conditions in the converter. The only practical way of removing heat in this kind of system is through a heat exchanger, and the Casale Isothermal Methanol Converter (IMC) combines the functions of a reactor with those of a plate heat exchanger (see *Nitrogen+Syngas* no. 352 pp. 51-54).

The choice between an axial or axial-radial flow path through the catalyst bed has to be based on a complete analysis of loop performance. Where it can be used, the axial-radial approach is preferred as it avoids the extra capital cost of installing multiple axial reactors.

Table 3 provides a summary of the IMC design option offered by Casale, according to feedstock.

Casale has successfully used axial-flow catalyst beds in coal-based methanol plants of up to 2,000 t/d capacity, reaching a satisfying compromise between pressure drop and vessel size.

For higher capacities from 2,500 t/d up to 10,000 t/d, a single, plate-cooled reactor with axial-radial layout is typically used. This minimises pressure drop but also allows a larger quantity of catalyst to be installed without raising the catalyst bed height above the limit set by the catalyst manufacturer. As long as the converter does not exceed transportation size limits, the main advantage of Casale's axial radial technology is the possibility of installing one single reactor instead of more than one axial converters in parallel.

Chinese experience

In the last decades, Casale has acquired wide experience in coal-based methanol plants in the Chinese market. Casale has designed 18 coal-based methanol synthesis loops with capacities ranging from 1,350 t/d to 4,000 t/d. Besides the challenging conditions already mentioned, Casale has also encountered other peculiarities in Chinese coal-based methanol plant projects as described below.

Synthesis loop make-up gas**Poisons**

Synthesis gas formed by coal gasification can contain poisons for methanol synthesis catalysts, such as arsenic and sulphur. These components originate as impurities in the coal feedstock, and during partial oxidation in the gasifier a portion of them is volatilized into the raw synthesis gas. They will normally be washed out in the acid gas removal section upstream of the synthesis loop, but upsets, mal-operation or under-performance of this unit may leave unacceptable concentrations of them in the gas.

As these substances poison the catalyst irreversibly, it is advisable to protect the catalyst by providing a guard bed on the make-up gas. The type of guard bed that is most frequently installed protects the synthesis loop from sulphurous components. It can be installed either at the suction or at the discharge of the synthesis gas compressor (before the circulator) and can work at a temperature above 100°C. A common vessel contains a layer of hydrolysis catalyst and a layer of zinc oxide catalyst. Usually the guard bed catalysts installed in Casale plants are manufactured in China, so they can be easily purchased by clients in the domestic market.

High CO content

High carbon monoxide concentration in the make-up gas may lead to the formation of metal carbonyls, which can reduce catalyst activity as well as promote undesired side reactions such as generation of waxes. Metal carbonyls can be prevented from forming by using appropriate equipment and piping metallurgy in the areas where carbon monoxide concentration is high and the temperature is in the range 100-200°C.

Low inert contents and low SN

The SN of synthesis gas produced in a natural gas-based plant is high: this means that it contains a substantial excess of hydrogen

over that prescribed by the methanol synthesis reaction stoichiometry. Together with inerts, the surplus hydrogen acts as a 'thermal buffer', reducing the total effective heat to be removed in the methanol reactor.

In a coal-based plant the content of inert gases (Ar, N₂, CH₄) in the synthesis gas at the converter inlet is very low: typically it is in the range 5-10%, while in a purely steam reforming natural gas-based plant it is generally higher than 15-20%. Since the SN and percentage of inert gases are both very low in a coal-based plant, there is no such 'thermal buffer', so the characteristics of the cooling medium and the specific heat exchange surface in the converter must be adequate for these challenging operating parameters.

By product formation

The high activity of the make-up gas in a coal-based plant, resulting from the high content of carbon oxides and low CO/CO₂ ratio at the converter inlet, promotes the formation of higher alcohols, especially ethanol. These chemicals are by-products and have to be removed from methanol in the distillation section if grade AA quality is desired.

On the basis of capex-opex parametric analysis and, especially, on operating experience acquired in Chinese projects, the best compromise between the capital cost of the synthesis loop and that of the distillation section has been selected: Casale has identified a design for the IMC and synthesis loop that minimises equipment size and running cost but, at the same time, reduces the concentration of higher alcohols in crude methanol and, thus, the column dimensions and capital costs in the distillation section. The peak temperature in the catalyst and, consequently, the formation of unwanted by-products can, of course, be reduced by increasing the recycle ratio and specific heat exchange surface in the IMC and increasing the CO₂ content in the make-up gas, but the additional capital and operating costs that these measures entail in the synthesis loop have to be compared carefully with the corresponding savings that are likely to result in the distillation section.

Reference

1. Muscionico I., Moreo P., Poletti R. and Bramé M.L.: "IMC technology for large coal-based methanol plants: A breakthrough", Casale Innovation Meets Experience Symposium, Venice (Oct 2016).

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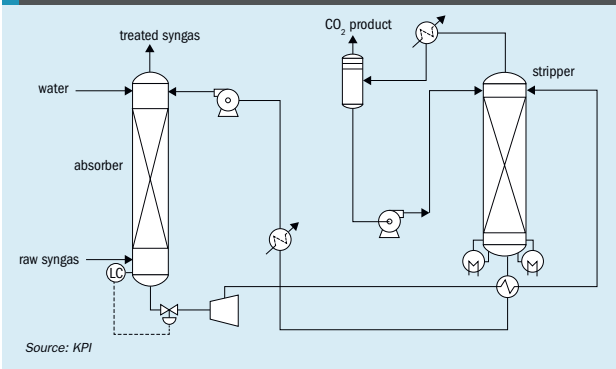
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Revamping for lower CO₂ slip

High CO₂ slip is a common problem experienced in ammonia plants. **V.K. Arora** of Kinetics Process Improvements, Inc. (KPI) discusses the cost-effective revamp experience of a CO₂ removal system of an ammonia plant with an attractive payback of just a few months.

Fig. 1: MDEA: piperazine CO₂ removal scheme



Source: KPI

An ammonia plant with an MDEA-based CO₂ removal system was earlier converted from an old MEA-based system as a part of the overall ammonia plant capacity revamp from the original nameplate capacity of 600 short t/d to approximately 1,100 short t/d. The original absorber and stripper columns were used with trays replaced with packings and other internals.

Fig. 1 shows the existing single-stage MDEA CO₂ removal system scheme.

The current operating capacity is 1,140 short t/d to 1,170 short t/d depending on the seasonal variation. This plant was well stretched to its design limits and beyond and experienced excessive CO₂ slip (up to 3,000 ppmv) at increased rates resulting in reduced plant efficiency.

A holistic review of the complete CO₂ removal system was carried out by KPI along with field measurements to identify

all the potential bottlenecks contributing to a shortfall in the performance. To support this, the following steps were taken:

- gamma scan of the columns to determine any maldistribution;
- representative operating data corresponding to the max operating capacity;
- reconciliation of the operating data;
- simulation of the existing scheme to match the reconciled operating data;
- evaluation of potential bottlenecks at the current operating conditions:
 - mass transfer limits of the existing packing type and height;
 - adequacy/limitations of the liquid distributor;
 - adequacy/limitations of feed vapour distributor;
 - hydraulic adequacy/limitations of the solvent circulation loop;
 - solvent and activator concentration for optimal performance.

Following this, several cost-effective and practical options were identified to reduce CO₂ slippage to a target value of less than 300 ppmv at the current capacity along with its maximum capacity of 1,170 short t/d and future capacity of 1,250 short t/d. A combination of new efficient packing and new distributors along with the increase in circulation were not enough to meet this target due to mass transfer limitations. To support the performance targets, the absorber column was closely reviewed for an increase in the packing height with different configurations.

Figs. 2 to 5 show the base operating performance at 1,140 short t/d as modelled and reconciled with the actual operating performance. The gamma scan of the absorber (Fig. 2) indicates the liquid density variation profile, with a variation of between 8 to 15 units indicating maldistribution. The absorber operating at ~85% flood while the stripper has enough hydraulic capacity available is shown in Fig. 5. The absorber temperature profile in Fig. 3 seems reasonable, while the CO₂ concentration profiles in Fig. 4 indicates approximately 2,600 ppmv of CO₂ slip.

Potential causes of high CO₂ slip

Based on the initial evaluation, the absorber column indicated the major limitations resulting in performance shortfall. The potential causes identified in the absorber system were:

- liquid maldistribution determined by gamma scan;
- undersized liquid distributor in the absorber leading to maldistribution;
- high momentum through vapour distributor in absorber leading to maldistribution;
- mass transfer limitations due to short packing height and incorrect loading;
- hydraulics and mass transfer limitations of the existing packing.

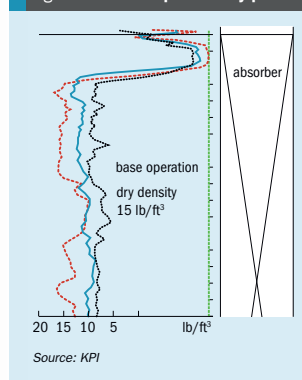
The stripper column did not indicate any hydraulic or mass transfer limitations or any performance issues.

