

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


Welcome to our interactive version of **Nitrogen+Syngas** Issue 361

Please use either the buttons on the left or top right of the page to navigate your way around this interactive PDF

IMPORTANT INFORMATION:
Copyright – Issued six times per year, or bi-monthly. All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means – electronic, mechanical, photocopying, recording or otherwise – without the prior written permission of the Copyright owner.

Number 361

September | October 2019



nitrogen **60** YEARS ANNIVERSARY 1959-2019

syngas

www.nitrogenandsyngas.com



CONTENTS

What's in issue 361

COVER FEATURE 1

Combatting AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

Combatting AN misuse

High temperature hydrogen attack

Green ammonia

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

JM

Making a difference to the world around us

With years of operating experience and expertise across the syngas, petrochemical, oil and gas markets, Johnson Matthey continues to invest in technologies that improve processes whilst looking after the environment.

Our gas heated reforming technology is a proven energy efficient solution for syngas generation across multiple applications reducing both CO₂ emissions and raw water consumption, whilst maximising the opportunity to use renewable energy.

Contact us to find out how our technology can benefit your business.

Johnson Matthey
Inspiring science, enhancing life

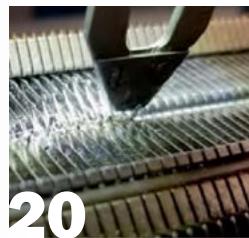
www.matthey.com



Cover: Detail of the domed golden roof of The Secession Building, Vienna. iStockPhoto.com/Emilie1980



16
Hydrogen attack
New developments in combatting HTHA.



20
Catalyst gauzes
Tailor-made catalyst gauzes for nitric acid plants.

Read this issue online at:
www.nitrogenandsyngas.com

Published by:
BCInsight

nitrogen 60 + syngas

YEARS ANNIVERSARY 1959-2019

www.nitrogenandsyngas.com

NUMBER 361
SEPTEMBER | OCTOBER 2019

CONTENTS

- 10 Preventing ammonium nitrate misuse**
The US has been pursuing regulation on controlling the misuse of ammonium nitrate-based compounds for nearly two decades, and arguably longer, but so far progress has been very slow.
- 12 The future of gasification**
While gasification, especially of coal, remains a common route to producing syngas, concerns over carbon emissions are slowly edging out new projects. But gasification remains a versatile process, and use of municipal waste, biomass and possibly carbon capture may yet see it flourish.
- 14 Profile: Umberto Zardi**
This year, on July 29th, Dr Umberto Zardi, president of the Casale Group, celebrated his 90th birthday. To mark the occasion, Nitrogen+Syngas looks back over the long and varied career of a nitrogen industry pioneer.
- 16 High temperature hydrogen attack**
High temperature hydrogen attack (HTHA) is a damaging form of corrosion of steels that occurs in high temperature, hydrogen rich atmospheres. While it was characterised in the 1940s via the so-called 'Nelson curves', recent incidents have indicated that the issue may be more complex than previously thought.
- 18 Green ammonia for a more sustainable future**
As the interest in sustainable ammonia, renewable energy and power-to-ammonia continues to grow, we report on some of the latest developments and technological advances that were presented and discussed at the 3rd European Power to Ammonia[®] Conference, organised by Proton Ventures BV.
- 20 Next generation catalyst gauzes for nitric acid plants**
Tailor-made designs according to specific customer requirements have led to catalyst gauzes with improved overall performance and minimise the total cost of ownership for customers. New and improved catalyst gauze systems from Heraeus, Johnson Matthey and Sabin Metal Corporation are discussed.
- 23 A unique alternative to RCF is born**
When it comes to lining fired heaters in the petrochemical industry, refractory ceramic fibre (RCF) has been the go-to material, but it has its drawbacks. S. Chernack of Morgan Advanced Materials looks at how these can be mitigated and discusses a new alternative material that meets stringent health and safety requirements.
- 24 A flexible concept for ammonia production**
K. Wawrzinek and C. Brunazzi of Linde describe the benefits and features of the Linde Ammonia Concept for large-scale and small-scale ammonia production. Recent ammonia plants built by Linde demonstrate the flexibility of the concept, which can be adapted for different feedstocks to produce co-products such as industrial gases and methanol or for small-scale modular plants.

REGULARS

- 3 Editorial** A tale of two urea plants
- 4 Price Trends**
- 5 Market Outlook**
- 6 Nitrogen Industry News**
- 8 Syngas News**
- 9 People/Calendar**
- 10 Plant Manager+** Problem No. 56: Oil fouling from ammonia plant

CONTENTS

What's in issue 361

COVER FEATURE 1

Combatting AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England

Tel: +44 (0)20 7793 2567

Fax: +44 (0)20 7793 2577

Web: www.bcinsight.com
www.bcinsightsearch.com

A tale of two urea plants



Just as this issue was going to press came news that Perdaman Fertilizers and Chemicals had finalised its licensing and technology agreement with Haldor Topsoe for the latter to supply its large-scale SyncOR technology as part of a project to build the largest single train ammonia plant ever to be built; a 3,500 t/d (1.2 million tonne/year) behemoth feeding 2 million t/a of urea production.

Perdaman's attempts to get a large-scale urea project off the ground in Western Australia have a long history. The company's chairman, Vikas Rambal, was between 2001-07 the managing director of Burrup Ammonia, the Indian-based company that developed and operated the Burrup ammonia plant on the Karatha Peninsula in the northwest of the state, before shenanigans centring around the company's owner Pankaj Oswal led to it falling into the hands of Yara and gas supplier Apache in 2012. Since Rambal's departure from Burrup Ammonia in 2007, the Perdaman Group has been involved in a variety of different industries, including pharmaceuticals and the ownership and operation of shopping centres. However, nitrogen fertilizer has clearly been close to his heart, as his Perdaman Industrial subsidiary was set up with the specific purpose of developing a new 2 million t/a urea plant in Western Australia. The main project proposal was submitted in 2009, based around a coal gasification fed plant in the southwest of the state, at Collie, 200 km southeast of Perth, in the heart of the state's coal mining region. The A\$3.5 billion project was approved by government in 2010, and the government had allocated space and performed improvement works at the Shotts Industrial Park.

However, the proposal ran into problems in 2011 on sourcing coal feedstock. Two major mining companies, Premier Coal and Griffin Coal operate mines at Collie, with the coal mostly going to local power generation. Perdaman had agreed to set up a long-term supply deal with Griffin, but in 2010 Griffin's owner, Rick Stowe, filed for bankruptcy and his share in Griffin Coal was sold to Indian-based Lanco Infratech. However, Lanco said that it was not bound by the agreement to supply 2.8 million t/a of coal because Perdaman had not yet achieved financial closure on the plant. The lawsuit rumbled on in the Australian courts for two years before being settled out of court, and Perdaman seeing little of the A\$3.2 billion in damages that it had been seeking.

While the project was not officially abandoned until 2018, the idea of building a coal gasification-

based plant in today's climate seems to be one whose time has come and gone. The heyday of coal gasification projects was the 1990s and early 2000s, when rising natural gas prices and cheap coal seemed to be pointing the industry in that direction. However, with increased focus on the carbon penalty of coal-based plants, as we discuss in our article this issue on gasification, the decision to focus instead on developing a gas-based plant seems a sensible one.

The new location chosen for the plant is the Burrup Peninsula, where it all started for Rambal. The project, now slated to cost A\$4.4 billion (US\$3.3 billion), will take gas from Australia's North-West Shelf. As before, the urea will be mainly for export, with India and south-east Asia likely to be target regions (although India's current move towards urea self-sufficiency may yet pose a problem). What is less likely to be a problem is feedstock, however. Australia has in effect two independent gas markets. Gas prices on the east coast of Australia have been impacted by several large LNG export projects. However, there are no pipelines running east-west across the country, so the west coast operates as almost a separate country, where gas is abundant and consequently cheaper. Perdaman signed a 20-year gas supply agreement with Woodside Petroleum last year. Perdaman's journey from Collie to Burrup has been a tale of two urea plants – one coal based, now abandoned, and one gas-based.

The Burrup plant still needs environmental approval – the draft plan was submitted in June this year – and financial closure, although Rambal remains confident that construction can still begin in early 2020, for completion in 2023. It will be a remarkable end to a long journey if it does so. However, a rumbling argument about Aboriginal rock art on the Burrup Peninsula and its susceptibility to emissions from the chemical industry in the region still remains a potential spanner in the works. ■

Richard Hands, Editor



Melamine...

is a key presence in our lives!

Euromel® Melamine is extensively used in the bullet trains for its superior performance. Driver's cabs, switch cabinets, doors and sidewalls rely on melamine for insulation, fire resistance and low weight.

Euromel® is the trademark for melamine produced at plants licensed, engineered and implemented by Proman Group's Eurotecnica Company, the leading melamine technology provider since 1978.

Contact us to find out more.



CONTENTS

What's in issue 361

COVER FEATURE 1

Combatting AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

NITROGEN

Natural gas prices have been falling in all major markets for most of this year, and the trend continued into July and August. A warm winter in the US and Europe means that there has been plenty of gas in stock. Henry Hub prices dropped as low as \$2.02/MMBtu in early August, but generally have been hovering around \$2.20-2.30/MMBtu, \$0.70-0.80/MMBtu below levels for the same time last year. Rising gas exports from Russia and the US to Europe have also brought European prices down – Dutch TTF prices touched historic lows of \$3.20/MMBtu in July, prices not seen in a decade, while European cross border import prices were as low as \$3.60/MMBtu.

Falling European gas prices have been a downward factor on nitrogen fertilizer markets, as was new supply; June saw the start-up of EuroChem's new 1 million t/a ammonia plant at Kingisepp near St Petersburg on the Baltic coast. EuroChem will supply ammonia to its fertilizer plants in Antwerp, Lifosa in Lithuania, and Phosphorit, at the Group's Kingisepp site, but a further 25% of output will be sold to third parties. Over the past few years, new capacity in the US has also reduced US import needs by around 1.7 million t/a. However, in the short term, outages and turnarounds in Algeria and Russia have helped keep a lid on excess ammonia supply in Europe. In particular, an unplanned outage at Ma'aden's ammonia plant in Saudi Arabia took the market by surprise and helped see prices rally slightly, with Asian prices up about

\$5/t on July to a range of \$260-280/t c.f. Longer term, however, as shut down plants return to production, the trend continues to be bearish. In the US, contract prices rolled over at \$215/t c.f. Tampa, Florida, but this has come after ten months of falling prices which began at \$355/t in October 2018.

In July urea markets were focused upon India's MMTC tender of July 1st, for 1.7 million tonnes of urea. Offers began at \$293-296/t c.f., with Chinese suppliers rushing to make offers at a netback around \$275/t f.o.b., \$15/t up on previous tenders but lower than anticipated. Around 1.0-1.1 million tonnes were said to be taken from Chinese suppliers, but it became clear many of these could not supply before the August 16th deadline, leading traders to try and cover sales to India from other sources, including 200,000 tonnes from the FSU. This supported prices in the Middle East and North Africa for most of July, although into August Arab Gulf prices had dropped back from \$282-284/t f.o.b. to \$270/t, as lack of demand from outside India drove bearish sentiment. North African was reported well supplied for the second half of August.

The US bucked the trend, with solid late season demand taking NOLA prices up from \$245/t f.o.b. to \$260/t, although this remains at a discount to international prices. Some of this is catch-up, after a poor spring planting season due to heavy rainfall and flooding led to lower US applications in 1H 2019. UAN netback prices at NOLA were around \$140-\$145/t f.o.b. Flooding on the Mississippi River in May and June led to

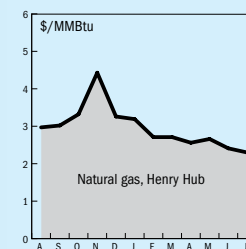
transport and distribution disruptions which led to a surge in US prices inland.

The US Department of Agriculture surprised the market in August by increasing corn production forecast to 13.9 billion bushels and raising the average national yield by more than 3 bushels to 169.5 bushels per acre. Farmers planted 76.7 million acres to soybeans, according to USDA's revised planting survey. With a national average yield of 48.5 bushels/acre, total production is forecast to be 3.68 billion bushels. The production estimate is a 19% drop from last year, however.

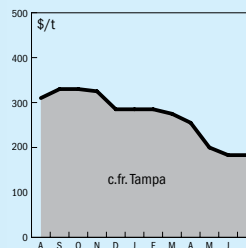
It is believed that there is more Indian buying ahead, although possibly not until September, but in the meantime higher Chinese exports have led to continuing softness in urea markets, exacerbated by the availability of cheap Iranian product, which has been a negative factor on prices in e.g. Brazil. Chinese urea exports fell to their lowest level in many years last year, but exports this year have rebounded and are expected to be at least double last year's record low. A devaluation of the Chinese yuan also helped lower Chinese urea prices by \$5-15/t f.o.b. at the start of August, falling to just above \$260/t f.o.b. Producers in most regions have found themselves with excess inventory, and offers from the Arabian Gulf and southeast Asia have fallen in line with Chinese supply, to \$260/t f.o.b. However, China's continued programme of urea plant closures is keeping the Chinese market tighter than it has been historically, which will set a limit on export availability.

END OF MONTH SPOT PRICES

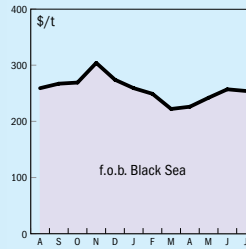
natural gas



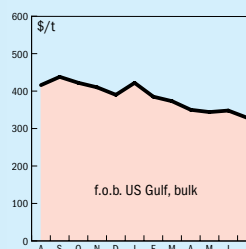
ammonia



urea



diammonium phosphate



METHANOL

Methanol prices have been on a long, slow slide this year that accelerated into July and August. Methanex's US Gulf Coast non-discounted reference price (NDRP) dropped 13 cents per gallon for August to \$1.03/gal (nominal \$342/tonne), while Southern Chemicals posted three cents lower at \$1.00/gallon, down \$0.17/gal, following a \$0.20/gal fall in July. The US methanol market has started to emerge from the issues caused by the fire earlier in the year at the Intercontinental Terminals Co storage facility at Deer Park, Texas. The fire closed the terminal for several weeks and particularly affected Methanex, which had to draw on supplies from Louisiana and Canada to fulfil customer contracts during Q2.

Over in Europe, the Q3 contract price was agreed at €305/tonne f.o.b. Rotterdam, a fall of 45 euros from Q2 2019, when it stood at €350/tonne, and down over €100/tonne on the Q1 price of €428/tonne. Even so, this adjustment still left European contract prices well above spot rates. European spot prices fell to three year lows in mid-August, dropping as low as €205/tonne on August 12th before rising back up to €215-217/t f.o.b. Rotterdam. The low spot rates were due to oversupply at Rotterdam, due to the lingering remains of the difficulty that traders had had from April onwards in securing storage tank space in Rotterdam, which was itself a knock-on effect of the high temperatures and low rainfall seen in Europe over the summer and consequent low river levels on the Rhine, making the usual barge transport upriver from Rotterdam difficult. A wetter August has seen river levels recover and more methanol start to move inland, which has finally taken the pressure off storage levels and allowed spot prices to recover a little. Another factor has been cargoes from the Caribbean and Middle East which had been scheduled to travel to Europe being diverted instead to Asia.

