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July | August 2015

nitrogen+syngas

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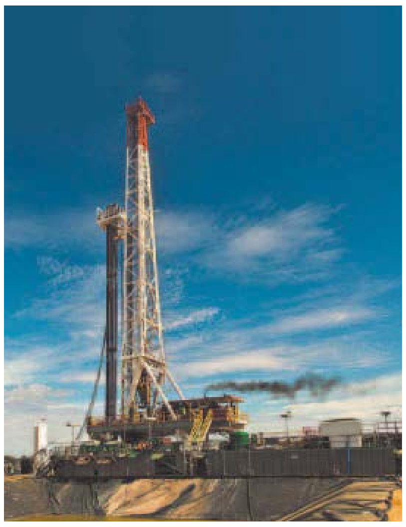

Cover: *Shale gas drilling. ribeiroantonio/iStockphoto.com*

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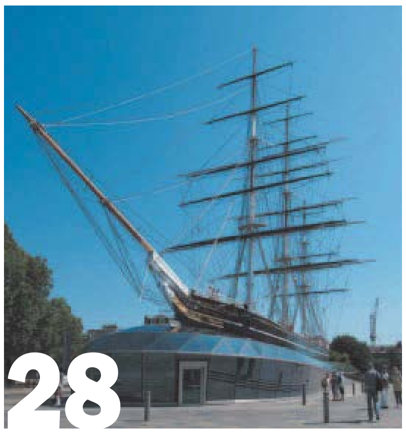

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Read this issue online at: www.nitrogenandsyngas.com

Published by: BCInsight

New technologies for old

> **The electric arc process for fixing nitrogen actually pre-dates Bosch-Haber.**

Fixation of atmospheric nitrogen by catalytic reaction with hydrogen in the Bosch-Haber process – which forms the basis of many of the industries covered by this magazine – is just over 100 years old now. However, while it forms the route for most of the nitrate that makes its way into soils in the developed world, it is not the only process. Some leguminous plants are able to process atmospheric nitrogen via root bacteria, and high energy electrical discharges can also oxidise nitrogen to NO which can then react onwards to nitrates – this is the way that new nitrates are formed in nature, during thunderstorms. The electric arc process for fixing nitrogen, which duplicates this effect, actually pre-dates Bosch-Haber, and formed the basis of Norsk Hydro's ammonia plant in the early years of the 20th century, using hydroelectric power to drive the electric arc generators.

Bosch-Haber proved to be far more efficient on an industrial scale than the electric arc process, and the latter fell into disuse, but at a recent meeting of the International Fertilizer Society in London, delegates heard from Rune Ingels – himself formerly of Norsk Hydro, now running his own company, N2 Applied AS – about advances in technology which may make nitrogen fixation from an atmospheric nitrogen-oxygen plasma a potential competitor once more.

The plasma reactor uses a concentric arrangement of electrodes with a perpendicular magnetic field for controlling the movement of the electric arc through the air in the annular space between the electrodes. The arc creates a plasma phase of exited molecules and atoms as well as ions with an equilibrium of NO vs. N_2 and O_2 that has more NO than the thermodynamic equilibrium of the gas phase at a similar temperature. The plasma temperature is 'low', and the materials used to contain the plasma and gas are thus just normal high temperature steels. Energy consumption is reckoned to be approximately 36GJ/tN, depending on the degree of heat recovery, which compares well to current world class ammonia plant technology of 32GJ/t NH_3, and far better than the 350-400GJ/tN that the old Hydro arc process used to use. The NO is removed by a water quench to continue to drive the equilibrium towards NO.

The key step is the next one downstream from here. N2 Applied AS wishes to combine it to scrub ammonia from ammonia-containing air to generate nitric acid or even ammonium nitrate on the spot. The concept is to develop this as a small-scale unit which can be used by a farmer directly, using locally generated renewable electricity. This holds out the potential of enriching manures with nitric acid or nitrate, effectively generating fertilizer on-site without greenhouse gas emissions, while recovering ammonia from manures which would otherwise be lost to air, causing further greenhouse effect. At a municipal level, it could be combined with sewage treatment or biogas processing. Ingels reckons that up to 54 million tonnes of ammonia is lost to the air every year from waste associated with meat production, waste water systems and human food waste, and capturing even a fraction of this in conjunction with the arc process could generate significant additional volumes of GHG-free (even GHG-negative) fertilizer. This he referred to as "fusion farming".

Of course, as with many such ideas, like the techniques for adapting leguminous root bacteria to other plants to allow them to fix nitrogen directly from the air that we mentioned back in September/October 2013, it is still very early days for this process. But it could be that innovative systems like this may find niches where they can compete against the conventional nitrogen industry, for a better future for all of us. ■

Richard Hands, Editor

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Price trends

MARKET INSIGHT

Laura Cross, Senior Analyst, Integer Research, assesses price trends and the market outlook for nitrogen.

NITROGEN

After a tough start to 2015, prospects for the nitrogen industry are looking up. Urea and nitrates prices hit five-year lows in April, but have since shown signs that a sustained period of recovery is set to begin. The ammonia market has fared better than its other nitrogen counterparts, although this is largely derived from the short-term bull run in prices at the end of 2014. Regardless, the key theme affecting all nitrogen product markets in the first half of 2015, and particularly in April and May, was that the industry had reached its floor. In capacity terms, the nitrogen market remains oversupplied, however, tightening supply from certain key exporters in the coming months has improved market sentiment significantly.

A prime example of lower nitrogen availability going into the third quarter of the year is Egypt. The country continues to suffer from a severe domestic gas shortage, and fertilizer producers have often lost out to the power sector, which has received priority for load balancing, and the result has been dwindling operating rates at Egypt's nitrogen plants. The situation became particularly fraught in March, when the government turned to urea imports to meet domestic demand, a surprise to the industry given that Egypt typically exported 170,000 tonnes of granular year per month in 2014. The country is certainly making efforts to address its domestic energy balance, both through long-term investment plans and short-term measures to meet temporary shortfalls, but the nitrogen industry continued to suffer from abysmal utilisation rates in June. It is expected that Egyptian export availability will be minimal in the coming months, and this has been a key contributor to strengthened marked confidence.

Another country facing extreme supply shortages that will have an impact on global trade is Ukraine. Ostchem, the holding group that owns four of Ukraine's six nitrogen plants, announced in June that the last of its facilities in the country will close temporarily. The company said that its last remaining operational nitrogen plants in the country, in Cherkassy and Rivne, would be shut down following "unprecedented pressure" from the Ukrainian government on the company. The company was forced to close its Stirol and Severodonetsk plants in May 2014 amid the ongoing separatist conflict in the Eastern half of the country, and turned its attention to maximising production at the group's two remaining plants. When operating, Ostchem's production facilities occupied the majority market share in the Ukrainian nitrogen market, as well as playing a vital role in global trade as a key exporter of urea and nitrates products.

Ukrainian shutdowns have been frequent in recent years due to the country's position at the high end of the nitrogen cost curve and as a swing producer, but there is far more uncertainty for Ostchem with an unstable political situation. Ironically, Ukrainian producers have seen their cost competitiveness actually improve in US dollar terms over the last 12 months based on lower gas prices, but this means nothing if plants are unable to run as gas supplies are cut off.

Ukraine's improved cost position is mirrored by developments in several other traditionally high-cost producing countries. Typically when the nitrogen industry is in a cyclically weak phase, the market becomes self-correcting as high-cost capacity leaves the market due to rapidly squeezed margins. The difference in this latest phase of the market has been that many of the industry's high-cost producers have seen improved production economics, primarily driven by lower energy prices, which we discussed in more detail the May/June issue. The result is that while falling nitrogen prices put pressure on margins, the impact has been offset by falling production costs. All of the above creates a unique situation where swing capacity that we would typically expect to close at recent price levels is able to continue operating, and the market oversupply becomes even more compounded. This is the where the unexpected supply disruptions in countries such as Egypt and Ukraine are in fact playing a vital role in propping up industry sentiment in the short-term.

On the demand side, a substantial urea tender from India was a key contributor to price increases in June. STC India purchased 849,000 tonnes of urea under the 19 June tender for shipment by 27 July, at prices higher than had previously been expected. With limited stocks at Chinese ports in the run-up to the closing of the tender, Chinese prilled prices rallied in late June to around US$310/tonne FOB, although it had been expected that offers under the Indian tender would be lower, closer to US$300/tonne FOB. The subsequent higher prices offered under the tender were therefore above expectations and far more in favour of producer ideas. Of the total volume purchased under the Indian tender, it was understood that about 450,000-500,000 tonnes of urea will be supplied from China, 200,000 tonnes from Iran, 50,000 tonnes from Oman and around 120,000 tonnes from Russia.

Table 1: **Price indications**

Cash equivalent	mid-May	mid-Mar	mid-Jan	mid-Nov
Ammonia ($/t)				
f.o.b. Caribbean	425	435	440-505	615
f.o.b. Arab Gulf	350-405	400-430	470-490	635
c.fr N.W. Europe	460-480	473-510	480-535	650-710
c.fr India	410-450	490-500	530-570	555-630
Urea ($/t)				
f.o.b. bulk Black Sea	275-283	270-280	320-325	315-318
f.o.b. bulk Arab Gulf*	308-335	270-275	320-325	307-320
f.o.b. bulk Caribbean (granular)	295-305	290-300	325-335	340-350
f.o.b. bagged China	293-308	275-283	280-285	289-294
DAP ($/t)				
f.o.b. bulk US Gulf	468-472	485	485	460
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	185-190	231-235	200-227	200-203

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

Source: Fertilizer Week

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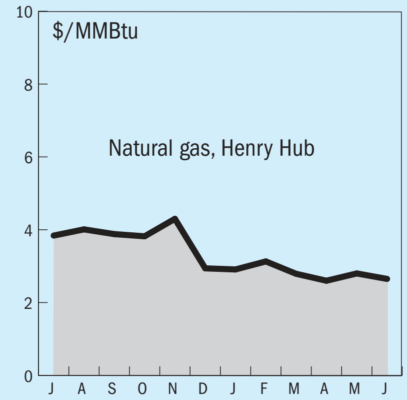
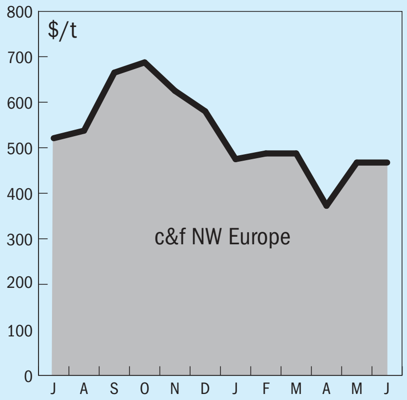
END OF MONTH SPOT PRICES

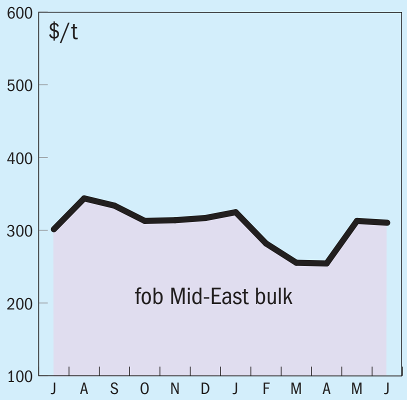
natural gas



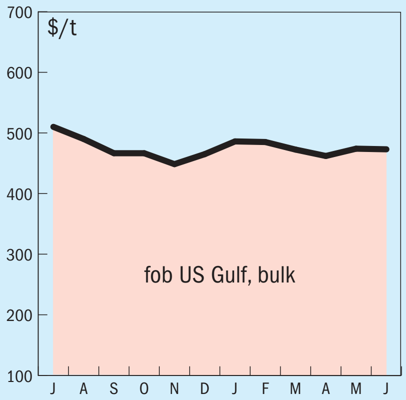
ammonia



urea



diammonium phosphate



MARKET INSIGHT

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

METHANOL

In North America, Henry Hub prices rose by $0.24/MMBtu from $2.61/MMBtu in April to $2.85/MMBtu in May. June prices looked to be fluctuating around the $2.85/MMBtu mark, with a high of $2.90/ MMBtu. In spite of the rise, these prices remain $1.50/MMBtu lower than for the same period last year, reflecting overall weakness in US gas prices.

US methanol spot prices had hit highs of $1.24/gal ($410/t) at the end of April, leading to a rise in Methanex's posted non-discounted reference price for May to $1.33/gal ($442/tonne) and similar rises for the Southern Chemical Company. However, spot rates were seen to decline again in May, trending back towards $1.11/gal ($368/tonne). Much of the weakness in May prices was blamed on additional availability from Trinidad, where natural gas curtailments, which had been at levels of up to 30%, had dropped back to around 15%. The US has already added over 1 million t/a of new methanol capacity in 2015 and this has begun to show in more comfortable availability in the markets, displacing imports as companies like Methanex make fewer spot purchases now that its Geismar 1 unit is operational.

Some of that methanol from Geismar has been finding its way to Europe, where there has been a supply shortfall for Methanex as the company has had operating difficulties with its 1.3 million t/a plant at Damietta in Egypt, which has been down since February because of gas supply constraints. However, overall EU imports of methanol were down 20% in April as compared to March, and 14% down on the same period a year ago, in spite of increased volumes of methanol being supplied from Russia.

In the Middle East, Iran is anxiously awaiting the outcome of the conclusion of long-running talks about its nuclear industry. The hope and expectation is for a lifting of sanctions to allow Iran to recommence exports of methanol to Europe again. Supply has been building in Iran in advance of the expected announcement, and production is running ar high levels. Fanavaran Petrochemical Co. reports that it produced a record 1.7 million t/a of methanol in the 12 months to March 21st. The company also produced 150,000 tonnes of acetic acid. Kharg Island also expects to top 1 million t/a this year.

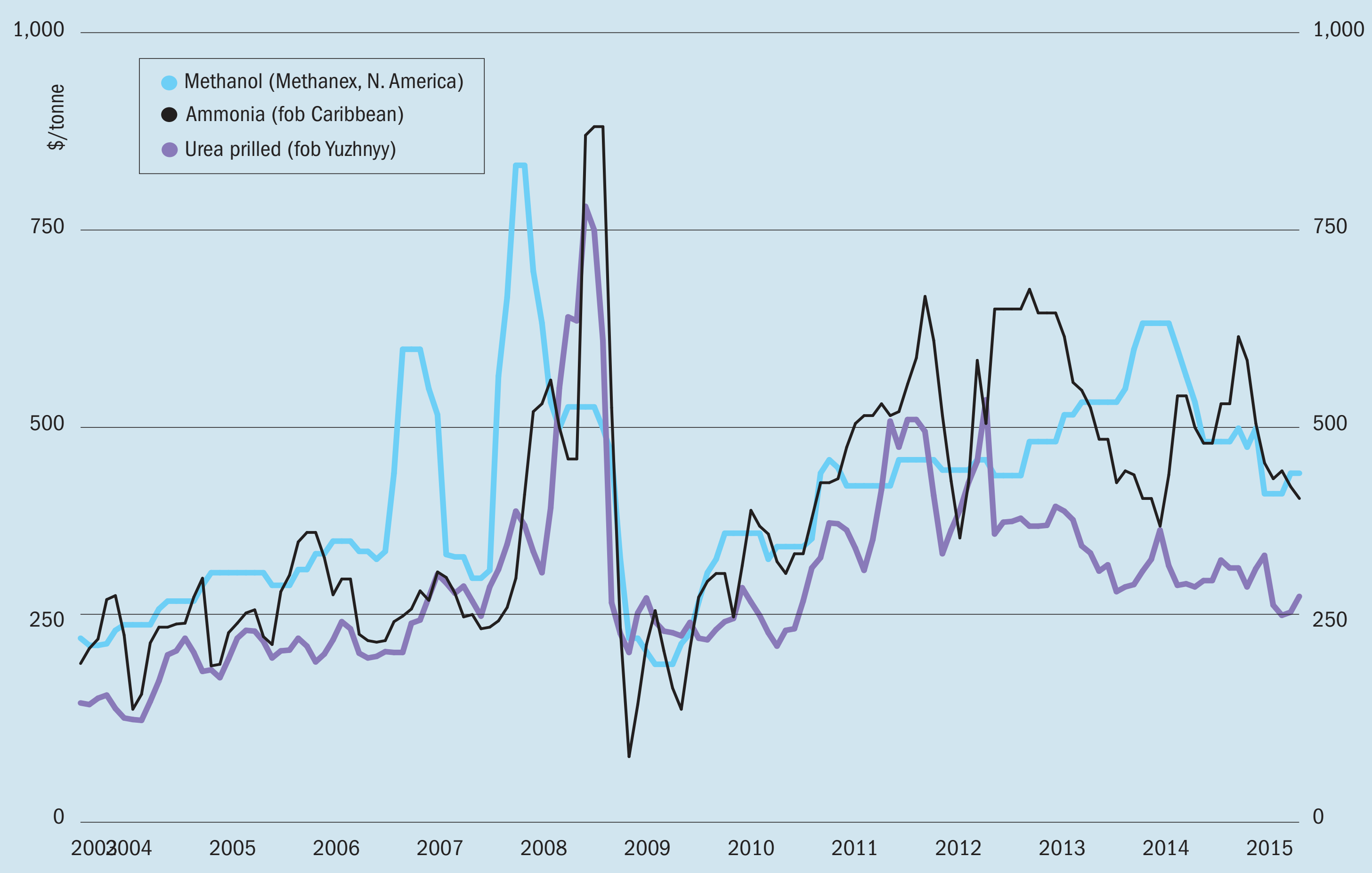
Chinese methanol markets appear to be facing weaker demand as the rainy season approaches, and downstream demand for formaldehyde is scaling back, with operating rates for the formaldehyde industry falling towards 40%. Demand into other derivatives also remains down – MTBE consumption has been hit by lower gasoline prices, and dinethyl ether (DME) has seen continuing low operating rates of 20-30% as the government cracks down on illegal DME blending. The main bright spot is acetic acid, where operating rates are relatively stable in the 70-80% region. Overall demand is not expected to recover until July, when the rainy season ends, and formaldehyde rates may increase to 50%. Domestic spot prices were around the $370/t mark.

For the new and burgeoning methanol to olefins (MTO) segment the decline in oil prices has affected product prices, and made competition from naphtha crackers cheaper, but there are now reported to be 17 MTO plants of varying sizes operational in China, and while Datang International Power's MTO plant has been down since April, most MTO operators have been running at high operating rates, and there has been another new startup – Shandong Yangmei says that it has achieved on-spec production at its new MTO plant, which can consume up to 900,000 t/a of methanol. Downstream demand for olefins has led to smaller plants to run their MTO lines and this additional capacity, coupled the off-season for demand has creates volatility in the market. Chinese demand growth is forecast to see methanol consumption increase by an additional 9 million t/a this year, compared to 1 million t/a in the rest of the world combined.

Elsewhere in Asia, June prices have been down slightly on May's, by an average of $5/tonne. Singapore imported 191,000 tonnes of methanol in January-April 2015, most of it from Saudi Arabia, and Japan reported 425,000 tonnes of methanol imports in Q1 2015. ■

Market outlook

Historical price trends $/tonne



Source: BCInsight

AMMONIA

- Ammonia prices continued their decline through the second quarter of 2015, falling to a low of US$375/tonne FOB in mid-May.
- Aside from the prevailing market oversupply, the key driver of this weak pricing was slow demand from regions that would usually be expected to make seasonal purchases.
- Market sentiment turned around in June as a result of lower availability from key ammonia exporters, and this will be the driving force behind price movements in the short-term.
- Plants in Russia, Ukraine, Egypt and Trinidad operated at lower utilisation rates through June, in the latter two cases due to gas supply curtailments, and ammonia export availability is likely to be affected into July at least, in spite of some easing in Trinidad.
- Demand for the US side-dressing period began in June and industrial purchases in the Asia-Pacific region are also expected imminently.

UREA

- In a similar vein to ammonia, the urea market remains oversupplied, although the short-term outlook is more positive than 2015 has been to date.
- The closure of Ostchem's last remaining plants in Ukraine and the ongoing gas supply issues in Egypt both carry a large degree of uncertainty that will keep some pressure on the urea market in the coming months, with the potential that the impact could be longer-lasting.
- Following on from the substantial volumes purchased under the Indian tender in June, other Asian demand is expected to follow, particularly from Pakistan, Sri Lanka and Bangladesh.
- Urea prices are expected to strengthen in the coming months, particularly in the run up to September, when buying interest for year end application begins.
- Urea prices have been rising in the US Mid-West, up $30/t at some upriver terminals, with expectations this will filter through to NOLA.

METHANOL

- New capacity additions in North America have combined with reduced gas supply curtailments in Trinidad to ease methanol supply constraints in the US and to begin to bring prices back down again.
- Supply from the new Methanex Geismar plant is however mostly covering for lack of availability from EMethanex at Dameitta at present and being exported to Europe.
- Chinese formaldehyde demand is down but startups and shutdowns of MTO capacity are leading to some volatility in the market.
- The results of Iranian nuclear talks could lead to a large tranche of fresh availability going forward. Production at some Iranian plants is running at record levels.
- Posted prices are down in most major markets, with expectations of slacker demand.
- Chinese demand is expected to pick up from July.

Nitrogen Industry News

RUSSIA

Contract signed for new ammonia plant

The engineering, procurement and construction (EPC) contract has been signed for a 2,700 t/d (890,000 t/a) ammonia plant at Kingisepp for EuroChem. The €660 million contract will be for the first of five fertilizer projects to be constructed under the MoU signed between EuroChem, Maire Tecnimont and Italian finance group SACE in April. SACE will provide a €575 million loan guarantee to EuroChem for the construction of the plant, which will license ammonia technology from KBR. The EPC contract will be delivered on a lump-sum turn-key basis, including utilities and off-sites, and is expected to be completed within 36 months from the commencement date. It will be executed by Maire Tecnimont's subsidiaries Tecnimont SpA and Tecnimont Russia OOO, the former having already completed front-end engineering design (FEED).

Dmitry Strezhnev, EuroChem CEO, commented: "the EPC contract for the Kingisepp ammonia plant continues our successful collaboration with Maire Tecnimont as we aim to develop five new ammonia-urea projects in three countries over the next 10 years. The project, based on the latest technology, will add new capacity to Russia, create new jobs and help EuroChem move towards its goal to become a top five global fertilizer producer."

Pierroberto Folgiero, Maire Tecnimont's CEO, added: "this contract will further strengthen our fruitful industrial cooperation with EuroChem with a long term spirit; its successful execution will best position Maire Tecnimont Group to collaborate on EuroChem's future investment road map globally. Further, such achievement offers sound evidence of Maire Tecnimont's leadership in the downstream business, and it also proves the effectiveness of the Group's strategy in focusing on an early involvement in clients' large-scale investment decisions".

INDIA

Government relents on naphtha-based urea plants

The Indian cabinet has relented on its decision force naphtha-based urea capacity in India to close and will now allow the three plants – owned by Mangalore Chemicals and Fertilizers Ltd, Southern Petrochemicals Industries Co, and Madras Fertilizers – to continue operation using naphtha feedstock until they can secure natural gas feedstock and complete work to convert the plants to run on gas. The government's aim is to secure urea supply in the south of India – the three plants are in the southern states of Karnataka, Tamil Nadu and Kerala. The total annual urea requirement of these states is around 2.3 million t/a, and production from the three plants totals around 1.5 million t/a of this. If these three units had been closed, the entire requirement of the southern region would have had to be sourced via imports.

Fertilizer minister Ananth Kumar has also said that the fertiliser sector will get a 500 billion rupee boost ($8 billion) over the next four years to boost the country's urea capacity by 8 million t/a and make it self-reliant in urea. The government's 'New Urea Investment Policy' has led to interest from around 12 companies in setting up urea plants in the country.

Gas prices to be unified from July

India's oil ministry has said that gas prices charged to urea plants will be 'pooled' at a uniform rate from July 1st. Under the plan, the price of cheaper domestic gas will be averaged or pooled with the cost of expensive imported LNG to create a uniform rate for fertiliser producers. India's ammonia plants currently consume about 42.25 million m^3/day of natural gas, of which 26.5 million m^3/d comes from domestic fields and the remaining 15.75 million m^3/d from imported liquefied natural gas (LNG). The unified price of $4.66/MMBtu is around half the delivered cost of LNG. State-owned gas utility Gas India Ltd (GAIL) will be responsible for the gas pooling, based on requirements set by the Department of Fertilizers.

UNITED STATES

Casale signs catalyst development agreement

QuantumSphere, Inc. a leader in nanoscale catalyst technologies, has entered into a multi-year joint development agreement with Swiss-based Casale SA. Casale technologies are used in approximately 38% of global ammonia production and 39% of global methanol production, according to the company. The agreement will cover development of commercial technologies for ammonia, methanol, and other industrial chemicals. Casale has also agreed to make QSI its exclusive provider of nanocatalysts for its chemical synthesis processes during the term of the agreement.

The first objective of the agreement is to validate and optimise QSI-Nano catalysts with Casale production reactor technologies. Following a successful validation phase, the second objective is to enter into a long-term agreement with Casale for the joint global distribution and sale of QSI-Nano catalysts with Casale reactor technologies to chemical plant owners and operators.

"Casale is a world-class partner. We look forward to working closely with their team to validate and optimize QSI-Nano catalysts along with Casale's new process technologies for ammonia, methanol, and other chemicals and then jointly sell these products," said Kevin Maloney, QSI president and CEO. "The joint development agreement with Casale follows the recent commercial validation of our *FeNIX*™ nano iron catalyst by a leading Chinese industrial chemicals partner, which opens up a large array of opportunities."

Federico Zardi, COO of Casale, said; "we are extremely pleased to be working with QSI, a proven leader in nanoscale technology. We have entered into this joint development agreement based on the very promising potential market opportunity of QSI-Nano catalysts combined with Casale's leading process technologies for the benefit of our customers around the world. We look forward to a mutually beneficial and long-term commercial relationship."

Borealis and Agrifos to set up ammonia plant in Texas

Borealis and Agrifos Partners LLC have reached a preliminary agreement to jointly develop a world-scale ammonia project via Gulf Coast Ammonia LLC (GCA), a company set up by Agrifos to develop the project. The plant will be located within an existing chemical site along the Texas Gulf Coast. GCA is in

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final negotiations with a short list of strategic site owners and expects to make a final site selection within the coming few months. The brownfield, hydrogen-based project is scheduled for mechanical completion and start-up in early 2019. The site will be supported by existing infrastructure and logistics capabilities. Borealis, says that it is likely to take a "significant" equity stake in the project, and that it will also enter into a long-term off-take agreement for approximately 40% of the ammonia produced by the plant.

Markku Korvenranta, executive vice president base chemicals, Borealis, said; "by participating in the development of, construction of and off-take from a world-scale project in the US, Borealis is able to secure long-term supplies of ammonia based on the attractive economics of US natural gas. It also is a key step in the Borealis goal to sell 10 million tonnes of nitrogen-based fertiliser products per year by 2020. Gulf Coast Ammonia's project is all the more compelling because it builds on existing site capabilities and assets along the US Gulf Coast."

Ammonia leak hospitalises 16

An ammonia release at Agrium's nitrogen facility in Borger, Texas, hospitalised 16 contract workers in late May. Officials said they believe a failure in an ammonia pump caused the leak at the urea plant, with around 40kg of ammonia released. The plant area was evacuated while the exposed workers were taken to area hospitals. The contract workers were from Houston-based engineering firm KBR, part of the crews working on the $720 million expansion project at the facility. The expansion will add a new urea unit with a capacity of approximately 610,000 t/a and increase annual ammonia capacity to approximately 635,000 t/a from its current 490,000 t/a.

ISRAEL

New research centre for plant nutrition

The Centre for Fertilization and Plant Nutrition (CFPN), a new institution for research and knowledge in the field of fertilizers and plant nutrition, is to be established under a cooperation agreement between the Israeli Agricultural Research Organization (ARO) and fertilizer manufacturer Israel Chemicals Ltd (ICL). CFPN will operate at the ARO Gilat Research Center in the Negev, with research conducted by ARO scientists in partnership with colleagues from other research institutions. The centre will also closely collaborate with the regional council representing farmers in the area. CFPN will also offer scholarships and research grants to graduate and PhD students from Israel and other countries, with funds allocated to dissemination and sharing of research findings to a global audience and to hosting international conferences, helping to cement Israel's place as a world leader in the field of fertilization and plant nutrition.

"Plant fertilization has a decisive impact on crop quantity and quality," said Nissim Adar, CEO of ICL Fertilizers. "Optimising and adapting fertilization to the needs of the crop leads to increased yield per unit area, greater plant resistance to stresses, and improved crop quality. It enables farmers to feed the growing population and to fight world hunger." However, the number of researchers in this field is diminishing. "It is important for us to produce a new generation of researchers in this field," said Prof. Yoram Kapulnik, director of ARO. "It is clear that this knowledge is needed today more than ever. Correct fertilisation increases crop resistance to diseases and pests and thus can help reduce the use of pesticides. It also allows plants to better cope with various stresses, and can enhance the nutritive and health value of the produce. The shelf-life of the crop after harvesting can also be extended."

AUSTRALIA

Collie urea project likely to move

Australia's A$3.5 billion coal-based Collie urea project is likely to move its projected location to the state of Victoria due to difficulties in sourcing coal in its original location near Perth, Western Australia. Developers Perdaman Industries had hoped to build the $3.5 billion plant at the Shotts Strategic Industrial Estate at Collie, 200 km south-east of Perth, adjacent to coal reserves there, but work on the project was halted in 2011 after Perdaman became embroiled in a legal dispute with coal supplier Griffin Coal after a change of ownership. The company says that it is now in formal negotiations with a coal miner in Victoria, and said it was "highly likely" to move the project in July. Analysts have questioned the viability of a coal-based urea project in Australia in the current urea price environment, but Perdaman Chemicals chairman Vikas Rambal says that "the economics of the project depend on capital cost and other related costs, which are now more favourable for the Perdaman project, and make the cost of urea produced comparable to, or lower than, the cost of urea produced in the rest of the world. Specifically, the exchange rate has come down, therefore reducing construction costs" – the EPC contract is likely to be priced in US dollars – "interest rates are lower; equipment and labour rates are more competitive; and the plant design has been improved, resulting in capital cost savings."