Options to reduce CO₂ slip

In the next step, several options were evaluated with relevant inputs gathered from vendors. The following options were further simulated and reviewed for improved performance including cost-benefit analysis:

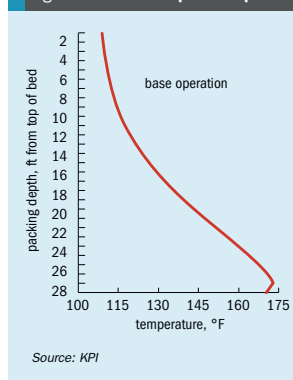
- new efficient packing configurations with improved mass transfer and hydraulics;

Fig. 2: Absorber liquid density profile



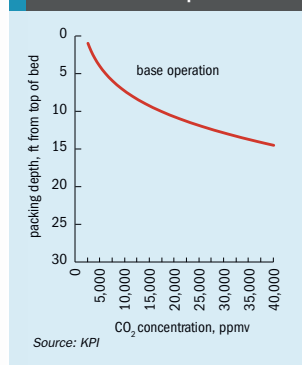
Source: KPI

Fig. 3: Absorber temperature profile



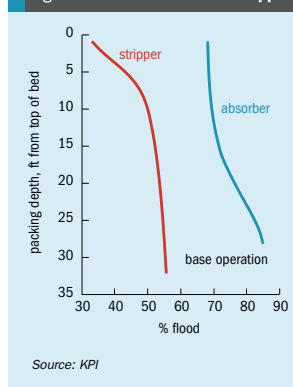
Source: KPI

Fig. 4: Absorber vapour CO₂ concentration profile



Source: KPI

Fig. 5: % flood-absorber and stripper



Source: KPI

- increase in packing height, as noted later for different options;
- new liquid distributor;
- new feed vapour distributor;
- increase in circulation rate;
- optimise solution concentration.

New liquid distributor

The existing trough-type V-notch liquid distributors were inadequate and considered less efficient for the service conditions. They were replaced with new efficient orifice-deck distributors, rated with sufficient design margin over the new service conditions for both the current and future operating cases. Most importantly, the new distributors were designed for installation and removal through the existing 17-inch manways to facilitate correct loading of packing.

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New feed vapour distributor

The existing feed vapour distributor was also found to be inadequate with a much higher momentum than recommended and also insufficient coverage of the cross-section. It was replaced with a T-type lateral distributor, rated with sufficient design margin over the new service conditions for both the current and future operating cases. Most importantly, the new distributors were designed for installation and removal through the existing 17-inch manways.

Increase in circulation and hydraulics adequacy

Increasing the solvent circulation rate was reviewed along with complete hydraulics evaluation of the lean circuit along with the

lean MDEA pumps with a clear premise not to replace any of the existing pumps and its drivers. Interestingly, a marginal increase in circulation rate was possible with the replacement of the existing impellers with the maximum possible size well within the maximum design rating of the existing drivers. Further, the impact of the higher circulation rate was also evaluated for both absorber and stripper columns with new packing type, size, and different bed configurations.

Impact of solvent concentration

Maintaining an optimal concentration of piperazine is quite important to reduce the CO₂ slippage. The optimal concentration of piperazine will vary depending on various factors including the MDEA concentration, CO₂ loadings, lean solvent temperature, vapour-liquid loads in the columns, etc.

New efficient packing

To improve the limitations of both mass transfer and hydraulics in the absorber, new and efficient packings from two reputed suppliers were evaluated with extensive in-house modelling for their quantitative impact on performance. The improved hydraulics with the selected new efficient packing with increased packing height (127% of the existing) is shown in Fig. 6 and compared with the hydraulics of the existing packing for both base and future. The hydraulic capacity of the absorber indicates a substantial improvement with new efficient packing.

New packing configurations

The latest and most efficient proven packings from two reputed suppliers were reviewed and modelled to evaluate their impact on CO₂ slip and hydraulics. A combination of split bed with two different packing sizes, with and without liquid redistributors, were also reviewed. Based on the detailed evaluation and modelled performance, it was decided to proceed with only one deeper bed for the most value.

Incremental packing height and practical constraints

The existing packing height was determined to be a limiting factor to achieve the target CO₂ slip despite changes with the most efficient packing and the vapour-liquid distributors along with optimised solution concentration. Therefore, several options

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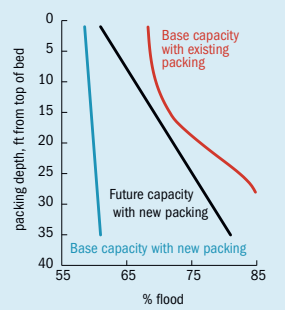
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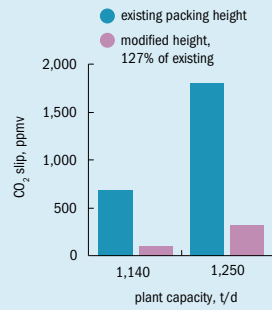
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Fig. 6: % flood absorber new and old packing



Source: KPI

Fig. 7: New packing and distributor performance estimate



Source: KPI

- base capacity (1,140 short t/d)
- future capacity (1,250 short t/d)

The additional packing height provides a significant reduction in CO₂ slip to achieve CO₂ slip well below 300 ppmv for the base capacity and <500 ppmv for the future capacity as indicated in the Fig. 7.

Incremental ammonia production

Reducing CO₂ slip benefits ammonia plant efficiency with a proportionate increase in ammonia production for the same amount of feed gas as used with high CO₂ slip. Incremental ammonia production with improved performance of the CO₂ removal system for the base operating capacity and the future operating capacity are estimated and shown in Fig. 8. It indicates a capacity and efficiency improvement of approximately 2.4% for the base case and approximately 3.6% for the future case.

Economics of CO₂ removal system upgrade

Based on the modifications being carried out and the expected performance improvements, the payback period for the base capacity is estimated to be less than eight months and the payback for the future capacity to be less than four months, as shown in Fig. 9. The basis of this estimate is the incremental ammonia production relative to the base ammonia production corresponding to high CO₂ slip for the two capacity cases and median net-back on ammonia.

Additional CO₂ removal schemes

Another MDEA-based two-stage CO₂ removal system has also been reviewed for high CO₂ slip and corrosion. The recommended changes are planned to be implemented in the turnaround next year. ■

Table 1: Options investigated to maximise packing bed height

Option	Packing height	CO ₂ slip target	Bed configuration	Tower modifications
Base	100% base	way below target	single	wall clips
1	112%	below target	single	wall clips
2	123%	closer to target	split bed	wall clips, complex supporting
3	127%	meets target	single bed	wall clips and ring

Source: KPI

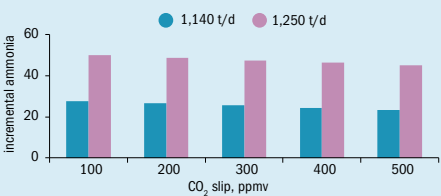
to maximise the packing bed height were closely investigated (see Table 1) with all the practical constraints for this old column.

The studied options along with the inspection history were jointly reviewed with the customer's operations, engineering as well as their construction group to select the most suitable practical option. It was decided to pursue the maximum height option 3 with some hot work within the absorber column. The selected option is currently in the implementation phase with all the hardware already ordered.

Estimated performance improvements

The new performance of the CO₂ removal is estimated using the new efficient packing, new efficient vapour and liquid distributors and an optimised solution concentration. The performance with new internals/packing with optimised solvent is further compared for two capacity cases using the modified packing height (127% of the existing packing height) in the existing absorber to provide the most value with the least cost. The two capacity cases compared are:

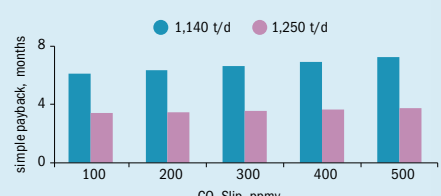
Fig. 8: Incremental ammonia production with reduced CO₂ slip*



* No additional feed

Source: KPI

Fig. 9: Payback estimate of modifications



Source: KPI



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The important role of DEA promoter in Benfield systems

Utilising the ProTreat® simulator, **R.H. Weiland, G.S.A. Weiland** and **M. Bailey** of Optimized Gas Treating, Inc. have investigated how DEA affects CO₂ removal in hot potassium carbonate solutions. It was found that if the CO₂ unit is properly designed, what really determines treated gas quality is the performance of the regenerator, which can be greatly improved by using DEA.

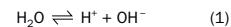
Hot potassium carbonate processes (also known as "Hot Pot" or Benfield) for carbon dioxide removal in ammonia production are characterised by both absorbers and regenerators running very hot (typically ranging from 100-130°C) so that heat integration in the form of large lean-rich cross exchangers is unnecessary. Regeneration is driven by a pressure swing from a high absorber pressure to a low regenerator pressure, but is aided by steam stripping, as opposed to the temperature swing and predominantly steam stripping typical of amine systems. Nevertheless, removing CO₂ remains energy intensive, and a variety of conservation schemes is used.