More relief on European supply came from delays to the restart of BioMCN's second methanol train, which was delayed from June, and maintenance at some facilities in Russia. Methanex's plant in Egypt remains offline due to technical issues. In the Middle East, Salalah Methanol Company in Oman was aiming to take a planned maintenance period from August 23rd for 18-20 days, removing its 1.3

million t/a plant from the market. Operating difficulties in Iran caused by the US sanctions regime have also seen Iranian plants running at lower operating rates. However, slowing European growth rates and a recession in Germany point to lower demand for the second half of 2019, coupled with continuing uncertainty over Brexit.

Meanwhile, the cargoes diverted from Europe helped contribute to a supply glut in Asia, Methanex's Asia-Pacific Contract Price fell by \$40/t in August to \$295/t. Chinese coastal storage was also reported nearing saturation levels, and there were some shutdowns of the crucial methanol to olefins (MTO) units that drive Chinese spot demand. Technical issues affected Ningbo Fund's 600,000 t/a methanol-to-olefins (MTO) plant from 11th August and were expected to last for a week, removing 36,000 tonnes of methanol demand based on its 1.8 million t/a nameplate consumption. Shaanxi Yulin Energy also took planned maintenance from August 20th. Chinese demand has been weak throughout the first half of the year, and prices have been at lower levels in spite of lower production from Chinese gas-based methanol plants due to lack of feedstock availability. Even so, the impact of the extra supply meant that East Chinese spot prices fell during August by about 70 yuan/tonne, to 2,005-2,030 yuan/t (\$285-288/t), and methanol futures were also down on the Zhengzhou commodity exchange.

Tariffs imposed by China on US imports of methanol have affected supply patterns slightly, but more serious has been US sanctions on Iran, which has left China as one of the few potential destinations for Iranian methanol, and which has contributed to Chinese oversupply. A little supply relief in the region was provided by continuing technical problems at Petronas, which suffered a short outage at its 660,000 t/a Labuan Island plant.

Elsewhere, Methanex subsidiary Waterfront Shipping has launched two more 49,000 dwt methanol tankers, the M/T Mari Couva and M/T Mari Kokako, both of which are powered by methanol to meet new IMO regulations on sulphur in marine fuels. Methanex has given the green light to its new 1.8 million t/a methanol plant at Geismar in Louisiana, which is expected to be completed by 2022, and which Methanex has said will be focused on supply to Asia.

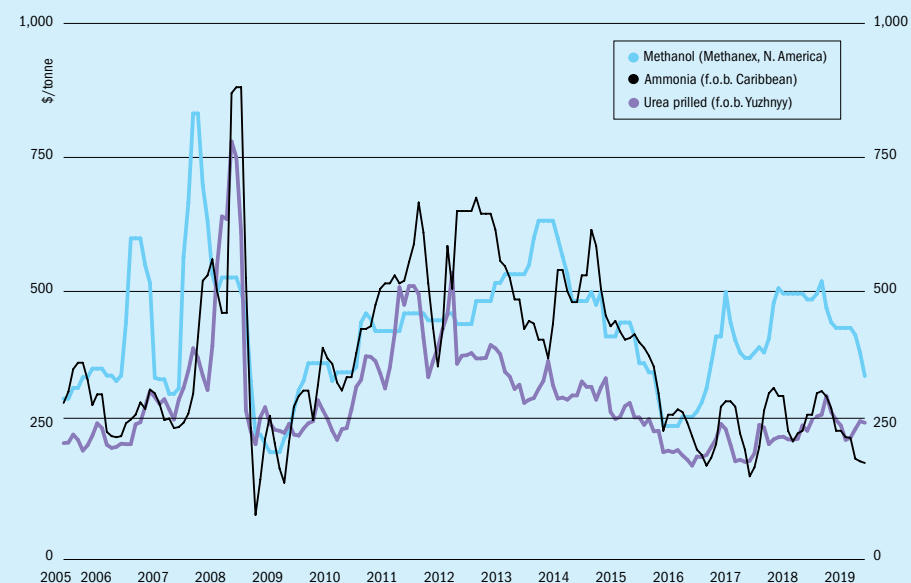
Table 1: Price indications

Cash equivalent	mid-Aug	mid-June	mid-Apr	mid-Feb
Ammonia (\$/t)				
f.o.b. Black Sea	195-215	200-210	242-250	260-280
f.o.b. Caribbean	170-190	175-190	223-228	240
f.o.b. Arab Gulf	190-205	200-215	245-255	270-285
c.fr N.W. Europe	225-265	230-265	275-290	310-325
Urea (\$/t)				
f.o.b. bulk Black Sea	245-260	250-266	224-230	230-240
f.o.b. bulk Arab Gulf*	256-270	285-295	247-272	233-255
f.o.b. NOLA barge (metric tonnes)		248	265	245
f.o.b. bagged China	277-295	285	300	260-285
DAP (\$/t)				
f.o.b. bulk US Gulf	313-326	346-349	353-369	390
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	197	205	235	238

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

Market Outlook

Historical price trends \$/tonne



Source: BCInsight

NITROGEN

- Natural gas prices continue to be much lower than 2018 values in all major markets, leading to expectations of continued lower floor prices for ammonia.
- Iranian ammonia supply continues to be a source of uncertainty due to US sanctions.
- A poor year for fertilizer applications and crop yields in the US has led to more positive forecasts for demand for 2020. In their second quarter results, Nutrien, CF Industries and Mosaic all outlined optimistic forecasts, with expectations of higher corn prices, strong spring demand next year, and an estimated 95-96 million acres of corn planted, all expected to boost urea demand.
- Downside factors remain US trade policy, especially as regards the ongoing trade war with China. The depreciation of the yuan has caught markets on the hop, but could be a sign of things to come. Slowing economic growth in China will reduce pressure on coal prices, and may lower Chinese and hence global market floor prices.

- There have been positives for demand from Brazil and Southeast Asia however. CF Industries says that it expects demand for urea from India and Brazil to remain strong over the next two years. Through the end of June 2019, urea imports to India were 3.5 million metric tons, an increase of 11% over the same period ending in June 2018.
- Overall, CF expects that global demand growth for nitrogen over the next four years will outpace net capacity additions. Net Chinese-produced urea exports are likely to be in a range of 1.3 million metric tons annually, with higher nitrogen prices bidding in additional Chinese export tons at times when urea supply is needed worldwide.

METHANOL

- Demand for methanol continues to be robust, up 3% in the US year on year. Globally, the methanol market has averaged a growth rate of 6.2% over the past five years, and Methanex has forecast 5% growth for this year. Globally, in spite of capacity additions such as Methanex
- at Geismar and EuroChem at Kingisepp in Russia, not enough new methanol capacity is being built to cover forecast demand increases, and at the moment the outlook is for tighter methanol markets over the next couple of years. Longer term, the US-China trade war has the potential to delay new capacity being developed in the US for export to China.
- Much of global demand growth continues to come from Chinese methanol to olefin plants, with some new plants expected on-stream during 2H 2019. However, the Chinese market is expected to remain under supply pressure as methanol from Venezuela, Iran etc continues to be funnelled there due to US sanctions. Overall, predictions are for Chinese spot prices to rise during 2H 2019, but not by a long way.
- The slowdown in the global economy is a slight counterbalancing factor to this, especially for traditional demand sectors like formaldehyde, acetic acid etc. Lower oil prices will also impact upon margins for MTO producers, potentially driving down production there.

www.nitrogenandsyngas.com

Nitrogen+Syngas 361 | September-October 2019

AMMONIA

Change your vision

INTEGRATED PROCESS

From feedstocks to any fertilizers and valuable chemicals.

AMMONIA
NITRATES & PHOSPHATES
UREA
MELAMINE
METHANOL
SYNGAS

CASALE

www.casale.ch
info@casale.ch

CONTENTS

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

EGYPT

MoU on new ammonia plant

Egypt's Al-Nasr Fertilizers Company (SEMADCO), a subsidiary of the Holding Company for Chemical Industries, has signed a memorandum of understanding (MoU) with Benchmark Power International to establish a new ammonia plant. The two companies have agreed to develop a plant with a capacity of 1,200 t/d in the first phase, at an estimated cost of \$600 million, with a potential identical second train in the second development phase.

The MoU was signed by the chairman of El Nasr Fertilizers Company Hamdy Gaber, and chairman of Benchmark Power International Ahmed Bahgat, in the presence of the chairman of the Holding Company for Chemical Industries Emad Mostafa and Egypt's Minister of Public Business Hesham Tawfik.

El Nasr Company will provide the project with an unused plot of land with an area of approximately 460,000 square meters for the establishment of the plant on a 25-year basis. The land is located in the company's complex at Ataka in Egypt's Suez Governorate. Benchmark, for its part, will bring in technical and financial partners, and provide knowledge and an information technology contract with a global knowledge resource provider in the ammonia technology industry.

This project is part of the Ministry of Public Business's efforts to modernise and develop its subsidiaries, support them with modern technology and harness the expertise of the private sector, as well as improve the utilisation of unused assets.

NETHERLANDS

Collaboration on ammonia-burning generators

In July Proton Ventures BV announced a strategic collaboration with Duiker Combustion Engineers for, among other things, the start-up of mini-ammonia plants using the Stoichiometry Controlled Oxidation (SCO) technology developed by Duiker Combustion Engineers, which converts ammonia into high temperature heat. Proton Ventures develops small-scale ammonia plants for conversion of wind and solar energy into ammonia, while Duiker CE technology burns ammonia-rich streams in a furnace environment with very low NOx formation and without CO₂ emissions. The companies say that SCO technology makes it possible to save fossil-based energy and produce less CO₂ and NOx emissions, because the ammonia containing fuels are oxidised in a controlled manner.

Hans Vrijenhoef, CEO Proton Ventures said: "We like to collaborate with partners to complete the chain of using ammonia as an energy solution. This includes also power and heat generation and solutions for energy storage. Duiker's SCO technology opens new possibilities for us in applying local ammonia production from small to large scale, such as conversion of power plants to cleaner fuels while maintaining the existing installations. A combi-

nation of our expertise leads to this unique collaboration."

Albert Lanser, Duiker CE Business Development Director added: "This collaboration offers us the opportunity to place our SCO technology worldwide in a completely different customer segment than we currently serve. Moreover, in combination with a 'green' ammonia production unit it is capable of making a real contribution to the climate because ammonia does not emit CO₂ during combustion.

SWITZERLAND

Casale buys Orica's LDAN technology

Casale and Orica have agreed on a deal for the acquisition by Casale of Orica's complete process and know-how to produce low density ammonium nitrate (LDAN). Casale says that this acquisition is in line with the company's long-term growth strategy in the syngas-based chemicals sector, aimed at offering complete production chains, from feedstocks to final products. In particular, the move strengthens Casale's technical and commercial footprint in the solid nitrates field by complementing its well-proven high density/fertilize grade ammonium nitrate technology.

The deal includes the right to use the technology in all new and revamped plants based on LDAN prilling technology, as well as Orica's proprietary additive *Sapphyr*, on commercial terms to be agreed. In addition,

during the technology transfer phase, Orica will provide assistance to Casale and grant access to Orica's plants. Casale says that it will continue to work on creating value for its customers through synergic acquisitions.

GERMANY

thyssenkrupp aims to be climate neutral by 2050

thyssenkrupp says that it is aiming to be climate neutral from 2050 onwards, based on the Paris Climate Agreement of 2015. As early as 2030 the Group plans to cut emissions from production and outsourced energy by around 30%. Emissions from the use of thyssenkrupp products are to fall by 16% by 2030.

The targets take in thyssenkrupp's own production operations, the energy it purchases and its products. In steel production, for example, thyssenkrupp is currently pursuing two approaches to reducing CO₂ emissions: the Carbon2Chem project, which is expected to be available on an industrial scale before 2030, and the so-called hydrogen route, which should take full effect by 2050 and make the biggest contribution to directly avoiding CO₂. Carbon2Chem converts steel mill emission gases, including the CO₂ they contain, into valuable chemicals. thyssenkrupp's hydrogen route involves replacing coal with 'green' hydrogen as the reducing agent for blast furnaces so that in the long term no CO₂ is created in the production of steel. These technologies are being funded by the German federal government and the state of North Rhine-Westphalia.

Meanwhile, under its Climate Action Program for Sustainable Solutions (CAPS) thyssenkrupp will also systematically work to make its products carbon neutral. The Group already offers a technology for the cement industry that permits CO₂ emissions from the combustion processes to be captured for subsequent storage or processing. In the area of sustainable mobility thyssenkrupp is working with European partners to produce fuel from biomass. These fuels reduce CO₂ emissions by up to 90% compared with conventional fuels.

Other key areas include the e-mobility sector, where thyssenkrupp supplies battery production lines and special steels for electric motors. The Group is also actively involved in the development of energy storage solutions, for example with electrolysis systems that convert electricity into hydrogen. These storage systems allow a con-

stant supply of electricity from renewables regardless of the weather.

thyssenkrupp CEO Guido Kerkhoff said: "the threats posed by climate change affect us all. As an industrial company with operations around the globe we are in a particularly good position to reduce greenhouse gas emissions through sustainable products and processes. We take this responsibility very seriously and have received several awards for this in recent years. Now we are setting ourselves clear targets for 2030 and 2050 as the next logical step."

ITALY

Tecnimont acquires Protomation

Maire Tecnimont Group has acquired Protomation via the Group's innovation and licensing company Stamicarbon. Protomation is a specialist Dutch IT company dedicated to developing software applications and state-of-the-art operator training simulators (OTS) for the chemical process industry, with an extensive track record of collaboration with fertilizer producers. Stamicarbon has been partnering with Protomation for more than ten years to develop software packages and OTS for urea plants using Stamicarbon designs and technology. Controlling and stabilising a processing plant in optimal operating conditions needs constant operator attention: OTS have already proven to be a valuable training tool for new personnel in existing plants and new operator teams in greenfield plants.

With this acquisition form's part of Maire Tecnimont's digital transformation roadmap, which aims to leverage digital tech-



Stamicarbon CEO Pejman Djavdan (right) with Leo Rams of Protomation (left) at the signing ceremony.

nologies to redesign its internal processes and enhance the Group's value proposition towards its clients through digitally enabled services. As part of this strategy the Group has designed a modular digital portfolio, across a range of activities from technology licensing to EPC contracting.

Pierroberto Folgiero, Maire Tecnimont Group CEO, commented: "Digital transformation is providing a much-needed boost to our industry, and our aim is to drive this digital advantage as an accelerator to speed up process improvements required to bridge the gap. The acquisition of Protomation fits with Maire Tecnimont's strategy for digital transformation, as we complement our value proposition with new services, and at the same time we improve our operational model through digital enablers.