Orica looking to increase ammonia production

Chemical giant Orica is seeking permission to increase ammonia production at its Kooragang Island facility above the original limit approved by planning officials. The present ammonia plant has a designated capacity of 360,000 t/a, and the company is seeking to increase its annual production limit by 25,000 t/a as a result of debottlenecking work. Orica says that if this is not approved, it will need to lower its production rate or stop ammonia production for more than three weeks over the course of the year. The company uses ammonia produced at the plant to manufacture nitric acid and ammonium nitrate at the same site.

UNITED KINGDOM

New sulphur enhanced urea technology

Shell has announced the development of *UreaPluS* technology, the second generation of its *Thiogro* sulphur-enhanced fertiliser technologies. *UreaPluS* technology for the first time enables fertiliser manufacturers to incorporate micronised sulphur particles into urea, producing a differentiated sulphur-enhanced urea product. "As Shell's integrated sulphur management business, we are proud to be able to help meet the global demand for sulphur as a plant nutrient by launching a technology that can deliver sulphur to plants through the most widely-used nitrogen fertiliser in the world – urea," said Mike Lumley, general manager of Shell Sulphur Solutions.

Shell's *Thiogro* team has already produced various high nutrient density grades of sulphur-enhanced urea, ranging from 7-18% elemental sulphur, over the course of two successful pilot runs at IFDC (the International Fertilizer Development Centre), in Muscle Shoals, Alabama. The team is now focused on testing this product in agronomic and scientific trials, and integrating the technology with various urea forming technologies. *UreaPluS* utilises Shell's micronisation technology to emulsify the particles of elemental sulphur evenly throughout the urea, forming a homogeneous granule, in contrast to existing elemental sulphur-containing urea technologies, which typically coat urea in a layer of elemental sulphur. The microscopic size of the sulphur particles, at under 40 micrometres (μm), promotes the oxidation of the sulphur within the crop season. It is expected that the technology will also be able to incorporate micronutrients like zinc and boron into the granule, enabling urea manufacturers to produce customised grades that meet local needs.

VIETNAM

Ammonia expansion for PetroVietnam

PetroVietnam Fertilizer and Chemicals Corp has awarded a $237 million expansion contract to a consortium including Technip and Thyssenkrupp Industrial Solutions. Under the deal, the company's annual ammonia capacity will rise by 20% to 540,000 t/a in 2017, it said in a statement. The extra ammonia will be used in a new unit to be built at PetroVietnam's Phu My complex to produce 250,000 t/a of NPK fertiliser a year from 2Q 2017. Vietnam consumes around 4 million t/a of NPK, with domestic supply currently meeting just 10% of that demand.

IRAN

Plans for petrochemical complex dusted off

Iran says that it is moving ahead with long-mooted plans to develop a massive gas based petrochemical complex at that port of Chabahar on the Gulf of Oman. The $12 billion project would consist of 17 petrochemical plants designed to produce 22 million t/a of petrochemical and polymer products destined for markets in Pakistan, India and China. The complex is intended to include four methanol units, each of 1.65 million t/a four ammonia/urea trains, each with a capacity of 1.275 million t/a, two methanol/ammonia units producing 1.0 million t/a of methanol and 300,000 t/a of ammonia, an 800,000 t/a DME unit and methanol to olefins production making 450,000 t/a, as well as aromatics, melamine and polyolefins production.

MALAYSIA

Samur running six months late

Petronas Chemicals says that it is expecting to start up its Sabah ammonia and urea (Samur) project early next year, about six months behind schedule. The plant was originally slated to be completed by August 2015 and is set to make Petronas Southeast Asia's second largest producer of urea. Arif Mahmood, chief executive of the downstream division of Petronas said at a conference in Kuala Lumpur that the start-up date for Samur is now the first quarter of 2016. The plant was delayed from its earlier start-up schedule after a vessel transporting critical equipment to the plant site caught fire early last year.

UKRAINE

Production stopped at two plants

Group DF said that it had ceased production at its Ostchem plants – Azot PJSC (Cherkasy) and Rivne Azot PJSC. As well as the ongoing conflict in the east of Ukraine, the company has blamed political pressure from the People's Front government, including what the company calls "deliberate fabrication of a range of criminal cases against Ostcehm executive officers and... absolutely unlawful cessation of supply of natural gas." Group DF stopped production at Concern Stirol and Severodonetsk Azot in May 2014 due to the military conflict with Russian-backed rebels.

AZERBAIJAN

Neste Jacobs to manage SOCAR urea project

The State Oil Company of Azerbaijan (SOCAR) has appointed Finland's Neste Jacobs Oy as project management consultant for SOCAR's ammonia-urea project at Sumgayit. The urea plant project is being developed by SOCAR jointly with South Korea's Samsung Engineering Co. Neste Jacobs will form a project management team to supervise the EPC contractor on behalf of SOCAR. The project is designed not only to meet domestic demand for fertilizers, but also to export to the world market through SOCAR's terminal at Kulevi. By the time the new complex is up and running it will produce 1,200 t/d of ammonia and 2,000 t/d of urea. The plant will be commissioned in 2017.

"We are proud to provide our strong knowledge to SOCAR in this state-of-the-art world scale fertilizer industry project. We understand the value of the project both for SOCAR and the Republic of Azerbaijan. This is also an important project for Neste Jacobs from a strategic point of view," said Jarmo Suominen, managing director of Neste Jacobs.

NETHERLANDS

OCI to buy BioMCN

Egyptian-based OCI says that it has reached agreement to buy Dutch methanol producer BioMCN for €15 million. The transaction will not cover BioMCN's glycerine activities, which will continue under the name Dutch Glycerin Refinery. BioMCN is one of Europe's largest remaining methanol producers and owns two methanol plants, of which one is operational (with a production capacity of 440,000 t/a) and the other, 430,000 t/a unit mothballed. Both plants are sited at the Chemical Park Delfzijl, with connection to the national natural gas grid and logistical access to major European end markets via road, rail, barge and sea freight. The plant uses glycerine waste from biodiesel production as a feedstock via a vapourisation process to produce what BioMCN describe as "bio-methanol". The methanol is certified as renewable by EU authorities and is then used in a variety of downstream products.

OCI has moved into the syngas industries originally via ammonia and urea production, with plants in Egypt and via the purchase of Dutch-based DSM Agro. It expanded into methanol via the acquisition and revamping of the Beaumont methanol plant in Texas, which operates 910,000 t/a of methanol capacity. The new acquisition will create a foothold for OCI in the European methanol market, which consumes more than 7 million t/a, of which approximately 30% is used in transportation fuel applications (biodiesel, MTBE etc).

Europe currently imports more than 5 million tons of methanol and this deficit is expected to continue to increase for the foreseeable future. OCI is also currently expanding its Beaumont plant via the addition of another 1.75 million t/a of methanol capacity in the Natgasoline venture.

"This is an important addition to our natural gas-based portfolio of products at a time when natural gas prices are becoming more favourable in Europe," said OCI chief executive Nassef Sawiris. "We are firm believers in the methanol industry and its growth prospects," he added. "Methanol is a diverse building block for industrial chemicals and can be used as a transportation fuel. This acquisition gives us a foothold in both the European methanol markets and in the bio-methanol market."

CHINA

Ethylene glycol from syngas

Leading Chinese energy and chemical engineering form Wison Engineering Services Co. Ltd says that it has signed a strategic cooperative agreement with Guizhou Xinxin Chemical Engineering Co., Ltd. and Tianjin University to jointly cooperate to commercialise their proprietary technology for production of ethylene glycol from syngas. Wison Engineering will also provide EPC services relating to a demonstration unit to produce 70,000 t/a of oxalic acid and 10,000 t/a of ethylene glycol under the strategic agreement. Tianjin University will provide the process design package of syngas-to-ethylene glycol technology, Wison Engineering will work on engineering design and project management services, and Xinxin Group will invest in the construction of the ethylene glycol demonstration unit as s pilot plant for further technology optimisation. Tianjin University's syngas-to-ethylene glycol technology uses gas-phase CO coupled with synthetic oxalate and oxalate hydrogenation to produce ethylene glycol.

Liu Haijun, senior vice president of Wison Engineering, said; "Wison Engineering is committed to continuous technological innovation and new technology engineering. We are very honoured to forge a strategic cooperative alliance with Tianjin University and Xinxin Group… to promote the rapid development of China's modern coal chemical industry."

Mr. ShenXin, President of Guizhou Xinxin Group, said "Xinxin Group fully recognizes the role of science and technology in the transformation and upgrading of traditional industries. Hence, in 2009, we entered into full cooperation with Tianjin University in the carbon-1 chemical industry, and have since made a series of achievements. We look forward to this fruitful tripartite cooperation that will lead to a new pattern of coal-to-ethylene glycol technology."

Coal to SNG project complete by 2018

Sinopec Xinjiang Energy Chemical Co Ltd, a 90-10 joint venture between oil major Sinopec and the state of Xinjiang, is to build an 8 billion Nm^3/year synthetic natural gas (SNG) plant at the Dajing industrial park in the Zhundong Economic and Technology Development Zone. Total investment for the project is put at 59.35 billion yuan ($9.5 billion). The project comprises a combined gasification unit which composed of 2.4 million Nm^3/h of pulverised coal gasification and 1.25 million Nm^3/h of powdered coal gasification. The project also includes an 8 billion Nm^3/year methanation plant, a 60,000 t/a sulphur recovery unit and a 500,000 t/a coal tar hydrogenation unit. The general construction period is scheduled to be 57 months, with completion and initial start-up expected in 2018.

Waste gas streams will be treated by desulphurisation/denitrification, dust removal, sulphur recovery, adsorption and incineration. A waste water treatment plant is designed to treat waste water from individual units as well as contaminated rainwater and domestic waste water. After pre-treatment, membrane concentration and vapourising crystallisation, recovered fresh water and distilled water will be recycled to process, while crystallised inorganic salt components will be sent to landfill. This means the project will realise zero waste water emissions.

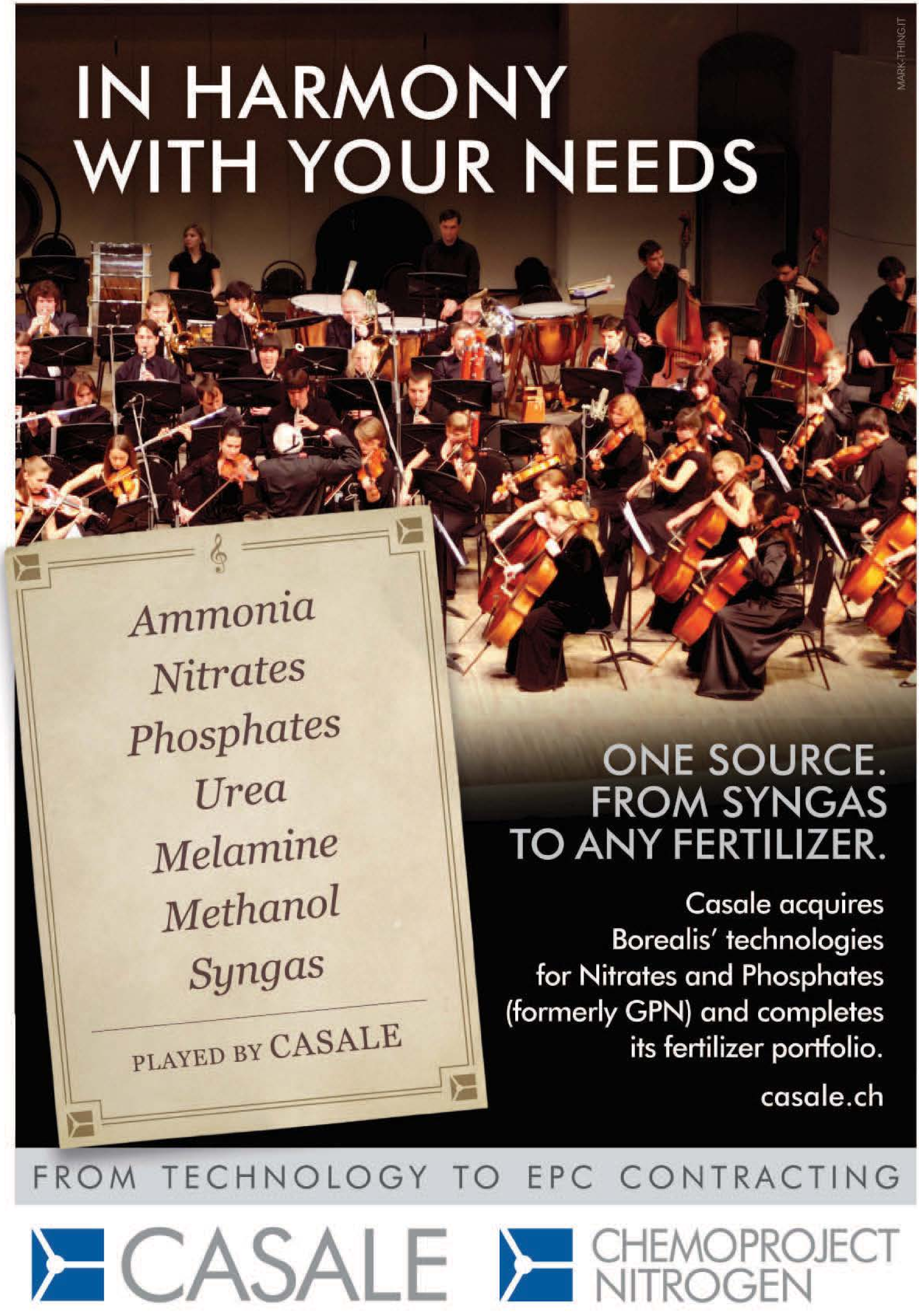
NDRC approves nine CTO projects

China's National Development and Reform Commission (NDRC) has approved the construction of nine coal to olefins (CTO) units across the country, subject to approval by state planning authorities. The projects, all based on methanol to olefins technology, are; CPI Ordos CTO project; Zhongtian Hechuang Ordos CTO project; Heilongjiang Longtai Shuangyashan CTO project; SSinopec/HNEC Hebi CTO project; Sinopec Bijie CTO project; ChinaCoal Yulin CTO project; Huahong Huijin Pingliang CTO project; Qinghai Mining Haixi CTO project; and the Shenhua Group Hulunbeier CTO project.

UNITED STATES

MTG licensing tie-up

Air Liquide's Global Engineering and Construction division has entered into a global technology licensing agreement with ExxonMobil Research and Engineering. Under the terms of the agreement, Air Liquide



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CASALE
CHEMOPROJECT
NITROGEN

will market and license its proven Lurgi MegaMethanol™ technology combined with ExxonMobil's proprietary methanol-to-gasoline (MTG) technology to convert natural gas into ultra-low sulphur gasoline. The combination of technologies will be marketed under the trademark G2G™. The partners say that the integration of Air Liquide Global E&C Solutions and ExxonMobil technologies into one combined solution will minimise project interfaces, off sites and logistics complexities, as well as overall investment for synthetic fuel production. The G2G™ technology offer will be licensed as an integrated solution and will be sold globally through Air Liquide Global E&C Solutions.

Air Liquide has signed nearly 20 licenses for its Lurgi MegaMethanol™ technology since 2000, especially recently in the US, while ExxonMobil has demonstrated its MTG technology in New Zealand from 1985-95 and at a second in China since 2009. A third facility is currently under construction, also in China.

Cristiano Tortelli, vice president and chairman, Air Liquide Global E&C Solutions, said: "methanol has become a promising energy carrier, enabling the market to fully utilise the potential of lower-cost energy sources into low-sulphur transportation fuels. This technology licensing agreement will further enhance Air Liquide Global E&C Solutions' technology portfolio, in line with Air Liquide Group's mission to create value over the long term by delivering high-quality solutions to customers."

GTL from shale

American GTL Energy Holdings LP has announced that it has completed a feasibility study for building a 20,000 bbl/d gas to middle distillates plant to process natural gas derived from the Marcellus and Utica shales. The study has been based on detailed information provided by BP and Johnson Matthey Davy Technologies ('JM Davy'), based on BP's fixed bed Fischer-Tropsch technology and licensed synthesis gas production technology from JM Davy.

Andy Hiles, business development and licensing director for JM Davy, commented; "this opportunity has been developed over a number of years and it is very encouraging to see the project taking the next step. The American GTL project team and JM Davy/BP technology team have worked closely together to develop a concept into a viable project and we look forward to the next stage of working with American GTL, their partners and their chosen detailed engineering contractor to realise this project in early 2020."

A project budget has been developed by an independent EPC contractor which has confirmed the feasibility of the project even in the current low oil price environment. The project financing is progressing in two stages, with the financing of stage one currently under way. A number of sites have been evaluated with one particular site now under detailed evaluation prior to purchase. The plant is expected to start production in early 2020.

American GTL CEO Steve Frobouck commented; "we are excited about the results of the study, as it has reinforced our strong belief that a project of this scale, executed with the right partners and technology providers, can be delivered in a cost-effective way. Choosing JM Davy and BP as our licensing partners has been vital in getting us to this position and we look forward to continuing the collaboration as we progress the execution of the project."

LNG exports approved by Department of Energy

Pieridae Energy has confirmed that the US Department of Energy (DoE) has granted its US subsidiary long-term multi-contract authorisation to export natural gas to Canada for end use in Canada and to export LNG produced from this natural gas in Canada to countries with which the US has entered into a free trade agreement. Pieridae Energy has requested being able to export up to 292 billion cubic feet (bcf) per year of natural gas (0.8 bcf per day) via the Maritimes Northeast US and Canada pipelines. The natural gas exported to Canada will be purchased by Pieridae and will then be processed at the proposed Goldboro LNG liquefaction facility located in Goldboro, Nova Scotia, and exported as LNG to FTA countries.

Ground broken on GTL plant

Envia Energy, a joint venture between Waste Management Inc., Ventech Engineers International LLC, NRG Energy Inc. and Velocys plc, recently held a ground breaking ceremony for its gas-to-liquids (GTL) plant, located adjacent to Waste Management's East Oak Landfill in Oklahoma City. The project will be the first of a series of GTL plants the Envia JV plans to develop to produce renewable diesel fuel, synthetic waxes and naphtha from a combination of landfill gas (LFG) and natural gas. The project will provide a commercial reference for Velocys' small-scale GTL technology. Ventech will design and build the project using its experience in the modular construction of process plants. The project will employ Waste Management's landfill gas recovery and clean-up techniques, and will use NRG's experience in energy project development. The joint venture, formed in March 2014, made a final investment decision in August. Permitting and procurement of all major equipment has been completed and fabrication of the FT reactors and plant modules is under way. Envia says that the facility is on track for commercial operation by the first half of 2016.

Velocys is also working on several GTL and biomass-to-liquid projects, such as the Red Rock Biofuels project in Lakeview, Oregon, which is looking to achieve an investment decision later this year. In addition, Velocys is developing a GTL project in Ashtabula, Ohio, and has a number of other projects in the pipeline in North America and internationally.

Linde expands syngas production at LaPorte

Linde has completed a $200 million expansion at its site at LaPorte, Texas. The expansion includes one of the largest air separation units (ASUs) in the country and a third partial oxidation reformer to process natural gas into syngas. The syngas goes to feed the 780,000 t/a LyondellBasell methanol plant at Channelview, restarted in 2013, as well as to provide hydrogen for local refineries and petrochemical facilities.

Methanol production begins at Pampa

G2X Energy says that the company's 65,000 t/a Pampa, Texas methanol plant is now fully operational and has completed its first shipment of methanol. After building commercial quantities of inventory on site, the plant shipped its first two railcars of IMPCA specification methanol and will continue to ship to customers throughout the Texas panhandle region. "We are extremely pleased to have achieved commercial methanol production at our Pampa, Texas facility," said Tim Vail, president and CEO of G2X Energy. He added; "this plant represents the rebirth of the petrochemical business in the Texas panhandle. By revitalising an abandoned industrial site and leveraging the widespread availability of low-cost of shale

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47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64

gas, we have brought high quality jobs and prosperity back to the area."

Through its partnership with Methanol Holdings (Trinidad) Limited and methanol wholesaler Southern Chemical Corporation, G2X is enlarging its North American operations with the construction of a world-scale methanol facility in Lake Charles, Louisiana as well as the acquisition of natural gas reserves in the Piceance basin of Colorado and other areas.

UNITED KINGDOM

Construction nearing completion on waste gasification plant

Construction work is nearly complete on Air Products' second 50 MW plasma gasification waste to energy facility on Teesside, in northeast England. Once the plant has finished commissioning, it will process 350,000 t/a of 'refuse-derived fuel' (RDF) at the Tees Valley gasification near Billingham. TV1 (Tees Valley 1) will be treating pre-processed municipal, commercial and industrial waste supplied by Impetus Waste Management, diverting it from the waste firm's landfill site which is nearby. The plant gained planning permission from Stockton-on-Tees borough council in 2011. The estimated cost of £320 million ($510 million) has been funded almost entirely by US-based Air Products.

SINGAPORE

Methanol Institute working to reduce methanol deaths

The Methanol Institute (MI) says that, as the trade association for the global methanol industry, it and its members are "saddened" by recent incidents of methanol poisonings in India from the illegal manufacturing and distribution of adulterated alcoholic beverages. The illegal manufacturing and distribution of contaminated alcoholic beverages carries serious consequences leading to injury and loss of life, either from deliberate adulteration or poor distillation of homemade alcohol.

MI says that it "strongly condemns" the illegal use of methanol in alcoholic drinks and has contacted the Indian government to volunteer its support and resources. The methanol industry contributes significant resources to educate consumers and the medical communities globally about the dangers of consuming adulterated alcoholic beverages and about how to prevent, identify, and treat successfully suspected cases of methanol poisoning.

Since 2014, MI and The L.I.A.M Charitable Fund have developed and implemented successful community and medical education programs in Indonesia. These programs have reached out to thousands of local residents and tourists in Bali, Lombok, and the Gili Islands, and have similarly provided medical and educational training to hundreds of local public health officials and medical personnel. The L.I.A.M Charitable Fund was founded in March 2013 by Lhani and Tim Davies, whose son Liam had died from unknowingly drinking methanol-tainted alcoholic spirits while on holiday in Indonesia's Gili Islands in January 2013. L.I.A.M is an international organization dedicated to providing alcohol poisoning prevention educational and training services to the public and medical community in Indonesia.

According to figures assembled by the Methanol Institute, methanol contamination or adulteration of alcohol resulted in 600 deaths in India from 2001 to the present, and 650 deaths in Kenya in the past two decades. ■

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People

Dr. Abdulrahman Jawahery

Gulf Petrochemical Industries Company (GPIC) President **Dr. Abdulrahman Jawahery** has been named President of the International Fertilizer Industry Association (IFA). This is the first time in 30 years that an Arab national has been elected to head the international body, representing the global fertilizer industry on issues related to the promotion of plant nutrients, improvement of the operating environment of member companies and the collection and compilation of industry information. In a statement, Dr. Jawahery expressed great pride and happiness at the appointment. He said it was a statement demonstrating IFA's confidence in the advancement of the petrochemical industry in the Arab world in general and the Gulf region in particular, reflecting global confidence in the Arab leadership cadres and their competence in handling specialised positions at international institutions. He added that the appointment would increase the responsibility placed on GPIC and all its employees to enhance sustainability, not only in Bahrain, but globally.

Dr. Jawahery, who holds a Ph.D in Engineering and a Master's Degree in Chemical Engineering from London, and is a fellow of the British Institute of Chemical Engineers; pledged to continue working with his colleagues at IFA to further develop the work systems and promote the exchange of experiences as well as contributing to developing new innovative ideas and successful programmes.

Mosaic has named **James 'Joc' O'Rourke** as the phosphate fertilizer giant's new president and chief executive. O'Rourke, 54, joined Mosaic in 2009 and since 2012 has served as executive vice president of operations and chief operating officer. He will succeed the retiring James Prokopanko as president and CEO on August 5, the company announced Thursday.

"The board has full confidence in Joc and the rest of Mosaic's talented management team," said Robert Lumpkins, chairman of the company's board. "Together, they will help Mosaic build on Jim's legacy of success for our employees, customers, investors, communities and other stakeholders."

Before joining Mosaic, O'Rourke was president of the Australia Pacific region for Barrick Gold Corp. and responsible for Barrick's 10 gold and copper mines in Australia and Papua New Guinea.

Prokopanko said he is confident of O'Rourke's leadership and of the company. "It has been a great privilege to serve as CEO and help build the world's leading crop nutrition company alongside some of the most talented people I have ever known," he said. "I deeply appreciate the outpouring of support I received during my illness last year, and I am happy to be healthy today. I plan to enjoy my good health with my family." Prokopanko had taken leave last summer because of cancer treatments.

EuroChem have announced that **Dmitry Boldyrev** will assume the position of managing director trading and relocate to Zug, Switzerland effective July 1, 2015. This is in addition to his current responsibilities as head of trade and operations. **Rudolf Graf von Plettenberg**, currently managing director of EuroChem Agro, will join Boldyrev as head of premium products and development. The role encompasses NPK and premium product strategies, research and development, marketing, and the development of international projects. **Andriy Savchuk** has been promoted to regional director for Europe and managing director of Eurochem Agro based in Germany. ■

Calendar 2015

JUNE

22-26

IFDC/IFA Nitrogen Fertilizer Production Technology Workshop,
VIENNA, Austria
Contact: IFDC, P.O. Box 2040,
Muscle Shoals, Alabama 35662, USA.
Tel: +1 256 381 6600
E-Mail: training@ifdc.org

AUGUST

30-3 SEPTEMBER

AIChE Ammonia Safety Symposium,
BOSTON, Massachussets, USA
Contact: AIChE Customer Service
Tel: +1 800 242 4363/
+1 212 591 8100
Fax: +1 212 591 8888
Email: xpress@aiche.org

SEPTEMBER

21-23

IFA Production and International Trade Conference, Florida, USA
Contact: IFA Conference Service,
28 rue Marbeuf, 75008 Paris, France.
Tel: +33 1 53 93 05 00
Email: ifa@fertilizer.org

OCTOBER

4-9

Ammonium Nitrate/Nitric Acid Conference,
JASPER, Canada. Contact: www.an-na.org

26-28

Asian Nitrogen+Syngas Conference,
JAKARTA, Indonesia.
Contact: CRU Events, Chancery House,
53-64 Chancery Lane,
London WC2A 1QS, UK
Tel: +44 20 7903 2444
Fax: +44 20 7903 2432
Email: conferences@crugroup.com

NOVEMBER

4-6

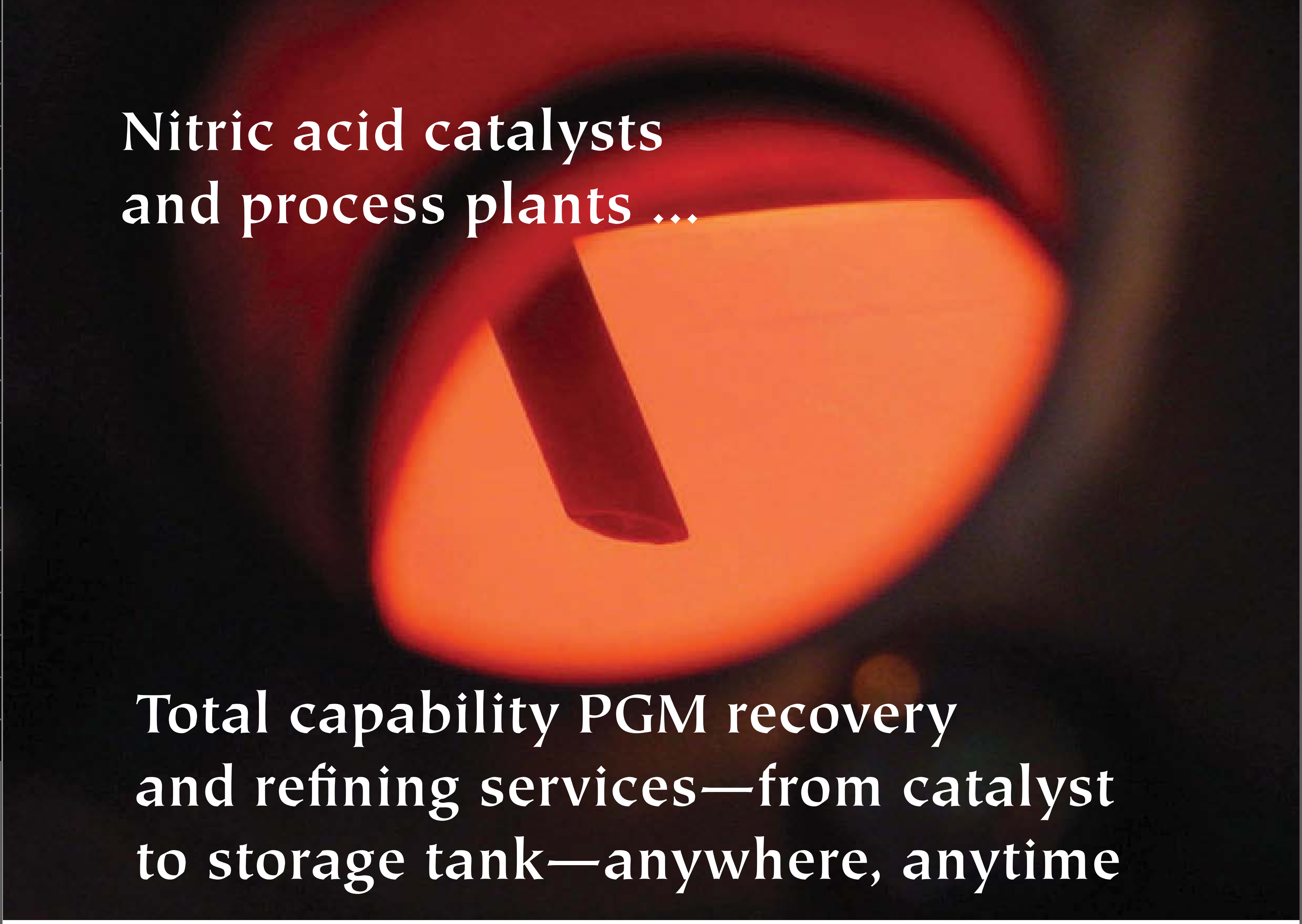
IMPCA Asian Methanol Conference,
SINGAPORE
Contact: Methanol Market Services Asia
Tel: +65 64 65 27 20
Email: services@methanolmsa.com

10-12

World Methanol Conference,
MUNICH, Germany
Contact: Lynn Urban, Sales Manager,
IHS Events.
Tel: +1 303 397 2801
Email: Lynn.Urban@ihs.com
www.ihs.com/events/world-methanol-conference-2015/overview.html

23-27

Training Programme for Urea Engineers,
DOHA, Qatar
Contact: UreaKnowHow.com
Email: mark.brouwer@ureaknowhow.com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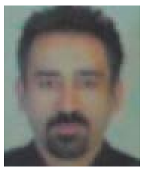
Problem No. 31 Insulation of high-pressure flanges in a urea plant

The intermediate product in the production of urea from carbon dioxide and ammonia is ammonium carbamate. Ammonium carbamate is very corrosive under the synthesis conditions in a urea plant. It is good practice to minimise the number of flange connections in the high pressure urea synthesis section. However some flange connections will be unavoidable. Typically two types of flange connections are applied in the high pressure urea synthesis section: ring type joints and lens ring joints. Once a flange connection leaks it is almost impossible to stop the leak by re-tightening the bolts. Due to the leak a crevice is created in which the oxygen dissolved in the carbamate containing liquid will be depleted and passive corrosion will become active corrosion. Active corrosion rates of stainless steel can be >50 mm per year and this means that in the case of a leaking flange connection one has to stop the plant immediately and service the leaking flange connection. This raises the question whether the flange connection should be insulated.