High temperatures in CO₂ service make for a very corrosive environment. To avoid the use of corrosion inhibitors, vessels are usually stainless clad and process piping is also stainless. Characteristically, the absorber and regenerator tend to be very tall (50-60 m overall) holding five or six beds of random packing, each between five and eight metres deep. Indeed, as will be seen, these towers tend to be grossly over height.

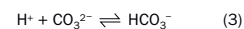
Process chemistry

Aqueous potassium carbonate and bicarbonate exist exclusively as K⁺, HCO₃⁻ and CO₃²⁻ ions. When CO₂ dissolves into water it forms carbonate and bicarbonate ions, and very little is present as molecular CO₂. Hot potassium carbonate solutions are an ionic soup and the notion that these ions are associated with each other in the

form, for example, of K₂CO₃ is quite fictitious. Carbon dioxide hydrolyses in solution with the hydroxide ion available from dissociated water:

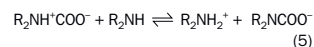
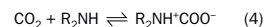


The hydrogen ion that remains after hydrolysis immediately and instantaneously reacts with carbonate to form bicarbonate:



Potassium is merely a spectator ion. It takes no part in any reactions and, beyond affecting the ionic strength of the solution and its non-ideality, potassium itself has no effect on the solubility of CO₂ in Hot Pot solutions. The vapour-liquid equilibrium associated with the solubility of CO₂ in Hot Pot is modelled in the ProTreat® simulator on the basis of a concentrated solution of electrolytes.

The rate of the CO₂ hydrolysis reaction (reaction 2) is fairly slow because the OH⁻ ion concentration is low, and CO₂ is a sparingly soluble gas. This leads to quite tall absorption and regeneration towers without a promoter. DEA is a secondary amine and reacts readily with CO₂, so its addition to carbonate solutions tends to speed up the absorption process considerably. DEA reacts with CO₂ according to the simplified scheme:



Reaction 4 occurs at finite rate while reaction 5 involves only a proton transfer and so is instantaneous. Apart from the three molecular species CO₂, DEA, and of course water, the solvent again is an electrolyte soup and when combined with Hot Pot, the correct way to determine CO₂ solubility is with an electrolyte model. This is the way ProTreat simulation does phase equilibrium calculations.

The amine of choice for promoting Hot Pot is DEA. As a secondary amine, DEA binds less strongly to CO₂ so carbamate decomposition in the regeneration step requires less energy. MEA reacts faster with CO₂, which for the same molar concentration would enhance the absorption rate; however, the cost is a higher regeneration energy requirement compared to DEA, and MEA's absorption rate advantage can be easily achieved using DEA with a small amount of additional packing. As will be seen, a small amount of DEA also somewhat lowers the CO₂ equilibrium backpressure over the treating solution.

Fractional conversion

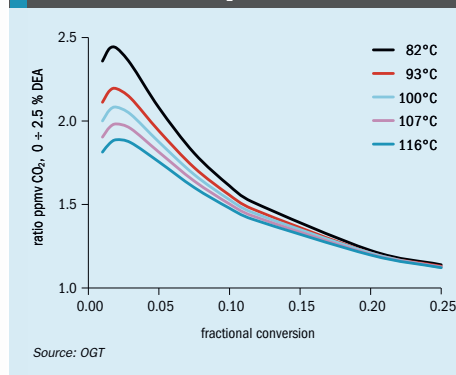
Fractional conversion, Fc, is the extent to which a carbonate solvent is saturated with CO₂:

$$F_c = \frac{\frac{1}{2} [\text{KHCO}_3]}{[\text{K}_2\text{CO}_3]_0} \quad (6)$$

If the solvent is promoted with DEA, then fractional conversion is:

$$F_c = \frac{\frac{1}{2} [\text{KHCO}_3] + [\text{DEACOOH}]}{[\text{K}_2\text{CO}_3]_0 + [\text{DEA}]_0} \quad (7)$$

Fig. 1: Effect of DEA on CO₂ in gas at equilibrium



Source: OGT

Table 1: Condition of raw syngas entering absorber (dry basis, stream 3)

Parameter	Value
Temperature, °C	124
Pressure, barg	31
Flow, Nm ³ /h	160,000
Composition, mole %	
Carbon dioxide	17.4
Methane	0.90
Hydrogen	60.6
Carbon monoxide	0.17
Nitrogen	20.7
Argon	0.23

Source: OGT

The subscript 'o' signifies the concentration of the component in the completely CO₂-free state, i.e., the fresh solvent before it has been exposed to carbon dioxide. The DEACOOH molecule is equivalent to R₂NCOO⁻ in reaction 5. These definitions are the exact equivalents of the term 'loading' as used in amine treating in the natural gas and refining industries.

Effect of DEA on equilibrium solubility of CO₂ in Hot Pot

The ProTreat® simulator was used to develop solubility curves for CO₂ in Hot Pot with and without DEA. The cases considered were 30 wt-% K₂CO₃ and 30 wt-% K₂CO₃ + 2.5 wt-% DEA because the latter corresponds to the solvent formulation in the case study to be considered later. Fig. 1 shows the extent to which 2.5% DEA reduces the CO₂ backpressure at absorber lean-end conditions. Fractional conversions between 0.1 and 0.25 have CO₂ levels in the gas between 100 and 3,000 ppmv. Using 2.5 wt-% DEA reduces equilibrium CO₂ pressures between 10 and 40% (i.e., the ppmv ratio is 0.6-0.9). As it turns out, this is a significant but not a large effect compared with the effect of the DEA reaction on absorption, and especially regeneration rates.

Case study - 1,000 t/d ammonia plant

This case study is based on a 1,000 t/d ammonia plant. The CO₂ section uses the two-stage DEA-promoted Hot Pot system shown in Fig. 2. The simplified drawing

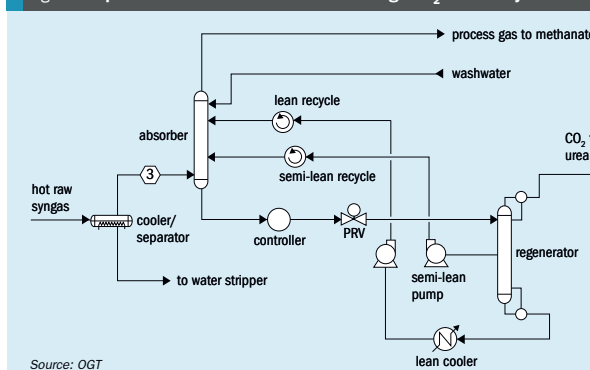
omits several energy conservation measures but retains the features essential to the discussion. Table 1 shows the parameters pertinent to the raw ammonia syngas (stream 3).

Both towers contained more than one type and size random packing in multiple beds. The absorber had two water wash trays at the top, and a total of 32 m of

packing distributed roughly equally between the lean (2,600-mm diameter) and semi-lean (4,250-mm diameter) tower sections. The regenerator was 5,000 mm diameter above the semi-lean draw point holding 25.6 m of packing and 3,050 mm diameter in the lean section with 18 m of packing.

This plant actually operates with 30 wt-% potassium carbonate and 2.5 wt-%

Fig. 2: Simplified schematic of a Benfield two-stage CO₂ removal system

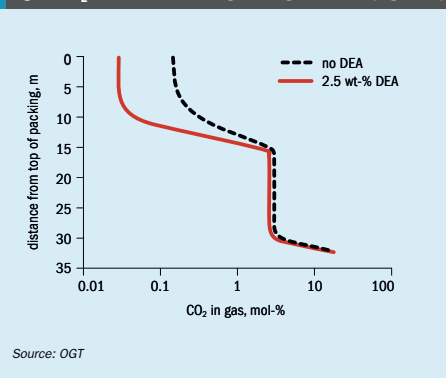


Source: OGT

Table 2: System performance using promoted vs. non-promoted Hot Pot

	DEA-promoted	Non-promoted
CO ₂ in treated gas, ppmv	350	1,530
Lean solvent fractional conversion	0.116	0.203
Semi-lean fractional conversion	0.541	0.563
Rich solvent fractional conversion	0.691	0.739

Source: OGT

Fig. 3: CO₂ concentration change through absorber (log scale)

DEA and the performance parameters predicted by the ProTreat® simulator were very close to measured data without the need for any adjustment or manipulation of any parameters to achieve agreement between simulation and measurement. In other words, the simulation is fully predictive without adjustable parameters. The same unit was simulated without DEA, all other parameters being identical between the two cases. The effect of DEA on overall performance of both absorber and regenerator is summarised in Table 2. Obviously, using 2.5 wt-% DEA provides a very satisfactory synthesis gas.

Non-promoted Hot Pot leaves enough additional CO₂ in the treated gas to result in roughly a 7.4 t/d loss in ammonia production. At the notional value of \$300 per tonne, this lost production is worth about \$2,220 daily in unrealised revenue. However, hydrogen makeup and energy are additional costs and, when these are factored in, the cost of the additional CO₂ slip is really about \$7,800 per day for this size plant. The question is what is happening in the columns to produce these not insubstantial differences.

Absorber

Fig. 3 shows and compares how CO₂ concentration is changing across the absorbers in the two cases. Apart from the obviously lower CO₂ slip with DEA promotion, there are several other notable observations.