POLAND

Tecnimont to build new granulation unit

Tecnimont SpA has been awarded an engineering, procurement and construction (EPC) contract by Anwil, part of Poland's Orlen Group, for a new granulation unit to produce various types of fertilizers. The contract concerns one of three packages related to Anwil's \$350 million expansion of its fertilizer production. Tecnimont will license granulation technology from CEAMAG for the project. Tecnimont's scope of work includes engineering, equipment supply, construction, commissioning and execution of performance tests as well as training of client's personnel, for the implementation of a new granulation plant with an average



Watch free fertilizer market presentations

Argus deliver concise and insightful webinars analysing the nitrogen, phosphate, potash, sulphur and sulphuric acid markets. The webinars are offered on-demand and live – and are completely free to watch.

Watch the free webinars here:
www.argusmedia.com/webinars



CONTENTS

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

capacity of about 1,500 t/d which will allow the simultaneous production of a wide range of products such as ammonium nitrate, calcium ammonium nitrate, and ammonium sulphate/ammonium nitrate (ASN) mixtures. The new plant will be built at Anwil's existing fertilizer complex in Wloclawek. Completion is scheduled for mid-2022.

FRANCE

IFA welcomes FAO sustainable code of conduct

The International Fertilizer Association has welcomed the UN Food and Agriculture Association's (FAO) Code of Conduct for the Sustainable Use and Management of Fertilizers, which was officially approved during the recent FAO Conference.

"IFA and our members around the world, welcome the Code as a useful framework for nutrient stewardship, which is aligned with the commitments of the fertilizer industry," said IFA director general Charlotte Hebebrand, "and we are pleased that several of the industry's suggestions for improvements of the Code are reflected in the final document."

IFA has embarked on developing an Industry Code of Practice which will incorporate relevant provisions of the FAO of Conduct, but be more specifically targeted at industry players, with the goal to facilitate adoption and practical implementation by IFA members in a measurable way.

"As the code makes clear, site-specific nutrient management incorporating the '4Rs' – ensuring the application of the right nutrient source, at right rate, the right time and in the right place – is a requirement to close remaining yield gaps as well to reduce the environmental footprint of fertilizers," said IFA's coordinator on UN issues Tip O'Neill. "Given the industry's expertise and global reach, we look forward to engaging in an effective public-private partnership with the FAO to promote nutrient stewardship across the globe."

AUSTRALIA

Santos and Perdaman sign pre-FEED agreement for ammonia/AN complex

Santos and Perdaman have signed a heads of agreement for the further study and design of Perdaman's planned new ammonia facility near Narrabri in New South Wales. The companies signed a non-binding gas supply agreement back in February 2019 for the supply of 14.5 PJ of natural gas per annum

over 20 years, subject to a final investment decision for Santos' Narrabri Gas Project. The new pre-FEED (front-end engineering and design) study is the next step in the development of the facility, which will use appraisal and early development gas. It will also further define hybrid power facility options, a combination of gas-fired power generation integrated with renewable power generation to provide electricity to both the Narrabri Gas Project and the downstream ammonium nitrate plant.

Speaking at the signing, Santos managing director and CEO Kevin Gallagher said these two projects will be a boost for small businesses and the communities in and around Narrabri, and indicated that the Narrabri Gas Project could ultimately produce enough natural gas to supply up to half of New South Wales' needs with a competitively-priced source.

Perdaman Group's founding chairman and managing director, Vikas Rambal said: "I hope the Narrabri Gas Project will proceed to a final investment decision as soon as possible to give certainty to this project and attract more to the region. If our plant goes ahead it will not only bring new jobs but competition, which is always good for prices, to the market in NSW and that will be good for farmers in the region."

UKRAINE

OPZ begins work on restarting ammonia, urea production

After more than a year of being idle due to feedstock issues, PJSC Odesa Port-Side Chemical Plant (OPZ) has begun work on



Odesa Port Plant, Ukraine.

PHOTO: OPZ

re-starting ammonia and urea production at the site, according to the plant's deputy director Mykola Schurikov, who described work as being "in the finishing straight." The plant will take 60 million m³ per month of gas on a tolling basis from Agro Gas Trading for at least the next four months (to 1st December 2019), with the potential for extension.

Ukraine's government has tried several times to find a buyer for the troubled facility, which owes more than \$60 million to state-owned natural gas monopoly Naftogaz, even at last year's knock-down price of \$54 million. The plant is contracted to pay off its debts to Naftogaz via sharing profits received from Agro Gas Trading for providing processing services (\$1.50/tonne of urea and \$1.00/tonne of ammonia).

INDIA

New fertilizer plants still scheduled for 2021

According to Coal India Ltd's (CIL's) latest report on the subject, construction works of all three urea plant revival projects are on track, and urea production is expected to begin at the start of 2021. CIL has a 29.67% stake in the joint venture company responsible for the restart projects, Hindustan Urvarak and Rasayan Limited (HURL). Four other public sector companies form part of HURL: NTPC and the Indian Oil Company (IOC), both of which also have a 29.67% share, as well as the Fertilizer Corporation of India Ltd (FCIL) and Hindustan Fertilizer Corporation Ltd (HFCL), with the remaining 10.99% stake between them.

The three ammonia-urea complexes will each have a capacity of 1.27 million t/a of urea when completed, and are sited at Gorakhpur in Uttar Pradesh, Sindri in Jharkhand and Barauni in Bihar. Total investment by HURL is put at \$3.08 billion, with the State Bank of India as lead lender for financing the consortium via a debt-equity ratio of 75:25.

Another new 1.27 million t/a ammonia-urea complex is expected to start up at the end of 2019 at Ramagundam in Telangana, one of the five closed units of FCIL and HFCL which are being revived. Operating company Ramagundam Fertilisers and Chemicals Ltd is a joint venture between National Fertilizers Ltd, Engineers India and FCIL.

BRAZIL

Gas sale contract signed

Bolivia's state-owned YPFB has agreed to sell 2.2 million m³/day of natural gas across the border to Acron's Tres Lagoas fertilizer plant in Brazil. The sales agreement lasts for 20 years from 2023. As part of the agreement, YPFB will also take a 12% stake in the plant, with the option to raise that to 30%. Bolivia's government is also looking at a joint venture with Acron for the sale of urea in Brazil, with gas exploration currently taking place in the Vitiacua region for the possible supply of gas to the new plant. Reserves in the region are put at 2.1 trillion cubic feet. Bolivia's hydrocarbons minister said that the gas development project would require an investment of \$1.1 billion, and could produce an estimated 12 million m³/d of gas by 2028.

CANADA

Nutrien reports second quarter earnings

In its second quarter earnings presentation, Nutrien reported adjusted net earnings of C\$1.58 per share, and adjusted earnings before interest tax, depreciation and amortisation (EBITDA) of C\$1.9 billion. This brought adjusted EBITDA for the first half of 2019 to C\$2.6 billion, supported by higher earnings in the company's potash and nitrogen businesses. Cash production costs were in line with the previous year, and general and administrative expenses were down 5%. On the nitrogen side, Nutrien's EBITDA was up 17% in the first half due to higher prices, lower North American natural gas prices, and increased earnings from equity investments.

In his remarks, President and CEO Charles Magro noted that North America had had "the worst nine-month weather period in history", with millions of acres going unplanted. This resulted in a lower spend on crop inputs by farmers, and was, he said, a major reason there has been a pause in global fertilizer demand growth this year. Even so, demand for grains and oilseeds is still growing, and supply is tightening. Magro said he expected US corn inventories to drop by as much as half this year. Markets have started to respond with corn prices up about 20% year-over-year, with the likelihood of a significant increase in US corn acreage and a strong rebound in crop input demand next year. Magro said that Nutrien was expecting a strong fall nitrogen application season in the US. Urea prices have outperformed other sources of nitrogen, in part due to continued strong demand from India. Global ammonia prices weakened in the first half of 2019, but Nutrien expects the seasonal curtailment of some production along with improved demand will provide underlying support to prices in the second half of the year.

Heraeus

YOUR GLOBAL PARTNER FOR CATALYTIC GAUZES

- A global partner for our customer
- Technical support for our customers' processes
- Perfect customized catalytic system
- Market leader in N₂O abatement

Meet us at ANNA Conference
08th - 13th September

Heraeus Precious Metals

www.heraeus-precious-metals.com
chemicals@heraeus.com

EMEA

Heraeus Deutschland GmbH & Co. KG
Heraeusstr. 12-14
63450 Hanau, Germany
Phone: +49 6181 35-4463

APAC

Heraeus Materials Singapore Pte. Ltd.
Loyang Industrial Estate,
30 Loyang Way #02-21
Singapore 508769
Phone: +65 8121 8324

AMERICAS

Heraeus Precious Metals North America LLC
15524 Carmanita Road
90670 Santa Fe Springs, CA, USA
Phone: +1 562 483-1891

CHINA

Heraeus Materials Technology Shanghai Ltd.
No. 1 Guangzhong Road
Minhang District
201108 Shanghai, China
Phone: +86 21 3357-5512

CONTENTS

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

UNITED STATES

Methanex makes investment decision on third US plant

Methanex's board of directors has reached a unanimous decision to go ahead with its plants to build a new 1.8 million t/a methanol plant at the company's existing site in Geismar, Louisiana. Methanex already operates two plants at the site, which it relocated from its Chilean facility at Punta Arenas, where they had been idled due to gas supply constraints. The company expects costs for the project to be \$1.3-1.4 billion, over and above the \$60 million that Methanex has already committed to the project. Methanex had been looking for a project partner to ameliorate shareholder concerns about geopolitical risks, but following reaching a deal with activist investor M&G Investments and bringing one of M&G's nominees onto the board, the company has now decided that the project fundamentals remain sound and it will proceed without an investment partner. The so-called 'Geismar 3' project is expected to begin construction later this year, with methanol production beginning in the second half of 2022.



PHOTO: METHANEX
Methanex's Geismar site, Louisiana.

"Our long-term outlook for the methanol industry is very positive. Demand forecasts for methanol are strong and new capacity additions will be needed to meet expected demand growth," said John Floren, president and CEO of Methanex.

"We are delighted to continue our work with Methanex and once again demonstrate our unmatched ability to execute large-scale, complex projects," said Stuart Bradie, KBR president and CEO. "We look forward to successfully and safely completing this world class methanol facility that will produce a product that is an essential ingredient used to produce hundreds of everyday industrial and consumer items and is also a clean-burning, cost-competitive alternative fuel."

KBR has been given approval to work on the detailed engineering, procurement and construction (EPC) phase of the project. KBR was awarded a reimbursable front end engineering design (FEED) contract with an EPC option for the project in July 2018.

Mabert buys gas to liquids plant

Greenway Technologies, Inc. says that Mabert LLC, a company controlled by Greenway Director, Kevin Jones, which also acts as agent for the Company's lenders, has acquired the INFRA Technology Group's gas to liquids (GTL) plant and

at Wharton, Texas. Mabert has bought the entire 5.2-acre site, plant and equipment, including INFRA's proprietary Fischer-Tropsch reactor system and operating license agreement. Greenway and Mabert have also agreed in principle to enter into a joint venture whereby GWTI, Mabert and a third party investment group will jointly

fund and participate in plant operations going forward.

The INFRA plant is a 75 bbl/d modular *G-Reformer*™ GTL demonstrator plant producing a 60-40 mixture of gasoline and diesel products via syngas generated from natural gas using a patent-pending *Fractional Thermal Oxidation*™ (FTO) natural gas reforming technology and a G-Reformer unit. Greenway is expected to contribute engineering and operations personnel to the joint venture, who will be responsible for integrating Greenway's G-Reformer technology with the existing INFRA FT system.

Ray Wright, Greenway's chairman said; "Greenway's anticipated participation in the joint venture's conversion of this existing GTL production facility marks a major milestone in our company's history. Not only will we be able to complete our engineering certifications, a necessary step for future G-Reformer licensing and sales, we expect that this facility will produce a substantial amount of saleable waxless liquid fuels, demonstrating what we believe will be the world's first economically viable commercial small-scale GTL plant."



PHOTO: INFRA

The Wharton GTL plant.

DENMARK

Demonstrator plant for green methanol

Haldor Topsoe says that it plans to build a 10 kg/hour methanol plant to demonstrate the company's electrified and extremely compact *eSMR Methanol*™ technology for cost-competitive production of sustainable methanol from biogas. The technology exploits the full carbon potential of biogas by utilising the 40% CO₂ content which is routinely separated and vented today. It heats the process using green electricity from wind turbines or solar panels instead of natural gas. The demonstration plant will be located at Aarhus University's research facility in Foulum, Denmark, and receives funding from EUDP – Energy Technology Development and Demonstration Program.

The demonstration plant, scheduled to be fully operational from the beginning of 2022, is expected to demonstrate that sustainable methanol production from biogas can compete with traditional methanol production based on fossil fuels.

"We want to show that sustainable methanol can be produced from biogas at a cost similar to that of traditional methanol produced from fossil fuels," said Peter Mølgaard Mortensen, Principal Scientist at Haldor Topsoe. "The *eSMR Methanol*™ technology is about 100 times smaller than a traditional unit, which makes it a very attractive solution for decentralised biogas sites and world scale producers alike."

Today, biogas in grid quality is much costlier to produce than the natural gas it replaces. However, Topsoe believes that if biogas producers can produce sustainable methanol instead, they will be able to increase their production value significantly and compete on commercial terms with fossil-based products.

eSMR Methanol™ is based on Topsoe's *eSMR*™ technology which was described in our previous issue (Nitrogen+Syngas 360, pages 14-15). The compact technology replaces the natural gas-fired heating of traditional steam reformers with direct electric heating of the catalytic process.

CHINA

China looking to switch to hydrogen-based transport

According to a recent Bloomberg report, China is considering state support for hydrogen-fuelled vehicles as part of a zero emissions transport concept. The country's 'father of electric vehicles', Wan Gang, said that he believed the ease of refuelling hydrogen-powered vehicles would make them a viable option, particularly buses and trucks, which are fuelled centrally and which often have to travel long distances.

China alone already accounts for more than half of all the electric vehicles (EVs) sold worldwide, but support for hydrogen vehicles could decisively alter the global landscape for zero emissions transport. The country has already slashed its support for EVs, and private investments in its EV start-ups have dropped to a mere 10% of 2018's record high of \$7.7 billion.

ESTONIA

Feasibility study on new methanol plant

Swiss-based chemical trading company Larkwater Group is seeking to build a €1 billion methanol plant in Estonia, according to local press reports. The project is said to be backed by former



Producing me uses loads of energy!



We save energy and increase efficiency.

Fans equipped with special impellers and retrofitted with speed control result in considerable energy savings.

- Detailed system checks
- Increased cost-effectiveness
- Extremely reliable



We make air work for you.