Mr Easa Norozipour of Khorasan Petrochemical Company in Iran starts up the round table discussion: What do people recommend as regards insulating the high pressure flanges in the high pressure section in a urea plant?

Mr Prem Baboo of National Fertilizers Limited in India responds: Insulating flanges is a generic term of pipe flange joints with requirements in sealing performance of buried steel pipes and insulation properties of electro-corrosion pipes. It includes a pair of steel flanges; easy to manufacture, strong, high pressure flange-type insulating coupling with wide separation between exposed metal parts. The insulating coupling is made up of two metal half flanges supported on a non conductive cylindrical non-metallic member. The space between the two vertical ends of the half flanges is wound in typical fashion with plastic impregnated glass fibres to provide the necessary working strength.

Easa asks further: Thank you for your reply, but my query is about insulation of high pressure flanges in the high pressure section of a urea plant for heat resistance, not for electrical isolation. If the flanges are covered by insulation leakages cannot be identified via a visual check. In this case the flange and bolts will be corroded (see picture).

Prem replies: In our plant the high pressure urea section flanges are non insulated so that a minor leakage can be easily detected at an early stage. The first sign of a leakage is vapour escaping, which can be easily seen by the rotating shift operator. The flanges are tightened when there is a leakage so it is not possible to have insulation on the flanges. Regular nut bolt cleaning of these flanges is routine practice in our plant checklist. Vessel manhole cover flanges are also non insulated so that leaks can be detected.

Easa asks further: Many thanks Prem. Do any other experts have any recommendations for the insulation of high pressure flanges?

Mr Shoaib Minhas of FFBL in Pakistan shares his valuable experiences: Apart from visual inspections, in my opinion no insulation at the flanges will lead to atmospheric corrosion, surface corrosion, moisture ingress and corrosion under insulation due to improper waterproofing of insulation. In our plant all flanges are covered with proper insulation and waterproofing.

Mr Mark Brouwer of UreaKnowHow.com in the Netherlands joins the discussion: Find below the philosophy of one expert in the industry: "Some of our plants have insulation over the flange joint and others have left flanges that are non insulated. For flanges in carbamate gas service, I like to insulate the flanges to reduce the risk of condensation corrosion (refer to picture). For flanges in liquid service, I like to keep flanges uninsulated to keep the stud bolts visible so that a small leak doesn't go unnoticed

and seriously corrode the bolts." Others apply a leak detection tube in the case of insulated flanges.

Mr David Smith of Startupdynamics in Canada shares his experiences: I have also worked in urea plants, which do both. My preference is to "not" insulate high pressure flange connections in the urea synthesis section. The flanges have a very large metal mass, which retains the heat from the line. In my opinion, the amount of condensation corrosion caused by a cold spot from reduced temperature would be small. The bigger concern would be early detection of leakage from the ring joints. I think most of the bolts used are some type of ferrous material, which may corrode if a leak begins.

Normally a leak is not difficult to determine, based on the ammonia smell or build-up of crystals. Should a leak occur, the first action that happens is to remove the insulation anyway to determine the size of the leak. If it is unmanageable, the plant is stopped and drained, but if it is a small leak, it is tightened or if unsuccessful, flushed by steam to avoid any build-up of corrosion material until the gasket can be replaced. We have used permanent and removable insulation, we have put leak tubes inside the insulation to detect an early leak, but personally I want to know about leaks as early as possible.

Mr Ali Salman Bokhari of Pak-American Fertilizers (Pvt.) Ltd. in Pakistan contributes to the discussion: As per TEC standards, all these flanges must be insulated. The reason behind this may be the following: Generally lens rings are used as a connector in high pressure piping but in some cases titanium gaskets are also used. During start-ups and shutdowns there is a possibility that titanium gaskets may undergo stresses due to uneven expansion of metals. This may weaken the gasket, which at some later stage causes leakages. Insulating the flanges will reduce the extent of uneven expansion of metal by reducing a significant delta temperature, which exists between metal and ambient temperature. The same standard exists in the case of manholes, which are insulated, generally at all plants.

Mr Pablo Gastón Schulz of Profertil in Argentina gives his opinion: We do not insulate flanges in the high pressure section so that bolts do not loosen with temperature, avoiding leaks and the need to tighten them in service.

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.

North American syngas: boom or bubble?

Has the global fall in oil and hence petrochemical product prices tempered the enthusiasm for people to develop new gas-based chemical projects in North America?

High gas prices closed down domestic US syngas-based chemicals production, and now the US is a major importer of both nitrogen fertilizer and methanol. The slump in domestic US gas prices caused by shale gas drilling has therefore led to a plethora of re-starts of mothballed facilities and new project announcements to try and use shale gas to produce downstream products to substitute for these imports. However, the first wave of new capacity is now either already on-stream or well under construction, while the number of new projects still under development has not yet significantly diminished. Is there a bubble about to burst for US gas-based production?

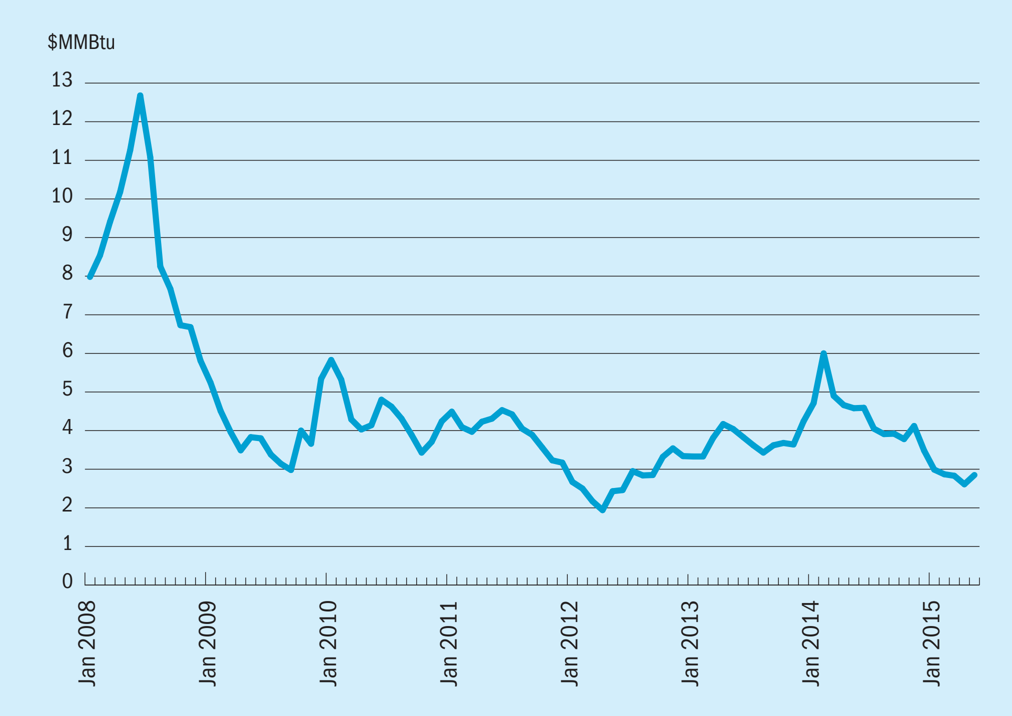
Natural gas

While the story of the US shale gas boom is a well worn one, it is worth briefly reflecting on the speed and scale of the change. In just a decade US gas output has increased by over 40%, from 510 billion cubic metres (bcm) in 2005 to 730 bcm last year according to BP, leaving the deficit from consumption of 760bcm of only 4%. US coal consumption fell by 22% over the same period, as power producers increasingly switch towards natural gas.

Gas pricing, meanwhile, has kept on falling, as Figure 1 illustrates, from peaks in the benchmark Henry Hub price of more than \$12.00/MMBtu in 2008 to just \$2-3.00/MMBtu in the past year. In spite of persistent calls that prices are "too low" to support production, and that producers were losing money, the run of low pricing has continued. Indeed, one of the most striking things about US gas production is that it does not even appear to have been affected by the fall in oil prices during 2014 as many thought it might. The theory was that 'wet' shale plays, which had depended on production and sale of natural gas liquids (NGLs) like ethane, propane and butane, whose prices were determined by the buoyant oil market, had subsidised shale gas production, and with their prices lower we would see margins squeezed and wells shut in. However, this has not happened, at least not yet. The reason is that gas production in the US seems to continue to become more and more efficient. In the northern Marcellus Basin, for example, the rig count has dropped by 50% since 2012 at the same time that production has almost tripled. Producing six times as much gas per rig has meant that the economics continue to remain favourable in spite of the oil price environment. And technology continues to improve, with 'smart' drill bits now able to adapt to rock conditions almost instantaneously.

The other major worry for North American syngas producers was that large scale exports of LNG from the US would drag domestic gas prices upwards, as has happened in Australia. Here, however, it is the slow pace of permitting which has helped the US nitrogen and methanol industries. The US Department of Energy (DoE) lists 54 applications for LNG export, totalling 46 bcf/d, of which only 10 have been approved for export to non-Free Trade Agreement countries. FTAs cover mainly countries in the Middle East and Central and South America – the only potential Asian LNG customer among them is Korea. Likewise, the fall in oil prices has led to a drop in LNG prices in Asia which alters the economics of LNG export projects. Nevertheless, four export plants are currently under construction with a total capacity of 40 bcm/year, with Sabine Pass in Louisiana set to begin commercial exports in February 2016. Construction at Cameron LNG in Louisiana, Freeport LNG in Texas and Cove Point LNG in Maryland started in 2014, and those projects are slated to come on line from

Fig 1: **US natural gas prices**, Henry Hub 2008-15



late 2017 to late 2018. However, even with LNG exports, higher gas prices should drive more gas production, and even the most pessimistic forecasts do not see gas prices rising beyond $5-6.00/MMBtu, making domestic nitrogen capacity still competitive when the cost of importing from overseas and the rising costs of gas elsewhere in the world are taken into account.

North of the border, Canada has also been affected by the changes in the US gas market. Canada still exports around a net 53bcm to the US (actually around 75bcm from Alberta and Saskatchewan, with 22bcm flowing in the opposite direction from the Marcellus Shale to the provinces of eastern Canada). Cheap US gas prices have undercut production of sour gas from Canada's western provinces, and Canadian gas production has dropped by 15% over the past decade.

In response, Canada has also looked to LNG exports to balance its gas production with consumption, sending gas west to gas-hungry Asia, but the cost of producing gas in Canada is generally higher than in the US, and although there are 19 LNG projects in British Columbia according to the BC provincial government, none so far has made a final investment decision – the collapse in LNG prices caused by the fall in global oil has drastically changed the economics of many of the projects, which are often based at greenfield sites with additional development costs. Two projects have seemed the most advanced – Petronas has been planning a 7.4 million t/a LNG terminal at Prince Rupert Island, and Shell is leading a consortium developing a 12 million t/a at Kitimat, but Petronas has deferred its investment decision and Shell says that it will make a final decision this summer. With costs put at $36 billion and $40 billion respectively, these are not decisions to make lightly! Some analysts believe that these projects could make money with oil at $70/bbl, but Brent crude remains stubbornly stuck at around $65/bbl and not forecast to reach $70/bbl until next year at the earliest. With LNG exports apparently off the table in Canada, there has been some interest in developing methanol capacity as a way of exporting gas instead, more on which later.

Table 1: **New nitrogen capacity, North America**

Company	Location	Capacity, million t/a	On-stream	Status
OCI	Beaumont, TX	0.24 ammonia	2014	C
Southern Co.	**Kemper Cty, MS**	**0.02 ammonia**	**2015**	**C**
CF Industries	Donaldsonville, LA	1.1 ammonia	2015	C
		1.16 urea		
		1.4 UAN		
	Port Neal, IA	0.73 ammonia	2015	C
		1.16 urea		
OCI (IFCo)	Wever, IA	0.73 ammonia	2015	C
		0.4 urea		
		1.4 UAN		
Incitec Pivot	Waggaman LA	0.8 ammonia	2016	UC
Agrium	Borger, TX	+0.145 ammonia	2016	UC
		+0.61 urea		
Koch Nitrogen	Enid, OK	0.9 urea	2016	UC
Dakota Gasification	**Beulah, ND**	**0.33 urea**	**2017**	**UC**
JR Simplot	Rock Springs, WY	0.18 ammonia	2017	UC
Mosaic	St James, LA	+0.32 ammonia	2017	CA
Cronus Chemical	Tuscola, IL	0.73 ammonia	2018	CA
		1.27 urea		
Yara/BASF	Freeport, TX	0.75 ammonia	2017	CA
Fatima Group	Posey Cty, IN	0.73 ammonia	2018	P
		0.73 urea		
		1.42 UAN		
CHS	Spiritwood, ND	0.73 ammonia	2018?	P
		Urea, UAN		
Ohio Valley	Rockport, IN	ammonia, urea	2018?	P
		0.9 UAN		
Gulf Coast N	TX	n/a	2019?	P
N Plans Nitrogen	North Dakota	0.73 ammonia	n/a	P
		+urea, UAN		
AM Agrigen	Killona, LA	n/a	n/a	FS
EuroChem	LA	0.89 ammonia	2019?	P
		1.16 urea		
Texas CEP	**Penwell, TX**	**ammonia**	**2019?**	**CA**
		0.76 urea		

Key: C = complete/commissioning. UC = under construction. CA = contracts awarded. P = planned. FS = feasibility study. n/a = figures not available. ***Coal-based plants in bold***

Nitrogen industry

The changing gas market has rejuvenated the US nitrogen industry, much of which had withered as gas prices rose during the 1990s and 2000s, with much ammonia production decamping to Trinidad. With a large and efficient agricultural sector, the US remains the world's third largest market for nitrogen fertilizer, and US agriculture has been boosted significantly by the use of corn-derived ethanol as a fuel blendstock, which has led to an extra 3 billion bushels/year of demand over the past decade. Corn planted area has grown to 90 million acres at the same time that yields have increased from 145 to 165 bushels/acre, according to the US Department of Agriculture (USDA).

Supplying this demand at the same time that domestic nitrogen production has closed has led to the US becoming the largest importer in the world of nitrogen fertilizer. The US imports 6-7 million

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64

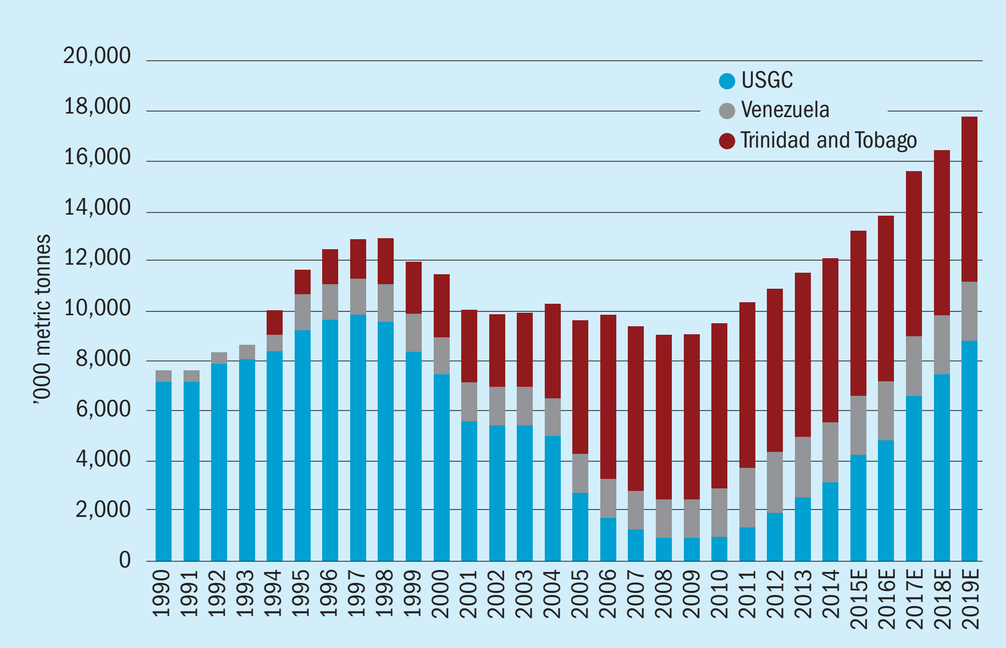
t/a of ammonia (6.0 million t/a in 2013, more than half of it from Trinidad), about 6-7 million t/a of urea (6.4 million t/a in 2013, mainly from Canada and the Middle East), and 2-3 million t/a of UAN (3.2 million t/a in 2013, with Russia and Trinidad the main suppliers). Now that gas prices are cheap once again, this has therefore led to a scramble to reopen capacity and develop new capacity to supply America's burgeoning fertilizer market.

PCS has restarted its idled ammonia plant at Geismar, Lousiana after revamping capacity to 495,000 t/a, replacing imported ammonia as a feed for downstream urea and UAN production. The restart of the Eastman methanol plant at Beaumont Texas, now owned by Egypt-based OCI, has also involved a side stream of 240,000 t/a of ammonia production, and there is a similar 20,000 t/a ammonia side stream from the Southern Company integrated gasification combined cycle power plant in Kemper County Mississippi. There are also revamps which will add capacity planned at Agrium in Borger, Texas and Mosaic's facility at St James, Louisiana.

However, Table 1 shows, most of the new capacity is coming from new plant developments. Most of these are, perhaps unsurprisingly, at existing brownfield sites, where there are experienced companies already running capacity, permitting issues are less fraught than for a greenfield development, and financing easier to come by for a company with a proven track record. CF Industries in particular is completing two large plants, one at its Donaldsonville, Louisiana site, and the other at Port Neal, Iowa. Incitec Pivot is adding ammonia capacity at its Waggaman site, and Koch Nitrogen a urea plant at Enid, Oklahoma and Dakota Gasification a urea unit at its Beulah, North Dakota facility.

Of the rash of greenfield projects, only one – OCI at Wever in Iowa – is currently under construction. All of the others have faced difficulties and delays, and most remain subject to a degree of uncertainty, while some projects have already gone by the board. Famers cooperative CHS has planned a large-scale plant in North Dakota but is having trouble sourcing water supply for the plant and although a decision to commit to the $3 billion investment was made last September, there has as yet been no beginning to construction. Agrium have put off a decision on new plant building, settling for the Borger revamp option instead. A plan by the India Farmers Fertilizer Collective to build a 1.6 million t/a ammonia-urea plant near Quebec was placed on hold earlier this year, and elsewhere in Canada Yara has delayed expansion of its Belle Plaine, Saskatchewan facility to include a 1.3 million t/a ammonia-urea line. Indeed, outside of the lower 48 states, there is only one current nitrogen project under development, as Agrium has been seeking to re-start its Kenai ammonia-urea plant in Alaska.

Fig 2: **Caribbean methanol production capacity,** 1990-2019



Source: MMSA

Other feedstocks

Most of these projects have sought to capitalise on cheap US natural gas, but there are still a handful of projects based on other feedstocks, especially coal. Some of these are relics of the era in the early 2000s when high US gas prices led to a number of projects aiming to develop domestic fertilizer capacity based on gasified coal, backed by George Bush's Clean Coal Initiative. As gas prices have fallen, so most of these projects have gradually fallen by the wayside, and others, like Hydrogen Energy California, which includes 825,000 t/a of planned urea capacity, remain highly uncertain. However, the Kemper County IGCC project, as noted above, has now been completed, and includes 20,000 t/a of ammonia capacity, and the $2.4 billion Texas Clean Energy Project (TCEP) still seems to be proceeding, with 90% CO_2 capture, some of which will be used for urea production of a projected 760,000 t/a.

The Dakota Gasification Co, which has operated the Great Plains Synfuels plant since 1984, and successfully demonstrated coal-based ammonia and methanol production, and, more recently, carbon capture for enhanced oil recovery, is now also developing downstream urea capacity, with a 330,000 t/a unit under construction and due for completion in 2017.

Meanwhile, there are proposals for ammonia plants based on hydrogen generated from wind-derived electricity, as a way of storing renewable energy in remote areas. A small-scale pilot plant has been built in Minnesota, and there is discussion about Juneau, Alaska as a site for a larger scale demonstrator unit, but so far little progress.

Methanol

As with ammonia production, so things have changed in similar fashion for methanol. The US methanol industry had suffered a double blow from rising gas prices on the one hand and the spreading ban on the fuel additive MTBE – which had been the major source of demand for methanol in the US in the early 1990s. As with ammonia production, Trinidad was the major beneficiary of the demise of the US methanol industry, which contracted from 18 plants producing 6.6 million t/a in 1998 to four plants producing 1.0 million t/a in 2005. Now, however, rising production in the US is threatening production in the Caribbean, as shown in Figure 2. The changes wrought by the shale gas boom start to show an effect from 2011, when Methanex restarted its mothballed 470,000 t/a plant at Medicine Hat, Alberta, which had been idled for nine years since its shutdown in 2002. This was followed by a re-start for Eastman's Beaumont, Texas methanol plant in 2013, now owned by OCI after a revamp to generate an ammonia side-stream. Methanex are now in the process of relocating two plants from Chile, where the company has faced gas curtailments, to Geismar, Louisiana, south of Baton Rouge, with one plant now operational and the second under reconstruction. LyondellBasell restarted its 800,000 t/a Channelview methanol plant near Houston, Texas in late 2013, which had been idle since March 2003 and came close to being sold off. These changes also come at a time when gas availability has been crimped in Trinidad and investment cash for production in Venezula has been in short supply.

But as well as restarts and relocations in North America, several large new methanol plants have been under development, most of them in the Gulf Coast region, as shown in Table 2. Celanese Corporation, the world's largest maker of acetic acid, is building a 1.3 million t/a methanol plant at its existing Clear Lake site outside Houston to supply its acetic acid and acetyl plants, and the company is now interested in possibly developing a second plant of similar capacity at its Bishop, Texas site. Both of these plants would be integrated into existing downstream production, and hence have a ready made market for their product, making them far more certain as project developments.

Other, more speculative developments include South Louisiana Methanol, owned by the Zero Emission Energy Partnership (ZEEP) and New Zealand's Todd Corporation, which has been securing gas supply and financing for their proposed 1.7 million t/a methanol plant near New Orleans. China's Yuhuang has also been seeking permits for a similar sized plant in the same location. So far there has been no ground broken on either project, though. Further west, major refiner Valero is studying the possibility of building a 1.6 million t/a methanol plant at the company's Lake Charles complex in Louisiana, with the possibility of downstream conversion to gasoline or olefins, but so far has not made a firm investment decision. The Big Lake Fuels project at Lake Charles, originally developed by G2X, whose small-scale plant recently came on-stream in Texas, now seems to have gained more momentum than these other three projects via the involvement of Methanol Holdings Trinidad Ltd (MHTL), one of the world's largest methanol producers. Big Lake is now looking at a 1.5 million t/a methanol plant with downstream methanol to gasoline production. Environmental permits were gained in June 2015 and construction is now slated to begin in early 2016, according to the developers.

More speculative still is Chinese involvement in two major methanol projects in the US Pacific Northwest. Chinese firm Northwest Innovation Works LLC has sites for two $1.0 billion plants to produce 1.7 million t/a of methanol each for onward transport to China to be use in methanol to olefins (MTO) production. China has a number of methanol to olefins plans under development which will use methanol from the merchant market as feed, and while there is plenty of coal-based methanol capacity, the theory is that cheap gas-based capacity could undercut this. However, it remains to be seen whether the economics and financing stack up.

Finally, there is a proposal in Victoria, British Columbia to use carbon dioxide from a natural gas power plant at Pine River, operated by Spectra Energy, together with electricity from BC Hydro's proposed new Site C dam, to produce methanol to blend as a fuel in the province of British Columbia. Blue Fuel Energy is proposing to build a C$1 billion methanol plant near Chetwynd that would use 4,500 GW hours of electricity per year – virtually the entire output of the new hydroelectric facility – to electrolyse hydrogen to combine with 2,100 t/d of carbon dioxide from the waste stream of the existing power plant, in order to make a provisional 390,000 t/a of methanol. Again, the likelihood of this project coming to fruition remains very uncertain.

Syngas to fuels

Is there room for all of this methanol capacity? One carrot dangled in front of the US methanol industry has been its potential use in fuel blending. Methanol has become a major component of the gasoline pool in China, and for a while was also used in California. The US also of course has considerable experience of fuel ethanol blending. During 2013 the Open Fuel Standard tried to mandate production of flexible fuel vehicles which would be able to use any combination of ethanol and methanol, but there was insufficient political will to pass this and government focus has instead moved on to a Renewable Fuel Standard.

In its wake, however, there have been some projects which have instead looked to produce gasoline from methanol via ExxonMobil's MTG process. As well as the MHTL project proposal at Lake Charles, OCI is developing an MTG project via a subsidiary called Natgasoline to tie in with the company's new methanol plant

Fig 3: **New North American syngas capacity**

at Beaumont, Texas. There is also a company called ZeoGas trying to develop a 1.7 million t/a methanol plant using Air Liquide technology with 16,000 bbl/d of downstream gasoline production in the US Gulf Coast. A debt offering is expected in 2Q 2016 with construction completion and start-up scheduled for 2019.

Moving away from fuels and towards petrochemicals, via methanol to olefins/methanol to propylene (MTO/MTP) – something which has been a major success story in China – BASF have plans to build a methanol to propylene unit in Freeport, Texas by 2019, with a large scale gas-based methanol front-end using Air Liquide technology.

GTL

Other projects have considered conversion of syngas directly to synthetic diesel fuel via Fischer-Tropsch polymerisation. Foremost among these was a Sasol project in Louisiana to convert gas to 96,000 bbl/d of liquids, and a second proposal of similar size in Alberta. Shell was also looking at a major GTL project in North America but abandoned this in early 2014, and Sasol rowed back on its GTL plans earlier this year, with a final investment decision now due for next year, all three projects presumably killed by low oil prices.

Instead, some smaller companies are considering more compact GTL operations closer to prolific natural gas fields. Juniper GTL is developing a 1,100 bbl/d plant in Louisiana co-financed by Calumet Speciality Products, and based on re-using a mothballed steam reformer at a brownfield site in order to reduce project costs. Elsewhere, Modular GTL reactor developer Velocys is participating in a couple of small-scale GTL projects, one for 2,800 bbl/d in Ashtabula, Ohio, acquired with the purchase of developer Pinto Energy, and based on local shale gas from the Utica shale, and the other at ENVIA Energy Oklahoma City, based on gasification of waste. Ground was broken on the latter project in May 2015, with commercial operation expected in late 2016. Velocys is also licensing its technology to Red Rock Biofuels, developing an 1,100 bbl/d biomass to liquids project in Oregon. Marcellus GTL also is planning a 2,000 bbl/d GTL plant in Duncansville, Pennsylvania, although another Pennsylvania GTL project, EmberClear, was recently abandoned due to local opposition. Sundrop Fuels has longer term plans for a biomass to liquids plant in Louisiana, although it is focusing first on methanol to gasoline. Finally, Enerkem Alberta Biofuels started up a plant gasifying 100,000 t/a of waste from the city of Edmonton, Alberta to produce methanol in 2014, with downstream pathways to ethanol, propanol, acrylic acid, acetic anhydride and others all under development.