Firstly, regardless of promotion, the full benefit of using a semi-lean stream is realised in the bottom 5 m of packing – the

next 12 m do absolutely nothing towards removing CO₂. Also the benefit of promotion is fairly small in the semi-lean section (lower half of the plot) because the fractional conversion is already high there, thus, most of the DEA has already been converted to carbamate.

The differences in the lean section of the absorber (upper half of the plot) are more striking. Without DEA promotion, CO₂ continues to be slowly removed across almost the entire lean (polishing) section. However, the addition of 2.5 wt-% DEA drops the CO₂ concentration to 350 ppmv so quickly that now the top five metres of packing are not even needed. Of perhaps greater value is knowing that the lean section is completely lean end pinched. This means simply that the final treating is determined by the lean solvent's fractional conversion. If there is enough packing in the absorber and if the split between lean and semi-lean sections is properly chosen, this will almost invariably be the case. This absorber (like many Benfield absorbers) is over-packed and over-height by about a factor of two; however, these profiles suggest that where one's attention should really be focused is on the regenerator because it is there that the lean and semi-lean solvents are produced.

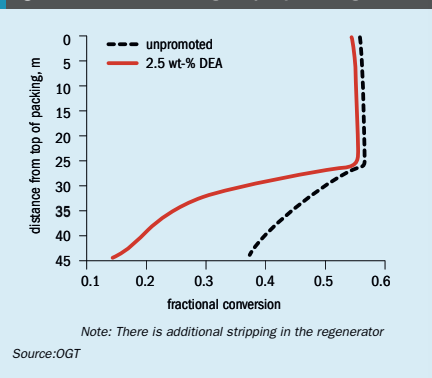
Regenerator

Fig. 4 shows how CO₂ strips out and reduces the fractional conversion to its final value in the lean solution as the solvent flows through the regenerator. In both cases a large fraction of the dissolved CO₂ in the loaded solvent flashes off in the PRV

(21.4% when promoted, 24.7% when not). As the solvent flows down the top 25 m of packing, no stripping at all takes place – the upper section might as well not be there! Indeed, the upper 25 m of packing, all the auxiliary internals such as distributors, and the 30 m or so of tower shell are an unnecessary capital investment. The primary reason for this is that the stripping steam is metered to provide proper stripping of the 10% of the total solvent flow that actually reaches the lean (lower half) section. The other 90% could be immediately withdrawn as an essentially flashed semi-lean solvent without entering the regenerator at all. Although it is contacted by a flow of stripping steam, the steam flow is inadequate and quite incapable of having a significant effect.

Below the semi-lean draw point the vapour-to-liquid flow ratio is high enough for the stripping vapour to actually strip CO₂ from the solvent. However, it is easy to see from Fig. 4 that CO₂ strips from DEA-promoted Hot Pot a lot more easily than from its non-promoted equivalent. With the non-promoted solvent, there are no reactions to enhance mass transfer – stripping is purely a physical process. With DEA promotion, however, the decomposition of DEA carbamate enhances the mass transfer rate of stripping by factors of from four in the semi-lean section up to 70 at the bottom of the lean section, and the lower the fractional conversion, the greater the enhancement to the stripping rate. Thus, the fractional conversion of the fully stripped DEA-promoted solvent is nearly one-half the non-promoted value (0.116 versus 0.203).

Fig. 4: Promotion with DEA greatly improves regeneration



Note: There is additional stripping in the regenerator
Source: OGT

Summary

There are a number of little-known (perhaps unknown) characteristics of Hot Pot and DEA-promoted Hot Pot that have a profound effect on the potential economics and efficacy of CO₂ removal using standard Hot Pot and Benfield processes. This article has discussed only one specific example of the CO₂ removal section of an ammonia plant; however, the operating conditions in this case are fairly typical, and the observations and conclusions have general validity. In particular the ProTreat® mass transfer rate-based simulator was used to show the effect of spiking a 30 wt-% Hot Pot solvent with 2.5 wt-% DEA on (1) CO₂ solubility, (2) absorber performance, and (3) regenerator performance:

- The equilibrium CO₂ partial pressure over the promoted solvent may be as low as one-half the value in the non-promoted case. However, the effect is already weakening when fractional conversions approach values typical of treating with Hot Pot and Benfield technologies ($F_c \approx 0.1$), and it weakens further as fractional conversions get even higher.
- The main effect of DEA is on the mass transfer (absorption and stripping) rates in both the absorber and regenerator as actualised by reaction kinetics enhanced by DEA.
- In an absorber, only the bottom few metres of packing in the semi-lean (bulk removal) lower section are useful for CO₂ removal. About the upper two-thirds provides no treating whatsoever.
- In the lean (gas polishing) upper section of the absorber, using DEA can reduce the amount of packed height needed for treating or it can extend the lean-end pinch region to insulate the column from process upsets. Even without DEA, the entire polishing section performs useful work.
- Benfield absorbers frequently contain at least twice the amount of packing that is actually needed.
- In a lean-end pinched absorber, the quality of the treated gas is determined almost solely by the fractional conversion of the lean solvent, i.e., by regenerator

performance, provided other operating conditions are what they should be.

- In the case examined here, the regenerator section used to produce semi-lean solvent could as well be replaced by a flash drum, saving about half the tower height.
- The presence of DEA allows the fractional conversion of the fully-lean to be reduced by a factor of two. This permits much cleaner syngas to be produced without incurring more than the cost of the additive.

With the exception of the effect of DEA on equilibrium CO₂ partial pressure, all the other findings are a direct result of using the ProTreat simulator's true mass and heat transfer rate-basis in the analysis. Without doing these calculations on a rate basis, none of these observations could have been made. There is no substitute for a simulator that does all calculations rate-based, without approximations or simplifications.

Perhaps the most important finding is that if the CO₂ unit is properly designed, what really determines treated gas quality is the performance of the regenerator, which can be greatly improved by using DEA as a promoter. ■



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The GV low-energy CO₂ removal processes

Giammarco-Vetrocoke's CO₂ removal processes have a long history. **L. Tomasi** of Giammarco-Vetrocoke describes the continuous developments to the GV low-energy regeneration processes, focusing on the main improvements and key benefits of the different process schemes.

Giammarco-Vetrocoke (GV) has been a leading licensor of CO₂ removal processes based on activated hot potassium carbonate (HPC) solutions since 1955 and has built up a reference list of more than 365 applications worldwide.

GV has placed significant focus on the continuous improvement of the CO₂ removal processes with the target to minimise energy consumption and maximise feedstock utilisation by optimising plant reliability and operation in new and/or revamped units.

In the field of CO₂ removal energy and/or capacity revamp, GV plays a leading role in the world with 95+ applications, including the GV processes as well as competing processes.

GV low-energy dual pressure regeneration (DPR)

The GV low-energy DPR process has been in commercial use since 1980 and has been extensively proven in 70+ new and/or revamped CO₂ removal units.

The simplified process flow diagram of a standard two-stage CO₂ absorption/regeneration system based on the GV low-energy DPR process is shown in Fig. 1.

The DPR process is based on the use of two strippers operating at different pressures, the HP (high pressure) stripper and the LP (low pressure) stripper.

The revamping of an existing conventional CO₂ removal system to the GV DPR process is achieved by implementing a new LP stripper operating in parallel to the existing HP stripper.

A particularly attractive configuration for revamp to the GV low-energy system comprises plants that have been originally designed with twin strippers operating in parallel. These plants can be profitably converted to the GV DPR process by

utilising the existing strippers as LP and HP strippers.

The rich solution from the bottom of the CO₂ absorber is shared between the HP stripper (about 60% of the total circulation amount) and the LP stripper (the balance).

The heat for the solution regeneration is supplied to the HP stripper only by process gas reboiler(s) and/or by direct or indirect LP steam.

The semi-lean solution withdrawn from the mid zone of the HP stripper feeds the mid zone of the LP stripper, from which, after releasing steam by flashing, it is recycled to the lower zone of the CO₂ absorber.

The lean solution withdrawn from the bottom of the HP stripper feeds the bottom of the LP stripper and, after releasing steam by flashing, is cooled and recycled to the top of the CO₂ absorber.

The LP stripper operates autogenously with the steam flashed from the incoming

lean and semi-lean solutions when they are depressurised flowing from the HP stripper to the LP stripper.

The pressure difference between the HP and LP strippers (typically 0.80-0.90 kg/cm²) is such that sufficient flashed steam is produced to strip out the CO₂ from the rich solution fed to the LP stripper achieving a similar fractional conversion (FC), before mixing with the semi-lean solution withdrawn from the HP stripper.