- ▶ Process gas fans
- ▶ Process gas cleaning plants
- ▶ Dust collection plants
- ▶ Recycling and waste treatment plants
- ▶ Ventilating and air-conditioning plants
- ▶ Exhaust air treatment plants



info@venti-oelde.de
www.venti-oelde.com



CONTENTS

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Estonian minister and current musician and entrepreneur Toivo Asmer. An application has been received for permission to build a new 5,000 t/d methanol plant in Lääne-Harju Municipality, 50km west of Tallinn, with a current projected start-up date of 2023. The local municipality has launched a planning application and environmental impact assessment (EIA) and a 60-hectare site has been selected for the project just outside Paldiski, close to a deep water port and railway network. Larkwater has reportedly been seeking a suitable location for the plant for three or four years, with sites examined in places such as Latvia, Lithuania and Poland.

TURKMENISTAN

Gas to gasoline plant starts production

A new 15,500 bbl/d plant has begun production in Turkmenistan, converting natural gas to gasoline. The plant, the only one of its kind in the world, is based on Haldor Topsoe's TIGAS™ technology. The official opening ceremony at the site, close to the capital Ashgabat, was attended by Turkmen president Gurbanguly Berdimuhamedov. Topsoe says that start-up of the plant has proceeded according to plan and that the initial product meets the agreed specifications. During the coming months, the performance test run is expected to be completed.

The plant is an important step in Turkmenistan's plans to monetise its huge natural gas resource – the fourth-largest in the world – and supply the Turkmen home market with synthetic gasoline that complies with the highest environmental standards, with no sulphur and very little unwanted by-products. Topsoe supplied the technology license, engineering, catalysts and hardware such as an autothermal reactor burner, and boilers for the plant. Kawasaki Heavy Industries was the EPC contractor, and Rönésans was responsible for construction.

"We are proud to be part of this forward-thinking and ambitious project. It sets a new world standard for monetizing gas resources in a very effective way and will be a model for other nations and companies around the globe. This is the definitive demonstration that TIGAS is a technologically and financially viable way to produce gasoline from natural gas," said Bjerne S. Clausen, CEO of Haldor Topsoe.

TIGAS is based on proven Topsoe technologies and catalysts, including the proprietary SynCOR™ technology. Utilisation is

high, with gasoline making up more than 85% of the product stream in addition to 11-13% liquefied gases (LPG).

AUSTRALIA

Kawasaki begins construction of Victoria coal-to-hydrogen plant

Kawasaki Heavy Industries has started building works on a government-backed pilot project in Victoria state's Latrobe Valley that will convert brown coal to hydrogen via gasification. The hydrogen would then be exported to Japan via a liquefaction and loading terminal. Australian Minister for Resources and Northern Australia Matt Canavan, Minister for Trade Simon Birmingham, Victoria Treasurer Tim Pallas and Japanese Ambassador to Australia Reichiro Takahashi launched the project in a ground breaking ceremony on July 19th.

"This project promises to be of huge benefit to both nations and particularly the state of Victoria, which has the opportunity to develop an alternative and value-adding use of its abundant brown coal reserves in the Latrobe Valley", Canavan said at the ceremony. "The use of hydrogen is part of Japan's vision of a clean energy future and any emissions from the pilot project will be fully offset, with commercial scale operations required to use carbon capture and storage to ensure a low emission source of hydrogen."

The Victoria gasification unit is merely a pilot unit, processing 160 tonnes of coal into 3 tonnes of hydrogen over its first year of operations. The project is part of the A\$500 million (US\$350 million) Hydrogen Energy Supply Chain (HESC) project, which is being developed in two phases. The pilot phase will demonstrate a fully integrated supply chain between Australia and Japan over one year by 2021, including the liquefaction plant and shipping facilities at Hastings and dedicated ship for transport to Kobe in Japan. The decision to proceed to a commercial phase will be made in the 2020s with operations targeted in the 2030s, depending on the successful completion of the pilot phase, regulatory approvals, social licence to operate and hydrogen demand.

The pilot unit is set for completion by June 2020, and is being delivered by a consortium of Japanese and Australian energy and infrastructure companies, in cooperation with the Victorian, Australian and Japanese Governments. The consortium partners include Kawasaki Heavy Indus-

tries (KHI), J-Power, Iwatani Corporation, Marubeni Corporation and AGL Energy, with KHI and Iwatani leading the build at the Port of Hastings. The pilot production phase is set to produce three tonnes of liquefied gas over a one-year period.

Japan is moving towards hydrogen-fuelled vehicle transport on a large scale, with next year's Tokyo Olympics intended to be a showcase for such technologies.

Leigh Creek Energy advances UCG project

Leigh Creek Energy says that it is another step closer to commercialising its underground coal gasification (UCG) project – now referred to as 'in situ gasification' after Australia's previous unhappy history with UCG. The company says it has concluded consultations with South Australian regulatory authorities and established a clear approval pathway. Talks have now moved to the South Australian Department of Energy and Mining regarding the operations and shut down process for its synthesis gas pre-commercial demonstration plant. Earlier this year, Leigh Creek hailed the pilot plant a "great success" after it produced proved that underground syngas production could be achieved at commercial levels. This was followed by a decommissioning and monitoring process which continues to reveal no reported environmental impacts or safety issues from the plant. According to Leigh Creek, monitoring data is required to be collected for up to three months to ensure the demonstration plant was compliant and operated safely with little or no impact to people or the environment. When all monitoring commitments have been completed, Leigh Creek will provide the regulator with a full report.

"We are pleased that following the shut-down of the pre-commercial demonstration plant, we have been able to work with the Department of Energy and Mining to confirm that the pre-commercial demonstration plant was operated with the approved Statement of Environmental Objectives, that there were zero environmental and safety incidents and that independent reports provided to the Department of Energy and Mining showed that the pre-commercial demonstration plant was operated safely and in accordance with all regulatory requirements," Leigh Creek managing director Phil Staveley said. "Additionally, a pathway to obtain commercial approval has been established," he added. ■

People

Swiss-based speciality chemicals and catalyst company Clariant says that **Ernesto Occhiello**, chief executive officer and member of the executive committee, has decided to leave the company for personal reasons with immediate effect. The company's board of directors has accepted his resignation and asked **Hariolf Kottmann**, chairman of the board, to assume his responsibilities in the interim as executive chairman until a successor is found.

"We thank Ernesto Occhiello for his support of the company in a challenging phase and his contributions to strengthening the company's position as a market leader in speciality chemicals during the past months," said Hariolf Kottmann. "Clariant will continue to implement its strategy and intends to continue to profitably grow in the market by providing specialised products and solutions that meet global challenges with attractive prospects and above average growth potential. This is safeguarded by a stable structure of shareholders who support our strategy."

The previous month, Clariant also lost **Christian Kohlpaintner** from its executive committee, who resigned to take on new challenges outside the company. Kohlpaintner led the growth Business Areas Care Chemicals, Catalysis and Natural Resources and was accountable for the regions Greater China, India, Japan, and South East Asia & Pacific. In addition, he was responsible for Group Technology & Innovation and Corporate Sustainability & Regulatory Affairs. For

the time being, Kohlpaintner's responsibilities will be assumed by the remaining members of the executive committee, which currently consists of: Hariolf Kottmann, executive chairman, Patrick Jany, chief financial officer, and Hans Bohnen, chief operating officer. In order to comply with Swiss governance rules, **Eveline Saupper** has been appointed independent lead director of the board.

Michel Prud'homme, the senior director of the International Fertilizer Industry Association's (IFA's) Production and International Trade Committee, retired on June 28th. Prud'homme held the position for 19 years, helping to produce all of IFA's trade forecasts and outlooks and representing the organisation at numerous international conferences and events. Prior to joining IFA, Prud'homme, a Canadian geology graduate from Montreal, worked for 19 years as an economist with Natural Resources Canada.

At IFA's international conference in mid-June in Montreal, the organisation elected **Mostafa Terrab**, chief executive of Morocco's OCP group, as chairman of the association. Terrab becomes the first chairman from the African continent of IFA in its 90-year history. He succeeds Rakesh Kapur, joint managing director of IFFCO, India. Terrab holds a Ph.D in Operations Research from MIT, and previously worked as the first Director General of the Moroccan National Telecommunications Regulatory Agency (ANRT) and at the World Bank before joining OCP in 2006.

"I am honoured to take on this important responsibility" said Mr. Terrab. According to IFA, sustainable nutrient use, science-based approaches to plant nutrition and capacity building are among Mr. Terrab's top priorities for his chairmanship. Soil fertility across much of Africa is low. Over 40% of African soils face nutrient depletion, partly because of a failure to apply sufficient levels of fertilizers. As a result, average crop yields are only a fraction of those enjoyed by other regions and risk not keeping up with the continent's growing need for food. To meet demand, sub-Saharan Africa must triple the amount of cereals it produced in 2007 by 2050. This is in the face of many challenges in the coming decades, such as water scarcity and climate change.

Mr Terrab also pledged to increase efforts to attract more youth and women into roles across agriculture. Despite most of Africa's population is under the age of 24, the average age of farmers is 60 years old. Nutrien CEO and president **Chuck Magro** was also elected vice chairman of IFA.

Another innovative feature of IFA2019 was a special session exploring how the traditionally predominantly male fertilizer industry can encourage greater gender diversity, showcasing the diversity programs of some IFA members. The interactive session also provided an opportunity to hear women in leadership positions within the industry offering invaluable lessons learned along their own professional paths, as well as from young women who are charting their careers in the fertilizer sector. ■

Calendar 2019

SEPTEMBER

8-12

64th AIChE Annual Safety in Ammonia Plants and Related Facilities Symposium, SAN FRANCISCO, California, USA
Contact: AIChE Customer Service
Tel: +1 800 242 4363/+1 212 591 8100
Fax: +1 212 591 8888
Email: xpress@aiche.org

8-13

Ammonium Nitrate/Nitric Acid Conference, VIENNA, Austria
Contact: Hans Reuvers, BASF
Karl Hohenwarter, Borealis
Email: johannes.reuvers@basf.com
karl.hohenwarter@borealisgroup.com
Web: www.anna-eu.com

23-25

TFI World Fertilizer Conference, CHICAGO, Illinois, USA
Contact: Valerie Sutton, The Fertilizer Institute, 425 Third Street, S.W., Suite 950, Washington D.C. 20024, USA.
Tel: +1 202 962 0490
Email: vsutton@tfi.org

24-26

GPCA Fertilizer Convention 2019, MUSCAT, Oman.
Contact: Anida Dcosta, Conference Producer, GPCA
Tel: +971 4 4510666
Email: anida@gpca.org.ae

OCTOBER

4-5

IHS Annual World Methanol Conference, BERLIN, Germany
Contact: Lynn Urban, IHS Markit

Email: Chemical.Events@ihsmarkit.com or lynn.urban@ihsmarkit.com

27-29

Nitrogen+Syngas Middle East, MUSCAT, Oman
Contact: CRU Events,
Tel: +44 (0) 20 7903 2444
Fax: +44 (0) 20 7903 2172
Email: conferences@crugroup.com

27-29

Global Syngas Technologies Meeting, AUSTIN, Texas, USA
Contact: Global Syngas Technologies Council, 3030 Clarendon Blvd. Suite 330 Arlington, VA 22201 USA.
Tel: +1 703 276 0110
Fax: +1 703 276 0141
Email: info@gasification-syngas.org
Web: www.gasification-syngas.org

CONTENTS

What's in issue 361

COVER FEATURE 1

Combatting AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Plant Manager+

Problem No. 56 Oil fouling from the ammonia plant

One of the most important control parameters in urea plant operation is the synthesis pressure and a sharp increase of this pressure is very dangerous for the urea plant. One cause for an increase of the synthesis pressure is oil contamination in the urea process which causes many abnormal variations

in many sections of the plant. This problem can be recognised by taking a sample from the ammonia feed and observing the colour change of the urea product. These samples and observations can prevent much confusion in determining the cause of the problem.

Ahmad Hussain of Engro Fertilizers in Pakistan starts this round table discussion: Since last month, the ammonia we receive at battery limits has had a high oil content due to a leaking low pressure stage oil seal of the refrigeration compressor in the ammonia plant. Our machinery team is dealing with this problem. Meanwhile can anyone suggest any filters that can be used in the urea plant to remove the oil from the ammonia that is received at battery limits?

Any respectable licensor (since 1960s) equips the suction drums and ammonia receiver with a permanent drain via the orifice to divert the ammonia contaminated with oil to the last drum and further to storage. Also, any low point of piping from the compressor discharge lines should be equipped with spring loaded valves so that operators are able to drain the ammonia during normal operation.

Tajinderpal Singh Bajwa of Canadian Fertilizers Industries in Canada faces a similar situation: We are currently facing the same problem, which is limiting us on total throughput and resulting in operating the plant below the nameplate capacity.

Prem Baboo of Dangote Fertilizers in Nigeria shares his valuable insights: The oil can be separated in the ammonia receiver (see diagram). In a newly built plant a partition plate was provided to protect the carry-over CO₂/carbamate from the MP absorber. A pot was also provided at the end of the receiver bottom for collecting the oil /sludge which can be drained while the plant is running. This modification can also be made to an old ammonia receiver.

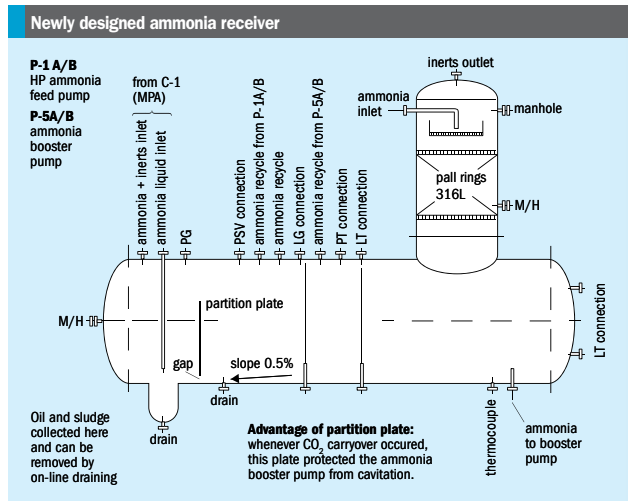
We know that the oil contamination in the ammonia feedstock is coming from an ammonia plant compressor seal leak. Is there a better oil sealing technology for the centrifugal compressor? Are any mechanical separation systems available upstream of the ammonia surge drum before the ammonia passes through the booster pumps and into the suction of the HP ammonia pumps?

Amir Hosein Tafazol of Shiraz Petrochemical Complex in Iran shares his experience: For several years we have been using a PALL coreless filter for the ammonia line in the urea plant, upstream of the ammonia HP pumps to prevent oil and catalyst powder from entering the urea plant. Previously we had a problem of clogging of the liquid dividers in the HP stripper. After installing this device we haven't had any problems.

Bhupen Mehta of IFFCO Kalol in India joins the discussion: Oil ingress in the ammonia product is mainly from the low pressure case oil seal leakage of the ammonia refrigeration compressor.

It is better to have a dry gas seal for the ammonia refrigeration compressor. However, for oil seals: 1) the buffer gas pressure of the low pressure case should be monitored (>0.07 to 0.2 kg/cm²g higher than suction pressure) and 2) the gravity drain from the trap may be limiting due to low suction side temperature, a level control valve in place of the trap can be checked to avoid oil hold-up in the trap due to malfunctioning.