Table 2: **New methanol capacity, North America**

Company	Location	Capacity, million t/a	On-stream	Status
G2X	Pampa, TX	0.07	2015	C
Celanese	Clear Lake, TX	1.3	2015	UC
	Bishop, TX	1.3	2019?	FS
OCI	Beaumont, TX	1.75	2017	UC
Methanex	Geismar, LA	1.0	2015	C
	Geismar, LA	1.0	2016	UC
Big Lake Fuels	Lake Charles, LA	1.5	2018	P
S Louisiana Meth	LaPlace, LA	1.7	2018	CA
Valero	Lake Charles, LA	1.6	2018	P
Yuhuang	St James, LA	1.8	2019?	P
NW Innovation	Kalama, WA	1.7	2019	P
	Westward, OR	1.7	2019	P

Key: C = complete/commissioning. UC = under construction. CA = contracts awarded. P = planned. FS = feasibility study.

Market changes

The new plants in Table 1 are set to radically reduce US dependence upon imported nitrogen, but not eliminate them. On the ammonia side, the current total of new, under construction and likely new capacity totals around 2.3 million t/a, still some way short of the 6 million t/a imported. For urea, the figure is about 3.7 million t/a of new and likely production out of imports of 6 million t/a, and for UAN 2.8 million t/a out of 3.2 million t/a. This still leaves some room for the new projects which remain at the planned/proposed stage, but not for all of them, and given the number of UAN projects, probably only if that displaces liquid ammonia as a fertilizer. Furthermore, the question of project cost is a very real one, especially for large new greenfield developments; the number of plants that are being worked on concurrently, together with similar developments in related industries, means that contractors time and slots in fabricators schedules are both at a premium, and the cost per tonne of installed capacity may have risen drastically for some of the later projects. Coupled with a depressed urea market because of Chinese capacity overbuild, many of these large greenfield projects begin to look distinctly dubious.

On the methanol side, US methanol imports run at 5-6 million t/a (5.1 million t/a in 2013). Current plants under construction already total 5.1 million t/a, already reaching this total, and the other plants listed in Table 2 total another 11 million t/a – far in excess of US methanol demand, unless large scale downstream uses like methanol to gasoline and methanol to propylene can be successfully developed, even granting that 2.4 million t/a of that total is aimed towards exports to China. The prospect of the US becoming a methanol exporter from the Gulf Coast is made problematic by the amount of written down export-oriented capacity already present in Trinidad and Venezuela, as demonstrated in Figure 2, while the margins for exporting from the US to China, given the cost of developing these massive greenfield plants, seem unlikely to be favourable at current methanol prices. Given that, it seems likely that there is not much room for new methanol plants to begin construction in the US without guaranteed downstream demand.

The area with the greatest market potential has been in fuel uses, but the fall in oil and hence domestic gasoline and other fuel prices in North America has reduced the attractiveness of large gas to liquids facilities, and outside a few niche waste or biomass to liquids plants, or cheaper, small-scale modular GTL production, there seems no great likelihood of any major development in North America until oil prices rise again.

1 47 2 48 3 49 4 50 5 51 6 52 7 53 8 54 9 55 10 56 11 57 12 58 13 59 14 60 15 61 16 62 17 63 18 64 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64

IMTOF 2015

The 13th International Methanol Technology Operators' Forum (IMTOF) was held at the Thistle Hotel in London from June 8th – 10th.

Above: On Monday evening a dinner was held at the Cutty Sark in Greenwich. One of the last surviving examples of a 19th century fast 'tea clipper', the ship and associated museum has been recently refurbished following a disastrous fire in 2007.

While methanol market conferences roll round on a reasonably regular basis, those focusing on methanol technology are much rarer birds. Beginning life in 1993 as the ICI Methanol Technology Operators Forum, IMTOF has been held every two years since then, and while the licensor for ICI methanol technology – developed in the 1960s and still the most popular technology for producing methanol – has been passed on through the years to ICI's Katalco division, then spun off as Synetix, and now finally having been bought by Johnson Matthey, the conference has continued to be a showcase for developments in methanol technology. And so, having overcome a last minute change of venue, IMTOF convened for its 15th incarnation near Marble Arch in London in early June.

Opening the conference, Peter Roberts, Methanol Technology Manager for JM, noted that methanol was one of the most rapidly growing bulk chemical markets, seeing 6-7% growth year on year. Chinese demand, much of it for downstream methanol to olefins (MTO) production now represents much of that, showing an amazing 12% year on year growth, while outside China growth is more subdued at closer to global GDP growth levels of 2-3% per year. In China there are now 13 commercial-scale MTO plants operational, and many more under development.

Giving the his keynote speech, JM's chief executive Robert MacLeod said that as a global commodity methanol was subject to a number of global drivers on both the supply and demand sides, including population growth, urbanisation, economic development and increased wealth, as well as natural resource constraints, environmental factors and energy efficiency, climate change and the continuing drive for cleaner air – methanol fuel blending has now moved beyond China to Israel and Australia, amongst others, and there is the possibility of methanol becoming more widespread as a marine fuel. As well as China's huge push on coal-based developments, the US, seen as a country with low sovereign risk, has attracted investment based on shale gas, with the possibility of some of this becoming gasoline or even being exported to China, but managing project construction costs remains key. Asset performance and integrity are also key concerns, as capex pressures lead to a drive for greater efficiency and increased plant reliability.

Commercial papers

The conference proper began as usual with a review of methanol markets, given by Mark Berggren of methanol consultancy CMAI. Mark reiterated that China is driving both methanol demand and supply, the latter increasingly substituting for refined products, and China will increasingly be the price dictator in spite of the US methanol renaissance. Global demand for methanol is expected to reach 83 million t/a this year, with MTO and formaldehyde now both representing about 25% of this. By 2020 this is expected to have risen to 118 million t/a. Supply has ramped up quickly, but the rate of addition is likely to slow from 2015-2020 and much of that new capacity will be integrated into downstream applications, especially in China.

Outside of China, the US is developing new merchant facilities, but South American production may provide a check on US exports and divert capacity instead to methanol to gasoline (MTG). Asia ex-China remains a net large importer, with strong growth in methanol derivatives. Europe still relies heavily on imported material, into which market Russia is a net exporter with room for additional production, and possibly longer term competition with the US for European markets.

Although the global operating rate for methanol plants is about 65-70%, Mark noted that there is about 22 million t/a of what he described as 'hindered capacity' around the world – plants running on coke oven gas, old gasification plants in China, and gas-based plants where the gas supply is reduced or intermittent, like Trinidad, Chile, Iran etc, implying a global operating rate closer to 80-85%.

Speaking to delegates about the work of the Methanol Institute, Greg Dolan of MI reviewed the institute's latest campaign; against alcohol adulterated with methanol – a major problem in countries like Indonesia. In India 600 people have died since 2001, and 650 people have died in Kenya over the past two decades. MI is working with local charities and community programmes in Indonesia to raise awareness of methanol poisoning and treatment. Fuller details can be found in our news story on page 17.

'Green' methanol

Several papers looked at ways of operating plants with lower greenhouse gas emissions. Firstly, Jim Abbott of JM discussed the prospects for syngas from renewables. He identified two main routes for this; firstly using hydrogen generated electrolytically from renewable electricity, although this also requires a source of relatively pure CO_2. However, renewable energy faces grid balancing problems once it reaches more than about 20% of a country's electricity supply, and this could be a way of 'storing' power when it is in excess. The other route is to gasify biomass. This has the advantage over other biofuels that it uses all available carbon, and is currently used for small scale power generation, and may soon be extended to methanol production. However, when using a low temperature fluidised bed system, there are by-products such as tars, methane and other hydrocarbons which can potentially represent a loss of product. JM is therefore working on a sulphur-resistant catalyst for 'tar reforming – steam reforming of the tar stream. Jim presented a case study of a 4,300 t/d wood gasification system. From a base 1,334 t/d of methanol production, the addition of a precious metal-based tar reformer can add another 40% to overall production, albeit requiring an additional 286 t/d of oxygen.

Alan Ingham of JM looked at ways of producing 'low carb(on) methanol'. The gas heated reformer and autothermal reformer combination generates the lowest CO_2 emissions compared to other flowsheets (by avoiding an auxiliary boiler), but it can achieve even lower emissions by using electrically driven compressors and importing renewable power, in which case up to a 50% reduction in greenhouse gas emissions can be achieved.

Stephen Stanbridge presented ways of improving the carbon efficiency of a methanol plant. Mechanical modifications can make the conversion better approach equilibrium, especially if a quench cooled converter is used, with an energy saving of up to 0.8 MMBtu/t of methanol. Reducing excess hydrogen and/or adding CO_2 and O_2 (while acknowledging that the latter has a cost in terms of capital and operating expenditure) can shave another 0.5-1.0MMBtu/tonne methanol. Other suggestions included using some of the fuel as process feed, or reducing reformer fuel requirements (eg by using a pre-reformer).

Finally of course the question must be asked: lower emissions that what? Guanhua Liu of the Clean Energy Commercialisation Co in China argued that using US shale gas to make methanol and ship it to China instead of domestic Chinese coal could save the planet over 3 tonnes of CO_2 per tonne of methanol produced as well as scarce water resources.

Improving efficiency

"Profiting from purge gas" was the topic for Charles Yiu of JM. A typical steam reformer will have a hydrogen excess after methanol synthesis, traditionally used as fuel for the reformer. A better use is to use it to produce more methanol, where additional CO_2 is available, but another option is to use the purge gas downstream of a parallel autothermal reformer (some is also used upstream to lower the autoignition temperature). The purge gas from one SMR can in theory support up to an additional 1.75 times that capacity in terms of autothermal reformers, with very simple tie-ins, if considering, for example, a phased new build complex.

Troubleshooting

Paul Jackson, standing in for Neil Henry of ABB Consulting, looked at the importance of asset analysis. While many methanol plants around the world are ageing and often subject to being operated at higher duties than originally designed for, when determining likelihood of failure, equipment condition is far more important than age, and a typical plant asset analysis finds that almost 75% of equipment items can still be operated safely for another 20 years, and only a relatively small number will require extensive work for continued service (as opposed to minor repairs or replacement). The results of such an analysis can also pay dividend in terms of plant safety and reliability.

Meanwhile, considering plant monitoring techniques, Dave Ferguson and Kevin Mowbray of JM both looked at methods for plant performance measurement and troubleshooting, ranging from the in-tube *CatTracker* heat sensing system, which can take temperatures at intervals within one or more reformer tubes or a radial catalyst bed, to the *Tracerco* suite of radioisotope measurement techniques, including gamma ray scanning, neutron backscatter, and radioisotope leak detection and residence time measurement.

Operator experience

Several papers dealt with the experiences of methanol plant operators. Tim Usher of Methanex New Zealand explained that his company had had persistent problems with hot bands in reformer tubes in their top-fired steam reformer. The root cause of this appeared to be carbon deposition inside the tubes. Carbon formation occurs when the deposition reaction rate runs faster than the reverse reaction, and in this instance appears to be due to the presence of higher carbon molecules (C5,C6 etc) in the main gas feed to the plant. As a stopgap, the plant is able to irregularly use a secondary, lower carbon number gas feed from another source, which reverses the deposition reaction and allows the carbon to be cleared, but this requires running the plant at reduced rates (8% down), and Methanex is currently looking for a longer term solution to the problem.

> **Carbon formation on syngas catalysts can be a significant problem.**

Ambrogio Stanghellini of Techint described lessons learnt during the commissioning of the 3,600 t/d Damietta Methanol plant in Egypt. Although a number of problems were experienced with the main air compressor, the biggest issue was a failure of the refractory lining of the ATR caused by a higher than expected gas flow causing suspended particles to abrade the lining.

Tang Huai Jiang of the China Coal Shaanxi Yulin Energy Chemical Co introduced his company's 1.8 million t/a methanol plant, which began operations last year, while Milind Summant of the Qatar Fuel Additives Company (Qafac) described the modifications to his company's 2,500 t/d methanol plant to revamp it to a 2,950 t/d capacity. Around 300 t/d of this capacity increase was gained by injecting 500 t/d of CO_2 into the synthesis section of the methanol plant, which had been recovered from the reformer flue gas.

Finally, although it was not quite (or perhaps not yet) an operator experience, Philip Lewis of ZEEP (ZEro Emissions Partnership) took delegates through the thinking behind and financing for his company's South Louisiana Methanol Project – one of the new shale gas based plants now under development in the US (see also the article on page 22).

Catalysts

The final day of the conference was what the organisers described as a 'science day', mainly covering the science of catalyst development and operation. Prior to that, however, Peter Farnell of JM reported on a new development courtesy of the completion of the acquisition of Ohio-based catalyst manufacturer Catacel by Johnson Matthey in 2014. The two companies have been looking at adapting Catacel's foil-based catalyst technology (used extensively in catalytic convertors in the auto industry) for use in reformers. Peter said that since the foil is the mechanical support, the catalyst itself can be optimised for improved intrinsic activity, using a higher dispersion of nickel in the alumina than in a conventional pellet, where the alumina must provide structural support. The result is up to 25% higher heat transfer and 20% lower pressure drop, and a 50% increase in surface areas as well as higher activity. The first reference for the new catalyst was in a small hydrogen plant in Turkey which had experienced very low catalyst lifetimes due to high rates of thermal cycling. The lifespan was extend from 18 months to over 4½ years. A key reference will be in a top fired reformer at a hydrogen plant in Mexico, which will see the new catalyst installed in September 2015.

In the meantime, most catalysts rely upon alumina support. Daniel Sheldon of JM described how the physical characteristics of alumina supported catalysts determines not just crush strength but also resistance to impact forces during loading, static loads in a catalyst bed, internal thermal stresses and thermally induced loads during cooling, and more besides. Modelling is used extensively to extrapolate from test results to plant conditions and provide insight into experimental results.

Norman MacLeod of JM discussed how the method of discharge of a catalyst could impact upon its subsequent examination and any conclusions drawn from that. To maximise the benefit from discharge samples it is important to take the right sample in the right way, and to preserve plant records over the lifetime of the catalyst through reduction, commissioning, operation, shutdown and discharge. Following on from this, Steve Bailer of JM took delegates through the techniques used for analysis and characterisation of catalysts.

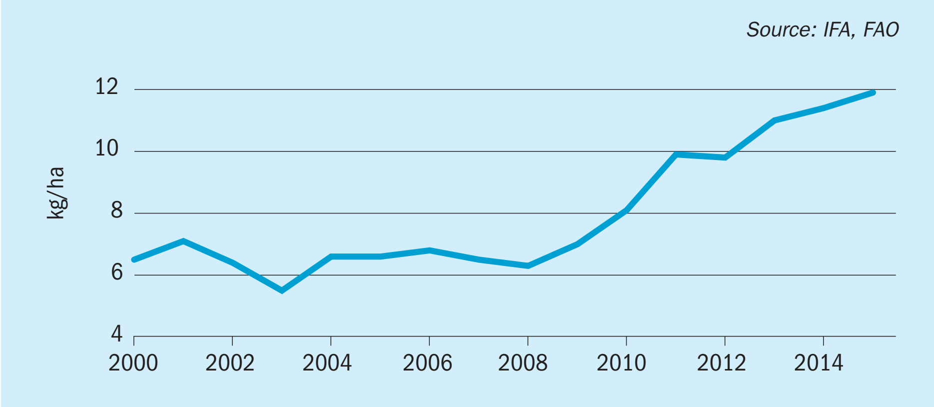
Carbon formation on catalysts can be a significant problem, as Methanex reported, above. The more acidic a surface, the higher the rate of carbon formation, and alpha alumina – a common catalyst support – contains acid sites which are generally neutralised with magnesium or calcium doping. A further way to increase the surface basicity is to add potassium compounds, as described by Mikael Carlsson of JM. It is important that the potassium dopant is added in optimised phases to give a controlled release rate, to keep tube walls free from carbon and assist recovery from plant upsets.

With the accent on methanol, Terry Fitzpatrick of JM explained what happens inside a methanol catalyst pellet. In recent years advances in computer modelling of diffusion inside the pores of catalyst pellets has assisted with understanding how to optimise methanol formation and reaction rate and minimise ethanol formation by ensuring that methanol molecules do not have too long a residence time at the reaction site.

JM has been working in collaboration with Eastman since 2006 on developing a methanol route to monoethylene glycol (MEG), as described by JM's Paul Harris. The MEG market is currently about 25 million t/a, but is expected to grow by 10 million t/a over the next 10 years, especially in China, where coal based syngas can compete economically with routes via conversion of ethylene. The route produces formaldehyde from methanol and then combines this with additional syngas in the step to MEG. The process achieves economies of scale at capacities above 200,000 t/a and can be built at capacities up to 500,000 t/a. Paul reckoned that a 7,000 t/d methanol plant could produce instead 5,400 t/d of methanol and 225 t/h of MEG.

Sub-Saharan Africa has the lowest rates of fertilizer application in the world, and hence some see it as having the greatest potential for new nitrogen demand in the years to come. But difficult issues surrounding infrastructure and rural poverty may cloud the rosy forecast.

Fig 1: **Estimated average fertilizer application rate in sub-Saharan Africa** (without South Africa)



African nitrogen demand

In the January/February issue of *Nitrogen+Syngas* we looked at the supply-side prospects for gas-based ammonia and downstream production in sub-Saharan Africa, some of it based on new gas discoveries in places such as Tanzania and Mozambique. However, almost all of the proposed new capacity is of necessity focused towards the export of urea to places like India, because there is insufficient demand domestically to justify investment. Africa has 13% of the world's arable land and 12% of the world's population, but consumes only 3% of the world's fertilizer, and when North Africa and the Republic of South Africa are removed from that, the figure falls to only 1%.

Not only is fertilizer demand in sub-Saharan Africa low, it has stagnated since the mid-1980s, growing only 15% from then to 2008 according to the International Fertilizer Industry Association (IFA), and many people have noted that, because of this Africa has not had a 'Green Revolution' in the same way that Asia and South America have done. As a consequence, at the African Union summit in 2006, African heads of state combined to make the Abuja Declaration: a commitment to raise fertilizer use to 50 kg/ha by 2015.

There has been a pick-up in demand since then, with application rates rising around 40% from 2008 to 2015, as shown in Figure 1, and growth does continue, especially in countries like Nigeria, Ethiopia, Kenya and Tanzania. According to the UN Food and Agriculture Organisation (FAO), while overall fertilizer demand around the world is growing at about 1.8% per year for the period 2014-2018, it is projected to grow fastest in sub-Saharan Africa, at 4.6% per year, with the figure for the region excluding South Africa (where demand is relatively mature) as high as 8% per annum according to IFA. However, as current usage across the region is low (about 1.8 million tonnes N in 2013 according to IFA), in 2018 sub-Saharan Africa will use only 340,000 additional tonnes of nitrogen as compared to 2014, accounting for less than 5% of the projected global increase during the period, and at present, average fertilizer application rates in sub-Saharan Africa are only around 12kg/ha, barely 10% of the global average. Fertilizer demand is also quite concentrated. At present, 23% of fertilizer demand in the region is represented by South Africa, with Nigeria another 14%, Ethiopia 13% and Kenya 7%. There is thus definitely huge potential for new fertilizer demand across the continent. The big question is how to achieve it.

African agriculture

The agricultural sector plays a prominent role in sub-Saharan Africa terms of economic growth, food security and poverty alleviation. Some 63% of the population live in rural areas, and agriculture employs 62% of the regional population, generating 27% of GDP. However, in spite of significant gains in some areas, malnourishment still affects over 200 million people, and leads to 5 million deaths every year.

African agriculture is based on smallholder farming (typically with less than 2 hectares of land. Around 80% of all farms are small and family-based. Women play a critical role in this kind of farming, performing most of the weeding, harvesting and processing and making up 60-80% of smallholder farmers and producing 90% of the food in Africa. However, only 15% of them possess land titles and only 10% can obtain credit.

Increasing agricultural productivity is thus a key developmental goal, helping not only to improve nutrition and food security but also alleviate the most serious poverty in such countries. However, it is often very much a 'chicken and egg' situation, as productivity cannot be improved without access to better quality and varieties of seeds, nutrients and fertilizers, crop protection products etc, but these cannot be afforded by the majority of poor farmers.

Indeed, fertilizer prices in some regions of Africa can be significantly higher than elsewhere in the rest of the world. IFA says that the elevated price of fertilizer in many regions of Africa is mainly due to high transport costs (itself a product of poor infrastructure development) and the lack of local production and blending facilities.

Other options

It has been argued that Africa can also learn from success stories in other parts of the world. For instance, Africa's Savannah regions could benefit from the model applied in Brazil's *Cerrados* region, where soils are also acidic and often nutrient-poor. In these areas, applying fertilizers is not enough; fertilizer use must be combined with the application of lime to improve soil pH, and use of crop residues and livestock manure to progressively increase the soil organic matter content. Organisations such as the FAO are pushing for 'green' solutions, including encouraging farmers to grow trees and legumes to fertilise the soil, and increased use of manures. However, while these can help, there is insufficient manure availability (due to lack of cattle etc farming), and these techniques can at best only supplement the soil, but cannot substitute for application of chemical fertilizer.

Chemical fertiliser, it is argued, can help kick-start Africa's farms and, as crop yields rise over time, farmers can use the extra crop residues as organic manure, and so reduce their dependence on chemical fertiliser. It can also help prevent the current on-going degradation of soils. Lack of fertilization management has been detrimental to African soils; the FAO estimates that 8 million tonnes of nutrients are lost per year and that 95 million hectares of land (75% of the continent) has been degraded to the point of greatly reduced productivity.

Are subsidies the answer?

One possible way of cutting this Gordian knot is to subsidise the price of fertilizer in an attempt to encourage farmers to use more. There is evidence that national subsidy schemes in Malawi and Rwanda have shown some success, for example, and it is argued that some of the success of Indian and Chinese agriculture in increasing yields has been down to government subsidies for fertilizers. However, the World Bank has cautioned that subsidies often benefit the wealthiest farmers rather the poorest, and that they can stifle the private sector and economic development. In India, the imbalances in the subsidy scheme have also led to imbalances in consumption of fertilizer, leading to over-application of urea and under-application of phosphates and potash.

Malabo declaration

In 2014, as part of its 'Year of Agriculture and Food Security', the 23rd African Union summit at Malabo in Equatorial Guinea renewed its commitment towards tackling some of these developmental problems, and produced the 'Malabo Declaration', in which AU countries pledged to:

- spend at least 10% of their national budget on agriculture;
- sustain annual agricultural GDP growth of at least 6%;
- double agricultural productivity;
- eliminate child under-nutrition in Africa, with a view to bringing down stunting to 10% and those underweight to 5% by 2025;
- triple, by 2025, intra-African trade in agricultural commodities and services;
- halve post-harvest loss and bringing stunting down by 10%.

The countries also agreed that "agricultural growth and transformation process is inclusive and contributes at least 50% to the overall poverty reduction target, and to this end we will therefore create and enhance the necessary appropriate policy, institutional and budgetary support and conditions."

Smallholder scheme

In September 2014 IFA followed this up with a programme to try and enable and enhance smallholders' access to fertilizer by engaging in partnerships with other stakeholders, aiming to provide improved access to credit, finance and insurance by retailers and farmers, and facilitated imports and the distribution of diverse fertilizer products. Via member companies, IFA is also hoping to encourage increased investment in infrastructure: transport, handling, storage, and blending facilities, and training of extension workers to help farmers organise themselves. IFA says that it is also "keen on developing mobile technologies to provide information on markets, extension services and prices". The organisation says that it is also working to disseminate best practices based on the integration of organic and mineral nutrients, balanced fertilization, and other good soil and crop management practices.

> "These techniques cannot substitute for application of chemical fertilizer.

Africa, it is argued, could also learn from initiatives in Asia in terms of distribution and outreach strategies. Models developed in India for knowledge transfer to the farmers, including the use of mobile phone technology to access agronomic and market information, are worth adapting for smallholder farmers in Africa.

A tailored approach

Alejandro Nin-Pratt of the International Food Policy Research Institute (IFPRI) in a recent report on Ghana argued that it is wrong to assume that solutions which worked in other continents will automatically work for African countries. One way in which Asian countries managed to increase productivity was via labour-intensive methods, but while Africa has high populations, this does not always translate to cheap agricultural labour. Solutions for Africa should concentrate on developing technologies that increase labour productivity in agriculture, it is argued, and therefore lower unit labour costs, such as mechanisation (especially for land preparation and weeding), laser land levelling, and high pressure irrigation, which may in turn generate sufficient productivity to allow more expensive technologies such as fertilizers, improved seeds etc.

Prospects for demand

Sub-Saharan Africa is a region that clearly has tremendous potential for new fertilizer demand. However, while developments such as the Abuja Declaration and the doubling of fertilizer application per hectare over the past decade are extremely encouraging after the region has languished for so long, average fertilizer application rates are only at the kinds of levels that, for example, India achieved in the late 1960s. It took India another 15 years for application rates to reach the 50kg/ha specified in the Abuja Declaration, and it does not seem unreasonable to assume that sub-Saharan Africa might take as long to achieve a similar feat. By way of comparison, this would equate to an additional 7 million tonnes N of nitrogen fertilizer demand by 2030 – equivalent to an additional 15 million t/a of urea demand. These figures are likely to be overshadowed by increased consumption elsewhere in the world, but could nevertheless provide the domestic underpinning to support several of the new fertilizer projects which we discussed in our January/February article. ■

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Issues in ammonia handling

Above: The Millard site, showing the facility and neighbouring industrial canal.

The US Chemical Safety Board's final report on an ammonia accident at a refrigeration plant highlights issues with process control and emergency response.

In January this year the US Chemical Safety and Hazard Investigation Board issued its final report on an anhydrous ammonia release at Millard Refrigerated Services, Inc., which took place in Theodore, Alabama on August 23rd 2010. Although there were no fatalities, several people were seriously affected by ammonia inhalation and the CSB took the incident as offering insights into ammonia handling, especially as regards refrigeration systems. The CSB notes in its report that, in addition to health and safety risks from ammonia exposure, these types of large-scale releases can result in deflagration if an ignition source is present with concentrations of ammonia in the flammable range. In 2007, hydraulic shock caused a similar ammonia release incident that resulted in an explosion at another cold storage company.

Ammonia release

Shortly before 9:00 am on the morning of August 23rd, 2010, the company was in the process of loading two ships with frozen poultry when the facility's refrigeration system experienced a hydraulic shock event that lead to a catastrophic piping system failure and the release of 16 tons of anhydrous ammonia. The majority of the ammonia was released through a compromised portion of the system's 12-inch suction pipe on the roof, and so the resulting cloud of ammonia vapour drifted with the wind several hundred metres to the south across the Theodore Industrial Canal (see picture), where contractors were working outside at a clean-up site for the Deepwater Horizon oil spill. One Millard employee sustained injuries after briefly losing consciousness from ammonia inhalation and falling from a height. Nine ship crew members and 143 of the offsite contractors downwind reported exposure. Of the exposed victims, 32 required hospitalisation, and four were placed in intensive care.

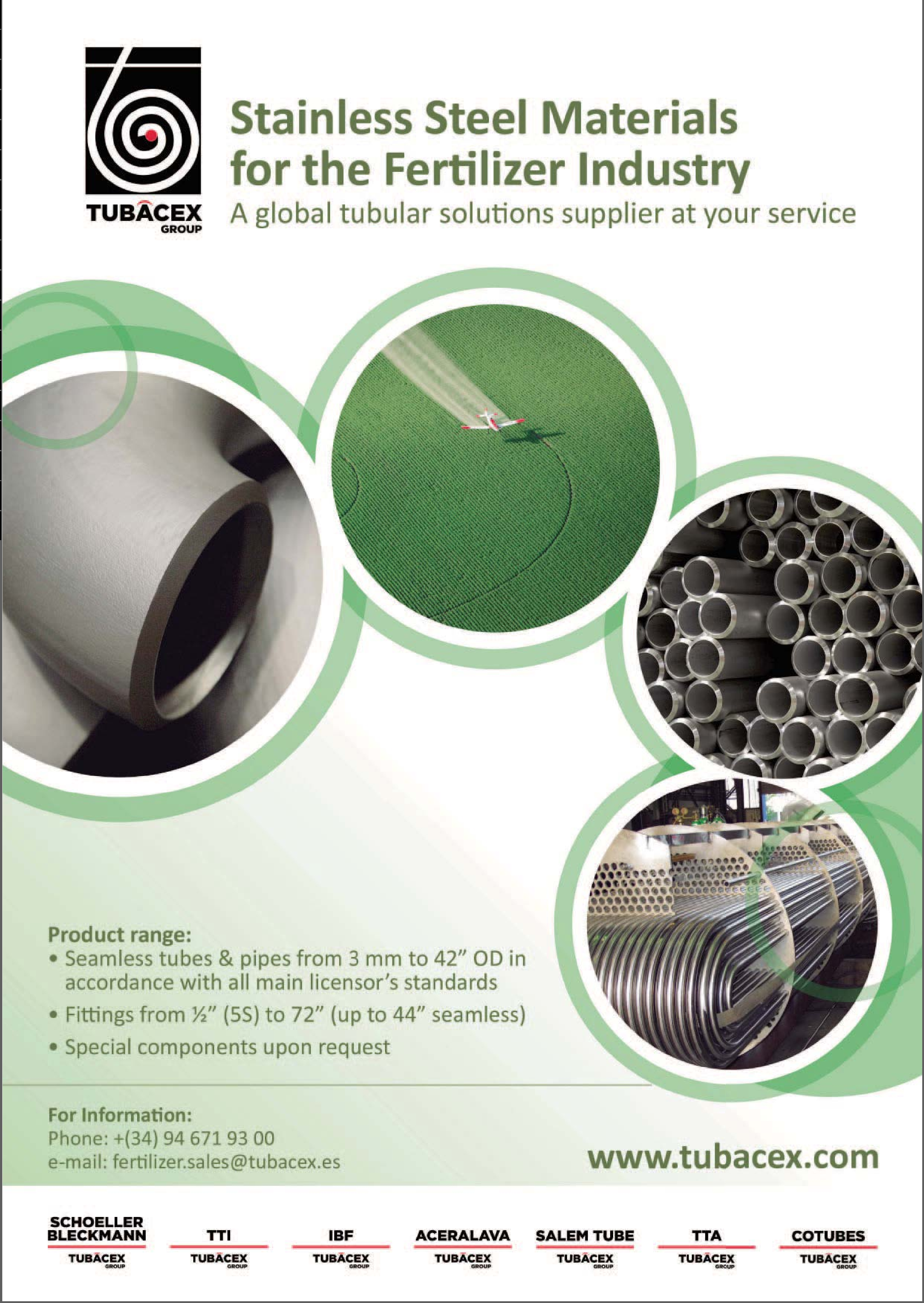
At approximately the same time, alarms sounded within the plant due to the detection of high concentrations of ammonia indoors by air-monitoring equipment in the freezers. This was the result of a second leak that developed because a portion of the system's blast freezer evaporator header ruptured.