GV low-energy multi flash regeneration (MFR)

The GV low-energy MFR process is an improved configuration of the DPR process profitably applied in the revamping of low-energy CO₂ removal processes operating with the multi stage flash tank ejector system. Four CO₂ removal system based on competing HPC processes have

Fig. 1: GV low energy DPR process

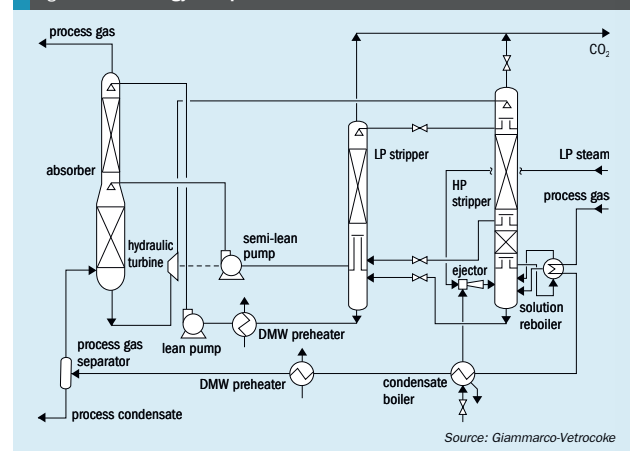


Fig. 2: Simplified PFD based on GV low energy MFR process

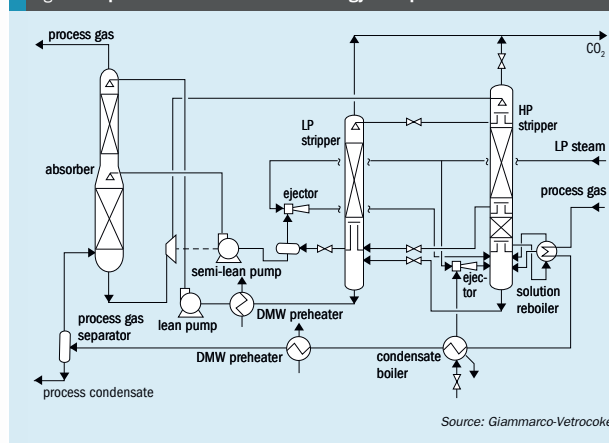
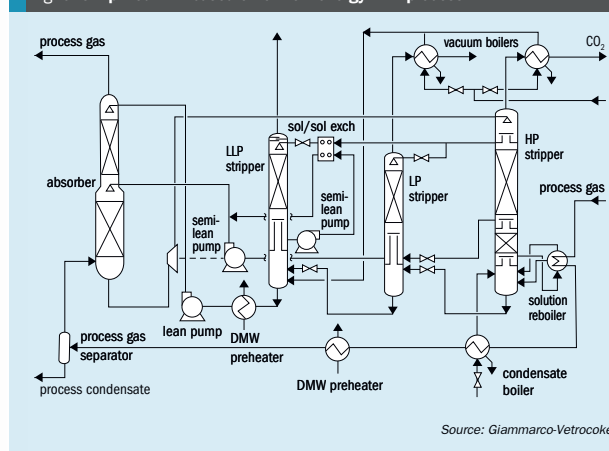


Fig. 3: Simplified PFD based on GV low energy VPR process



been converted to the GV low-energy MFR process.

A simplified process flow diagram of a standard two-stage CO₂ absorption/regeneration system based on the GV low-energy MFR is shown in Fig. 2.

The revamped configuration is achieved by implementing a new stripper LP in between the existing HP stripper and the flash tank.

The HP and LP strippers are operated at different pressures by retaining the existing flash tank for a final mild flash of the semi-lean solution withdrawn from

the LP stripper upstream of the circulation pump. The final flashed steam is recombined by a steam ejector to the bottom of the HP stripper.

The MFR process is an attractive revamping option easily achieving 10% energy saving over the DPR process at a very low capex by reutilising existing equipment.

GV low-energy vacuum pressure regeneration (VPR)

The GV low-energy VPR process is a substantial evolution of the MFR process

where the final flash tank is replaced by a low-low pressure (LLP) stripper operating under mild vacuum.

The simplified process flow diagram of a standard two-stage CO₂ absorption/regeneration system based on the GV low-energy VPR is shown in Fig. 3.

The concept of the GV low-energy VPR process is based on the implementation of the final regeneration stripper LLP operated under vacuum which, by reducing the boiling point of the lean solution below 100°C (typically 80-90°C), allows heat to be recovered at low temperature from the top head of the HP and LP stripper to produce LP steam at low thermal level suitable for the regeneration at the lower boiling point of the solution stream fed to the LLP stripper.

By optimising the process parameters, up to 35% of the total amount of the rich solution can be diverted to the final LLP stripper to be regenerated with recovered heat at low thermal level allowing a dramatic saving (up to 40%) of the required regeneration heat supplied through the process gas reboiler(s) connected to the HP stripper.

The GV low-energy VPR process can be operated without any import of LP steam and at a steam to carbon ratio (S/C) in the primary reformer assessed to be the lowest figures proposed by the most efficient technologies currently available on the market.

The VPR process is particularly attractive for grass root units but can also be profitably applied for revamping of the GV DPR/MFR processes.

GV low energy hybrid scheme (GHS)

The proposed GV low-energy hybrid revamp scheme is an innovative CO₂ removal concept, based on the integration of physical CO₂ absorption and low-energy chemical CO₂ absorption (Fig. 4).

A small-sized CO₂ physical absorption column is implemented as a standalone unit upstream of an existing GV low-energy scheme (DPR or MFR) or a multi-flash steam ejector system to absorb the portion of CO₂ at higher partial pressure. Typically 30-35% of the CO₂ is easily absorbed from the process gas in the pre-absorber and is then stripped by flash only, with no need for stripping energy.

The existing low-energy system remains as it is. All the existing equipment is reutilised for the absorption/regeneration of

Fig. 4: GV low energy hybrid scheme

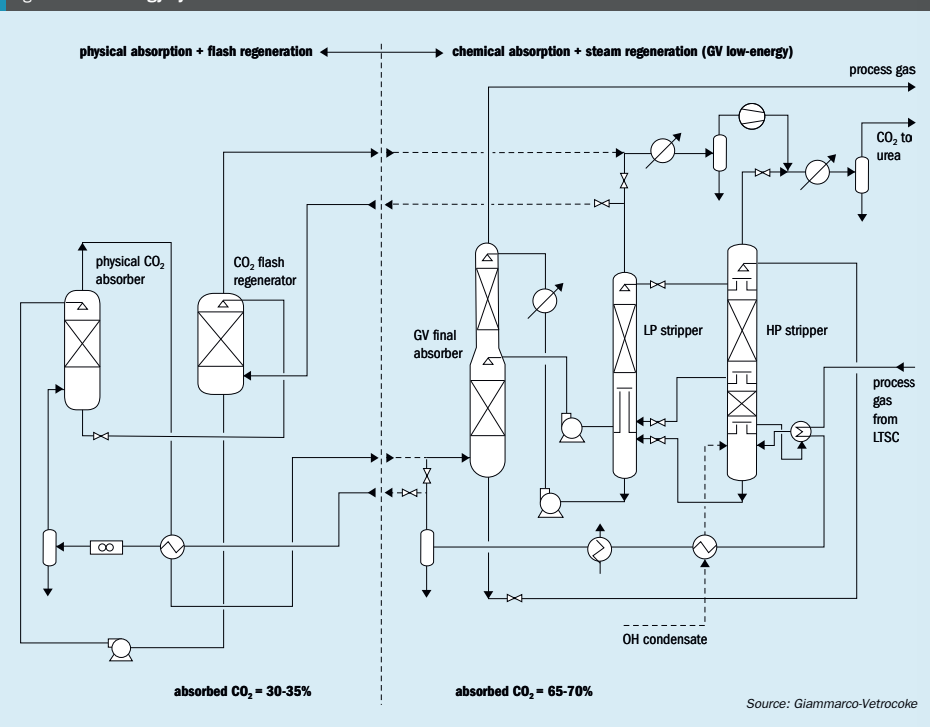


Table 1: Typical features of GV low-energy processes

	DPR	MFR	VPR	GHS
Specific regeneration energy (kcal/Nm ³ CO ₂)	700-800	630-730	400-500	400-500
CO ₂ slip (ppm)	<500	<500	<500	<500
DMW final preheating temperature (°C)	>115	>115	>115	>115

Source: Giammarco-Vetrocoke

the balance amount (65-70%) of CO₂ contained in the process gas.

Accordingly, the regeneration heat required for a GV low-energy scheme operating according to the DPR or MFR configuration is drastically reduced to 65-70%.

The proposed revamping scheme has good flexibility to further increase the plant capacity.

The revamping can be implemented in a very short time, typically during a planned

plant annual turn around (ATA), because the additional new small physical absorption/flash regeneration unit can be erected while the existing CO₂ removal unit is in operation and hooked up within the normal ATA time.

The extent of the flash regeneration can be adapted according to process requirements by integration with the GV steam regeneration, by diverting, if required, a stream from the top of the LP stripper.

Main features of the GV low-energy processes

The typical features of the GV low-energy processes for the different configurations are summarised in Table 1.

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Lessons learned from urea incidents

P. Baboo of National Fertilizers Limited, M. Brouwer and J. Eijkenboom of UreaKnowHow.com, B.V. and M. Mohammadian of OCI N.V. provide a detailed analysis of the first 100 urea safety hazards registered on the UreaKnowHow.com open source risk register for urea plants. The most critical safety hazards are described and prevention and mitigation measures are provided.

In 2017, AmmoniaKnowHow.com and UreaKnowHow.com introduced global open source risk registers for ammonia and urea plants. As of January 1, 2018, the "UreaKnowHow.com Risk Register Safety Hazards in Urea Plants" contained its first 100 safety hazards related to more than 100 safety incidents, which led to at least 65 casualties and 217 people injured.