Mark Brouwer of UreaKnowHow.com in the Netherlands replies to two questions from Taj: An upgrade to dry gas seals will definitely solve this issue. On the other hand these are more sensitive during operation, especially for water ingress. The dry gas seals skid should be carefully designed for start-up conditions. The temperature of the seal gas should be kept above the dew point. Oil separation takes place in the ammonia receiver, and intermediate suction drums.



Preventing ammonium nitrate misuse

The US has been pursuing regulation on controlling the misuse of ammonium nitrate-based compounds for nearly two decades, and arguably longer, but so far progress has been very slow.

a threshold percentage for ammonium nitrate in a substance that will be subject to regulation. In 2008 the department therefore published a Notice of Proposed Rulemaking (NPRM), seeking public comment on a Secure Handling of Ammonium Nitrate Program, and a period of public comment and discussi on lasted until 2011. The DHS proposal, based on a review of detonability studies, was to consider all AN mixtures with a composition of more than 30% by weight and a weight of more than 25 lbs (11.3 kg) as being potentially threatening.

While ammonium nitrate (AN) remains the most widely used component of commercial explosives, especially ammonium nitrate/fuel oil (ANFO), and, in Europe and the CIS, also one of the main nitrogen fertilizers, its potential for misuse by criminal and/or terrorist groups or individuals remains a potential headache for lawmakers and security organisations. The use of AN in some high profile bombing attacks, such as the Oklahoma City bombing in 1995, the World Trade Center bombing of 1993, and the Delhi and Oslo bombings of 2011, have led to a continued push from regulators to try and control the use and manufacture of AN and AN-based products. The fear of the industry has always been that creeping regulatory environment will result in a 'death by 1,000 cuts', as it slowly becomes too onerous for manufacturers and wholesalers to deal in such products in terms of regulatory compliance and additional costs.

United States response

In spite of the seriousness that the US government appeared to attach to the subject, the progress of regulation on this issue in the US has been surprisingly slow. Following the Al Qaeda attacks on the US in September 2001, and the subsequent establishment of the Department of Homeland Security (DHS) in November 2002, the US has been looking at ways of dealing with this issue. However, it was not until 2008, the Department of Homeland Security Appropriations Act directed DHS to "regulate the sale and transfer of ammonium nitrate by an ammonium nitrate facility to prevent the misappropriation or use of ammonium nitrate in any act of terrorism."

The DHS was directed to consult with the heads of Federal departments and agencies and seek public comment in developing and implementing ammonium nitrate regulations, including establishing

However, following the comment period the DHS decided to seek additional scientific data on the feasibility of weaponising commercially available products containing ammonium nitrate before establishing a threshold percentage and quantity of ammonium nitrate that would be subject to regulation. This led in 2012 to the commissioning of Sandia National Laboratories (SNL) to perform testing and collect data on this. SNL performed its own literature review to determine areas in need of technical assessments, and then designed technical assessments to determine the effects of total mass, physical form, and dilution on

CONTENTS

What's in issue 361

COVER FEATURE 1

Combatting AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

the detonability of ammonium nitrate mixtures using materials and under conditions realistic to terrorism bomb design.

The SNL report was not released until 2015, and only in redacted form. It concluded that formulations of ammonium nitrate and pre-fabricated ammonium nitrate mixtures with various fuels would detonate with one pound of ammonium nitrate, the lowest mass tested. The results also showed that a minimum concentration level of 15% ammonium nitrate diluted with dolomite in a mixture containing a fuel detonated and that dilutions of ammonium sulphate detonated at a concentration level of 25% ammonium nitrate. The panel of subject matter experts concluded that mixtures containing 1 lb (454 g) of ammonium nitrate were detonable on the test diagnostics and that a minimum detonable level of 10% AN as nitrogen by weight could be technically defended, providing a small margin of safety beyond the 15% level, which showed a weak detonation.

The report has now (July 2019) been added to the NPRM and there has been an official request for public comment on it, especially the scientific methodology and test plans SNL employed, technical data generated by SNL and test results, and factors affecting detonability thresholds.

Taggants

As to how the DHS might actually tackle potential misuse of AN, various means have been suggested. Following the Oklahoma City bombing in 1995, which used ammonium nitrate, the idea of 'tagging' commercial explosives, or possibly even all ammonium nitrate compositions was raised. There are essentially two types of taggants – detection taggants, which make an explosive or potential explosive easier to detect in security screening, either via some kind of RFID chip, or a chemical additive which is more easily detectable (similar to the mercaptam which is added to natural gas to identify leaks) – and identification taggants, which act as a kind of 'fingerprint' so that the source of the explosive can be identified after the blast. Detection taggants are widely used in plastic explosives to assist sniffer dogs and chemical sniffers identify them at airports and other sensitive areas.

During the 1980s, so-called Microtaggant Identification Particles ('microtaggants') were developed by 3M, the technology being bought by Microtrace. Microtaggants are

chip made of multiple layers of plastic and metal which could be placed in explosive products with the hope that investigators could find them at a bombing crime scene, after an explosion, and trace them, through the manufacturer, to the bomber.

However, the Institute of Makers of Explosives has highlighted concerns over and above the expense that such a scheme would have if widely adopted, such as the possibility that the metal and plastic components could destabilise explosive mixtures – there have been tests confirming this and one suspected industrial accident. The environmental effect of tagging AN fertilizer in this way is also potentially problematic.

Authentix of Dallas, Texas, says it can chemically tag any fertiliser during manufacturing. In the case of ammonium nitrate, molecules that contain different isotopes of nitrogen and hydrogen can be added in concentrations of parts per billion. However, the cost of such an additive remains prohibitively expensive for widespread use.

Switzerland is the only country in the world to currently require taggants in explosives. The Swiss law was adopted primarily to stop undesirable trans-border trade in explosives. Imported explosives must be tagged only if competing products are also made in Switzerland. Swiss manufacturers are required to change the taggant code in their products only every six months. The actual law enforcement utility of such a program remains open to question, however.

The economic consideration is not a small matter either. In 1994 the quoted price for Microtaggant was \$326/lb. If this covered the AN used in the mining industry in the US, it would cost approximately \$750 million per year just in materials cost, with additional costs coming from processing costs, re-engineering, record keeping, the shutting down of equipment for cleaning between each batch of explosives, and the disposal of excess hazardous waste during a taggant changeover.

Lower explosive mixtures

One concept that came out of bombing campaigns in the UK and Ireland in the 1970s, conducted by the Irish Republican Army (IRA), often using fertilizer grade AN as a bomb component, was of desensitising AN by changing its bulk composition with additives. In 1972 Northern Ireland banned the sale of AN mixtures with more than 79% AN, and calcium ammonium

nitrate (CAN) became the preferred fertilizer instead. While this could still be (and was) used in explosive mixtures, it increased the technical proficiency required to make such an explosive.

The concept resurfaced in the US following the Oklahoma City bombing, based on a patent issued to Samuel J. Porter in 1968, based on a mixture of AN with diammonium phosphate (DAP). While Porter's detonation tests had indeed showed that his mixture was non-detonable in small quantities, tests conducted in the 1990s using larger diameter samples confirmed that the mixture could still detonate.

Committees in both Northern Ireland and the US which have considered the use of additives to make AN non-detonable have concluded that there is no additive which can do so at a level which does not invalidate the use of AN as a fertilizer. Nevertheless, Honeywell developed an ammonium sulphate nitrate compound which it calls *Sulf-N 26*, which is 26% nitrogen and 14% sulphur by weight, and which the company claims has a 'double salt' matrix with two AN molecules for each molecule of AS which "dampens the rate of AN combustion", and which it markets as a low-detonability product.

Access

The other focus on preventing AN misuse concerns who has access to such chemicals. The issue is one of security vetting and employee credentials, and in the US a similar program has been proposed such as occurs for airport personnel. However, the practicality of vetting tens of thousands of workers in road haulage, warehousing and possibly even extending to farm workers in the case of fertilizer grade AN is dubious.

Precursor chemicals

With both taggants and additives providing only questionable benefits, one suggested way of tackling the issue of misuse of chemical compounds is to look at regulation of precursor compounds that can be used to make homemade explosives. The US National Academies of Science, Engineering and Medicine produced a report in 2018 on 'Restricting Access to Explosive Precursor Chemicals'.

Its committee developed a prioritised list of precursor chemicals, reasoning that; "It would be impossible to restrict access to all precursor chemicals without disrupting people's lives and commerce."

As a result "ubiquitous" chemicals and foodstuffs were not considered, nor those only used in small quantities. A shortlist of 28 was then whittled to 10 by considering those which were considered to pose the greatest threat. As well as aluminium, hydrogen peroxide, nitromethane, and sodium and potassium chlorate and perchlorate, the list also included ammonium nitrate, calcium ammonium nitrate, and urea ammonium nitrate (UAN) as potential targets for regulatory control.

The committee next considered trade-offs among security, economic, and other factors associated with a small set of possible control strategies; a ban, licensing, or a registry, as well as augmenting existing controls with supplemental measures and activities, such as outreach, training, and reporting. Six recommendations emerged:

(i) Agencies attempting to reduce the threat of IED attacks by restricting access to precursor chemicals should focus on both person-borne and vehicle-borne IEDs, (ii) should consider multi-chemical, rather than single chemical strategies and (iii) should focus on retail-level transactions of precursor chemicals, especially e-commerce. Various mandatory and voluntary monitoring programmes are already in place in the industry. For example, the ATF runs programs like Be Aware for America to educate the fertilizer industry on illegitimate use of precursor chemicals. Likewise the DHS already identifies and regulates designated 'high-risk' chemical facilities, subject to thresholds for monitoring, such as 2,000 lb for ammonium nitrate. However, the committee felt that this may not be sufficient for preventing access to quantities which could be used in person-borne IED attacks. Of 38,000 unique facilities, only 2,570 are currently covered as high risk. However, the committee felt that the point of purchase rather than manufacture, transport or storage should be the area subject to most control.

(iv) Agencies should explore strategies for harmonising oversight of the sale and use of commercially available kits that contain precursor chemicals that are specifically designed to be combined to produce homemade explosives.

(v) The DHS should engage in a more comprehensive, detailed, and rigorous analysis of specific provisions for proposed mandatory and voluntary policy mechanisms to restrict access to precursor chemicals by malicious actors.

(vi) The federal government should pro-

vide additional support for voluntary measures, activities, and programs that can contribute to restricting access by malicious actors to precursor chemicals used to manufacture IEDs.

The report also recommended additional research into standardisation of explosive incident data collection, standardisation of regulatory thresholds, substitution of precursor chemicals in commercial products, and understanding behavioural responses, including those of terrorists to proposed controls and those of policy makers to terrorist attacks.

International regulations

The report's authoring committee assessed the regulations in place to restrict access to precursor chemicals in Australia, Canada, Singapore, the United Kingdom, and the European Union (EU) for insight into possible control strategies.

Nationwide control strategies for precursor chemicals are already in use in some countries. The EU, which like the US has had to grapple with the diverse circumstances of many member states, passed a regulation in 2013 on the sale and use of certain precursor chemicals that defaults to a ban on sales to non-commercial users, referred to as "members of the general public," but allows member states to instead use licensing or a registry. Since the regulation passed, the EU reports that the amount of precursor chemicals for sale has decreased and that authorities' capacity to investigate suspicious incidents involving the chemicals has increased, but with some cost to commerce and legitimate users. However, the EU has also noted challenges: for example, authorities face difficulties reaching retailers and enforcing restrictions on internet sales, imports, and intra-EU product flows; differences among member states' programs can obstruct legitimate commerce; and retailers have had difficulty identifying which products fall under the regulation and which purchasers are legitimate commercial users.

JIDO

Outside the US, the Pentagon has looked at reducing the threat posed by improvised explosive devices (IEDs) via a sub-organisation originally called the Joint IED Defeat Organisation (JIEDO), and now broadened in scope to become the Joint Improvised Threat Defeat Organisation (JIDO). JIDO

has also focused on ammonium nitrate, as it was behind most of the IEDs used by militants in Iraq and Afghanistan, much of it smuggled across the border from Pakistan as calcium ammonium nitrate (CAN). JIDO recently reported at a conference on IEDs that it is pursuing new capabilities that could be used in future combat environments, including attempts to render AN-based explosives ineffective using chemicals delivered by unmanned aerial vehicles (UAVs). Reportedly means considered include a reactive mixture to burn the explosive mix, or a polymer-type solution that rendered the explosives inert for several days.

No end in sight

At the moment, legislation on the misuse of ammonium nitrate and other potentially explosive precursor chemicals is still at the discussion stage. However, the attaching of the SNL report to the notice of proposed rulemaking does seem to indicate the direction of travel, with any ammonium nitrate mixture more than 10% nitrogen and in a quantity more than 1 lb might become subject to regulation, with some form of restricted access to the compound at point of sale becoming the norm. The fertilizer and explosives industries will fight their corner, no doubt, and there still does not seem to be an end point in sight for the Department of Homeland Security's legislation. ■

References

1. *Reducing the threat of IEDs by restricting access to explosive precursor chemicals*, National Academies of Science, Engineering and Medicine publication, 2018.
2. Testimony before the House of Representatives Committee on Homeland Security, Subcommittee on Cybersecurity, Infrastructure Protection, and Security Technologies, 2012, GAO-12-907T.
3. Institute of Makers of Explosives, statements on AN detonability, explosives precursors, taggants, April 2019.
4. K. Lappo et al, Ammonium Nitrate Security Program, Technical Assessments (redacted), Sandia National Laboratory, February 2015.
5. Honeywell, *Sulf-N26* fact sheet, July 2011.
6. *Containing the Threat from Illegal Bombings: An Integrated National Strategy for Marking, Tagging, Rendering Inert, and Licensing Explosives and Their Precursors*, National Academies of Science, Engineering and Medicine publication, 1998.
7. US Department of Homeland Security, AN Security Program website. www.dhs.gov/cisa/ammonium-nitrate-security-program

The future of gasification

The Tees Valley
1 & 2 sites,
Billingham, UK.

While gasification, especially of coal, remains a common route to producing syngas, concerns over carbon emissions are slowly edging out new projects. But gasification remains a versatile process, and use of municipal waste, biomass and possibly carbon capture may yet see it flourish.

Production of syngas can take various forms. Where a gaseous feedstock is available, reforming or partial oxidation are the preferred routes. However, where solid or liquid matter is the feed, the process usually involves some form of gasification. Gasification is a mature technology; coal gasification was the feed for the first ammonia plants, going back to the 1920s. However, cheap and abundant natural gas gradually came to dominate the production of syngas because it was cheaper and avoided the additional capital costs required for feed pre-treatment in a gasification-based unit. The main exception to date has been China, where lack of natural gas and abundant coal has led to a concentration on coal and coke gasification as the main feed for ammonia and methanol plants.