After the operations manager announced the release on the facility intercom, three Millard employees went onto the roof in an attempt to mitigate the leak by closing manual valves that supplied ammonia to the blast freezer. All other employees evacuated the facility to a location upwind of the ammonia release. The employees on the roof closed valves and reported the release secured by 1:20 pm, about 4 hours after the initial release. Industrial hygiene technicians contracted for post-incident remediation recorded ammonia concentrations as high as 7,275 parts per million (ppm) in the contaminated blast freezer later that day.

About 15 minutes after being notified of the release, the plant manager called 911, triggering a response from the City of Mobile Fire Department (MFD), which arrived on-scene 16 minutes later with hazardous materials technicians to assess and mitigate the release. The MFD called the County Emergency Management Agency and advised shelter-in-place for the surrounding community, and the US Coast Guard halted water traffic on the industrial canal.

Hydraulic shock

Millard Refrigerated Services operated a 70t ammonia refrigeration system that supplied five product storage freezers and three blast freezers. The CSB's report identifies the main cause of the release as hydraulic shock, which caused a roof-mounted 12-inch suction pipe to catastrophically fail, leading to the release of more than 16 tonnes of anhydrous ammonia. The hydraulic shock was enabled during the restart of the plant's ammonia refrigeration system. In addition to the catastrophic failure of roof-mounted piping,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the pressure developed by the hydraulic shock event also caused an evaporator coil inside the facility to rupture.

Hydraulic shock is a sudden localised spike in pressure that can occur in piping or equipment when there is a rapid change in the velocity of a flowing liquid. In ammonia refrigeration, such events can generate extremely high pressures with the potential to cause catastrophic failure of piping, valves, and other equipment. Damaging hydraulic shock events are typically condensation-induced, often associated with the transition from high temperature and pressure to low temperature and pressure during and after defrosting of evaporators with hot gaseous refrigerant.

On the afternoon before the incident, the facility experienced a loss of power that lasted more than seven hours. While attempting to troubleshoot equipment issues after the system regained power, the Millard refrigeration system operator manually cleared an alarm in the system. This resulted in an interruption of a defrost cycle that was in progress for a blast freezer evaporator. The evaporator switched directly from defrost mode into refrigeration mode without bleeding hot gas from the evaporator coil. Because the operator manually intervened to clear the alarm and thus reset the control system, the control system did not recognise that the blast freezer evaporator unit contained high-pressure hot gas when it allowed the suction stop valve to open during the system restart. This manual bypass of the programmed defrost sequence allowed the low-temperature liquid and hot gas to mix in the same pipe, causing the hot gas void to collapse as it rapidly condensed to a liquid, creating a hydraulic shock that ruptured the evaporator piping manifold and the low-temperature suction piping on the roof.

Contributory factors

According to Millard documentation, the control system contained a programming error that permitted the system to go from soft gas directly to refrigeration mode without bleeding the high pressure from the coil or preventing the low-temperature suction valve from opening. The error with the software logic in the control system went undetected because under normal operations, in its programmed sequence, the defrost cycle would not allow the ammonia liquid to enter the evaporator until the coil was properly depressurised via the bleed cycle. In Millard's investigation report for the incident, the company found that the manual clearing of the ammonia alarm in the control system interrupted the defrost cycle. This was enabled by a lack of restricted access to control system modifications. Had password-protected controls been in place, they could have been used to restrict access to only authorised personnel trained to modify the refrigeration system sequence and pump-out times.

After an unintended interruption, process upset, or power outage, refrigeration system operators can avoid the need for manual intervention to the defrost cycle sequence by programming the control system to automatically bleed any coil that was in defrost prior to the power outage upon restart. The CSB also argues that control system designers can program the control sequence logic on a restart following a power outage to identify evaporators in defrost prior to the power outage. The sequence would be programmed to assume that those coils are pressurised and thus initiate a bleed cycle prior returning the evaporator to refrigeration mode. These features will reduce the need for manual intervention and the risk of hydraulic shock after an unplanned shutdown.

> **"These types of large-scale releases can result in deflagration if an ignition source is present.**

Immediately after discovering the release, two Millard employees went to the roof to mitigate the release by manually closing valves to isolate the associated equipment and processes. The employees attempted to isolate the source of the leak, but all other equipment connected to the low-temperature suction header was still in operation. Based on a review of control system data, other evaporators kept operating and ammonia fed to the ruptured suction line. This caused an intermittent expulsion of ammonia as pressure from the evaporators increased upstream of the failure.

The use of the emergency stop button, located in the Millard control room would have shut down the compressors and pumps and de-energised valves. Shutting down these components would have stopped the circulation of ammonia into the other evaporators and decreased the quantity of ammonia that flowed out to the failed suction line located on the roof. Because the employees attempted to isolate the release to avoid shutting down refrigeration for the entire facility, the release quantity was significantly greater than it would have been had they simply shut the system down.

Lessons learned

- For the design of ammonia refrigeration systems, avoid grouping multiple evaporators to a single set of control valves. This is especially important for large capacity evaporators in excess of 20t. Evaporators with hot gas defrost systems should be controlled by individual valve control groups dedicated to each evaporator coil.
- Program or configure defrost control systems with interlocks to ensure the low-temperature liquid feed and hot gas remain isolated during the initiation and termination of the hot gas defrost cycle in the event of a power outage, cycle interruption, or other abnormal situation. Program the defrost control sequence to automatically depressurize or bleed the coils in defrost upon restart after an outage or interruption, prior to opening the suction stop valve to set the evaporator into cooling mode.
- Avoid the manual interruption of evaporators in defrost and equip control systems with password protected controls to ensure only trained and authorised personnel have the authority to manually override system processes.
- For time-initiated hot gas defrost systems, ensure pump-out times are long enough to remove a sufficient amount of residual liquid refrigerant in the evaporator coils prior to introducing hot gas, especially after low-load periods or power outages.
- Design and operational considerations are most important in the prevention of hydraulic shock incidents and other events that could result in an ammonia release. If an ammonia release does occur from ruptured equipment, lessons learned from the Millard incident can also be applied to reduce the quantity of released ammonia from the refrigeration system. In the event of an ammonia release that cannot be promptly isolated, activate the emergency shutdown switch to de-energize pumps, compressors and valves instead of attempting to isolate leaking equipment while the refrigeration system is running. Shutting down the equipment will stop the circulation of ammonia and limit the release of additional ammonia from components running upstream of failed equipment or piping. ■

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Avoiding tube failures in ammonia condensers

Carbon steel is the most commonly used material for tubes in heat exchangers, yet more than 50% of the yearly maintenance replacements are in this grade. Operators require a replacement material that enables superior erosion corrosion resistance and reduced maintenance costs. **Marcelo Senatore**, Sandvik Global technical marketing specialist, explains the benefits that duplex stainless steel have to offer.

Year after year, large amounts of money are spent on replacing materials that have corroded to the point of failure in the ammonia units of fertilizer plants. Heat exchangers are especially vital in the ammonia production processes, and are dependent on the efficient transfer of energy from one point to another.

Tubing must be versatile in order to be relied upon in a variety of applications such as waste heat recovery boilers, shift conversion heat exchangers, lean amine coolers, carbon dioxide stripper overhead condensers, sync gas compression coolers, ammonia condensers and convertor effluent coolers. The physical properties of steel grades selected for these demanding applications should offer design advantages, with ease of fabrication and good toughness and good weldability.

As mentioned, carbon steel is the most commonly used material for heat exchanger tubing, followed by austenitic grade 304L. Initial low cost does not always justify the subsequent high maintenance and plant shutdown costs that are necessary when failures occur. Corrosion failures have been reported in the ammonia plants of several fertilizer units in India and further afield, specifically in the heat exchangers. Inadequate performances of steels have led to premature equipment failures, loss of production, higher maintenance and replacement costs and, not least, greater safety risks.

Upon closer examination, some tube failures can be attributed to pitting and crevice corrosion initiated by chlorides in cooling water, while others are due to stress corrosion cracking (SCC) caused by process media. In some cases it was necessary to replace the carbon steel tubes three times within a total life span of 15 years, incurring significant maintenance and shutdown costs for the operator.

It is with a view to solving these issues that companies require replacement materials that are more economically viable, and which also meet the specific requirements of their unique heat exchanger equipment and processes.

Identifying replacement materials

Operators must deal with a number of factors that create varying levels of corrosion. One approach is to control process parameters as an ongoing process, while the other is to replace the existing tube material with corrosion-resistant alloys. Practical considerations, such as component lifecycles and their effects on overall cost must be taken into account when choosing alternative materials.

Many studies have been conducted by various organisations to identify a ‘middle ground’ between low cost, low corrosion resistant carbon steels and high cost, high corrosion resistance alloys. This search to combine the best of both options has hit upon one solution in particular: lean duplex stainless steel. In terms of performance, lean duplex falls midway between the cheaper traditional materials, such as carbon steel and AISI 304L with low lifecycles, and more costly and heavier alloyed materials which have proven economically impractical.

Chloride containing water

One of the most common causes of deterioration in heat exchanger tubing is chloride containing water, measured as pH. It can initiate SCC, pitting corrosion and/or crevice corrosion depending on the amount of chlorides present and the temperature.

Stainless steel’s resistance to pitting and crevice corrosion is influenced largely by the amounts of chromium (Cr), nitrogen (N) and molybdenum (Mo) within its metallurgy. The effects of alloying steels with Mo or N on pitting corrosion resistance have been investigated yet are still not fully understood. Observed phenomena in steels alloyed with Mo include improved metal passivation when pitting attack occurs; Mo is shown to assist in repairing the passive steel layer and stop pit nucleation.

One theory for this behaviour is that molybdate ions form in the dissolved Mo and remain on the outer surface of the diffusion layer, causing the layer to become cation selective. This means that only certain positive ions (cations) can pass through, while aggressive ions (or anions) such as chlorides, are prevented from reaching the surface. Due to this anion selectivity, oxide growth can continue to form a layer on the steel and protects against pit nucleation. In support of this theory, increased amounts of molybdate ions have been detected in pitting areas after the initiation of attack.

The effects of Mo seem to be enhanced by N which influences the molybdate concentrations on the surface. This has been explained by the production of ammonium ions which increases the pH and, in turn, makes the formation of molybdate ions more likely.

Pitting resistance in steels

A more exact parameter for assessing and comparing the pitting resistance of different steels is the PRE (Pitting Resistance

Equivalent) number, defined as:

PRE = % Cr + 3.3 % Mo + 16 x % N.

This formula takes into account that pitting resistance is determined primarily by the steel's Cr and Mo contents, while the N content also has an effect.

Sandvik SAF 2304, a lean duplex (austenitic-ferritic) stainless steel, has a PRE value of 24, which is considerably higher than the PRE value of 18 typically found in the standard austenitic steel grade AISI 304L, and more comparable to AISI 316L, which also has a PRE number of 24. The Sandvik lean duplex grade is characterised by very good resistance to SCC, good resistance to general corrosion and pitting, and high strength that is approximately twice the proof strength of typical austenitic stainless steels.

Potentiostatic tests in solutions with different chloride contents (pH = 6) show how the different PRE values of steels affect their performances in chloride containing water, as shown in Figure 1. Each curve in Figure 1 is based on at least four measuring points, each of which is derived from a minimum of three separate measurements, and variation in the measurement results lies within the range +/5°C.

The results make it possible to identify the critical temperature for pitting (CPT) of each grade; Sandvik SAF 2304 has a higher CPT than AISI 304L and its properties are more comparable to that for AISI 316L. Further to this test, the results for AISI 316L have been compared to results obtained under practical conditions of service and the correlation is good. Overall, the results correspond with the PRE rankings of the three grades.

Stress corrosion cracking

Compared with the nominal chemical compositions (%) of carbon steel, AISI 316L and AISI 304L steels, lean duplex Sandvik SAF 2304 stainless steel has a two phase microstructure with about 50% ferrite. The duplex microstructure imbues the grade with twice the yield strength of austenitic stainless steels, and also enhances the steel's resistance to general corrosion with very good resistance to SCC. Table 1 further illustrates the chemical composition of SAF 2304, in comparison with standard austenitic stainless steel and traditional carbon steel.

Sandvik SAF 2304 has an enhanced nominal Cr content of 23% which is one of the drivers for its high corrosion resistance. N is also added to the material to further increase its strength and improve its weldability and resistance to pitting corrosion. Because of its twophase structure and well balanced composition, SAF 2304 possesses very good resistance to SCC.

The properties were put to the test both in concentrated chloride solutions and oxygen containing dilute chloride environments. Figure 2 shows the results of examinations carried out in 40% CaCl solution at 100°C (210°F) and illustrates that the stress required to cause fracture due to SCC, known as the threshold stress, is much higher for Sandvik SAF 2304 than it is for AISI 304/304L or AISI 316/316L.

In addition, welding of Sandvik SAF 2304 does not appreciably reduce the resistance to SCC, provided that certain welding recommendations, as advised by the manufacturer, are followed. The threshold stress of material that has been TIG welded with Sandvik 22.8.3.L or MMA welded with Sandvik 22.9.3.LR is on a level with that of the parent metal.

Fig 1: **Critical pitting temperature for SAF 2304 AISI 304L and AISI 316L in neutral chloride solutions** potentiostatic determination at +300 mV/SCE

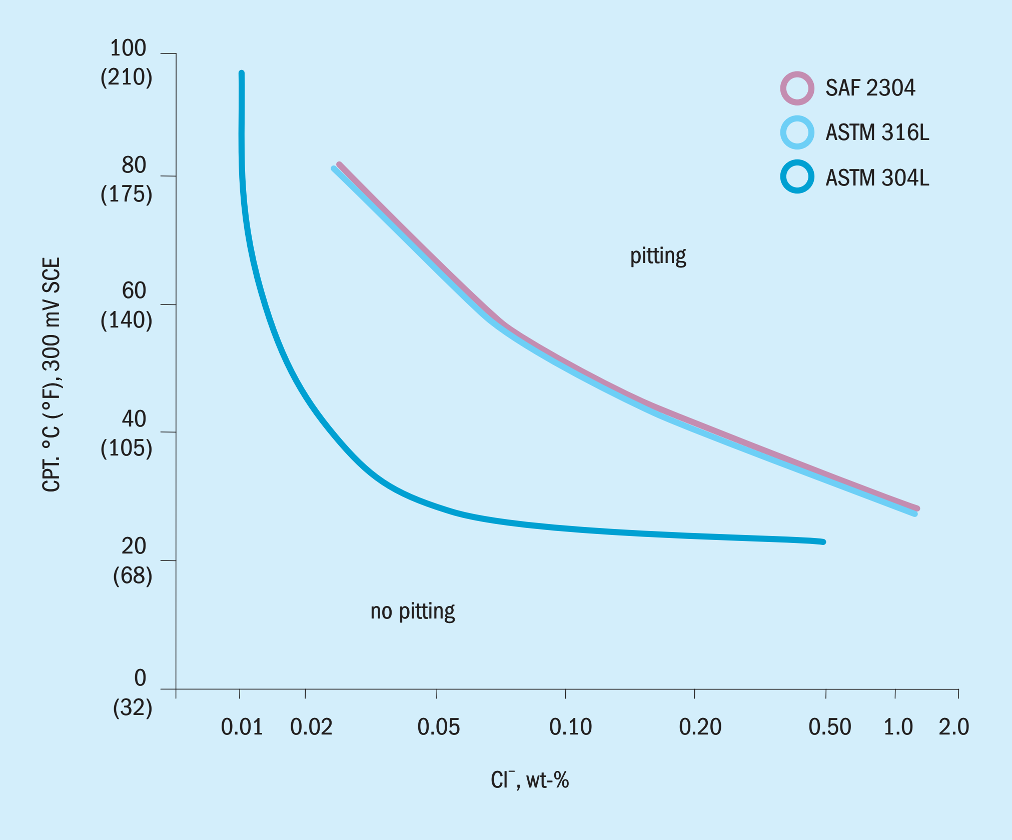

Table 1: **Chemical composition SAF 2304 vs standard steel grades**

Grade	UNS No.	ASTM	Cmax	Cr	Ni	Mo	N	Pmax	Smax	Mn
SAF 2304	S32304	A789	0.03	21.5-24.5	3-5.5	0.05-0.6	0.1	0.04	0.04	2.5
AISI 316L	S31603	A213	0.035	16-18	10-14	2-3	-	0.045	0.03	2
AISI 304L	S30403	A213	0.035	18-20	-	-	-	0.045	0.03	2
Carbon Steel	-	A179	0.06-0.18	-	-	-	-	0.035	0.035	0.27-0.63

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64

High temperature operations

SCC resistance of the lean duplex grade was further assessed in chloride solutions at high temperatures and pressures. Presented in Figure 2, the curve for Sandvik SAF 2304 is based on tests performed in various chloride contents and at different temperatures usually with six separate measurements performed at each measuring point.

The testing method involved spring-loaded specimens stressed to the proof strength (R) at the testing temperature, or U bends in which the stress at the apex is at least equal to the proof strength of the solution annealed material. Oxygen content of the inlet water (refreshed autoclaves were used) was between 4.6 to 10 parts per million (ppm) and the pH 4.5 to 7. The curve for AISI 304/304L and AISI 316/316L is based on published test results and on practical experience.

Results in Figure 2 indicate that SAF 2304 can be used in oxygen bearing chloride solutions at temperatures of up to about 125°C (260°F) without any risk of SCC. This is more than double than for AISI 304/ 304L and AISI 316/316L, neither of which should be used above 60°C in such environments.

With a dual phase metallurgy, where the trans-granular corrosion of one phase tries to nullify the intergranular corrosion centigrade without the risk of cracking, Sandvik SAF 2304 can tolerate low oxygen contents that are common in the process and power industries, and also considerably higher chloride contents and greater temperatures, without any risk of SCC. With these properties, the Sandvik grade offers a greater

Fig 2: **SCC resistance in oxygen bearing (>8ppm) neutral chloride solutions. Testing time 1000 hours. Load > yield strength at testing temperature.**

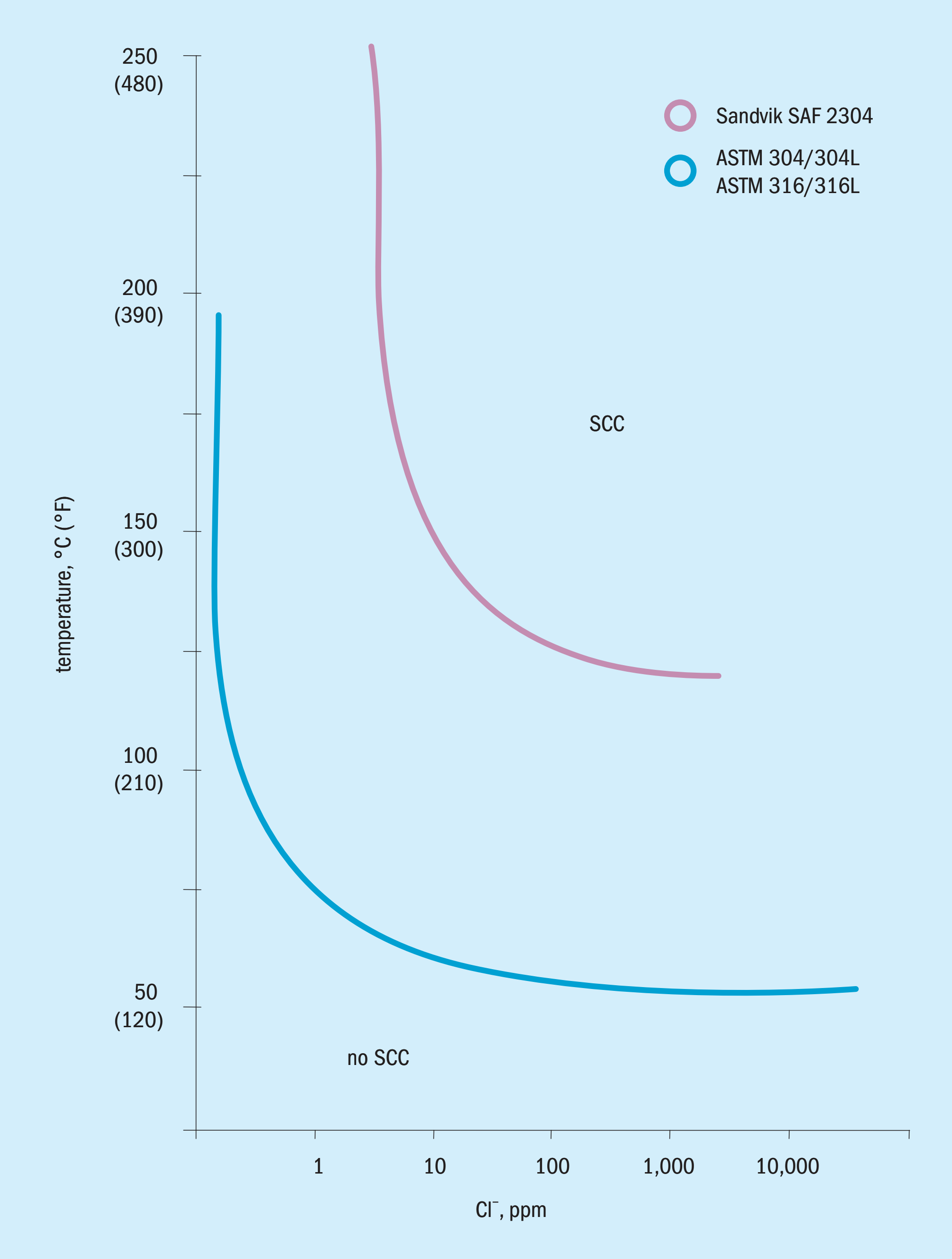

Table 2: **Mechanical properties of steels at recommended temperature**

Grade	Yield Strength min		Tensile Strength	Elongation %min	Hardness; Vickers (typical values)
	0.2% offset N/mm² (ksi)	1.0% offset N/mm² (ksi)	N/mm² (ksi)	-	-
SAF 2304	400 (58)	450 (65)	600-820 (87-119)	25	230
AISI 316L	210 (30)	240 (34)	500-700 (73-100)	35	200
AISI 304L	190 (27)	220 (32)	500-700 (73-100)	35	155
Carbon steel*	180 (26)	-	325 (47)	35	130

**Common values*

Fig 3: **Impact strength Charpy – V for UNSS2304 and carbon steel**
specimen size 10 x 10mm

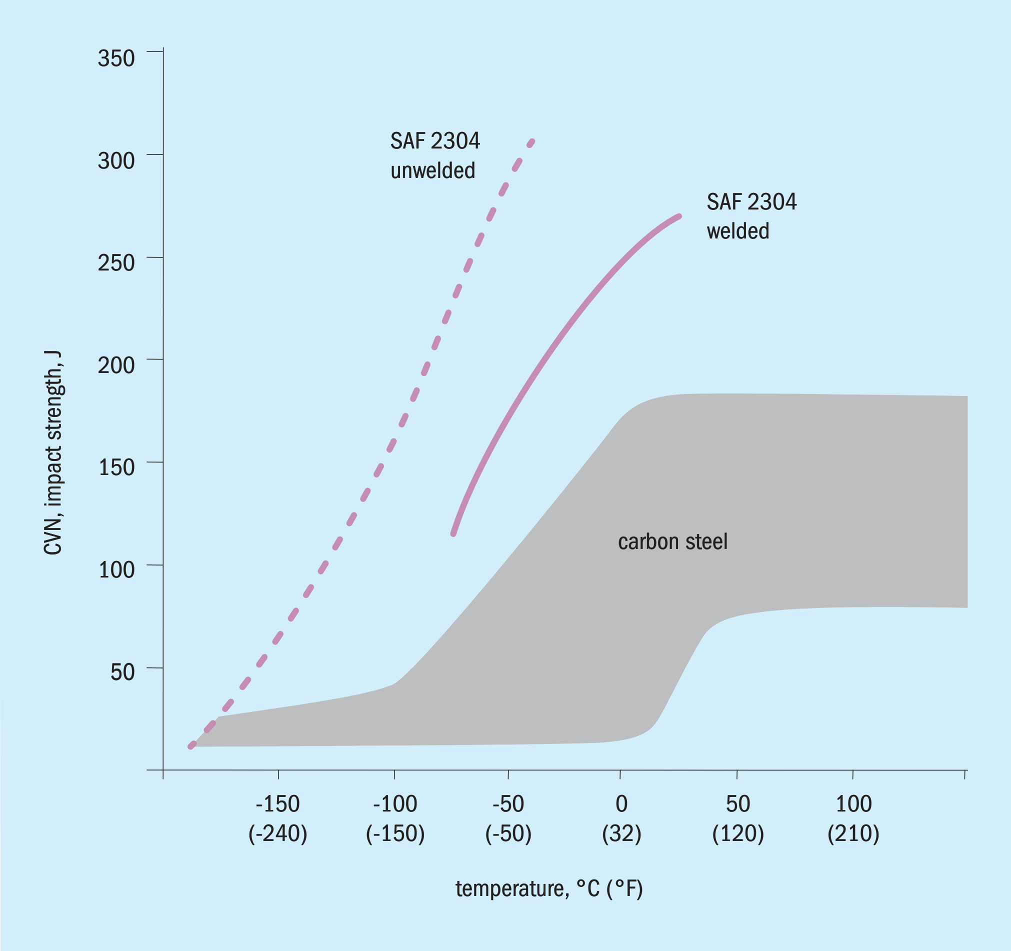

Table 3: **Thermal expansion, mean values (x10^{-6})**

Temp °C	**20-100 per °C**	**20-200 per °C**	**20-300 per °C**	**20-400 per °C**
UNS S32304	13.0	13.5	14.0	14.5
Carbon Steel	12.5	13.0	13.5	14
S31603/S30403	16.5	17.0	17.5	18

performance advantage for demanding heat exchanger applications. Nevertheless, SAF 2304 should not be used in oxygen bearing solutions in environments with more than about 10 ppm Cl. For such conditions, the manufacturer recommends Sandvik SAF 2205, SAF 2507 or Sanicro 28.

Mechanical properties

It is established that lean duplex stainless steel has higher yield strength, almost twice that of standard austenitic steel 316L/304L and low carbon steel, due to its the duplex microstructure. Consequently, Sandvik SAF 2304 has considerably better fatigue strength under corrosive conditions than such steels. A direct comparison of the mechanical properties of lean duplex stainless steel with austenitic stainless steels and local carbon steel is shown in Table 2, illustrating that the ultimate tensile strength and hardness values are higher for lean duplex stainless steel.

Welding, manufacturing and fabrication practices are of vital importance for actual performance in service and, provided that the welding recommendations by Sandvik are followed, welding of Sandvik SAF 2304 does not appreciably reduce its resistance to SCC. The impact strength of UNS S32304, at various temperatures in both welded and un-welded condition, is shown in Figure 3. The material has good toughness both at high and low temperatures. It possesses better properties than most carbon steels, which normally have ductile to brittle transition temperature in the range of 0-80°C (0-176°F).

UNSS32304 has much lower thermal expansion than standard austenitic stainless steel, close to that of carbon steel, see Table 3. Reduced expansion enables better component behaviour during performance for smoother operations, and can also open up considerable design advantages, especially where carbon steel and stainless steel are used in the same construction (e.g. in tubular heat exchangers).

Economics

Further to examining the corrosion properties of lean duplex, and examining possible applications based on corrosion resistance needs, price is also a major consideration. Although the initial investment cost has been a hindrance for operators looking to make a transition from traditional carbon steel or standard austenitic steel, lean duplex is a better solution to reduce the tube replacement cycle and thereby achieve reduced maintenance costs overall. A lower wall thickness can be used for lean duplex which means that its overall life cycle cost will be less than that of carbon steel and 304L, provided that the customer can fully utilise the strength to reduce wall thickness.