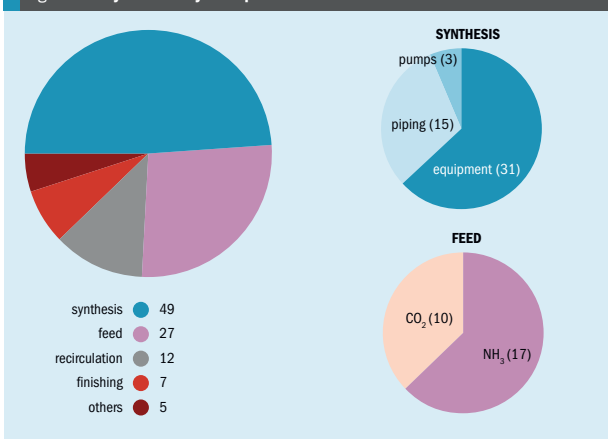
These 100 safety hazards originate from incident databases¹, hazard and operability (HAZOP) study results reported in the public domain and incidents reported by the members of UreaKnowHow.com. These 100 safety hazards are believed to represent a significant part of the most critical safety hazards in urea plants as these hazards relate to serious incidents that have the potential to lead to casualties, injuries, loss of containment, risk to the integrity of equipment or cause serious damage to critical and expensive equipment.

The number of safety hazards grows each month, mainly due to its global open source character where all members of UreaKnowHow.com can easily contribute. The more people contribute the more valuable these risk registers become for all of us.

Some safety hazards refer to two or more incidents indicating that its frequency may be higher than other safety hazards. This is valuable input when performing safety assessment exercises.

The risk register provides an overview of the safety hazards involved in a urea plant. Not only are the hazards identified and listed, each hazard is quantified by means of a risk factor, prevention and mitigation measures are suggested, and reference is made to companies who are able to provide support for implementing

Fig. 1: Safety hazards by urea plant section



these measures. Risk registers are a valuable information source for any HAZOP and safety study of a urea plant.

Where do most safety hazards occur?

Fig. 1 shows the plant sections in which the 100 safety hazards occurred.

Safety hazards mostly occur in the high-pressure synthesis section (49), the feed section (27), the recirculation section (12) and the finishing section (7).

The safety hazards in the high-pressure synthesis section were 63% related to high-pressure equipment, 31% related to high-pressure piping and 6% related to high pressure pumps. Any leak in this section leads to a critical situation due to the release of toxic ammonia, its high

pressure, high temperature and the corrosive ammonium carbamate. High pressure equipment is more vulnerable because of its carbon steel pressure bearing wall; corrosion rates of ammonium carbamate of carbon steel can be 1,000 mm per year.

A significant number (27) of safety hazards occurred in the feed section, of which 60% were related to ammonia and 40% to the carbon dioxide feed system. A significant part of the feed section is made from carbon steel, and any backflow from the high-pressure synthesis will lead to a situation that corrosive carbamate will come into contact with carbon steel. Note that during a HAZOP it is generally accepted that a backflow scenario is sufficiently protected by applying two non-return valves, each with a different design. This assumption/

solution now appears to be questionable in urea plants as a result of this analysis. The carbon steel ammonia lines can also suffer from other failure mechanisms like vibration, weld failure, corrosion from process side, erosion from process side, atmospheric corrosion and corrosion under insulation.

The carbon dioxide feed system has another specific critical safety hazard: a small unnoticed carbon dioxide leak can lead to asphyxiation if it occurs in a built-up unventilated section of plant.

In the recirculation section, various important safety hazards exist such as backflow of carbamate from the high-pressure synthesis to the centrifugal high-pressure carbamate pumps, damage of buffer tanks, and hydrogen explosion risks.

In the finishing section, there are safety hazards related to crystallization risks of the urea melt and cleaning and maintenance activities in the prill tower, granulator and warehouse.

The top ten equipment items with the most safety hazards are:

1. High-pressure heat exchangers
2. High-pressure vessels
3. High-pressure piping
4. Ammonia piping/valves
5. Ammonia pumps
6. Atmospheric tanks
7. Carbon dioxide piping/valves
8. Carbon dioxide compressor
9. Low-pressure piping (melt, flare headers)
10. High-pressure carbamate pumps

When do these safety hazards occur?

Fig. 2 splits the 100 safety hazards according to the project phase when the safety hazard occurred. In total, 74 of the safety hazards occurred during the operations phase. A relatively large number of safety hazards occurred during the maintenance (16) and commissioning/start-up (9) phase. A relatively large number of people are affected by these hazards because during these project phases a larger number of people are typically present in the plant.

Safety hazards during construction phase

Performing work at elevated heights is an important safety hazard during construction and maintenance and needs proper attention. Although only one construction hazard was identified related to one accident during the construction of a prill tower, that incident led to at least 12 casualties.

Elevated work safety risks also exist when working inside a vertical urea reactor. It is remarkable that no incidents related to working in urea reactors are reported in the public domain (yet) as it is also a confined space.

Safety hazards during commissioning and start-up phase

Nine safety hazards were identified during the commissioning and start-up phase, which has led to at least one casualty and 20 people injured. Noteworthy are:

- Four safety hazards were related to not properly tightening flange connections of high-pressure equipment and piping leading to leakages and even two ruptures. Of these four, one safety hazard is related to a leaking flange connection of a carbon dioxide pipeline causing one person to pass out.
- Two safety hazards were related to the damage of a sight glass leading to one casualty and 18 people injured. Sight glasses are a major safety risk factor in urea plants.
- In one case a high-pressure ammonia pipeline severely vibrated during start up flow conditions: Vibrating pipelines require proper attention.
- Damage to atmospheric storage tanks or loose liners of equipment can occur in case one or the other reason is able to condense and create vacuum pressure.
- Another safety hazard was related to the high-pressure flush pump.

Safety hazards during maintenance

During maintenance 16 safety hazards were identified and led to at least 20 casualties and 19 people injured. Similar to the construction phase, there was a relatively high number of casualties and people injured during the maintenance phase, most likely because more people are involved in the job and present in the plant.

In addition, nearly half of the safety hazards during maintenance are related to situations where a part of the plant was in operation or contained some process fluid. These hazards should be mitigated by applying double block and bleed designs and being aware of crystallisation properties of urea melt and carbamate (risks of high pressure pockets), the explosion risks of hydrogen and ammonia during hot work and the toxic effects of ammonia.

Safety hazards can also occur when entering a prill tower or granulator for cleaning activities. Entrants should be aware that urea lumps can fall down, and in a granulator the entrance door can close unexpectedly when the fan is put in operation.

Typical safety hazards associated with maintenance in any chemical process plants are also valid in urea plants such as working at high elevation, asphyxiation in confined areas and accidents with cranes.

Safety hazards during operation

During operation, 74 safety hazards were identified, which have led to at least 28 casualties and 173 people injured. A significant part of the 74 safety hazards during operations were related to leaks of process fluids.

In a urea plant, ammonium carbamate present in a crevice leads to crevice corrosion (active corrosion of stainless steel), which will lead to a leak after some time. A crevice can occur due to improper aligning/tightening of flanges or to improper design of valves or accessories.

Leaking ammonium carbamate is very corrosive and ongoing corrosion of stainless and carbon steel parts and piping must be avoided. Proper design, operation and maintenance of leak detection systems for high pressure equipment, high pressure flanges, and high-pressure valves are very important.

Leaking ammonium carbamate from higher pressure forms very hard crystals, which erode the sealing areas. Once a leak occurs it is nearly impossible to stop the leak by tightening the bolts. In a urea plant proper tightening of flanges and other connections is challenging because of the

Table 1: Risk matrix of 100 safety hazards before implementing any mitigation measures

Risk factors before prevention and mitigation measures		Likelihood					
		Rare	Unlikely	Moderate	Unlikely	Almost certain	
		<1% chance	1-20% chance	21-50% chance	51-80% chance	>80% chance	
		1 per 100 years	1 per 10 years	1 per 5 years	1 per year	1 per 3 months	
Consequence	Category	Safety	Never heard of in the industry	Heard of in the industry	Happened in the organisation or more than once in the industry	Happened at the facility more than once in the organisation	Happened more than once at the facility
	Catastrophic	≥1 fatalities / 6 serious injuries requiring hospitalisation		17	36	7	3
	Major	<6 serious injuries requiring hospitalisation for ≥24 hr		2	10	4	2
	Moderate	Single serious injury requiring hospitalisation for ≥24 hr		1	7	3	3
	Minor	Injury requiring hospitalisation for <24 hr			2		1
Insignificant	First aid / minor injury		2				

limited choice of suitable materials of construction. Proper attention by experienced fitters is important. Hot bolting/torquing and installing clamps during operation to stop leaks has led to five casualties and four people injured and should be avoided at any time.

Safety hazards like backflow, contamination, vibration, atmospheric corrosion, or corrosion under insulation should receive proper attention.