However, the carbon dioxide generated from coal gasification is about 50% higher than that for a comparable sized ammonia or methanol plant based on natural gas feedstock. As measures to tackle climate change become more urgent, the additional carbon cost of coal gasification has begun to make permitting and other environmental issues far more difficult in the developed world, and increasingly more difficult in the industrialising world as well.

Carbon capture and storage

The solution that the industry coalesced around in the 1990s and 2000s was to capture the carbon dioxide produced in the process and divert it to long-term storage, probably in an underground reservoir. The enclosed nature of the process gas stream means that adding an amine-based or similar absorption system to absorb the CO₂ generated in gasification is costly but possible. However, the challenge has been to find suitable long term storage sites – these are often exhausted oil or gas reservoirs, but they are often not found near to the large sources of coal needed to run a gasification plant. Furthermore, carbon dioxide at high pressures and in the presence of water can be extremely acidic, leading to potential corrosion issues in piping that is carrying the CO₂. These issues can be overcome by using corrosion resistant steels, but that again increases the cost. At time of writing, while there have been numerous CCS projects that have used carbon dioxide to pump into oil reservoirs for enhanced oil recovery (EOR), actual CCS projects remain mainly pilot studies and demonstrator plants. The Global CCS Institute reported last year that there were

no large-scale CCS projects under construction anywhere in the world, and the prospect of large scale adoption of CCS as a way of dealing with the carbon dioxide emissions from gasification at present remains a remote prospect.

Biomass

What, then is the future of gasification? Using biomass as a feedstock rather than coal has been proposed as a solution to the carbon dioxide issue. While gasification still generates the CO₂ from the feed, it is at least in theory from a renewable source which would generate CO₂ and even methane (far more damaging in terms of carbon equivalent) during the process of natural decay anyway, and which is presumably also drawing CO₂ from the air as replacement biomass is planted and grown. It is, in theory at least, a renewable source of energy.

The question is what the source of biomass might be. Biomass feedstocks are generally classified into four main groups¹: woody biomass, herbaceous biomass, marine biomass and manures. Woody biomass and herbaceous plants with low moisture contents are the primary choices because they do not require as much energy in drying to remove the moisture; every kilogram of water requires an additional 2.2 MJ of energy to process. Agricultural wastes such as bagasse, sugar cane trash, rice husk, rice straw, coir pith, groundnut shells etc are also potential feedstocks, although pulverisation is needed prior to use as feedstock to enhance their bulk density and reduce transportation cost.

All biomass contains cellulose, hemicellulose and lignin in varying percentages, along with an inorganic component which is the source of ash. All of these components decompose at different temperatures and hence the type of biomass can have a significant effect on energy produced and the composition of the syngas generated. In general, the higher the cellulose and hemicellulose content, the greater the volume of gaseous products formed. Therefore, softwood, hardwood, wheat straw and bagasse with much higher cumulative percentages of cellulose and hemicellulose are preferred over sunflower seed hull, coconut shell, almond shell, larch plant or poultry litter, when attempting to obtain gas as the final product. Other important constituents are silica, which can cause fouling and slagging and ash disposal issues, chlorine and sulphur, and alkali metals. Tar is also a significant potential problem in the gasification of biomass as it can lead to equipment blockages, increased maintenance and makes operation difficult.

Pulp and paper

One of the issues for large scale use of biomass gasification is the collection step; generating enough biomass to run a reactor at constant rates. Attention has therefore focused on the paper process-

ing industry, where large scale collection of trees already occurs. Sweden, Canada and the US, as major pulp and paper producers, have all experimented with gasification of so-called 'black liquor', a liquid mixture of pulping residues like lignin and hemicellulose together with inorganic chemicals from the Kraft process such as sodium hydroxide and sodium sulphide, for example. Black liquor is a toxic waste stream which paper producers must treat and dispose of and so gasification to produce useable products or energy seems a good fit. However, while this remains a promising angle, take-up so far has been limited and only four black liquor gasification plants are currently in operation.

Municipal waste

As we discussed in our article last year³, the slow growth of recycling and the filling up of landfill sites in the developed world has led to an increasing focus on incineration as a way of disposing of municipal waste. A study by the International Solid Waste Association (ISWA) showed that annual global waste generation accounts for 7-10 billion tonnes in total, of which approximately 2 billion tonnes is made up of municipal solid waste (MSW). Typical waste is made up of 24% MSW, 21% industrial waste, 36% construction and demoli-

tion waste, 11% commercial waste, and 5% due to waste water treatment. Only 3% of the total solid waste is currently used for energy production, and there is a considerable potential to use the remaining waste for energy recovery. However, incineration produces a number of toxic by-products when the waste residue is burnt at high temperatures, including dioxins, furans, polycyclic aromatic hydrocarbons, and oxides of sulphur and nitrogen. A logical step from incineration is to gasify the waste and use it to produce energy or chemical products, while producing an enclosed gas stream which can be more easily cleaned.

The UK government has provided subsidies in the form of Renewables Obligation Certificates (ROC) for municipal waste utilisation, which has created a big shift towards the UK becoming a market leader in waste to energy. There are currently 14 waste to energy plants in the UK, mostly based on gasification technology, and more are under construction.

As with biomass gasification, in urban areas the centralised collection and sorting of waste is generally already being performed by local authorities, reducing the cost of generation of the feedstock. Table 1 shows the different types of waste material that are generated by modern life.

Of these, municipal solid waste (MSW) is generally the preferred feed for gasifica-

Table 1: Types and sources of waste

Source	Type	Composition
Municipal solid waste (MSW)	Residential	Food wastes, paper, cardboard, plastics, textiles, leather, yard wastes, wood, glass, metals, ashes, special wastes (e.g., bulky items, consumer electronics, white goods, batteries, oil, tires), household hazardous wastes, e-waste.
	Industrial	Housekeeping wastes, packaging, food wastes, wood, steel, concrete, bricks, ashes, hazardous wastes.
	Commercial & institutional	Paper, cardboard, plastics, wood, food wastes, glass, metals, special wastes, hazardous wastes, e-waste.
	Construction & demolition	Wood, steel, concrete, soil, bricks, tiles, glass, plastics, insulation, hazardous waste.
Process waste	Municipal services	Street sweepings, landscape & tree trimmings, sludge, wastes from recreational areas.
		Scrap materials, off-specification products, slag, tailings, topsoil, waste rock, process water & chemicals.
Medical waste		Infectious wastes (bandages, gloves, cultures, swabs, blood & bodily fluids), hazardous wastes (sharps, instruments, chemicals), radioactive wastes, pharmaceutical wastes.
Agricultural waste		Spoiled food wastes, rice husks, cotton stalks, coconut shells, pesticides, animal excreta, soiled water, silage effluent, plastic, scrap machinery, veterinary medicines.

Source: Gasification for Low Grade Feedstock.²

CONTENTS

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England

Tel: +44 (0)20 7793 2567

Fax: +44 (0)20 7793 2577

Web: www.bcinsight.com
www.bcinsightsearch.com

tion, as it is highly calorific and, as noted, already gathered and sorted by municipal authorities. However, it has huge variations in composition, particle size, density, calorific value and contaminants. Due to these variations in MSW, waste feedstock after sorting valuable components such as metals, plastics, and paper is standardized into solid recovered fuel (SRF) or refuse-derived fuel (RDF), which are often commoditised and sold on international markets, prepared into pellets for easier transport and higher energy density.

As with biomass, the gasification process follows four steps: drying of feedstock, pyrolysis, oxidation, and finally reduction. Feedstocks are dried above 100°C to remove moisture before pyrolysis, where the feedstocks begins to decompose in the absence of oxidant at elevated temperatures. Next comes oxidation; at elevated temperatures and in the partially oxidized environment, heterogeneous reactions take place between oxidant and feedstock forming carbon monoxide (CO) and water vapour. Oxidation is influenced by the chemical composition of feedstock, type of oxidants (oxygen, steam, CO₂ or air) and operating conditions. This step is mostly exothermic and results in heat energy released for energy self-sufficiency to sustain the process heating needs. Finally there is reduction, a net endothermic step during which high-temperature chemical reactions take place in the absence of oxygen. Various reactions between products of oxidation and char take place to form new hydrocarbons. Ash and some char are the by-products of this reaction step.

Tar formation

One of the major issues with biomass and waste gasification is tar formation. Benzene and other heavier molecular weight compounds are present in pyrolysis bio-oil, and their presence in syngas tends to cause problems, leading to incomplete combustion. High molecular weight tars act as promoters of high viscosity, and limit the atomisation of the fuel, and can cause blockages in fuel pipes and injector lines by condensation. Avoiding tar formation is a key consideration in biomass gasification, and usually requires a fluidised bed gasifier. Feedstock enters the bed and finely ground bed material is fluidised by air or oxidising agent at a temperature of around 700-900°C. Biomass is thermally broken down into gaseous compounds,

and char is produced. The hot char and fluidised bed material cause further reactions to break long-chain hydrocarbons or tars into syngas components. Thus, a syngas product with very low tar content is produced with tar content less than 3 g/Nm³.

The advantages of fluidised bed gasifiers include more uniform syngas product composition, uniform temperature distribution throughout the gasifier, and rapid heat transfer between the feedstock, bed material, and oxidant. The effectiveness of tar removal can be further enhanced by using catalytic bed materials such as olivine, dolomite, and other industrial nickel-based catalysts, and, after removing solids through hot gas filtration, thermal tar cracking can be performed by oxygen injection to raise the temperature (1,200°C) of the syngas. The resulting syngas is then further cleaned before being used either in the gas engine, gas turbine or in chemical synthesis.

Plasma gasification

An alternative method that is attracting interest is plasma gasification, where the extremely high temperatures help to reduce tars and convert all the organic material into syngas. Tar content as is reported to be up to 0.1% of that of an autothermal gasification processes. Arc discharges obtain thermal plasmas from DC or AC current or through radio frequency or microwaves. Mostly DC plasma technology is preferred for waste gasification plasma processes. Plasma is formed by high energy from AC or DC sources through the plasma torch close to the bottom of reactor and fuels are gasified through the plasma flames. The oxygen demand in this process is small as compared to conventional gasification as most of the thermal energy is coming from an external energy source rather than exothermic reactions between the fuel and oxygen.

Underground coal gasification

Finally, a mention needs to be made of underground coal gasification (UCG). UCG revolves around gasifying coal in situ underground by pumping air or oxygen underground and using underground water to control the extent of the reaction zone and provide steam. The syngas mix can then be withdrawn from a second borehole and cleaned and processed and used for power or chemical production. UCG is no 'greener' on the face of it than above ground coal

gasification. However, as it takes place underground, carbon dioxide separated from the syngas stream can more easily be pumped back underground into the cavities produced by UCG, and the boreholes sealed, producing a form of carbon capture and storage that is cheaper and easier than that from conventional coal gasification. Although UCG has a long history, with Soviet experiments going back to the 1930s, and the US in the 1970s, control of the reaction has always been an issue, and UCG has not made much headway until the past decade or so when new drilling techniques and advanced computer control mechanisms became feasible. There are now UCG projects active in Pakistan, Australia, Canada, the US and Poland, with South Africa and some other countries also interested. However, commercial projects with CCS remain elusive, and the technology remains under development.

Market consolidation

A notable feature of the past couple of years has been consolidation among the main players in the large scale gasification technology area. The field is now dominated by industrial gases companies. Air Products has acquired the gasification businesses of the two largest licensors of gasification technology, Shell and General Electric, and has been actively pursuing new avenues, licensing its technology to projects totalling \$14 billion in capital expenditure in China and the Middle East. The other two major players remaining are Air Liquide and Linde. Air Liquide bought into gasification via the acquisition of Lurgi a decade ago, while Linde PLC, via its Linde Engineering division has plenty of experience with gasification but appear to limit its scope of supply to air separation units and syngas clean-up systems, rather than gasifiers.

References

1. Vineet Singh Sikarwar, et al, An overview of advances in biomass gasification, *Energy Environ. Sci.*, 2016, 9, 2939.
2. Yongseung Yon (Ed.), *Gasification for Low Grade Feedstock*, published IntechOpen, July 2018. ISBN: 978-1-78923-289-9.
3. Waste to Syngas, *Nitrogen+Syngas* 356, Nov-Dec 2018, pp32-35
4. Siming You et al, *Critical Reviews in Environmental Science and Technology*, Vol. 48, 2018, Issue 22-24.

NITRATES & PHOSPHATES

Change your vision

INTEGRATED PROCESSES

From feedstocks to any fertilizers and valuable chemicals.

AMMONIA
NITRATES & PHOSPHATES
UREA
MELAMINE
METHANOL
SYNGAS

CASALE

www.casale.ch
info@casale.ch

CONTENTS

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

PROFILE

Umberto Zardi

This year, on July 29th, Dr Umberto Zardi, honorary president of Casale Group, celebrated his 90th birthday. To mark the occasion, *Nitrogen+Syngas* looks back over the long and varied career of a nitrogen industry pioneer.

Umberto Zardi was born in Bologna on 29th July 1929 to Vincenzo and Clelia Bianconcini. He describes himself as still “very fond” of the city where he grew up, and where he graduated in mechanical engineering in 1954. After graduation, he began work at Montecatini’s Projects Division, working on innovations in urea technology, and later, during his 10 years with the company, extending that to the ammonia and methanol sectors.

His first career move was to Snamprogetti, in 1964. Here he successfully developed the ‘total recycle’ stripping technology for the urea process, thanks to which Snamprogetti has become one of the most important licensors for urea in the world, with over 130 plants built. Dr Zardi remained head of the company’s inorganic engineering division until 1978, during which time numerous patents for urea technology were filed on his behalf and about 20 industrial plants built.

Urea technology

In the 1960s and 70s, Snamprogetti shared the urea field with other established process licensors, such as Stamicarbon, Montecatini, Toyo and Chemico. Stamicarbon was working on the idea of distilling the urea solution from the reactor at high pressure by decomposing the carbamate with the help of a stripping agent. In this way most of the carbamate and ammonia not transformed into urea in the reactor were recycled in an isobaric loop at the reactor pressure with considerable energy savings and investment and maintenance costs.

A Snamprogetti patent of 1962 followed the same concept; Snamprogetti tried to compete with Stamicarbon on urea by introducing a different urea stripping process that would use ammonia as an



“Through a culture of innovation that is sometimes pushed to the limit by my nature... I like to think that I have led the company to become the only company in the world to own such a vast range of linked technologies.”

external stripping agent instead of carbon dioxide. The results of a pilot plant in San Donato Milanese during 1962-3 were not, however, sufficient to make the new Snamprogetti process competitive. In the spring of 1965 the construction of a 50 t/d demonstrator plant at ANIC Gela was finally approved in order to use the plant for the development of the technology using the new generation of stripping processes.