Conclusion

Sandvik SAF 2304 possesses good mechanical and physical properties, excellent resistance to SCC and other forms of corrosion as well as good weldability. Such advantages lead to longer equipment lifecycles, unlike low alloys such as carbon steel which necessitate re-tubing every three to four years in aggressive environments. As demonstrated in tests and lifecycle cost analysis, lean duplex stainless steel is an economical solution compared to carbon steel and 304L and, when used within the recommended safe working parameters, offers a solution that is midway between low cost carbon steels and austenitic and more expensive and highly alloyed steels. ■

> **“As demonstrated in tests and lifecycle cost analysis, lean duplex stainless steel is an economical solution compared to carbon steel and 304L.**

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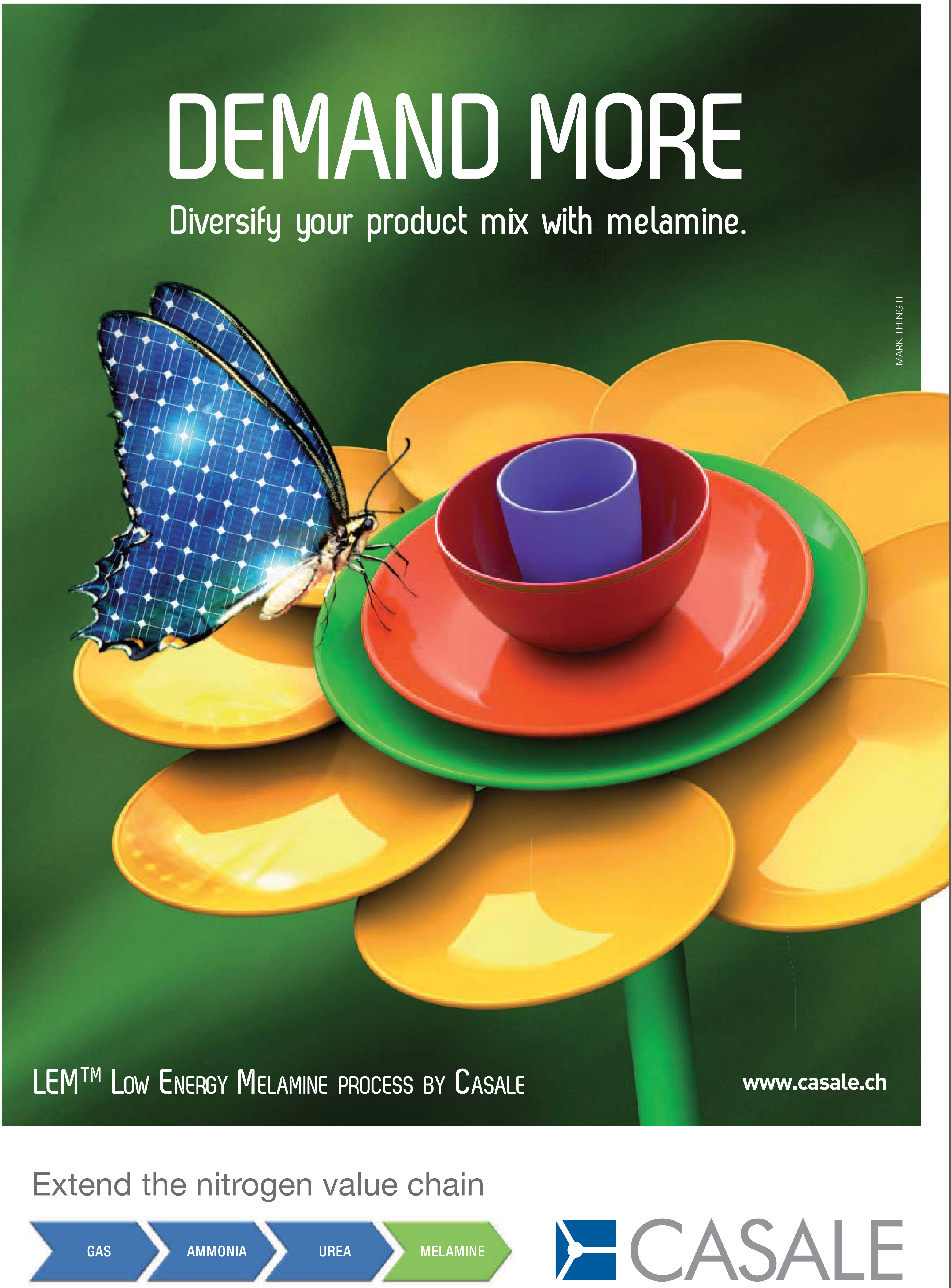
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Combatting corrosion in urea plants

Ammonium carbamate produced in the synthesis section of urea plants is highly corrosive. Although corrosion cannot be fully avoided, the risk of corrosion damage causing leakages or plant shutdowns can be minimised by proper material selection, quality control on fabrication, inspection and maintenance of equipment.

In general, all urea processes fit the following description. Urea is formed together with carbamate from CO_2 and ammonia in the high-pressure urea synthesis section. This section is the most critical from a metallurgical and mechanical point of view on account of the high pressure, medium temperature and the corrosive character of the fluids treated.

The urea solution, still containing unreacted NH_3 and CO_2 in the form of carbamate, is sent to single or multiple decomposition/condensation stages, where generally unreacted NH_3 and CO_2 are recovered in the form of a carbamate solution.

Though these stages are less critical than the synthesis section, material selection and mechanical aspects are challenging nonetheless, especially if a medium-pressure stage is present, since it involves fluid compositions and temperatures not far from those in the synthesis section.

The urea-water solution containing small quantities of NH_3 and CO_2 is then further treated in a vacuum evaporation section to obtain a urea melt for the prilling tower or the granulator. Even if conditions are less corrosive than in the higher pressure sections, material selection and equipment design should be carefully evaluated to avoid corrosion problems.

Process condensate obtained from the vacuum condensers is usually purified in the water treatment section in order to eliminate all NH_3, CO_2 and urea. This section also requires careful material selection, especially for the medium-pressure hydrolysis section.

All urea processes utilise stainless steel, but while the low-pressure, evaporation, vacuum and waste water treatment sections use standard commercial stainless steels (AISI-304L or AISI-316L), the synthesis loop is manufactured with special steels for urea application.

Urea synthesis section

The main items of equipment in the urea synthesis loop are the most critical in the urea plant. Their reliability is essential, as a plant cannot run without them and repairs are generally expensive and time consuming. In addition, they operate at high pressure, generally ranging from 130 to 260 bar, and therefore, catastrophic failure is possible, threatening the safety of the plant and its operators. The risk is increased, compared with common high-pressure equipment, by the corrosion characteristics of the process fluid.

Equipment safety and reliability are closely related and can be achieved by:

- accurate material selection
- proper design
- well controlled construction
- accurate maintenance and inspection.

Corrosion processes

In the manufacture of urea (NH_2CONH_2) there are three basic steps. The first step is the formation of ammonium carbamate according to the reaction:

$$2NH_3 + CO_2 \rightarrow NH_2COONH_4$$

This reaction is fast and highly exothermic. Ammonium carbamate (NH_2COONH_4) is generated as an intermediate product and is highly corrosive to metals.

The second step is the decomposition of ammonium carbamate to urea according to the reaction:

$$NH_2COONH_4 \rightarrow NH_2CONH_2 + H_2O$$

This reaction is weakly endothermic and slow. The carbamate is only partially converted into urea; therefore the unconverted portion must be separated. This can be done by lowering the pressure in one or more steps or by a stripping process where, with the aid of heat, the carbamate is decomposed to NH_3 and CO_2, which are removed with the aid of a sweep gas (such as NH_3 or CO_2) and recirculated into the process.

Urea synthesis solutions are very corrosive. The aggressive component is ammonium carbamate.

There are three main types of corrosion mechanisms associated with ammonium carbamate:

- active corrosion
- passive corrosion
- corrosion erosion

The first two are typical for stainless steel materials, whereas the third tends to occur on titanium.

Active corrosion (Fig. 1) would corrode stainless steel at an unacceptably high rate were it not for the fact that stainless steel surfaces form a protective oxide layer that can withstand it. This process is called passivation and requires the presence of free oxygen.

If the oxide layer is removed by any cause, active corrosion will start unless the medium contains sufficient oxygen or oxidation agent to build up a new oxide layer. If the oxygen content drops below this limit, corrosion will start. Therefore, introduction of a sufficient quantity of oxygen is needed to prevent stainless steel corrosion.

Usually as little oxygen as possible is added to reduce inert pressure, avoid explosion hazard and limit purge losses. However, sufficient oxygen must be present even in the least accessible areas in the system to ensure passivity.

Fig 1: **Active corrosion on stainless steel**

PHOTO: CASALE

Fig 2: **Intergranular corrosion**

PHOTO: CASALE

Fig 3: **Impingement damage on titanium**

PHOTO: CASALE

Extensive experience and knowledge are required to evaluate the right quantity of oxygen. Any modification to the process may change the situation.

Intergranular corrosion (Fig. 2) occurs even if appropriate passivation air is present. This phenomenon is called passive corrosion. However, in this case, the corrosion rate is generally low, so it can be managed by providing an appropriate corrosion allowance to the components.

Carbon steel in carbamate solution corrodes fast and is not suitable. Reactive materials such as titanium and zirconium are not susceptible to active/passive corrosion, but titanium is subject to erosion-corrosion in areas where it is exposed to high-velocity flow, direction changes or impingement of the process medium (Fig. 3). That limits the life of various components. Zirconium is virtually free from this phenomenon, but apart from its high intrinsic cost, it is challenging to work with and full reliability is hard to attain.

Different process choices for the synthesis section greatly affect the material selection of the equipment; therefore, the same equipment in a different process scheme may require a completely different approach.

Corrosion-resistance is not the only factor determining the choice of the construction material. Other parameters like mechanical properties, workability and weldability as well as economic considerations like prices, availability and delivery also deserve attention.

Casale urea plants

Through Its activities in the field of urea plant revamping and the design of new urea plants, Casale has wide experience in all types of processes and materials used in urea plants, such as urea-grade stainless steel, duplex stainless steel, titanium and zirconium.

Materials

Austenitic stainless steel

Austenitic stainless steels are almost immune to erosion and have good corrosion-resistance but require passivation air to avoid active corrosion.

They have found wide application in urea plants also because they have many advantages in construction on account of the ease of welding and forming, lower sensibility to heat treatment and long experience of manufacturing.

As explained, stainless steels are subject to intergranular corrosion in urea plant environments.

Intergranular corrosion is a form of relatively rapid and localised corrosion associated with a defective microstructure known as carbide precipitation.

When austenitic steels have been exposed for a period of time in the temperature range of approximately 425 to 850°C, or when the steel has been heated to higher temperatures and allowed to cool through that temperature range at a relatively slow rate (such as occurs after welding or air cooling after annealing), the chromium and carbon in the steel combine to form chromium carbide particles along the grain boundaries throughout the steel. Formation of these carbide particles in the grain boundaries depletes the surrounding metal of chromium and reduces its corrosion-resistance, allowing the steel to corrode preferentially along the grain boundaries. Steel in this condition is said to be "sensitised".

It should be noted that carbide precipitation depends upon carbon content, temperature and time at temperature. The most critical temperature range is around 700°C, at which 0.06% carbon steels will precipitate carbides in about two minutes, whereas 0.02% carbon steels are effectively immune from this problem.

A method used to overcome intergranular corrosion is to use the extra low-carbon grades such as grades 316L and 304L; these have extremely low carbon levels (generally less than 0.03%) and are therefore considerably more resistant to the precipitation of carbide.

The most common types utilised in urea plants are grades AISI 316L and 316L 'urea grade' (UG) steels, which are molybdenum-containing stainless steels that have shown a higher corrosion resistance in carbamate environments than those without.

On the other hand, high molybdenum content increases the likelihood of intermetallic phase formation during welding.

Austenitic stainless steel may form ferritic pools in the welding process. A certain amount of ferrite in the weld is usually beneficial to avoid hot-cracking sensitivity, but it should be avoided in urea applications because this may increase selective attack of the ferritic phase in carbamate-containing media. This is especially true for AISI 316L.

To ensure the minimum ferrite content, a special 316L type containing an extra-high guaranteed Ni percentage has been developed, which is usually called 316L urea grade (UG).

To avoid hot cracking with such low ferrite content, proper electrodes and low impurity materials must be used.

Type 316L-UG is widely used in urea plants, mainly because of its excellent weldability, fair corrosion-resistance and relatively low cost. However, the large amount of passivation air required and limited corrosion-resistance in harsher conditions prevents its application for the most critical components.

In any case, good performance in the harsh environment of the urea synthesis process requires careful material screening and specific construction procedures. Usually, specific standards are developed by the engineering company to guarantee the quality of the material and assure that its characteristics do not deteriorate during the manufacturing process.

These standards demand chemical analysis, microscopic examination and corrosion tests.

The Huey test is the corrosion test most commonly used because it detects carbide precipitation, sigma phase and intergranular attack, not because it will give any specific information on corrosion in carbamate.

However, since the structure of the material determines its stability in urea synthesis solutions to a very high degree, past experience shows that there is a close correlation between the behaviour in the Huey test and in the urea synthesis solution.

25Cr-22Ni-2Mo

The super-austenitic stainless steel type 25Cr-22Ni-2Mo is an upgrade of 316L-UG, but it has better corrosion-resistance than 316L-UG, higher passivation and re-passivation capacity and excellent weldability. This material is generally Casale's basic selection when the presence of passivation air allows stainless steels to be used.

Typical applications are: lining, tubes and nozzles in the HP carbamate condenser and HP stripper; lining, nozzles and internals trays in the urea reactor.

This type of material has been used for many years in urea plants and has proven to be reliable within its operating limits. The performance of this material has always been satisfactory, even in the most critical items such as the HP stripper.

As for 316L-UG, since the introduction of 25-22-2 Casale has developed the relevant specifications aimed to define the technical requirements, acceptability criteria and qualification tests for base material to be used in Casale equipment as well as all the requirements for welding 25-22-2. These specifications are the result of Casale experience in the field of urea and are continuously updated on the basis of the improved experience and the technical progress.

Bi-metallic tubes

The most challenging component is generally the HP stripper tube. This component reaches the highest temperature while the falling-film design makes it difficult to achieve homogeneous passivation of the surface. For these reasons, stainless steels impose limitations in the operating temperature and need effective passivation air.

On the other hand, reactive metals are expensive, their construction is very complicated, and their reliability is in any case limited.

When process conditions do not allow using stainless steels tubes, a possible solution is the use of bi-metallic tubes. These are composed of an external part fabricated in stainless steel and an internal part, made in zirconium, joined together by a drawing process. This kind of tube combines the constructability of stainless steel with the corrosion-resistance of zirconium, which is the part in contact with the process fluid.

All the other components in contact with the fluid are made of 25-22-2 stainless steel, which requires some passivation oxygen to be present.

Casale has applied this technology in NH_3 stripping plants, where a special process design ensures a higher amount of passivation air to the stripper bottom without the use of a dedicated additional passivation air compressor.

Duplex stainless steel

While austenitic stainless steels are susceptible to stress corrosion cracking (SCC) by chlorides which may be present in the utility fluid, especially in carbamate condensers, type 25Cr-22Ni-2Mo is expensive due to tits high nickel content.

Duplex stainless steels have lower nickel content and have high resistance to SCC. They have been used in some plants for urea synthesis components such as mixers, valves and piping for more than 30 years. But experience shows that common duplex stainless steels are not suitable for the harsher conditions, such as stripper or reactor components.

Specific duplex steels have been developed for the urea process conditions, to extend their use to more critical components. These types of duplex usually have high levels of chromium, which is favourable to passivation of steel. As a consequence, duplex stainless steel is easier to passivate than austenitic steels, which means duplex stainless steel requires less dissolved oxygen compared to austenitic stainless steel.

However, it has to be remembered that the dissolved oxygen content in the liquid phase varies, even if the oxygen feed is constant. The excessively low dissolved oxygen content, not oxygen feed, could cause active corrosion even in high-chromium duplex stainless steel. Therefore the quantity of oxygen feed must be determined on the basis of an analysis of the complete system.

Moreover, it should be noted that the O_2 concentration can only be reduced when all materials in contact with the process medium in the synthesis section are made out of duplex material.

The passive corrosion rate of duplex stainless steel developed for urea application is generally comparable to that of 25Cr-22Ni-2Mo.

Other applications of duplex material in the synthesis section are valves plugs, ejector nozzles, mixers and similar application. Special duplex materials developed to increase their already high resistance to erosion are selected for these components.

DP28W

In selected applications Casale utilises DP28W, a licensed material developed specifically for use in urea plants. DP28W is a super duplex stainless steel, with excellent resistance to corrosion in urea carbamate solution, very high mechanical strength, good weldability and formability, yet retains all the good characteristics of duplex stainless steels.

Thanks to its excellent strength, DP28W allows the tubes to be made with thinner walls, minimising the overall weight and cost of the equipment.

Typically DP28W is used for the tubes in carbamate condensers and has also been tested in the stripper with excellent results (Fig. 4).

Titanium

Titanium is a reactive metal which owes its corrosion-resistance to its ability to passivate. The addition of oxygen to the process is not required to passivate titanium. Moreover, titanium is not subject to intergranular corrosion in urea synthesis conditions. Therefore titanium is not susceptible to active/passive corrosion, which makes it an ideal candidate for the most critical components in the urea synthesis, where it has been widely utilised in the past.

Although not subject to purely chemical corrosion, titanium is subject to erosion-corrosion where exposed to high velocity, change of direction or impingement of the process fluid flow. This characteristic limits the life of such components where

Fig 4: **DP28W tubes in a HP stripper**

PHOTO: CASALE

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64

this phenomenon cannot be avoided, for instance stripper tubes.

Moreover, titanium is costly and manufacturing requires specific experience. High purity is required in all construction steps: typically a clean room is required, especially for welding.

Titanium cannot be welded to other steels (except zirconium) and therefore special construction features are required, involving the use of loose lining and explosion bonding.

Equipment made of this material is suitable for the highest temperature, even in absence of oxygen, but it is expensive and its life is limited due to erosion, especially in the case of strippers.

In addition, reliability is lower compared with stainless steel equipment because of the construction difficulties; therefore, maintenance costs are higher. Nonetheless, titanium strippers are still used in some plants, where the specific conditions make it the better choice.

For this material also, Casale has developed technical specifications to define material and construction requirements.

Zirconium

Zirconium is a reactive metal similar to titanium. In urea environments it has the same characteristics, but it is not subject to erosion-corrosion. It is even more expensive than titanium and the construction requirements are also higher, as both welding and forming have more stringent purity requirements.

This aspect lays many doubts over the reliability of a big welded construction made of this material, which has rarely been attempted. Consequently, apart from bi-metallic tubes, zirconium is used for small special components involving no or few welds, where its excellent corrosion-resistance can be fruitfully exploited without reducing the overall reliability (Fig. 5).

Fig 5: **Titanium – zirconium component**

PHOTO: CASALE

Material selection and design

Material selection is never separate from design, because for each material specific measures are needed to exploit the material's better characteristics and to cope with its limitation and construction restrictions. For instance, titanium does not need passivation air, but fluid velocities have to be limited and it cannot be welded to steel.

Therefore even an accurate material selection cannot by itself guarantee the reliability and safety of equipment, without correct design, quality construction, and proper operation and maintenance, since corrosion, even if under control, is always present.

The urea synthesis environment involves highly corrosive mixtures requiring special materials, which are not generally suitable for the heavy-gauge construction needed to withstand the high operating pressures on the scale typical of modern plants. In general, such equipment would be too expensive, and for some materials the procedures involved in fabrication would impair the corrosion-resistance properties, such as stainless steel and, especially, duplex steels. For others, construction would be practically impossible (titanium and zirconium).

For these reasons in nearly all applications the corrosion-resistant materials are applied as a lining to a pressure-resistant shell made of steel. Different choices are available, related both to the materials selected and to the design philosophy.

The easiest way is to apply the corrosion resistant layer directly to the pressure bearing steel. That can be done by weld overlaying, but only for material which can be welded to steel, such as stainless steel or duplex, not titanium or zirconium. Alternatively the layer can be clad by co-rolling on plates or by explosion on forgings.

Specific measures have to be employed at welded joints to correctly restore the protective lining, but the main problem with this type of design is that any damage to the protective lining can be detected only through an internal inspection. So, in the event of a failure in the protective lining during operation, however little, there is a high possibility of catastrophic failure of the pressure retaining shell, considering the corrosion rate of carbon steel, with potentially severe consequences. Such damage would be difficult to repair.

This solution has been used in the past, but it is not generally considered nowadays for the synthesis equipment. The common solution is to apply the corrosion-resistant material as a loose lining to the pressure casing. The loose lining seals the corrosive fluid, while the external casing has only a structural function.

In general, a leak detection system is provided between the internal layer and the pressure casing to inform of any damage to the corrosion-resistant lining, before the fluid can corrode the pressure components. This feature is essential for the safety of the equipment, since early detection of any failure of the corrosion-resistant layer could prevent damage to the pressure shell that could result in the equipment collapsing or, at least, to damage that is difficult to repair.

It is generally possible for a specialist company to repair the corrosion-resistant layer, but that is not always true for damage to the pressure casing.

Casale has an after-sales service specialised in equipment inspection and repair, which exploits experience acquired during the revamping of all types of plant to treat equipment of any kind, not just that supplied directly by Casale.

There are different philosophies in the design of the leak detection systems. Casale's design provides a specific leaking path that avoids any contact between the process fluid and the pressure-resistant carbon steel components in case of leakage to maximise safety and limit damage to the equipment.

Usually the leak detection is made visually by the operators on a daily basis or even more often.

This can be further improved providing an automatic leak detection system, which continuously monitors the integrity of the equipment.

All the components in the urea synthesis section are critical and need special care in the design.

Casale synthesis section design

Urea reactor

Here ammonia, CO_2 and carbamate are partially converted into urea. The two-phase mixture is quite corrosive and becomes more so as the reaction progresses and the temperature increases. The reactor is a simple vessel with adequate volume to let the reaction progress. But the pressure, the large dimensions and the huge surface to be lined make it a critical construction, where each detail must be designed according to specific features to guarantee the expected reliability.

The reactor has been layered with titanium, zirconium, austenitic stainless steels (316L-UG and 25Cr-22Ni-2Mo) and duplex stainless steel. The choice depends on the type of process and the specific experience of the engineering company. 25Cr-22Ni-2Mo has been the typical choice for modern plant, giving excellent results in terms of reliability and endurance.

From the point of view of corrosion, the internals of the reactor operate in very critical conditions.

Casale has developed special internal trays that increase the conversion rate in the reactor while optimising the liquid-gaseous interface. These trays have to be removable to permit inspection of the reactor lining and must not damage the lining itself in case of pressure hammering. These requirements involve the use of bolts and other types of joints which are more subject to corrosion

owing to the presence of dead areas, where passivation air may be deficient.

Reliability and corrosion resistance are guaranteed by specific design and by utilising 25Cr-22Ni-2Mo material expressly specified, selected and tested to this application.

Stripper

The stripper is possibly the most critical equipment in the urea process.

Different process designs have different requirements; that is why so many materials have been used in the past. As already discussed, the type of process, the operating temperature and the oxygen amount define the material selection, especially for the tubes, where the highest temperatures are reached.

The equipment itself is generally a falling-film evaporator, and different details in design are generally related to the different material requirements. Casale has experienced all type of materials and design in various revamping, but in its new plants utilises 25Cr-22Ni-2Mo.

In NH_3 stripping plants, where the stripper bottom typically operates without added oxygen, Casale has studied alternatives instead of using of titanium strippers. The first one is the use of Zr-lined 25Cr-22Ni-2Mo tubes. There is experience of this in a large number of plants operating with NH_3 stripping technology, where some corrosion drawbacks were detected.

Casale made some detailed analyses and studied some process modifications for this kind of stripper. This arrangement has been implemented and confirms that, by providing proper passivation of stainless steel through certain amount of oxygen to be ensured at the bottom part of the equipment, corrosion is kept within acceptable limits.

Compared with titanium, this first alternative results in cheaper equipment, even maintaining the same reliability in terms of corrosion-resistance and mechanical performance. Furthermore, the use of 25Cr-22Ni-2Mo simplifies maintenance and repair of the equipment, without any need for the specialist welders that are required for titanium. In addition, the stainless steel material is not subject to the erosion that occurs at the tube ends and inside the top portion of titanium tubes.

The second alternative is the newest one, since it proposes the use of super duplex stainless steel DP28W. This option is even cheaper than the bi-metallic one, since – thanks to the excellent strength of this material – the thickness of the tubes can be reduced, minimising the overall weight and the investment cost. From the process point of view, the same conditions are needed for DP28W tubes as for Zr-lined tubes (passivation system and low temperature on stripper bottom).

One of the most important features of the stripper is the liquid distribution. The correct distribution guarantees a homogeneous load for each tube, which is a prerequisite for reduced corrosion and maximum efficiency. In Casale's strippers distribution is made in more steps than one, to assure the correct efficiency at all plant loads.

Carbamate condenser

The design of this equipment can vary substantially according to the technology selected.

Casale has patented the Full Condenser™, which is a vertical condenser that works in a flooded condition so as to increase process performance and, at the same time, minimise corrosion. Special internals recirculate the fluid inside the equipment to maximise the efficiency.

The materials normally selected for this equipment are austenitic or duplex stainless steel. Casale usually considers either 25Cr-22Ni-2Mo or DP28W. Where stress corrosion can be a problem, the material for the tubes should be a duplex stainless steel such as DP28W.

Other equipment

Also the other equipment of the synthesis section is critical and requires specific design and features to maintain functionality in such a corrosive environment. Casale has specific solutions for each item of this equipment and some patented components such as special ejectors and mixers. In these items special materials such as erosion-resistant duplex and also zirconium are used for some component.

Piping

The piping and all its components must be as corrosion-resistant as the equipment. Several materials have been used in the past, but the choice between austenitic stainless steel (25Cr-22Ni-2Mo or 316L-UG) and duplex is generally based on economic considerations, balancing corrosion resistance, cost and mechanical properties, which are higher for the high grades of austenitic and duplex steel.

Each piping component must be designed for this environment, which does not forgive a standard design not specifically tailored. Therefore all components, from valves to bends, from pressure connections to thermocouples, from gaskets to flanges, cannot be selected from standard components but has to be designed specifically.

Other sections

The same principles apply to the design and selection of materials for the equipment in all other sections of the plant, although fluids are less corrosive and pressures lower.

In general, but not always, common stainless steel and standard components can be used. Only with experience and deep process knowledge is it possible to know when this is not true, making the difference between success and failure. Sometimes more troubles arise in this area than in the synthesis loop because less diligence has been exercised in materials selection.

Although common stainless steels can be used, the appropriate limits on chemical composition must be observed and quality checks carried out in many components to avoid corrosion which, when starts, can be fast. Casale has developed specifications that cover material requirements for all the plant sections.

The same is valid for component selection: in general, standard components can be selected but not all standard components are suitable. A typical case is the hydrolyser in the waste water treatment, where the stripping action of steam is used to remove the NH_3 and CO_2 from the treated urea plant waste water condensate so as to maximise the hydrolysis of the urea content. That actually increases the corrosiveness of the fluid.

In the high efficiency Casale hydrolyser technology, special test and chemical composition limits are prescribed for the type 316L stainless steel employed. Further tests are provided on the welds to assure the reliability of this equipment.

The same requirements apply for the patented internal trays provided in the Casale hydrolyser similar to those in the urea reactor.

Apart from material selection and design, construction and maintenance are also fundamental for the reliability and safety of the plant.

Construction

Equipment construction (Fig. 6) is one of the most sensitive phases, because all the advantages of a good design can be lost in an inaccurate construction. Defects, mistakes or incorrect procedures during construction are the first cause of equipment failure.

Casale philosophy is to utilise only a few selected manufacturers with a long experience in high pressure urea equipment. These manufacturers, which work continuously with Casale, are familiar with Casale's specifications and designs. All the critical construction phases are monitored by experienced inspectors. Accurate tests, well beyond code requirements, are specified to certify the accuracy of each specific construction.

Maintenance and inspection

Plant equipment must undergo continuous monitoring and testing all through its life to guarantee trouble-free operation. Casale equipment is typically designed for a three-year campaign between overhauls, assuming that all the required maintenance and inspection activities are adequately performed as scheduled.

Fig 6: **Stripper construction**

PHOTO: CASALE

To closely monitor all the equipment throughout its life, Casale has defined a specific program, the pro-active maintenance system (PAMS). Its prime purpose is to monitor equipment reliability and integrity and suggest corrective actions to ensure reliable and efficient plant operation.

Inspection and repair strategies are mainly focused on the following objectives:

- to safeguard pressure-bearing components from exposure to highly aggressive carbamate environments.
- to discern important findings requiring immediate actions and consideration.
- to extend reliability and life-integrity of operating components.
- to ensure compliance with pressure system safety regulations.
- to assess the remaining life of the equipment
- to propose proactive repair activities to extend equipment operating life

Snamprogetti™ Urea Technology

Material 25Cr-22Ni-2Mo is widely used in Snamprogetti™ urea plants, mainly for equipment linings, because it has a higher resistance to corrosion than the previously employed 316L-UG. On the other hand, 316L-UG is applied and provides good performance for piping in the high pressure section.

Compared to other materials, 25Cr-22Ni-2Mo also has the advantage of requiring less passivation air, with consequently smaller amounts of inerts and oxygen circulating throughout the plant and the benefit of reducing ammonia losses and risk of explosion.

In Snamprogetti™ Urea Technology continuous research and development of new materials is performed to find new and competitive materials, with the aim of reducing weight of piping and equipment and, at the same time, extending their lifetime.

The most critical item where materials play a fundamental role is urea stripper, which has a significant history in material selection.

The early strippers, with titanium lining and tubes, suffered of erosion in the upper part of the tubes. The above can be explained by the fact that pure Ti easily forms a thin layer of TiO_2 which protect the Ti itself from corrosion in both strong acids and alkali; however, since TiO_2 layer is characterized by poor mechanical strength is prone to be eroded especially when flashing of liquid takes place.

The solution was found with bimetallic tubes, where zirconium inner tubes (inserted through and extrusion process in those in 25Cr-22Ni-2Mo) assured resistance to corrosion and made the bimetallic design the leading one for urea strippers.

Applying the same concept of having zirconium inside the tubes, OmegaBond® material has been developed in collaboration with ATI Wah Chang for tubes of urea stripper. Zirconium tubes are in this case metallurgically bonded to titanium tubes, assuring resistance to erosion. With the use of OmegaBond® tubing, the temperature in the bottom of the stripper can be higher compared to bimetallic stripper (reducing the load on downstream decomposition section) and the total amount of passivation air required to the urea process is further reduced since no passivation air is required for the stripper.