Seven safety hazards were related to hydrogen, which is present in the feed streams to the urea plant. Hydrogen can also enter the urea plant when one integrates the ammonia plant with the urea plant, for example, via process water and/or drain systems. Hydrogen dissolves to a certain extent in the liquid streams leading to the presence of hydrogen in unexpected sections of the urea plant.

Which safety hazards have the highest risk factor?

Table 1 shows the risk matrix applied to each safety hazard and shows in each cell the number of safety hazards with a certain risk factor.

In the authors' view there are 55 safety hazards in total with an intolerable risk

factor (red colour in table). Appendix 1 lists the most critical safety hazards.

Even if one implemented all recommended prevention and mitigation measures, a significant number (63) of the above safety hazards would still remain a high-risk factor (catastrophic consequences and rare likelihood). It is not feasible to mitigate these consequences further against reasonable efforts (refer to Table 2).

This means continuous attention and awareness of these 63 safety hazards is very important.

Leaks with toxic ammonia release

In 76 of the 100 safety hazards a leak could occur whereby toxic ammonia would be released. This has already led to at least 36 casualties and 198 people injured. It is remarkable to notice that in nearly 90% of these incidents (during which a toxic ammonia leak occurred), the leak occurred suddenly, without any pre-warning. Here one should think about failure of high pressure flange connections, rupture of high-pressure equipment and piping, failure of an isolation block valve, atmospheric corrosion phenomena, backflow of corrosive ammonium carbamate into the carbon steel feed lines, failures of high-pressure

equipment and piping due to carbamate corrosion phenomena, tube ruptures and explosions caused by hydrogen.

In five incidents, there was a pre-warning in the form of heavy vibrations or a small leak, but the incident still happened because action was taken to try and stop the vibrations or leak instead of shutting down the plant. This led to nine casualties and four people injured. In case of a leak, the only advice is to stop the plant, trace and repair the leak. Do not try hot bolting/torquing or to install a clamp. Pay attention to heavy vibrating pipelines by performing a pulsation and mechanical analysis.

Main safety hazards, prevention and mitigation measures

Preventative and mitigation measures to avoid leaks with toxic ammonia release are listed below:

- proper design related to backflow, crystallisation and explosion risks, dead-ends in pipelines, crevices, double block and bleed and blind flanges for isolation purposes, carbamate safety valves, avoid cooling jackets of carbon steel vessels;
- proper design and fabrication quality related to high-pressure equipment, piping, accessories, valves and pumps;

Fig. 2: Safety hazards by project phase

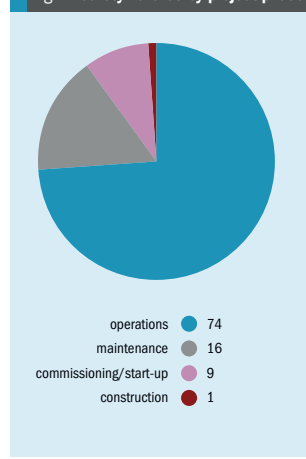


Table 2: Risk matrix after implementing all prevention and mitigation measures

Risk factors after prevention and mitigation measures		Likelihood					
		Rare	Unlikely	Moderate	Unlikely	Almost certain	
		<1% chance 1 per 100 years	1-20% chance 1 per 10 years	21-50% chance 1 per 5 years	51-80% chance 1 per year	>80% chance 1 per 3 months	
Consequence	Category	Safety	Never heard of in the industry	Heard of in the industry	Happened in the organisation or more than once in the industry	Happened at the facility more than once in the organisation	Happened more than once at the facility
	Catastrophic	≥1 fatalities / 6 serious injuries requiring hospitalisation	63				
	Major	<6 serious injuries requiring hospitalisation for ≥24 hr	15				INTOLERABLE RISK
	Moderate	Single serious injury requiring hospitalisation for ≥24 hr	14				HIGH RISK
	Minor	Injury requiring hospitalisation for <24 hr	3				MODERATE RISK
	Insignificant	First aid/minor injury	5				LOW RISK

- proper quality of welds in ammonia pipe-lines;
- proper operational procedures related to heating up with steam, chloride and nickel analysis, flushing equipment for maintenance entry, blocking in, sampling, carbon dioxide contamination of ammonia and operation of flares, ammonia detection sensors;
- continuous leak detection systems for loose liners, for heat exchanger tubesheet connections and for rupture discs and safety valves;
- operator plant tour inspections for leakages from flange connections, overlay welding, valves, pump seals severe vibrations and proper housekeeping;
- risk based corrosion inspections for high-pressure equipment, piping, accessories, valves and corrosion under insulation and atmospheric corrosion;
- risk based preventive maintenance related to sight glasses, flange connections (proper installation of gaskets and tightening procedures) and seals/stuffing boxes of pumps.

It is important to pay more attention to pre-warnings or precursor failures so that more incidents can be avoided².

Once an ammonium carbamate leak occurs it cannot be stopped indefinitely;

one may be able to stop the leak path but a crevice will remain. In this crevice ongoing corrosion will take place leading to another leak or possible rupture in the future. It is risky to stop flange leaks by hot torquing. Installing a clamp to stop the leak is not done in the urea industry as one cannot assure no crevice will remain. The best and only advice is: In case of a leak one should stop the plant and repair the leak.

To realise a safe and reliable urea plant, it is therefore important to pay proper attention to the design of flange connections and tighten flange connections in the right manner and with the right torque and right sequence. Best practice is to use (hydraulic) bolt tensioners for the high-pressure equipment and to use torque wrenches for flanges in piping in the high-



Fig. 3: Tightness test for large size flanges.

pressure and other sections of a urea plant. The optimum choice of materials of construction and a good understanding of the sealing mechanism and failure modes also have a large impact on the reliability of flange connections. It is best practice to perform a tightness test before introducing ammonia and carbon dioxide feed. Large flanges can be taped off and via a small hole a flange leak can be identified by means of a soap solution (see Fig. 3).

Crystallisation risks

Ammonium carbamate and urea crystallise easily at lower temperatures. During shut-down conditions it is possible that pockets of ammonium carbamate and urea remain in the equipment or piping even when flushing has been applied. Incidents occur

because these pockets can be encountered unexpectedly during maintenance activities. Also, incidents occur when trying to open up clogged urea melt pipelines. This is a difficult and risky exercise requiring proper personal protection as the main mitigation measure, and proper attention to tracing and insulating cold parts of the pipelines as the main preventative measure.

Attention should also be paid to a proper design, flush system and quality of safety valves handling the ammonium carbamate stream, assuring no passing and clogging of upstream and downstream piping.

Vibration risks

Certain pipelines are prone to vibrations like two-phase flow pipelines (for example, the pipeline from the high-pressure stripper to the recirculation section, minimum flow pipelines of high-pressure pumps) and discharge lines of high-pressure reciprocating pumps. A proper pulsation and mechanical analysis during the design phase of these critical lines is an important prevention measure. These pipelines should be included in a risk based inspection program (fatigue cracks) and in case of abnormal vibrations the plant should be stopped and the situation rectified.

Backflow risks

The high-pressure synthesis section is fed with carbon dioxide and ammonia. The typical material of construction in the feed section is carbon steel while the high-pressure synthesis contains the very corrosive ammonium carbamate. Backflow of this carbamate is therefore a critical safety hazard and several incidents have occurred. A further complicating factor is that crystallisation can easily occur, which can lead to non-return valves not functioning. Backflow can more easily happen when the feed line enters at the bottom of a vertical reactor which is completely filled with liquid and continuously a liquid head pushes back the feed flow.

Best practice for the ammonia feed system are two non-return valves in series and two fast closing motor-operated-valves. Preferably the non-return valves should be of different designs and high quality, but do not apply a non-return valve design with vanes as the weld of the vanes with the body is prone to corrosion failure. Non-return valves should be installed in a vertical line and a flushing connection should be installed upstream of the non-return valve to be able to flush away any solids. Install fast closing motor-operated-valves control-

lable from the DCS and apply the material specification break upstream these motor-operated-valves. Attention should also be paid to bypass/start-up lines. For carbon dioxide, additional measures like a third non-return valve and a buffer vessel can be installed to protect the carbon dioxide compressor against the corrosive carbamate.

Hydrogen explosion risks

Hydrogen is present in both the carbon dioxide as well as the ammonia feed. Further, oxygen is added in the plant to assure a passive chromium-oxide layer on the

applied protective layers. In several sections of the urea plant the concentrations of hydrogen and oxygen increase and the composition may enter the explosive area, so the risks for hydrogen explosions become realistic. Recommended preventative measures include adding a hydrogen removal converter in the carbon dioxide feed, an atmospheric flash step in the ammonia feed and adding methane to reduce the explosive area. Recommended mitigation measures are an expansion volume or a design pressure seven times higher than the operating pressure. Note that part of



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the hydrogen and oxygen will dissolve in the liquid phase and can reach and accumulate in less expected sections like the ammonia water tank and other low-pressure equipment³. Also, when one connects the ammonia plant with the urea plant, hydrogen containing streams can enter the urea plant creating explosion risks.