Zardi had the idea of using a film stripper without any external stripping agent (self stripper) to achieve both heat and mass transfer at a single surface. The gaseous stream, generated by the decomposition of the solution, would flow counter-currently to the stripped liquid film of the solution. The idea itself was original,

although the use of film exchangers was widely known, albeit in different applications. The titanium stripper tests were important, as they made it possible to establish that the residual ammonia content in the urea solution at the stripper exit could be contained at values of around 30% with the use of a film exchanger. The analysis of the results obtained during the operation of the ANIC plant in Gela gave Zardi the intuition that the stripper could operate without the introduction of any external ammonia stripping.

At the time, the idea of his “self-stripping” patent ran counter to the prevailing direction of the industry. Both Snamprogetti and Stamicarbon had new stripping processes, but both processes used an

external stripping agent. There was also a fear that the patent could harm the image of the new Snamprogetti process developed according to the standard stripping scheme, with the introduction of an external stripping agent.

Despite the fact that the carbamate condenser was installed at the highest point of the plant, the operation of the Gela plant with the reactor and stripper at the same pressure and the recycling of liquid carbamate back to the reactor by gravity also proved the criticality of this system based on natural circulation, which was via the simple hydrostatic liquid head. Zardi decided to install an ejector in the high-pressure loop circuit to facilitate circulation. The ejector could be installed in the gas circuit or on the carbamate solution and it was decided to install an ejector to pump the carbamate solution directly into the reactor using the liquid ammonia feed stream (liquid-liquid ejector). There were objections to this decision; that there would be problems of clogging or strong corrosion, given the fact that the carbamate solution was highly corrosive. However, he was able to prove that this was not occurring.

He also developed other original equipment, besides the stripper, for the Gela plant, for example, simple high-pressure carbamate tube bundle condensers: previously all urea processes used more complex heat exchangers.

In 1967, Zardi was the one to have significant experience in designing urea plants in his working group and therefore he was responsible for making all of the major decisions, but he was also involved in promotional activities for ammonia and hydrogen processes, managing a team of 16-17 collaborators, specialists in the field of ammonia, urea, hydrogen and methanol, until 1978.

Ammonia Casale

In 1978 came the turning point in Dr Zardi’s career: he joined Mr Salimbeni, the former CEO of Snamprogetti, in a new challenge in Switzerland. Salimbeni was no longer the CEO of Snamprogetti at the time, and had set up his own group of engineering companies, the Altech group. This group, comprising Italian (Ingeco SpA) and foreign contractors (Ingeco International SA, Ingeco Laing Ltd), had bought almost all of the shares of Ammonia Casale SA in 1976.

Ammonia Casale had been the company created in 1921 by Luigi Casale, the skilled Italian chemist and pioneer of the catalytic



Ammonia Casale staff in the early 1980s.

process for the synthesis of ammonia from nitrogen and hydrogen. Luigi Casale died prematurely, and after various vicissitudes, the company had entered into a technical and financial crisis from which it did not seem it could rise again. In order to generate the necessary resources to carry out research and development the company was sold to the Altech group. Salimbeni knew Zardi from his time in Snamprogetti, and contacted him to join him in the task of restoring and re-launching Ammonia Casale. So in 1978 Zardi moved with his family to Lugano in Switzerland, to take up this new challenge. From that moment on, his professional life was and remains inextricably linked to the relaunch and expansion of Ammonia Casale.

Relaunching the company drew upon several of Ammonia Casale’s existing technical experts as well as other experts in the field. Dr Zardi became General Manager, but continued to dedicate himself personally to the administration and management of research and development and technology licensing to third parties.

Revamping

It was in the early years of the company that Zardi, with the help of its highly experienced and creative staff, developed the new so-called axial-radial reactor design, with high efficiency and low pressure drop. At the same time he also pioneered the development of a new concept for the revamping of existing ammonia plants, a field in which Casale could take a leading position against its competitors, rather than trying to compete in the area of new plant design and construction in which the competition was too well established. The result of this strategy was the revamping

of about twenty plants in a very short time, even if those plants had originally been based on different technology.

Unfortunately, in 1984 the Altech group, which had been heavily engaged in Iraq via its contracting company Ingeco International SA, found itself in a serious financial crisis due to the ongoing war between Iran and Iraq and had to dispose of its Ammonia Casale shares to raise capital.

Nevertheless, the company, with management unchanged and Dr Zardi at its head, enjoyed the trust of its new shareholders and was able to continue its activity in Lugano with the high-value technical team put together a few years earlier. Thanks to its new owners, Ammonia Casale was able to reaffirm the validity of the company worldwide, with epoch-making innovations in the ammonia field.

Technical achievements in the early days of Ammonia Casale included the launch of the new axial radial synthesis reactor design at the British Sulphur Nitrogen conference in London in January 1981. This reactor (later called the “first generation”) successfully formed the core of the modernisation of numerous ammonia plants. The innovation has since been applied in practically every type of axial reactor, considerably improving its performance. However, this alone would not have led to the rebirth of the company if it had not also developed a new winning commercial strategy to ally to its technological innovation.

Large US and European companies, long-established in the sector, were dominant in the licensing of new ammonia plants, making it extremely difficult, if not impossible, for Ammonia Casale to be awarded contracts for new ammonia plants. Therefore, from the 1980s, Casale decided to develop and

CONTENTS

What’s in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
 SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
 London SE1 7SJ, England

Tel: +44 (0)20 7793 2567

Fax: +44 (0)20 7793 2577

Web: www.bcinsight.com
www.bcinsightsearch.com

promote the introduction of the so-called "in situ retrofitting" method for the modernisation of 'bottleneck' reactors like Kellogg and Chemico, which were the dominant designs in use at the time. This 'surgical' retrofitting method allowed Casale to bring the performance of these reactors to levels comparable to those of newly built reactors today, in an extremely economical way. Fortunately for Casale, hundreds of plants had been operating for many years with low conversions and yields, and above all with high energy consumption. Those plants were the perfect targets as they benefited most from what was a relatively simple modification, while at the same time being extremely profitable for the operators.

Via this simple but effective strategy, neglected by competitors, Ammonia Casale was able to tackle the challenge of regaining market share: revamp existing ammonia plants, whatever the original technology was, simply by modifying the existing synthesis reactor and replacing the catalyst. The first important milestone was reached in 1984: the revamping of four Kellogg reactors owned by CFI in the US achieved an increase in yield of 40% and consequent important reduction of specific energy consumption and increase in capacity. The contract for this operation was obtained on the basis of theoretical calculations only, because at the time Casale had not yet had the opportunity to test the modifications on a pilot plant, much less to indicate a reference plant.

The second milestone was the direct consequence of the first: immediately after this success, in 1986, as China began to open her doors to the world, Ammonia Casale entered the Chinese market and then, the retrofitting sector also rapidly moved into markets such as Russia and India. Since the relaunch of Ammonia Casale, its technology has been applied to 150 plants all over the world, i.e. more than 40% of the world's ammonia production.

Beyond ammonia

After the success of the ammonia plant revamping strategy, Ammonia Casale began to diversify into related markets, entering into the retrofitting market for urea and methanol plants. Again it achieved exceptional results, with the modernisation of approximately 35% of the plants that currently exist in the world. Subsequently, after entering into these new market, Zardi decided to consolidate and further expand the company by creating three new companies:

- Urea Casale, founded in October 1991, inherited and continued the activity, started by Ammonia Casale in 1985, of retrofitting urea reactors with the newly developed high-efficiency reactor trays. Casale subsequently developed other innovative technologies that have been used in the modernisation of various types of urea plant, such as the so-called Split Flow-Full Condenser CO₂ stripping technology promoted since the late 1990s, which represents the latest significant technological innovation in terms of the urea process scheme.
- Methanol Casale, founded in March 1994, started its activity mostly retrofitting ICI 'lozenge' converters. The company has subsequently developed various technologies for plant revamping.
- Casale Chemicals, founded in January 1995, focused on processes and products related to and complementing the activities of the other companies of the group. The company was active and successful in the field of syngas generation with the design of special burners for partial oxidation and autothermal reforming processes.

From revamping to new plants

With the three new companies in the group Casale not only consolidated its diversification into new markets but also took the strategic step to expand its range of revamping activities from focusing mainly on the synthesis reactor to offering revamping of the entire plant. In line with this strategy, Casale Group developed several breakthrough technologies to improve the design of the key elements of the plants and also to improve the production process itself. The group was gradually able to build up a complete technology package for plant revamping that also included new processes for the production of ammonia, urea and methanol.

This, together with experience gained through many revamping projects, was the basis for the development of innovative technologies for the design of new plants up to very large capacities. And so at the beginning of the new millennium Casale was able to close the loop of its initial strategy: through the comprehensive portfolio of technologies and the considerable market share gained with its revamping activity Casale was also able to compete with the long-established giants on the design of new plants.

May 27th 2014 was another very important date for the activities of the Casale

group: Ammonia Casale, Urea Casale, Methanol Casale and Casale Chemicals were merged back into a single entity, which operates under the name Casale SA. By simplifying the corporate structure, Casale wished to coordinate and integrate its services, talents and creativity more closely, thus strengthening its market presence and becoming even more competitive. The merger of the companies also enabled the new Casale SA to take on larger world-scale projects.

Since then, the strategic expansion of Casale has continued in two directions:

- the extension of its portfolio of technologies;
- the extension of its range of its services up to the supply of projects on a turnkey EP and EPC basis.

In line with this new strategy, in 2013 and 2014 Casale acquired world class technologies for the production of melamine, nitric acid, nitrates and phosphates and in the same year it also acquired Chemoproject Nitrogen, which subsequently become Casale Project, an important Czech engineering company active in the basic chemical and fertilizer industry.

Today

Dr Zardi currently holds the position of honorary president of the company, leaving his eldest son Federico, who has been working for Casale since 1986 and has participated with his father in the company's development, with the task of continuing the journey that Dr Zardi began forty years ago. Dr Zardi adds:

"When I think back on the almost one hundred years of the company's life, to that idea born from the intelligence of Luigi Casale, I can't help but consider that Casale has greatly contributed to the history of ammonia production. Today it is a licensor and a worldwide engineering contractor, a leader in designs for the production of ammonia, urea, melamine, methanol, nitric acid, nitrates, phosphates and synthesis gas and its expansion seems to be unstoppable.

"Through a culture of innovation that is sometimes pushed to the limit by my nature, and with the working group of engineers and designers as a driving force, I like to think that I have led the company to become the only company in the world to own such a vast range of linked technologies, ranging from ammonia to methanol, nitric acid and derivatives, urea and melamine, now consolidated in the current Casale SA, for the modernisation and construction of new plants." ■



Mixing and granulation systems for different kinds of fertilizer including nitrates, sulphur bentonite, urea, urea + ammonium sulphate, urea + micronutrients, and urea + sulphur (in partnership with Shell Thiogro).

- Ideal solution for de-bottlenecking or revamping existing facilities.
- Highly versatile process – parallel Rotoform installations enable flexibility and easy expansion for increased capacity.
- Environmentally-friendly – low dust emissions, low air scrubbing requirement, closed loop cooling (no cross contamination between water and product).
- Global service support operation.

ipco.com/fertilizer

CONTENTS

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com



High temperature hydrogen attack

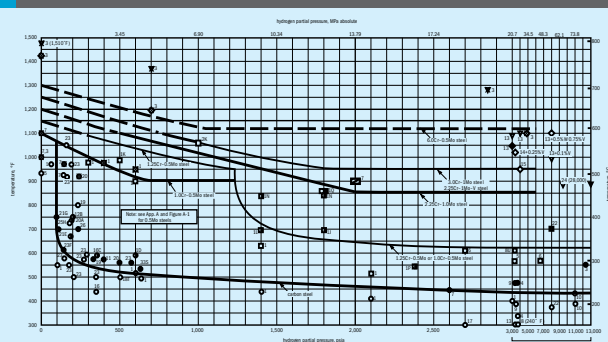
High temperature hydrogen attack (HTHA) is a damaging form of corrosion of steels that occurs in high temperature, hydrogen rich atmospheres. While it was characterised in the 1940s via the so-called 'Nelson curves', recent incidents have indicated that the issue may be more complex than previously thought.



PHOTO: CSB

Damage caused by the explosion at the Tesoro refinery, due to HTHA corrosion.

Fig. 1: Nelson curves



Source: API RP941 (7th edition)

The effects of hydrogen on carbon steel and its alloys has been known for some years. At elevated temperatures and pressures, atomic hydrogen is able to enter the microstructure of the steel and react with the carbon present to form larger methane molecules. The removal of the carbon embrittles the steel, and as the hydrogen penetrates further through the steel structure, over time, tiny pockets of methane coalesce, leading to fissuring and ultimately crack development.

During the late 1940s, G.A. Nelson and J. Shuyten of Shell Oil drew on a history of HTHA-related failures in refinery operations to produce operating safety guidelines via what became known as the so-called 'Nelson curves'. Essentially they plotted carbon and alloy steel compositions vs operating conditions on a graph, and drew a series of curves which distinguished between those where no HTHA failure had occurred or no serious HTHA microstructure corrosion had been detected, and those where it had occurred. The curves were re-drawn several times over the next two decades, as more operating experience and hence data points became available, and in 1970 these then formed the major part of the American Petroleum Institute's (API) Recommended Practice guide number 941 (RP941)¹. A recent iteration of the Nelson curves can be seen in Figure 1. One issue with the curves is that they provide only a record of pass/fail, and no safety margin – it is therefore down to operators to include a safety margin into their operating practice; 30°C is considered good practice.

The API has continued to issue and re-issue API RP941 over the succeeding years, each time with a copy of the Nelson curves enclosed, revised in 1977, 1983, 1990 and 1996. These have lowered the curves for various carbon-molybdenum steels in the light of new empirical data, and removed the distinction for carbon-0.5% Mo steel from carbon steel – the two now use the same curve.

However, in 2010 there was a fatal accident in the US at the Tesoro Anacortes

refinery which appeared to show that the Nelson curves were not a perfect predictor of steel behaviour. As a result, the US Chemical Safety Board (CSB) began a major investigation into the incident and produced a comprehensive report on the subject in 2014².

The Anacortes incident

On April 2nd, 2010, the Tesoro Refining and Marketing Co refinery in Anacortes, Washington State experienced a catastrophic rupture of a heat exchanger in the catalytic reformer/naphtha hydro-treater unit. The heat exchanger ruptured because of high temperature hydrogen attack, releasing hydrogen and naphtha at more than 260°C (500°F), which ignited, causing an explosion and an intense fire that burned for more than three hours. The explosion killed seven Tesoro employees who were working in the immediate vicinity of the heat exchanger at the time.

Amongst its findings, the subsequent US CSB report looked at API RP941 and its applicability to protection against HTHA. It concluded that; "The Nelson curves are predicated on past equipment failure incidents and are plotted based on self-reported process conditions that are ill-defined and lack consistency." It further stated that the CSB had learned of at least eight recent refinery incidents where HTHA reportedly occurred below the carbon steel Nelson curve, at operating conditions where carbon steel was previously thought to be resistant to HTHA. The CSB found that the carbon steel Nelson curve "is inaccurate and cannot be relied on to prevent HTHA equipment failures or accurately predict HTHA equipment damage."