Proper design

Another important factor to be considered where corrosion is an issue, is the design of equipment. A proper and accurate design is essential to reduce the risk of corrosion and losses of production.

In the design of equipment, in particular for those items prone to corrosion issues, Snamprogetti™ Urea Technology also takes into account the needs for inspections, maintenance and repairs, on the principle that the simpler such activities are, the less time they require. The great advantage of this philosophy is that after scheduled activities urea production can be restored fast.

A leading requirement of clients is to have equipment that lasts for many years so as to avoid economic effort for procurement of new items and loss of production due to aging of items. On this aspect Snamprogetti™ Urea Technology has from the beginning proposed equipment designed and constructed so as to extend their lifetime.

An example of this are reversible strippers: as said above, in titanium stripper it was noted that tubes got eroded after years of operations; since erosion occurred just in the upper part of the tubes, to overcome such an issue and avoid complicated activities of re-tubing and refurbishment, Strippers were designed to be reversible so as to double their life.

Fluid-dynamic of liquid and vapours inside the equipment is also to be considered in design: if passivation air is not properly distributed inside the equipment or dead areas where fluid is not circulating are present, thus limiting passivation of surfaces, corrosion may occur.

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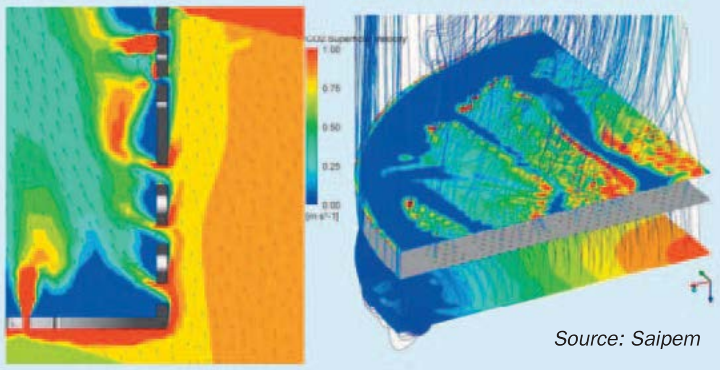
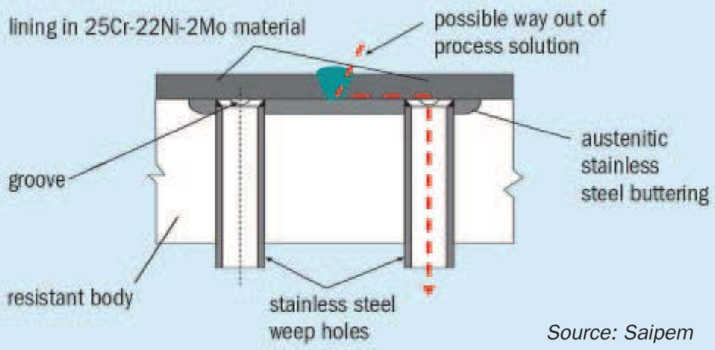
Fig 7: **CFD study of reactor internals**



Source: Saipem

Fig 8: **Simplified scheme of weep hole system**



Source: Saipem

These are important aspects well known to Snamprogetti™ Urea Technology, which are duly considered during design phase.

Recently a new design for reactor trays, Snamprogetti™ SuperCups, has been developed and installed by Saipem. During the conceptual and design phases of the new trays, computational fluid dynamic studies (CFD) were carried out to analyse and optimise the mixing phenomena that take place in the reactor and to check that all internals are properly passivated, thus reducing the risk of corrosion. CFD studies (Fig. 7) are also particularly important to verify the suitability of the new internals design for their installation in old equipment, which may have a design (e.g. materials) different from the one currently adopted.

Fabrication follow-up

Attention is paid by Snamprogetti™ Urea Technology during the construction phase of new items to check that all requirements with regard to process, materials and mechanical aspects are considered and properly applied by manufacturers, in order to supply clients with equipment that is reliable and durable.

Procedures for inspection and manufacturing are prepared by Snamprogetti™ Urea Technology and are constantly updated thanks to experience, feedback and fruitful interaction with manufacturers.

Leak detection

The peculiarity of equipment designed by Snamprogetti™ Urea Technology is that they are intrinsically safe. In the case of a leak, carbamate is routed outside of the equipment through the weep-hole system thus allowing any leak to be identified. (Fig. 8) An important aspect of this design is that carbamate will never come into contact with the carbon steel of the pressure resistant body (the presence of buttering in stainless steel material safely conducts the possible leak to the weep holes).

Assistance and inspection

Snamprogetti™ Urea Technology attention is not limited to the manufacturing phase of new items; assistance is also provided during commissioning of equipment and for inspections during turn-around.

As part of after sales services, qualified personnel are dispatched to clients workshops or to the plant site to check the integrity and status of equipment through a meticulous analysis of internals, welds and whole items.

Practical solutions from Toyo

Toyo Engineering Corporation (Toyo) has constructed urea plants all over the world since the 1960s As a process licensor, Toyo also provides inspection and diagnosis services for the safe and reliable operation of high pressure equipment in urea plants. Through these activities and root cause analysis of corrosion related damage, technical and practical solutions have been developed to overcome different corrosion problems.

In the following case studies Toyo discusses two corrosion related issues and their prevention to help plant owners minimise the potential of similar problems from occurring in future.

From the first case study one can conclude that even a small pinhole can be a potential source of severe active corrosion, especially for austenitic stainless steels in ammonium carbamate solution. The second case study emphasises the importance of understanding the potential risks of heat treatment for duplex stainless steels in order to avoid unexpected corrosion during operation.

Support ring on high pressure equipment

Corrosion by ammonium carbamate solution was observed in the welds of the baffle support rings of pressure equipment. The material of construction of the support ring and welding consumable were 316L-UG. The support rings were welded to the lining plates of the equipment. Initially, pinhole like corrosion was found on the weld deposit as shown in Fig. 9. Due to improper repair of the pinholes, severe corrosion occured through the pinhole. If a repair is not conducted properly, the inside of the pinhole is continuously filled with ammonium carbamate solution. Once the ammonium carbamate solution reaches a space behind the weld as shown in Fig. 10, the possibility of active corrosion becomes high since there is insufficient air to form a passivation film on the metal surface. When active corrosion takes place, the corrosion rate of 316L-UG can be 60 mm/year or more.

Based on these findings the following conclusions can be drawn:

- ingress of ammonium carbamate solution happened through pinholes

Fig 9: **Pinhole on weld deposit of support ring and lining**

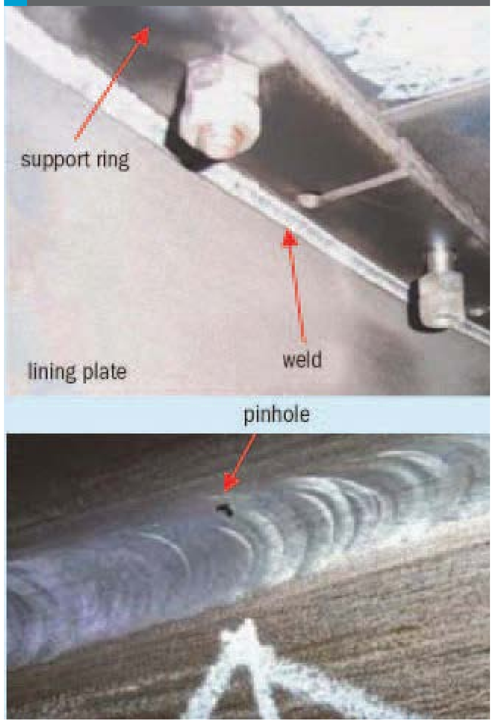


PHOTO: TOYO

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Fig 10: **Pinhole on weld deposit of support ring and lining**

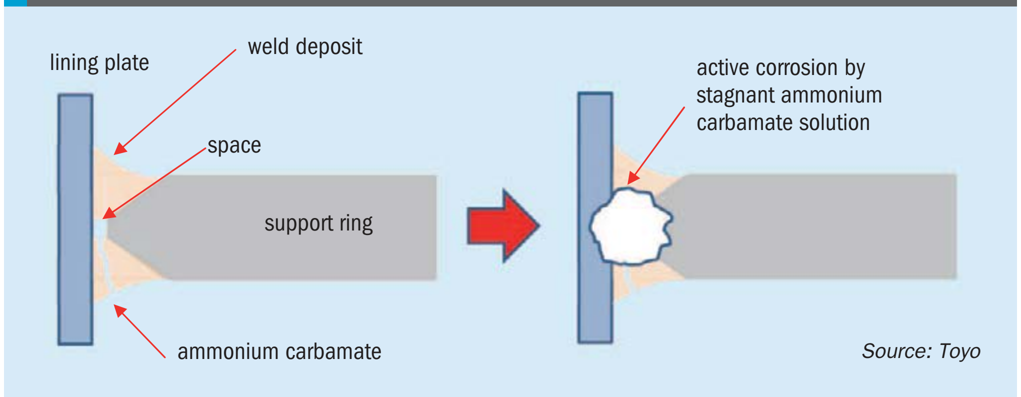
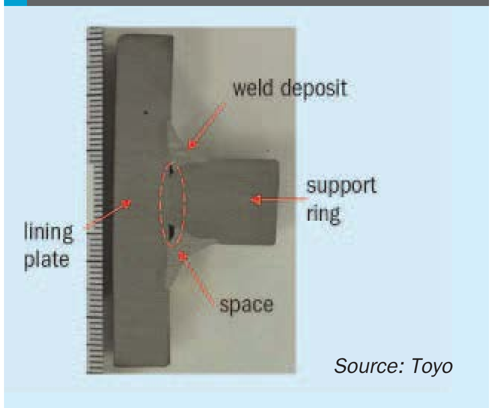


Fig 11: **Partial penetration**



- stagnant ammonium carbamate solution in the spaces resulted in a lack of passivation air
- severe active corrosion happened because no passivation film was formed on the surface of 316L-UG.

Lessons learned and corrosion prevention

The original joint design requested full penetration on the welds but this is not always achievable due to difficulty in geometric complexity. An Investigation with mock-up test pieces was carried out and revealed that the root cause of the generation of the space behind the weld was improper groove design, especially too narrow a root gap between the support ring and the lining plate. The space behind the weld due to partial penetration is shown in Fig. 11.

Fig 12: **Appearance of seat ring**

PHOTO: TOYO

This kind of weld is widely used for equipment in industry and small spaces generated by partial penetration do not cause problems in most cases. However, the corrosion observed on the weld deposit on the lining plate and the support ring suggest that even a small space behind the weld can lead to active corrosion by stagnant ammonium carbamate solution. The corrosivity of the solution should therefore be taken into account for the welds of internal parts in urea high pressure equipment. In addition to groove design, the thickness of the support ring also affects root penetration. If the support ring is unnecessarily thick, full penetration is difficult to achieve.

In addition to changing the groove design and optimising the thickness of the support ring, qualification of welders was also carried out. It was concluded by cross sectional observation of the new weld joints that 100% full penetration was attainable with these improvements. To ensure the integrity of the production welding of high pressure equipment, UT was carried out during fabrication. No space behind the weld was detected by the UT.

In Toyo's urea process, duplex stainless steels are currently applied instead of 316L-UG for linings and internal parts, including support rings of high pressure equipment. Toyo's laboratory test suggest that the active corrosion rate of duplex stainless steels in ammonium carbamate solution is less than about 0.5 mm/year. Therefore, even if there is a space behind the weld and ammonium carbamate solution reaches it, severe corrosion will not take place on the duplex stainless steel.

Seat ring of high pressure control valve

Severe corrosion was observed on a 25Cr duplex stainless steel forged seat ring of a high pressure control valve which was used in ammonium carbamate solution for several years. The appearance of the seat ring is shown in Fig. 12. The seat ring was inspected to find a root cause of the corrosion. A cross section of the seat ring is shown in Fig. 13.

Severe intergranular corrosion on the inner and outer surface was clearly visible especially at the bottom of the seat ring where the microstructures seem to be much coarser than that on upper parts. The microstructure of the seat ring is shown in Fig. 14. The microstructure of the bottom side of the seat ring includes a small amount of austenite (γ)-phase. Almost all of the microstructure of the corroded part on the seat ring consisted of ferrite (α)-phase only, and grains were coarse. The microstructure of duplex stainless steels, however, should consist of two phases, α and γ, in equal ratio. Once the microstructure becomes α-phase rich, solute carbon and nitrogen are precipitated at the grain boundaries as carbides or nitrides, and tends to be followed by severe intergranular corrosion.

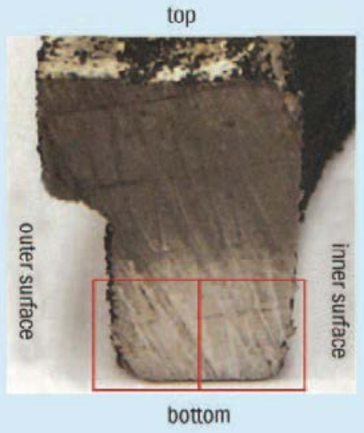
In addition, the finer microstructure observed at the top part shows better corrosion resistance because intergranular corrosion of passive steel selectively attacks the grain boundaries of metals in ammonium carbamate solution. Therefore, it can be considered that the lack of γ-phase in microstructure and coarse grain caused the severe corrosion in the seat ring.

Both of these causes would result from heat treatment at higher temperature during the forging process of the seat ring. Experimental tests indicated that γ-phase in duplex stainless steels can change into α-phase and its grain can coarsen with aging treatment at 1,200°C or higher, and the γ-phase can be generated again with aging treatment from 1,000 to 1,100°C. This means that the final heat treatment greatly affects the ratio of α and γ-phase in duplex stainless steels.

The seat ring was produced in the process shown in Fig. 15. Final heat treatment in the process was performed after second forging and the temperature specified for the heat treatment was 1,050°C. However, the actual temperature of the final heat treatment was not recorded which infers that the temperature was likely higher than 1,050°C during the final heat treatment, which resulted in growth of α-phase content and coarse grain, and consequently lowered corrosion resistance of the seat ring.

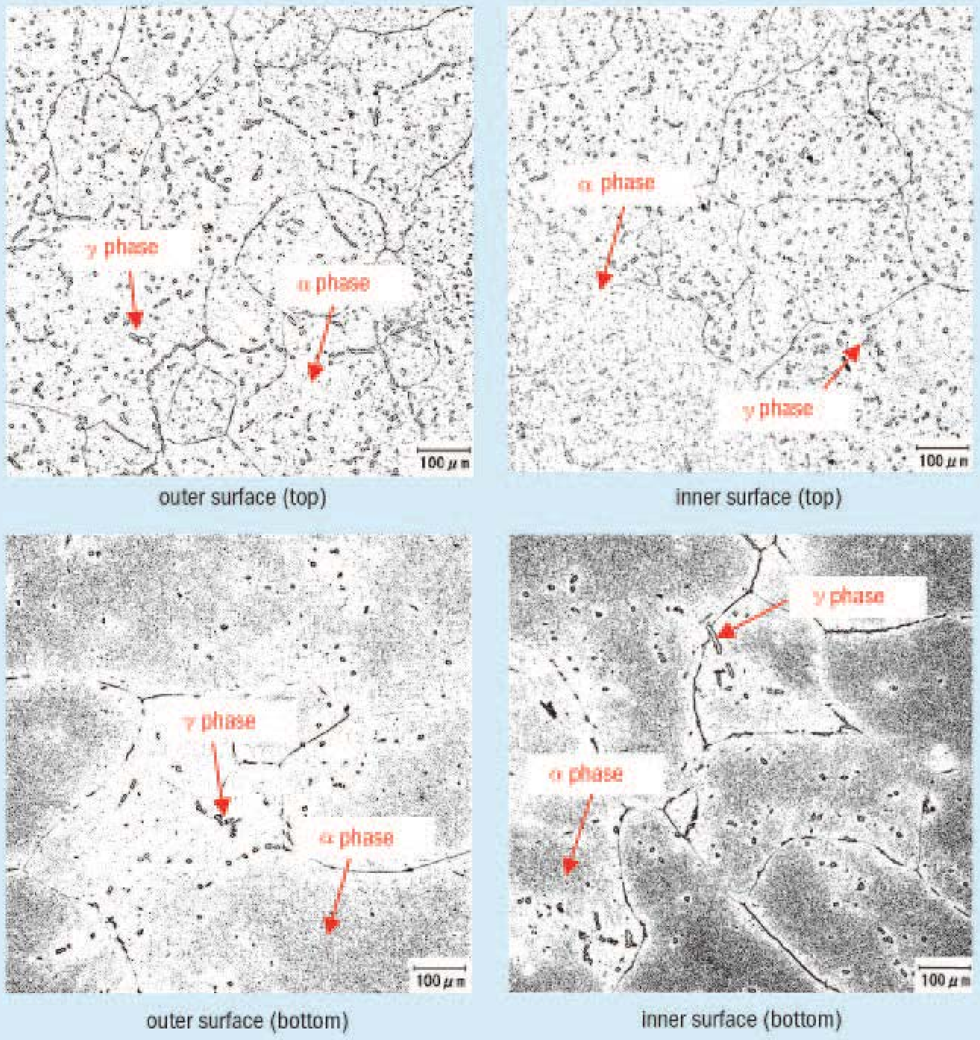
Based on the results of the metallurgical inspection of the corroded seat ring, the following conclusions can be made:

Fig 13: **Cross sectional observation of seat ring**



Source: Toyo

Fig 14: **Microstructure of seat ring**



Source: Toyo

- an increase of α-phase in the microstructure and coarse grain caused the severe corrosion on the seat ring
- final heat treatment at a higher temperature would result in the growth of α-phase content and coarse grain.

It is thought that the temperature was higher than 1,050°C during the final heat treatment.

Lessons learned and corrosion prevention

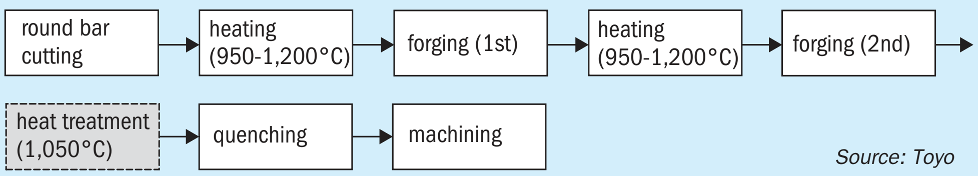
The grain of forged materials can be coarser than that of hot rolled products due to lower reduction ratio. Intergranular corrosion is normally observed on stainless steels in ammonium carbamate solution even under sufficient oxygen content. The grain size influences the corrosion rate and a larger grain size results in a higher corrosion rate. This means that different metal forming processes will affect the corrosion rate differently even if materials have the same chemical composition.

While duplex stainless steels, including forged material, are widely used in the urea process, especially for the synthesis section due to its excellent corrosion resistance, the steels still need intensive quality control regarding heat treatment during the production process. Toyo has applied several types of duplex stainless steels in commercial urea plants and has experienced both successful and unsuccessful applications. Detailed instructions to manufacturers for the heat treatment is one of the key factors to ensure the integrity of products. Toyo's specification includes ferrite content examination and Huey tests for each product used for critical equipment. These tests are conducted at an appropriate time during the material production and equipment fabrication in order to ensure its quality.

In addition, in the case of duplex stainless steels there is a possibility of sigma phase formation, nitride and carbide precipitation due to improper heat treatment, which resulted in deterioration of corrosion resistance in ammonium carbamate solution. Consequently, compared to austenitic stainless steels, duplex stainless steels require strict temperature control throughout the material production and equipment fabrication process, such as heat treatment and even machining to avoid degradation of corrosion resistance. Susceptibility to degradation depends on the types of duplex stainless steels.

Toyo has developed extensive test and inspection programmes to eliminate the possibility of degradation of corrosion resistance in production and fabrication, which ensures safe application of duplex stainless steels for intended service without any corrosion problems. ■

Fig 15: **Production process of seat ring**



Source: Toyo

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Added value with steam reformer solutions

K. Svennerberg of Haldor Topsoe discusses steam reformer solutions that add significant value throughout the whole operating cycle, providing industry examples where Topsoe's solutions have enabled customers to improve feedstock utilisation, increase synthesis gas production, prolong operating cycles and save valuable days during shut-down due to innovative loading methods and services.

"Successful plants can't afford to underperform". This quote comes from the technical director at a large ammonia plant in Southeast Asia. And he is right, in today's competitive market a successful plant cannot afford to underperform in any area. With the steam reformer being right at the heart of ammonia plants, it has a strong impact on the overall plant performance and ultimately, the bottom line.

Steam reforming

Reforming reactions are typically carried out in a heated furnace over a nickel catalyst. The Topsoe furnace consists of a box-type radiant section with side wall burners and a convection section to recover the waste heat contained in the flue gases (Fig. 1).

In the radiant section, a nickel catalyst is loaded in a number of high alloy reforming tubes placed in rows along the furnace. The outer diameter of the tubes ranges typically from 100 to 150 mm and the tube length from 10 to 13 m. Typical inlet temperatures to the catalyst bed are 450-650°C, and product gas leaves the reformer at 800-950°C depending on the application. Tubular reformers are designed with a variety of tube and burner arrangements[1] including: side-fired furnaces, top-fired furnaces and terrace wall furnaces.

Developments in metallurgy have allowed steam reformers to operate at increasingly higher levels of temperature, pressure and heat flux. Use of a variety of feedstocks as an alternative to natural gas has made selection of proper catalyst more important than in the past. New process technology in other parts of the plants has in many instances made the steam reformer the bottleneck for further capacity increase. Hence, optimising the steam reformer operation is crucial for getting the most possible out of the available natural gas.

Topsoe has delivered catalysts, technology and services for the steam reforming process for more than 35 years. Topsoe's catalysts are used in all types of reforming furnaces and have achieved some outstanding lifetimes. Services for catalyst loading and reformer assessment further boost reformer operation.

Fig 1: **Topsoe side-fired steam reformer – waste heat recovery placed at side**

Catalysts for the steam reformer

Developments in reforming technology have been considerable in the last decades, and with the rapid pace of developments in downstream process technologies, there is continuous pressure to achieve even small improvements in reformer performance. Here, the quality of the catalyst in the reformer plays a large role in determining plant performance. With a well-performing steam reforming catalyst it is possible to achieve excellent conversion due to high catalyst activity, operation at the lowest possible tube wall temperatures, and low and stable pressure drops. This translates into maximum synthesis gas production while ensuring long tube and catalyst lifetimes.

Topsoe's steam reforming catalysts combine high activity with favourable heat transfer and pressure drop characteristics, making it possible to significantly increase the throughput at unchanged pressure drop and tube wall temperatures. The R-67-7H (shown in Fig. 2) can operate at very high heat flux and take on even the toughest feedstocks. In situations where there is little risk of carbon formation, such as after a pre-reformer, you can load the R-67-7H can be loaded alone. Where there is a risk of carbon formation, such as when reforming natural gas in a top-fired reformer, it is loaded in the bottom of the tubes beneath an alkali-promoted catalyst, such as the RK-400. In less demanding heat-flux conditions, it can be loaded beneath the pre-reduced R-67R-7H.

For a given reformer and process conditions the approach to equilibrium at the exit of the tubes is a function of catalyst activity. Ammonia plants using Topsoe's steam reforming catalysts can achieve an approach to equilibrium below 10°C for many years, which means that the methane will be at a low and stable level throughout the whole operational cycle.

Indian plant obtains 12 years of lifetime

An Indian ammonia producer operating a 2,000 t/d plant has experienced exceptional performance with R-67-7H. The graph below shows the measured methane leakage and pressure drop for the whole lifetime of the catalyst. As can be seen in Fig. 3, R-67-7H was in operation for 12 years with consistently low methane leakage and stable, low pressure drop. After six years the plant increased the feedstock rate by 10% maintaining the steam rate and firing input to the reformer furnace and this resulted in a slight increase in methane leakage and pressure drop.

Being able to operate with the same catalyst charge for 12 years, with low methane leakage and pressure drop saves not only the investment in a new catalyst

Fig 2: Topsoe's 7-hole steam reforming catalyst R-67-7H

charge, but also valuable time during turnarounds since no re-loading is necessary.

R-67-7H performance in American plant

A low and stable pressure drop across the steam reformer is highly desirable, it reduces energy consumption due to savings in compression power and enables operation at high plant load. Here, the shape and mechanical stability of the reforming catalyst plays an important role. The graph in Fig. 4 shows the experience from an American plant, where Topsoe's R-67-7H was in operation for more than six years, without any significant increase in pressure drop over the lifetime. Experience at the same plant with a non-Topsoe catalyst is also shown, where the pressure drop was initially higher and continued to increase throughout the entire lifetime.

The experience from this American plant shows that choosing the right catalyst for the steam reformer is essential. As can be seen in the graph, the pressure drop over Topsoe's R-67-7H has been consistently lower, with the difference ranging from about 0.5-2 kg/cm². On average, the pressure drop over the R-67-7H was more than 1 kg/cm² lower throughout the whole catalyst lifetime. This adds up to a significant value, both in energy savings and the possibility to operate the plant at high and stable plant load at all times.

Additionally, should a plant have the possibility to increase the feed to the plant, the pressure drop across the reformer might be a bottleneck. However, choosing the right catalyst for the steam reformer can enable a boost in capacity, allowing the plant to produce more ammonia and increase profitability. Increasing the plant load with 2% in a typical 2,000 t/d plant corresponds to a yearly gain of around $6 million.

Preventing carbon formation

Carbon formation is a major challenge in the steam reforming process. The deposition of carbon may lead to several damaging effects, including catalyst deterioration and disintegration, encapsulated catalyst pellets, and build-up of carbon on the reformer tube walls. Depending on the type and severity of the carbon formed, this may further lead to the development of hot spots/hot bands, elevated pressure drops, or in the worst case, costly interruptions in production for replacement of catalyst and/or reformer tubes. In nickel-based steam reforming catalysts, alkali promoters are used to suppress harmful carbon formation. The disadvantage of alkali addition is a decrease in reforming activity, but Topsoe researchers have found a unique solution to this problem.

Alkali catalyst RK-400

RK-400 is Topsoe's most recent innovation in alkali-promoted catalysis, providing superior protection against carbon formation in conjunction with enhanced catalyst activity and lifetime. The ingenuity of the RK-400 catalyst lies in the method by which the alkali promoters are incorporated into the catalyst carrier material. Normally, the promoter is spattered onto the surface of the carrier material and the nickel particles. To compensate for the slow loss of alkali

Fig 3: R-67-7H in operation for 12 years in a 2,000 mt/d ammonia plant

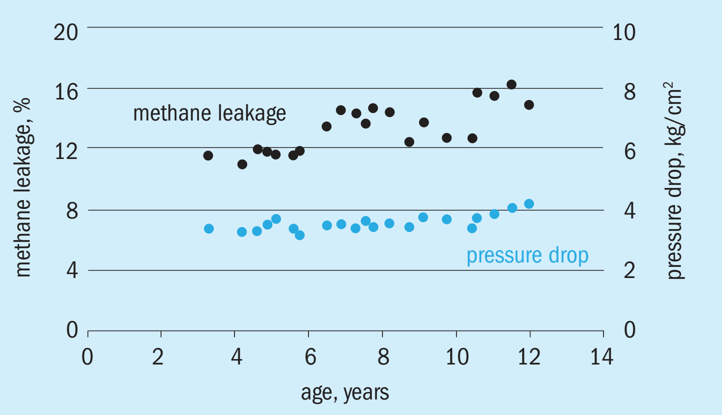
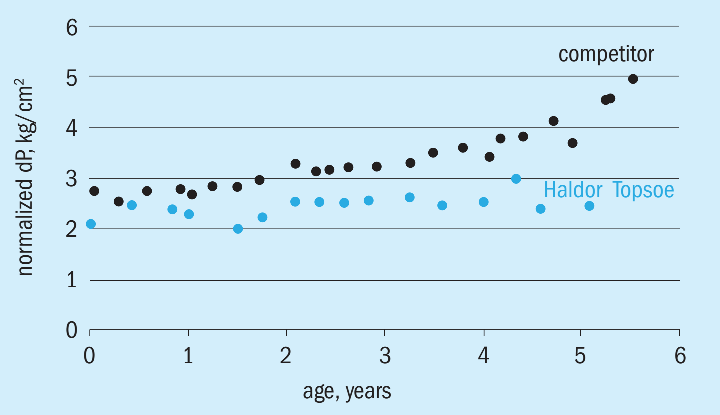


Fig 4: R-67-7H outperforming competitor catalyst in an American plant



over time and to ensure that sufficient protection is available for operation at end-of-run, the amount of promoter added is more than required for operation at start-of-run. The RK-400 catalyst, on the other hand, has been engineered to have a reservoir of potassium promoter integrated within the carrier material. The ability to replenish the potassium over time not only eliminates the obvious challenge of maintaining sufficient alkali at the surface but also allows for an initial surface coverage of only the essential amount of promoter material. In this way, more nickel surface is available for steam reforming catalysis, and a considerable increase in catalyst activity over those previously seen is achieved. RK-400 is suitable for all types of reformers and is also available in a pre-reduced version.

Proven performance of RK-400

The first charge of RK-400 was installed in 2012 in an ammonia plant in North America (Kellogg design). Regular evaluations of operating data confirm the expectations and superior performance of the RK-400 reforming catalyst. Table 1 shows a comparison between the current RK-400 charge and the previous charge after one year in operation. The numbers illustrate that after around one year of operation, both the methane leakage and pressure drop for RK-400 was lower than for the previous charge.

RK-400 has currently been in operation for almost three years and performance is continuing on the same high level.