Carbamate corrosion risks

Ammonium carbamate is the intermediate product when converting ammonia and carbon dioxide into urea and is the most common and most corrosive component in a urea plant. Corrosion rates can be controlled by assuring sufficient oxygen being present, but corrosion rates can become very high in cases where oxygen gets depleted. There are several reasons why this can occur (for example design with dead-ends or crevices, loss of oxygen supply, condensation of carbamate vapours, etc.) leading to several corrosion failure mechanisms. In some cases, carbamate corrosion leads to a "controlled" leak first via a leak detection system and proper action can be taken. In other cases, a sudden leak or failure occurs and one has to rely on preventive maintenance procedures, risk based inspection techniques, regular visual inspections and ammonia leak warning systems.

For example, a leak in a loose liner of a high-pressure vessel will lead to a situation that a large area of the carbon steel is exposed to corrosive carbamate and typically a break-before-leak scenario will be valid. The integrity of overlay welding in high pressure equipment cannot be monitored continuously and leaks should be avoided by preventive maintenance (corrosion inspections during a turnaround). A leak in the overlay welding will lead to a situation that only a limited area of the carbon steel will be exposed to corrosive carbamate and typically a leak-before-break scenario will be valid. Regular inspection rounds by operators to identify such a leak are recommended.

Atmospheric corrosion or under insulation risks

Atmospheric corrosion or corrosion under insulation is an often underestimated form of failure. In urea plants, atmospheric corrosion risks do occur. Special attention should be paid to the carbon steel high pressure carbon dioxide and ammonia feed lines and to stress corrosion cracking risks of nitrates and (bi)carbonates with

carbon steel and chlorides with stainless steel. Neighbouring plants and prevailing wind directions are important and sufficient attention to proper insulation is vital especially after a turnaround. A protective shield against rain above high pressure equipment is recommended.

How to behave safely in a urea plant

The fact that many leaks and failures can occur suddenly without any pre-warning has consequences on how to behave safely in a urea plant. One should avoid any leak and adhere to a zero-tolerance philosophy regarding leaks. This is vital for ammonia and carbamate leaks but also good practice for steam, carbon dioxide and other leaks. In a sudden large ammonia cloud one will only remain conscious a few seconds. Know the escape routes blindly, escape lateral/upwind direction, have readily available a wet cloth or better still a full face mask and move away quickly. Assure that all safety devices are ready to work such as safety showers and eye washes. Further, in case of a leak, stop the plant, do not apply hot bolting/hot torquing, do not apply clamping and limit the number of spectators.

How to identify a maximum number of safety hazards

It is commonly accepted that by performing a proper HAZOP study with experienced participants at regular time intervals one is able to identify most safety hazards. It is good practice to invite an experienced urea expert from outside into the HAZOP. It has been seen that for urea plants, HAZOP studies do not always identify commonly accepted assumptions. For example, the assumption that backflow can be avoided by installing two non-return valves with a different design as described in one of the previous sections.

Also, corrosion is typically excluded from a HAZOP study and should be covered by maintenance and inspection programmes. In a urea plant however, corrosion from the process side and also atmospheric corrosion or corrosion under insulation are major causes for safety hazards. For example, the risk register identifies 50 safety hazards for the urea reactor of which most are related to corrosion⁴.

Finally, one is able to identify more safety hazards by performing a HAZOP study also for transition phases like com-

missioning, start-up and shutdown situations and by using transition guide words like too fast, too slow, wrong sequence and control changes². For example, in urea plants the blocking-in of the high pressure synthesis is a specific situation, which can occur quite often and needs proper attention in a HAZOP study.

The quality of the HAZOP can be improved by making use of available incident databases and risk registers, by keeping track of incidents and near misses within the company. The authors invite all to share incidents and near misses within the industry to support each other improving safety studies in the belief that global open source risk registers⁵ and specific industry operational risk databases⁶ are best practice to keep track and share safety hazards in the industry, leading to a safer workplace for everyone.

Conclusions

Most safety hazards in a urea plant involve a release of toxic ammonia of which 90% can occur suddenly, without any pre-warning. Other main safety hazards are crystallisation risks, vibration risks, backflow risks, hydrogen explosion risks, ammonium carbamate corrosion risks, atmospheric corrosion and corrosion under insulation risks. The fact that in a urea plant many safety hazards can suddenly occur releasing toxic ammonia has consequences as to how to safely behave in a urea plant. To identify the maximum number of safety hazards, it is recommended to involve an experienced urea expert in HAZOP, include transition phases in the HAZOP and make use of available incident databases, risk registers and specific industry operational risk databases. ■

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Appendix 1: Most critical safety hazards

Catastrophic consequences and almost certain likelihood:

- rupture of carbon steel ammonia pipeline due to backflow from corrosive carbamate from synthesis;
- rupture of the high-pressure scrubber due to hydrogen explosion;
- rupture of high-pressure equipment due to high process pressure.

Catastrophic consequences and probable likelihood:

- large ammonia leak due to blowing out of a plunger from the stuffing box of a high-pressure reciprocating pump due to broken bolts of plunger yoke;
- leak/rupture of high-pressure flange connection in synthesis section;
- leak in loose liner of urea reactor due to no proper leak detection system (a proper leak detection being an active vacuum based leak detection system with a continuous, accurate and reliable ammonia detector);
- failure of urea reactor due to no proper leak detection system;
- failure of high-pressure flange connection due to hot bolting;
- asphyxiation/unconscious while working on tank;
- asphyxiation/unconscious when entering a pipeline/vessel (confined space) while welding was performed and welding gas was applied.

Catastrophic consequences and moderate likelihood:

- failure of a valve in an ammonia line due to human error to solve a vibration problem;
- ammonia leak due to a sight glass failure during start-up;
- isolation valve fails during maintenance of high-pressure ammonia pump;
- significant wall thickness reduction of high-pressure ammonia line due to atmospheric corrosion;
- ammonia leak due to loosening packing ring of stuffing box on a high-pressure reciprocating pump;
- explosion due to atmospheric corrosion of ammonia pipeline and/or erosion from process side;
- large uncontrolled ammonia emission when suction line of high-pressure ammonia pump fails due to unwanted backflow scenario;
- rupture of pipeline due to clogging of pipeline upstream or downstream safety valve due to crystallisation of carbamate;
- rupture of 316L Urea Grade (UG) high-pressure pipeline at inlet of reactor (conventional plant) due to erosion corrosion close to thermowell;
- high-pressure butterfly valve twists leading to leakage;
- high-pressure carbamate gas line ruptures due to strain induced intergranular cracking;
- 316L UG liquid outlet line of high-pressure ammonia stripper leaks due to relatively high temperature and as a consequence higher corrosion rates;
- rupture of high-pressure drain valve due to corrosion of threads during leakage;
- crack in stripper liquid outlet pipeline due to heavy vibrations;
- leak of high-pressure flange connection with titanium gasket manway cover of urea reactor;
- high vibrations of discharge line of high-pressure reciprocating carbamate pump;
- major leak at main flange of high pressure carbamate condenser during start-up;
- failure of flanged head connection of a urea reactor;

- reactor ruptures due to bad maintenance practice of closing the manway cover;
- vent line of ammonia water tank explodes during grinding;
- rupture of valve due to high pressure pocket during maintenance;
- failure of sight glass;
- high-pressure equipment ruptures due to not commissioning all leak detection holes;
- severe damage of loose liner in high-pressure equipment (cause not clear);
- liner bulges and ruptures due to too high pressure behind the liner or due to draining the synthesis;
- damage of carbon steel pressure bearing wall due to leakage of protecting sleeve in nozzle;
- rupture of high-pressure stripper due to fabrication defect;
- rupture of reactor due to active corrosion at a weld defect in weld clip to liner;
- rupture of reactor due to stress corrosion cracking of carbon steel pressure bearing wall due to flushing of leak detection system with water and bad design of leak detection holes in multi-layer vessel;
- rupture of urea reactor due to cracks in carbon steel behind the liner;
- rupture of urea reactor due to defect in titanium liner;
- tubesheet of pool condenser damaged due to erosion corrosion steam side;
- tube rupture in high-pressure heat exchanger leads to high pressure on steam or cooling water side;
- failure of the tube to tubesheet weld, potential damage of carbon steel tubesheet;
- failure of tube in tubesheet due to chloride stress corrosion cracking;
- chloride from atmosphere (cooling water effluent, marine atmosphere) entering the steam condensate system via atmospheric steam condensate tank;
- rupture or crack in pressure bearing wall due to atmospheric corrosion (nitrate stress corrosion cracking).

Major consequences and almost certain likelihood:

- rupture of carbon steel carbon dioxide feed line due to backflow from corrosive carbamate from synthesis;
- carbon dioxide breakthrough with ammonia recycle leading to failure of pipeline.

Major consequences and likely likelihood:

- excessive ammonia emission due to mechanical seal failure of high-pressure centrifugal ammonia pump due to dirt, oil in flush lines;
- significant ammonia and carbamate leak when plunger flows out from stuffing box of high-pressure reciprocating pump due to broken bolts of plunger yoke;
- rupture of tank due to vacuum pressure created;
- crane collapses during maintenance job.

Moderate consequences and almost certain likelihood:

- during cleaning or maintenance activities in the prill tower or granulator heavy lumps fall down causing casualties;
- while trying to open clogged melt line, melt splashes out of 3-way valve or flange;
- granulator door jammed close unexpectedly. ■

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