Table 1: **Industrial experience with RK-400 after one year in operation**

	Previous charge	RK-400 charge
Catalyst age, months	12	14
Plant rate, %	125	126
O/C ratio	3.57	3.59
Outlet temperature, °C	781	785
Methane leakage, mol-%	12.50	12.04
Pressure drop, kg/cm^2	3.14	2.54
Relative pressure drop	100	80

Time savings during start-up with pre-reduced catalyst

Using pre-reduced steam reforming catalyst in the top part of the tubes enables reforming to start immediately upon exposure to the process gas. The hydrogen generated in the top layer then quickly activates the catalyst in the lower part of the tubes, accelerating start-up time dramatically. The 'R' versions of Topsoe's steam reformer catalysts are pre-reduced at Topsoe in dry hydrogen and at an optimal temperature, resulting in higher activity than would be possible with in-situ reduction. The combi-loading in an ammonia plant could typically consist of R-67R-7H/R-67-7H or RK-400R/RK-400/R-67-7H.

To show the advantage of using a pre-reduced catalyst in the top part of the tubes, the key-steps of a typical start-up procedure for Topsoe's combi-loading with pre-reduced catalyst in the top part of the tubes is outlined in Fig. 5. Additionally, a typical start-up procedure for a non-Topsoe charge (full loading of unreduced steam reformer catalyst) is outlined for comparison.

Several benefits can be gained from using combi-loading with pre-reduced catalyst. Total start-up time required for combi-loading is about half of the time required for a full unreduced charge. This corresponds to a time saving of around 15 hours at initial start-up.

The catalysts can at all times be kept in the reduced, high-activity state, due to the fact that natural gas can be introduced already at 550°C (outlet). Avoiding unnecessary catalyst re-oxidation is desirable for achieving good catalyst activity.

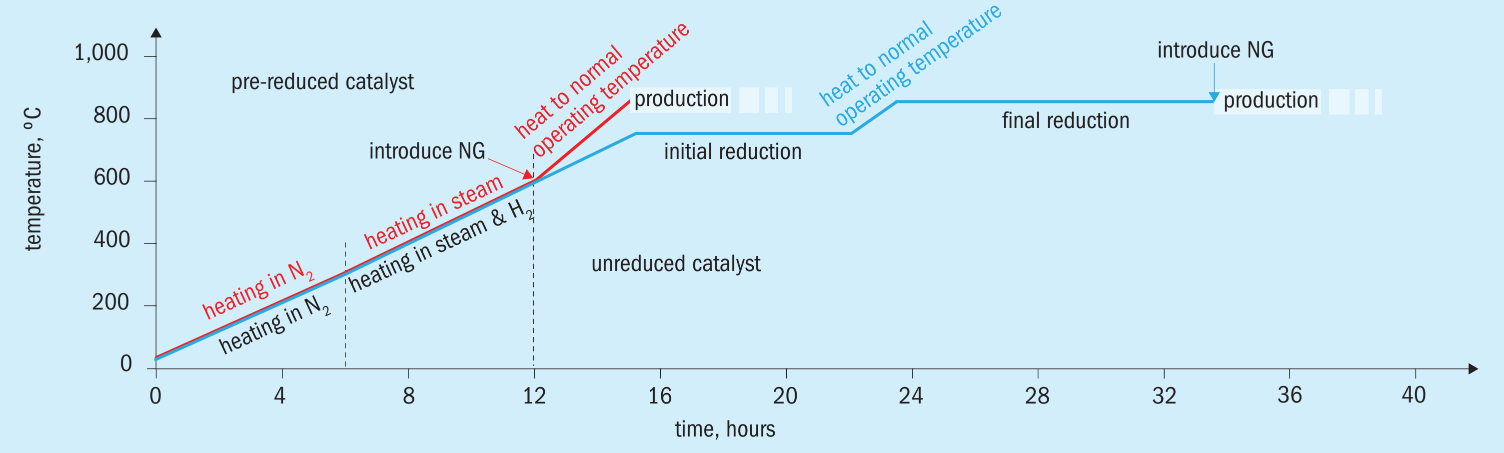
Since natural gas is introduced at lower temperature levels, the thermal shock for the reformer tubes as reforming reactions start is lower. This has a positive impact on tube lifetime.

No hydrogen source is needed during start-up, which both saves on hydrogen and eliminates any possible logistical challenges that might arise if hydrogen is not readily available.

Innovative loading method

The way catalysts are loaded into the steam reformer can affect performance for years and save valuable time during plant turnarounds. Topsoe's proprietary loading method for tubular reformers, SpiraLoad™, offers some significant benefits when it comes to fast and efficient loading of steam reformers. One of the main advantages of this method is the very uniform pressure drop that can be achieved across the tubes, typically the deviation in pressure drop when using SpiraLoad™ is around ±2%. That means that very few tubes have to be unloaded (see Fig. 6), actually less than one in a thousand loaded tubes has to be re/unloaded. The uniform density is also

Fig 5: **Time savings during start-up with pre-reduced catalyst in top part of steam reformer tubes**



1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64

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key when it comes to good performance of the steam reformer. Uniform density results in uniform tube wall temperatures (TWT), which increases the lifetime of the reformer tubes and ensures optimal conversion across the reformer. Hence, using SpiraLoad™ not only saves time during catalyst installion, but also gives a better reformer performance throughout the lifetime of the catalyst. Topsoe has around 200 references for this method, with a total of more than 40,000 tubes loaded with SpiraLoad™. It provides a fast and very uniform loading density, regardless of the reformer design.

Ammonia plant saves four days using SpiraLoad™

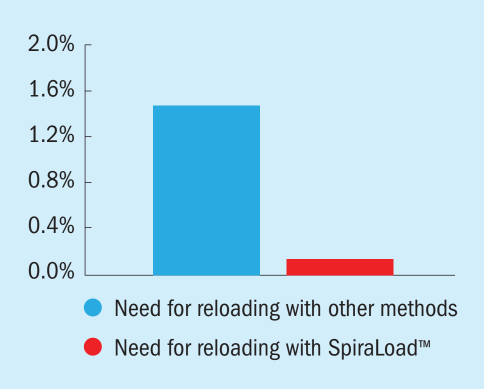
A few years back, an Indian ammonia plant operating two identical ammonia trains decided to evaluate the potential of alternative loading methods compared to the traditional sock loading of their steam reformers. They have two identical reformers, with close to 300 tubes in each and they decided to try two different loading methods in parallel. One reformer was loaded with traditional sock loading, the other one with SpiraLoad™. To ensure a fair comparison, the same loading team loaded both of the reformers.

As expected, the SpiraLoad™ loading process proved to be significantly faster. When using SpiraLoad™, the team managed to complete their work in about half the time compared to sock-loading, thereby gaining four days of valuable ammonia production. Additionally, a much better pressure drop uniformity was achieved. Because of the accelerated loading time, more uniform pressure drops and minimal need for tube reloading, this ammonia producer is now using SpiraLoad™ for all reformer loadings at their facilities. Catalyst performance is also very high, enabling operation of the reformers at close to 130% of their design capacity.

Steam reformer assessment

Optimising the performance of the steam reformer can potentially have a large impact on the overall plant performance, production and profitability. A thorough assessment of the steam reformer is not only an important tool to verify whether the reformer operates within its design limits but also when it comes to identifying bottlenecks in the plant. Moreover, it can also enable a reduction in energy and fuel consumption and increase tube life.

Fig 6: Reloading frequency, SpiraLoad™ vs other methods



Topsoe's steam reformer assessment/optimisation process involves a thorough analysis of process, catalyst and flue gas sides, examining factors such as:

- conditions in the radiant chamber
- interaction between the radiant chamber and heat transfer to the tube
- heat consumed by reactions inside tube
- conditions inside the tubes
- catalyst activity
- heat going to the waste heat section.

The aim is to generate detailed insight into steam reformer performance, showing the actual operation and temperature levels compared to mechanical design limits. This knowledge can then be used for trimming of the reformer to ensure consistently efficient, stable and high-throughput operation. Additionally, the knowledge can be used for assessing the remaining lifetime of the reformer tubes, which is valuable knowledge when it comes to maintenance planning. In the following case, a recent experience with steam reformer assessment in an ammonia plant is described.

2.6% higher ammonia production achieved

A Southeast Asian ammonia producer was looking to fine-tune the operation of its 1,500 t/d ammonia plant. Specifically, their goal was to optimise the performance of their steam reformer. The company turned to Topsoe to examine the reformer, verify actual conditions compared to design limits, and optimise the reformer to maximise performance.

When carrying out a steam reformer assessment at this plant, Topsoe engineers identified a number of issues that needed to be resolved. It was for instance observed that there were combustion air deficits in the furnace. Also, the vacuum pressure was too low, which created positive pressure in the upper part of the furnace. To optimise the reformer, the Topsoe service team adjusted the combustion air being sent to the burners to achieve a more uniform distribution of excess air. They then trimmed the firing profile and increased the furnace draught.

Topsoe's assessment and subsequent optimisation resulted in a more uniform distribution of heat and excess air in the furnace box. Moreover, better utilisation of excess burner capacity in the top-row burners could be achieved. The Topsoe team also made the plant aware of the fact that the flue gas temperatures at the inlet to the convection section were too high. Combined, these changes enabled this plant to increase its ammonia production by 2.6%, while also saving on specific natural gas consumption. For a 1,500 t/d plant, a 2.6% increase in production corresponds to a yearly gain of around $6 million.

Gold Cup – a valuable tool for steam reformer assessment

Accurate and detailed measurements of the tube wall temperatures (TWT) are essential when it comes to optimising the steam reformer operation. For advanced TWT measurements and steam reformer assessments, Topsoe uses the Land Gold Cup Thermometer as reference method.

The Gold Cup is the only instrument that can provide a repeatable, reliable reference temperature. It cancels out all the inherent errors typically found within other infrared thermometer devices. The Gold Cup produces a measurement area on the reformer tube wall, which is emissivity independent when placed upon the surface. Hence, it eliminates the uncertainty that the tube emissivity typically represents during TWT measurements. Simplified, it can be said that the Gold Cup measures the true TWT while TWTs measured with standard pyrometers are less reliable

This means if a plant is using only standard pyrometers to measure TWTs, the exercise might indicate that the reformer is operating closer to mechanical design limits than what is actually the case. Using the Gold Cup can therefore unleash previously undiscovered potential for optimising the steam reformer operation, something that can bring huge value to any plant operating a tubular reformer. ■

Reference

1. Rostrup-Nielsen J.R., Dybkjær I., and Christiansen L.J., Proc. NATO ASI Study "Chemical reactor technology for environmentally safe reactors and products", Ontario, Canada, Kluwer Academic Publishers, Dortrecht, p. 249. (Aug/Sep 1991).

Improving flue gas tunnel reliability

J. Quintiliani and **W. Russell** of Blasch Precision Ceramics discuss how the reliability of primary reformer flue gas tunnels can be improved through the application of engineering design and improved material selection.

Steam methane reforming is one of the most prevalent routes for the conversion of methane (CH_4) to petrochemicals. The process produces a mixture of hydrogen and carbon monoxide referred to as “synthesis gas” or “syngas”. In the most common configuration, methane is put through a primary reformer which is essentially a large refractory lined furnace with centrifugally cast chrome-nickel tubes mounted vertically in the furnace. The process gas and steam are fed downward over a catalyst which is heated by burners mounted in the side or top of the furnace. Along the bottom of this unit are refractory tunnels that function to distribute exhaust discharge uniformly from the furnace, optimising process efficiency and tube reliability. These tunnels have always suffered from reliability issues which can lead to unexpected shutdowns, losses in efficiency, or at the very least high turnaround costs.

Existing designs

The current design and construction of flue gas tunnels in steam methane reformers is relatively simple. The sidewalls are typically constructed directly against the furnace shell floor starting with insulating firebrick then transitioning to regular firebrick configured with either a flat face or tongue and groove. The bricks are all secured with refractory mortar. As the walls are constructed, half blocks are left out in regular patterns to provide holes to allow gas passage from the furnace through the wall into the tunnel. Once the walls of the tunnel have been constructed, the tunnel covers are placed on top. These lids, often called coffin covers, are often made from large slabs of refractory. In order to account for thermal expansion, large expansion gaps are created at regular intervals. This expansion gap is a critical feature, necessary to accommodate for anticipated thermal growth. In order to support these tunnel walls, intermediate support structures, or pilasters, are often integrated into the outer walls of tunnels in an effort to prevent the walls from leaning and collapsing.

Failure due to thermal stress

One of the prevalent tunnel failure modes seen in the field is the collapsing of the lids. Once installed, the lids are viewed to act as a simply supported beam. The belief is that a crack in the middle of the lid is the result of the ratio between the span and the material thickness. However, calculations indicate that the static load alone imparts very little stress on the lids, and will not likely result in a failure. Fig. 1 is a finite element analysis (FEA) of a typical extruded lid installed on a tunnel at a constant service temperature of 1,038°C (1,900°F). The lid has no external forces acting upon it other than its own weight, which resulted in a maximum stress of just 0.69 bar (10 psi); well below the hot modulus of rupture (HMOR) of typical refractories. In order to find the source of these failures, it is necessary to also consider thermal stress. Thermal stress is generated by temperature gradients within a body resulting in strains associated with differential thermal expansion. These strains drive a corresponding stress proportional to the modulus of elasticity of the material. Failure results when the thermal expansion from one area of a component is different than another area. Failure occurs when the resulting stress exceeds the rupture strength of the refractory. If the temperature in the convection section of the furnace is different than the temperature inside the tunnels, even for a short period of time, the potential for thermal stress is present. Fig. 2 shows an FEA of

Fig 1: **FEA of tunnel lid at constant 1,900°F**

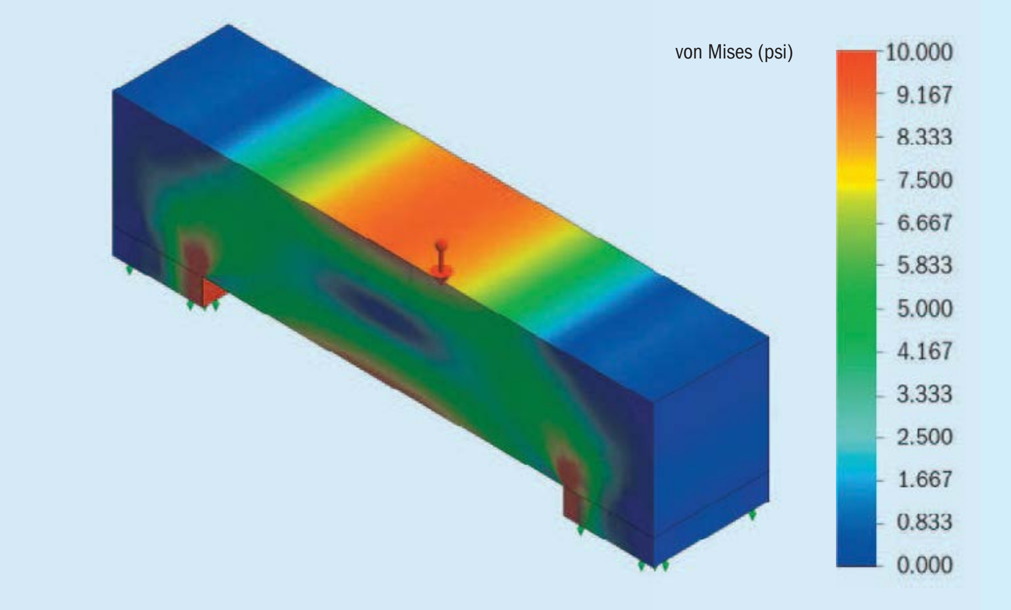


Fig 2: **FEA of tunnel lid at variable temperature between 1,900°F and 1,910°F**

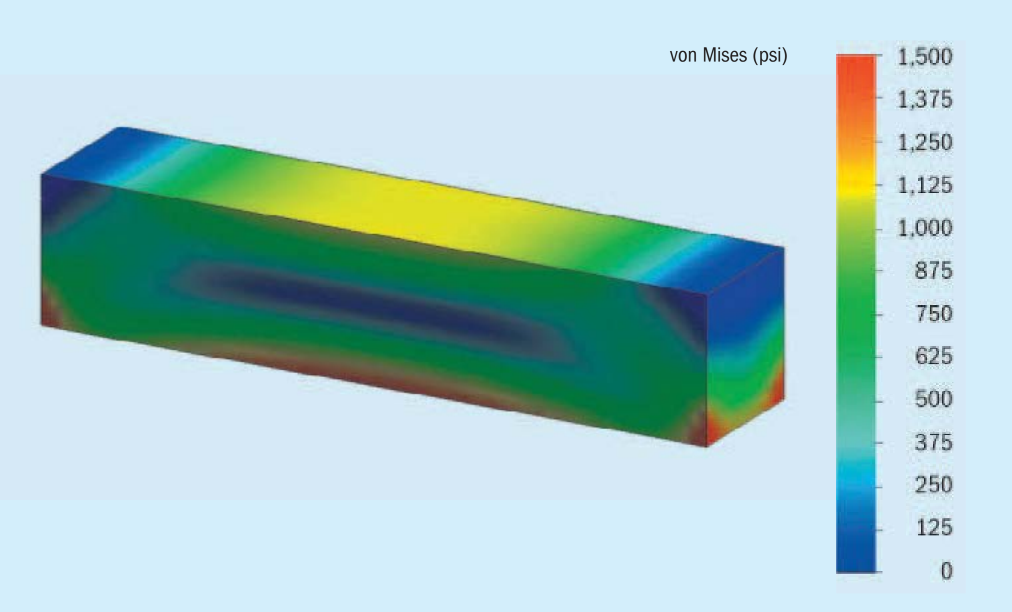
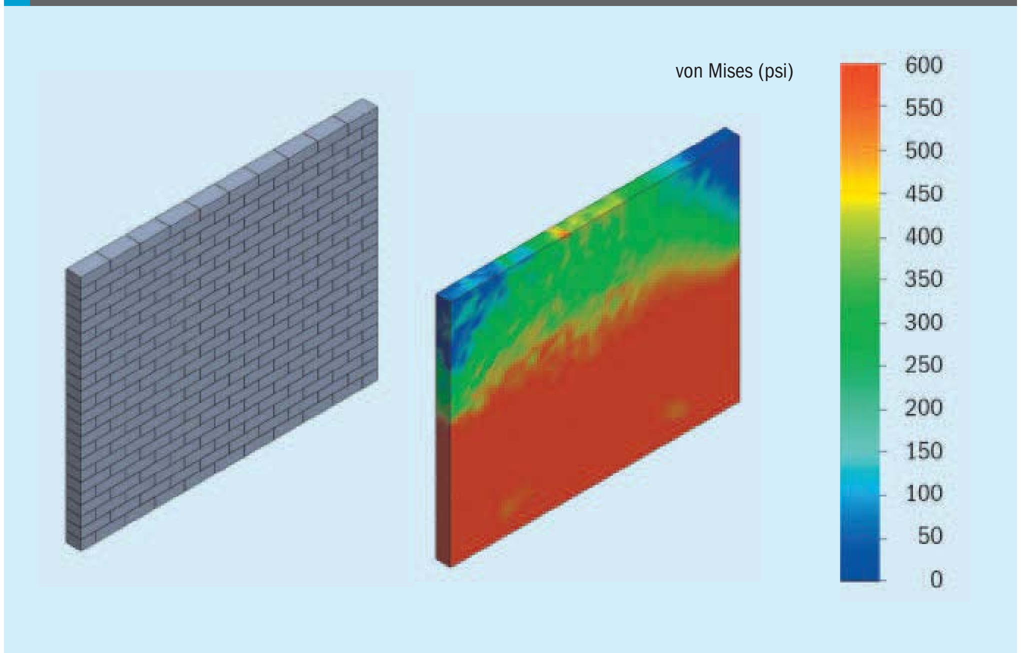


Fig 3: **FEA of a fully mortared 10' tunnel wall section with variable temperature**



the same lid used in Fig. 1, installed on a tunnel with the temperature on the top surface of the lid at 1,043°C (1,910°F) and the temperature on the bottom surface of the lid at 1,038°C. The lid has no external forces acting upon it other than its own weight. A differential temperature of 10 degrees across the lid results in a maximum stress of 103 bar (1,500 psi), above the HMOR of many refractory materials. In a particular instance where a very large number of the lids of a tunnel failed during the same campaign without any of the walls collapsing, the mode of failure was most likely thermal stress.

Decreasing the lid thickness will lower the thermal mass and increase the bulk conductivity resulting in reduced thermal gradients and lower resultant associated stresses. In general, the wall thickness should be as thin as possible without sacrificing the overall stability of the tunnel.

Failure due to material selection

Another important factor in the performance of the tunnel lids is the material selected for construction. There are several properties to consider when selecting a material including HMOR and creep resistance. Creep occurs when a material slowly but permanently deforms under long-term exposure to high levels of stress that are still below the material rupture strength. Creep of a lid will result in a "sagging" of the centre span and will change the interaction force between the lid and the tunnel walls, and eventually lead to a failure. The result on the tunnel walls is a transmission of the lid's mass at an angle that is a few degrees off of the vertical axis and will encourage the walls to separate further apart at the top than at the bottom. This phenomenon is not limited to tunnel lids; the base of the tunnel is also subject to this type of time dependent deformation. Conventional tunnel construction uses hundreds of thousands of pounds of refractory brick and lids. All of this mass rests on a final base layer of insulating fire brick. A conventional tunnel cross section with a solid lid will result in a load on the supporting IFB layer of over 0.69 bar. Published data using ASTM testing suggests that at the temperatures present in the reformer furnaces the IFB layer will deform a full% under those loads in 100 hours. The deformations of the IFB layer can prematurely compress the fiber allowances for thermal expansion, reduce the overall insulating value of the IFB, and impact the stability of the foundation of the tunnel walls, either of which can result in failure. The effects of temperature and tunnel mass are not limited to the internals of the furnace, but can also cause deformation of the supporting steel furnace structure, leading to a non-uniform furnace floor.

Proper material selection should include confirmation that the modulus of rupture at the service and excursion temperatures of the furnace has a sufficient factor of safety when compared to the associated static load stresses. Also, any material being selected for use in the reformer furnace should have the highest resistance to creep reasonably available, as a reduced creep will prolong the life of the tunnel system and prevent premature failures. Finally, reducing the component wall thickness will reduce the overall weight of the tunnel which greatly decreases the pressure load on the IFB base. A 60% reduction in weight will translate to an order of magnitude less load on the IFB layer. The design of the tunnel could also incorporate a "base" component that spreads the weight of the tunnel over up to five times the area of conventional designs.

Failure due to thermal expansion

Differential thermal expansion can occur not only in situations with different design materials, but also across large sections of materials that are expected to act as a single body. A conventional tunnel design will use fibre expansion joints roughly every

Fig 4: **FEA of a non-mortared 10' tunnel wall section with variable temperature**

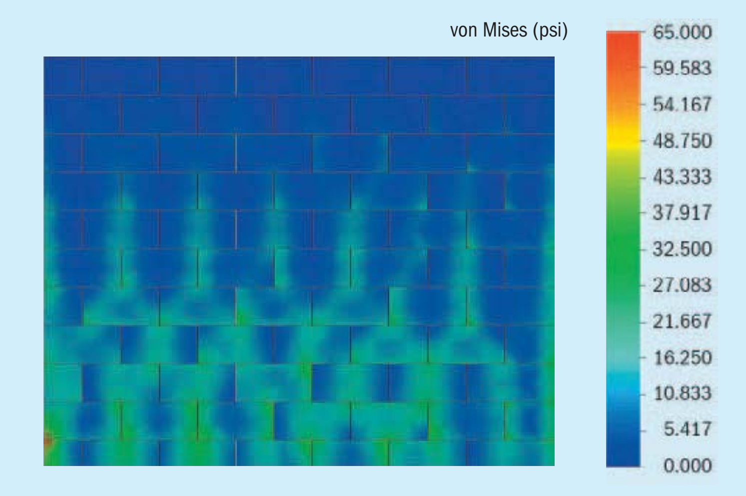
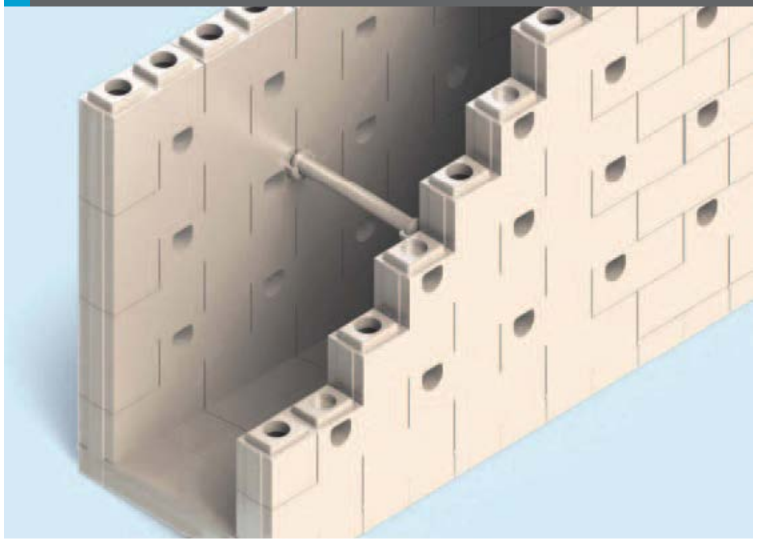


Fig 5: **Cross beam support for tunnel system**



183-305 cm (6-10 feet) of wall length, with all of the building components in between adhered to one another with a refractory mortar causing the wall sections to behave as a single body. Fig. 3 shows an FEA performed to determine stress levels associated with a differential temperature from the top of a fully mortared 305 cm wall section to the bottom. The fully mortared wall section was treated as a single body for the purposes of the analysis. The wall section has a uniform temperature distribution with 1052°C at the bottom and 1,038°C at the top. The FEA also included a simulated weight of the tunnel lids and gravity, but no other external forces. This analysis showed that the stress of this system exceeds the 34 bar HMOR typical of a standard refractory mortar. Since the mortar joints are the weakest point on the wall, they will crack to alleviate the stress, often resulting in overall wall stability issues. Fig. 4 shows an FEA performed to determine stress levels associated with a 3.05 m wall section comprised of 46 cm W x 23 cm T blocks that have individual expansion gaps. The conditions and external forces for this analysis are identical to that of the mortared wall section. The result is a system with a peak stress of less than 4.5 bar.

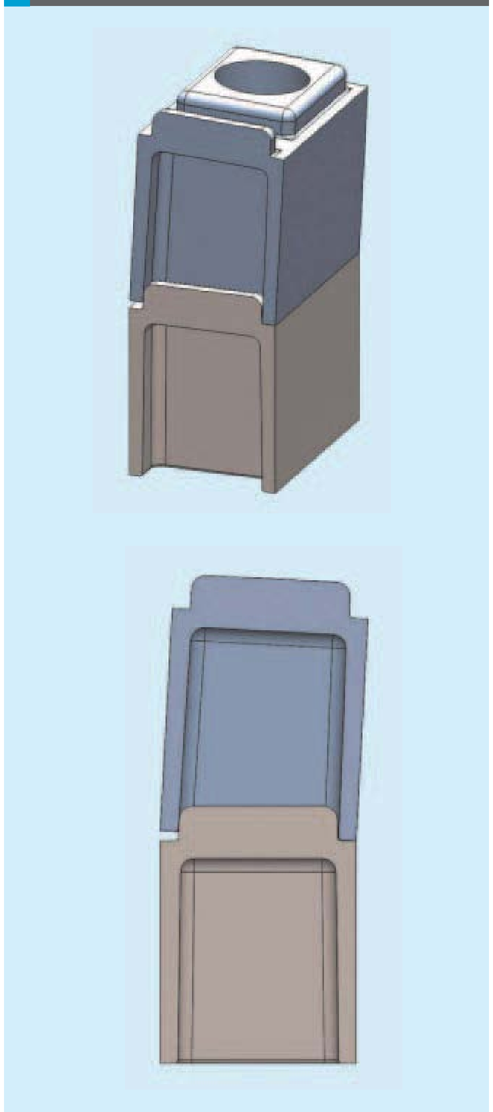
Properly accommodating for thermal expansion is one of the most difficult aspects of any thermal application design. A conventional tunnel design has a different material, conditions and design for the tunnel lid and the tunnel base. Often tunnels are designed with low density refractory or fiber insulation in the "base" area in between the wall supporting IFB columns. By design, the tunnel base area is cooler than the lid. The tunnel lid can expand as much as 9.5 mm pushing the tunnel walls apart with it, whereas the fibre insulation imparts far less expansion on the tunnel walls. The resulting trapezoidal tunnel cross section is far more susceptible to buckling and ultimate collapse.

In certain situations tunnels have been found at the conclusion of a furnace campaign to have alternative movement in the lateral direction. This is known more commonly as "snaking" and is the result of the overall length of the tunnel attempting to expand to a greater extent than that allowed by the expansion joints. Snaking can crack the mortar, separate walls from lids, and push the walls off of the IFB base; all of which can lead to failure. Proper material selection and installation procedures are important to prevent "snaking". Many materials will increase in overall dimension when re-heated, increasing variability and adding challenge to the thermal expansion management. Because the coefficient of thermal expansion for refractory components is nonlinear, it must be fully characterised and understood to ensure that proper expansion joints are created.

In order to best accommodate thermal growth, every block should manage its own thermal expansion and the entire system must be mortar free, but for stability reasons must be completely interconnected. Proper thermal expansion management also suggests a tunnel system should utilise a "base" component that has the same material and similar dimensions to the "lid" component. This will ensure that the tunnel expands and contracts equally on both the top and bottom of the wall. Cross beam supports can be added into the system at predetermined locations to arrest buckling if it does begin (Fig. 5).

Buckling can also be arrested with a tight tolerance mating feature in the wall components, such that the rotation of a block in relation to the block below it results in direct contact. This resulting tunnel system now requires a sufficient amount of stress to break the block wall (Fig. 6). ■

Fig 6: **Tight tolerance engaging mating features**



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