The report concluded that the most effective safeguard against HTHA was better design; including the application of high chromium steels with greater resistance to HTHA. An alternative approach to replacing all equipment with higher performance materials would be to improve the detectability of defects at an early stage and focus replacement where the risk is greatest. However, it considered that the effectiveness of risk-based inspection (RBI) was limited by current technology and the effectiveness of operator skill, although it acknowledged that "advances in inspection system capability combined with effective training of operators coupled with effective RBI could mitigate the risk for existing carbon-steel plant".

RP941 revision

API revised RP941 in February 2016 (8th edition) to take account of the CSB report findings. In addition to the eight incidents that CSB had identified where HTHA had occurred below the carbon steel Nelson curve, the 2016 edition of API RP941 reported 13 new failures below the Nelson curve. The API believed that, since the failures at Anacortes had occurred in areas which on or near to welds, but which had not been subjected to post-weld heat treatment (PWHT), the solution was to provide milder operating condition guidelines for welded equipment. Therefore, as well as adding 12 new data points to the Nelson curves, the 8th edition also added a new curve labelled as "Carbon steel (welded with no PWHT)" for HTHA of carbon steel not subjected to post-weld heat treatment (PWHT), which was below the carbon steel curve appearing in all previous editions – the latter of which was now labelled as "Carbon steel (non-welded or welded with PWHT)."

The revision also made more conservative recommendations as regards safety margins from the curves, especially for carbon steels and carbon-0.5% Mo steels, describing temperatures above 350°F (177°C) and a partial pressure of >0.345 MPa (50 psia) as 'highly susceptible' to HTHA.

CSB response

However, the CSB was of the opinion that the API revision did not sufficiently address the issues that their report had raised, and issued a subsequent Safety Alert in August 2016. In particular, the CSB said that: "API's updated carbon steel Nelson curves do not take into account all of the estimated process conditions where the catastrophic failure occurred due to HTHA at the Tesoro Anacortes Refinery. As a result, the new curves allow refinery equipment to operate at conditions where HTHA severely damaged the Tesoro heat exchanger. The use of a curve not incorporating significant failure data could result in future catastrophic equipment ruptures."

The Safety Alert provided additional guidance to the industry, recommending that it:

- Identify all carbon steel equipment in hydrogen service that has the potential to harm workers or communities due to catastrophic failure.
- Verify actual operating conditions (hydrogen partial pressure and temperature) for the identified carbon steel equipment.

- Replace carbon steel process equipment that operates above 400°F (205°C) and greater than 50 psia hydrogen partial pressure.
- Use inherently safer materials, such as steels with higher chromium and molybdenum content.

Risk-based inspection

API941 acknowledges that inspection techniques to look for HTHA can be problematic, with widely variant results reported on the same piece of equipment by both the same and different techniques. Consequently it argues that no one method in isolation is ideally suited to detection of HTHA, especially during its incubation stage, when microfissures are just starting to develop. Ultrasonic inspection techniques have been found to have the best chance of detection, but only once fissures have already started to develop. Advanced backscatter ultrasonic technique (ABUT) can be a useful initial screening technique, but is not suitable near welded joints as it cannot see the full volume of the weld region, and requires a high degree of skill in interpreting results; one reason why the CSB was slightly dismissive in its own report on the use of risk-based inspection as a defence against HTHA.

However, a blanket replacement of all vessels and piping which meets the CSB criteria above would be prohibitively expensive, and may be regarded as something of a sledgehammer to crack a nut. Risk based inspection is still a useful technique when used correctly. Therefore, as reported at last year's AIChE Ammonia Safety Symposium³, in the wake of the API941 change and the CSB Safety Alert, Yara International updated its own risk assessment for HTHA using the most recent HTHA damage progression modelling technology.

Yara initially identified 263 carbon steel and carbon-0.5 Mo steel pressure vessels and pipes in hydrogen service (defined as operating conditions above 200°C and >0.5 bara H₂ partial pressure). The identified items were ranked in terms of risk based on how closely the equipment was operating to Nelson curve limits. Based on the new CSB guidelines, Yara calculated that it should technically be replacing 94 out of 109 pressure vessels, which seemed excessive. These risk categories were therefore also combined with a consequence of failure (COF) analysis of each item. Based on this initial outcome, Equity Engineering Group was contracted to perform a more detailed

CONTENTS

What's in issue 361

COVER FEATURE 1

Combatting AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

HTHA evaluation on items determined to be 'high' and 'medium-high' risk.

Equity had developed an API579-like Fitness for Service model with eight major oil industry sponsors which formed the basis of the assessment methodology. Although this remains proprietary, briefly it involves equipment evaluation for both volumetric and crack-like flaw damage. Volumetric HTHA is defined as a layer by layer attack of the material where decarburisation leads to methane generation across the material in a more uniform manner, whereas crack-like flaw damage occurs when an existing crack is accelerated by the presence of hydrogen, with modelling studies to predict crack propagation based on stress concentration, hydrogen partial pressure and temperature.

The results of this analysis produced five categories of HTHA risk, with 14 of the 49 pressure vessels in the highest risk category and recommended for replacement at the soonest opportunity, and another 15 at high or medium risk recommended for future inspection and possible replacement.

Non-destructive evaluation

Equity further elaborated on its non-destructive HTHA testing regime in another paper at the same conference⁴, noting that the 8th edition of RP941 was not updated to take into account ongoing refinement of non-destructive evaluation (NDE) techniques. Equity has collected over 200 samples of HTHA damaged equipment since 2012 and analysed these using a variety of different techniques to identify those that produce the most reliable assessments. The company uses time of flight diffraction (ToFD) and phased array ultrasonics (PAUT) using trained operators, which provides, it believes, the most reliable results, in tandem with a fitness for service methodology, to assist plant operators to manage life cycles of equipment items. The model has been benchmarked against Nelson curves, to ensure accurate predictions.

Post-weld heat treatment

Given that the new, lower Nelson curve is for welded equipment that has not been post-weld heat treated, is one solution to simply PWHT an item of equipment? The answer is yes, but PWHT of an entire vessel is often impractical. Local PWHT of the repair weld also includes challenges from local thermal stresses that could potentially lead to

further HTHA damage. Hau⁵, cited by Equity, found that HTHA damage propagation could occur during a short timescale (a few hours) of PWHT despite prior bake-out treatment. If local PWHT is performed, special consideration must be given to 'bullseye' heat treatments (concentric circle heating elements resulting in local thermal gradients) to ensure local distortion is avoided.

Case studies

Johnson Matthey has also noted⁶ that one area that needs additional attention is refractory line equipment, such as the transfer line from a primary reformer to a secondary reformer, historically often designed as a refractory-lined non-PWHT carbon steel system. As originally designed the carbon steel part of the transfer line would operate with a shell temperature below 200°C. However, over time the refractory may degrade, leading to an increase in the temperature that the steel experiences. JM showed thermal imaging pictures of such a transfer line operating at 240°C – outside the Nelson curve for non-PWHT steel under the new guidelines.

The company also presented two case studies in the same paper. The first concerned an ammonia plant of 1970s vintage with a non-PWHT transfer line system with refractory hotspots. A replacement was scheduled to coincide with a radiant section re-tubing, and new inlet and outlet pigtails, reformer tubes and supports and outlet manifolds were installed as well as the replacement refractory-line transfer pipe. These latter were designed to have a larger internal diameter to enable easier inspection and future maintenance as well as a lower pressure drop. The shell temperature was designed to be lower than 180°C in still air.

The second case study concerned methanol converters in older (pre-1981) Davy-designed plants. These are typically quench converters using carbon -0.5% Mo steel, and peak temperature occurs at the exit of each catalyst bed, reaching up to 290-300°C at high H₂ partial pressure. Although there have been no reported HTHA failures of such equipment, they are susceptible to HTHA and Matthey recommended operators make a risk assessment and management plan for such assets.

Equity Engineering also reported a case study in their own paper⁴, concerning a carbon-0.5% Mo reactor with 300-series stainless steel cladding. The reactor operated above 315°C at 13.8

bara H₂, well above the PWHT Nelson curve. The vessel had been operating for over 40 years, with the last nine years documented via time scaled operating temperatures and H₂ partial pressure. The HTHA model showed that the vessel to have a high likelihood of cracks rather than volumetric damage. An inspection plan for time of flight diffraction analysis was created, accounting for difficulties such as the re-pad on the outside of the nozzle and cladding on the shell and loose liner in the nozzle bore. Inspection found a flaw comprising 33% of the wall thickness at a nozzle to head weld (high stress location). The model predicted a 10 year remaining service life with a 5 year inspection interval.

Duration in service

One of the issues with the existing Nelson curve approach to HTHA protection is that it does not consider duration in service of equipment items, which would be normal for any other type of corrosion risk assessment. The ammonia industry has a large number of plants still operating from the 1960s and 1970s, far above the 30 year recommendation in the original RP941. Work is ongoing to try and characterise the ageing characteristics of HTHA and produce a more 'three dimensional' Nelson curve based on operating lifetime as well as temperature and hydrogen pressure. In the meantime, intelligent use of risk-based inspection and use of the most up to date inspection techniques remain crucial tools in preventing accidents from HTHA. ■

References

1. API RP941 (8th Edition)
2. US Chemical Safety Board Investigation Report 2010-08-I-WA, Tesoro Anacortes Refinery, May 2014.
3. G. Franceschini et al, Yara International, *Fitness for Service Case Studies in HTHA Equipment*, paper presented at 59th AIChE Ammonia Safety Symposium, September 2018, Toronto.
4. Trace Siffes et al, Equity Engineering Group Inc, *Fleet-Wide HTHA Risk Assessment Using Latest Methodologies*, paper presented at 59th AIChE Ammonia Safety Symposium, September 2018, Toronto.
5. J.L. Hau et al, *Material Damage Implications of Post-Weld Heat Treating H₂ Blisters in Carbon Steel*, paper presented at Corrosion 2001, Houston, 2001.
6. J. Brightling, S. Shapcott, Johnson Matthey plc, *Risk Reduction Projects Combating High Temperature Hydrogen Attack*, paper presented at 59th AIChE Ammonia Safety Symposium, September 2018, Toronto.



WE KNOW OUR WAY AROUND ENGINEERING

Think about thousands of highly skilled professionals operating in the **petrochemicals, fertilizer and oil&gas refining industries:** this is Maire Tecnimont Group, a plant engineering leader dedicated to providing consumers at the end of the value chain with **energy in its different forms.**

We create value with innovative products for a countless number of industrial applications embedded in everyday life.

 **45**
COUNTRIES

 **~1500**
TOTAL DELIVERED
PROJECTS

 **50**
COMPANIES

www.mairetecnimont.com



CONTENTS

What's in issue 361

COVER FEATURE 1

Combating
AN misuse

COVER FEATURE 2

High temperature
hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid
catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England

Tel: +44 (0)20 7793 2567

Fax: +44 (0)20 7793 2577

Web: www.bcinsight.com
www.bcinsightsearch.com

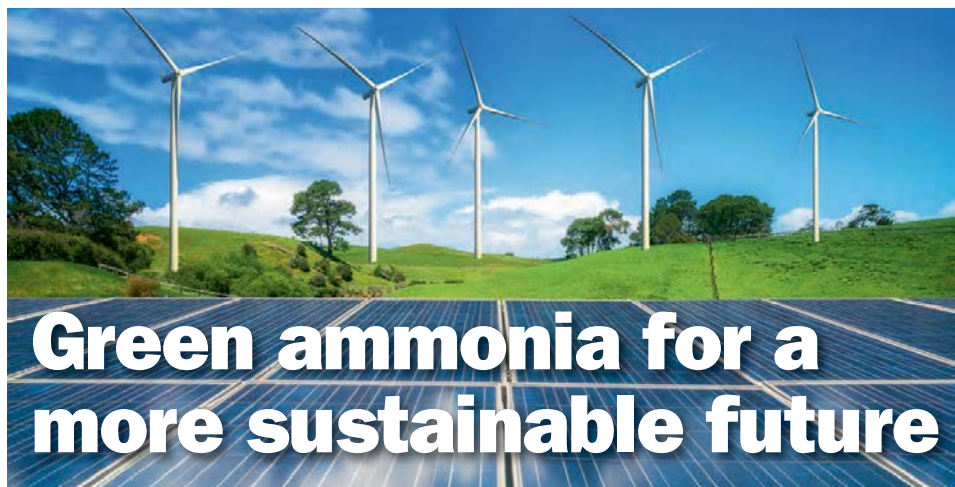


PHOTO: ISTOCKPHOTO.COM/ANANOSTOCK

Green ammonia for a more sustainable future

As the interest in sustainable ammonia, renewable energy and power-to-ammonia continues to grow, we report on some of the latest developments and technological advances that were presented and discussed at the 3rd European Power to Ammonia® Conference, organised by Proton Ventures BV.

In June 2019, industry experts, scientists, researchers and developers gathered for two days at the NH3 Event 2019 in Rotterdam, the Netherlands to present their recent work, developments and visions for the future for ammonia and its role in the energy transition to a greener and more sustainable future. In this article we highlight some of the key topics discussed.

Ammonia and hydrogen from solar and wind energy in China

China is the world's largest consumer of ammonia for fertilizers (approx. 56 million t/a). The majority of China's ammonia is produced from the partial oxidation of coal which generates the highest CO₂ emissions (approx. 200 million t/a).

However, China is blessed with immense solar and wind resources, particularly in the north and west, and ammonia from renewables is getting close to becoming competitive with coal-based ammonia.

Solar and wind energy can be harnessed by transforming it into hydrogen locally close to the point of consumption. For the harnessing of remote solar and wind resources, hydrogen is not easy to ship or pipe over long distances and many end-use applications require storable and transport-

able liquids so it is better to transport it as ammonia via pipelines. The world's longest (2,470 km) ammonia pipeline links Togliatti in Russia to Odessa in Ukraine.

Renewable energy from five sites in five provinces in China with excellent solar and wind resources have been studied and the preliminary results were presented at a workshop in Beijing. The five sites are Xinjiang, Qinghai, Tibet, Hebei and Fujian. Solar dominates in Qinghai, wind dominates in Hebei, while Tibet uses a more even mix. Some regions with abundant resources e.g. Fujian and Hebei are located close to industrial centres, while other regions, e.g. Qinghai and Tibet, are more remote.

Green ammonia for energy systems in developing countries

In May 2019, UN Secretary General António Guterres called for an end to building new coal plants by 2020. New research at Oxford University is underway to investigate the impact of green hydrogen and ammonia on energy infrastructure in developing countries. A key challenge in developing countries is building energy infrastructure to meet growing demand without entering traditional carbon-intensive development pathways, such as coal and natural gas.

Take India as an example, where approximately 75% of electricity generation is currently based on coal, there is no natural gas network and annual electricity demand is projected to double from 2016 levels (1,066 TWh) by 2025 and triple by 2040.

Local green ammonia production could be economically, politically and socially valuable for developing countries like India to meet their rapidly growing demand for energy. But it's not as simple as just building a green ammonia plant, there are many questions still to be answered: How will the ammonia be transported? What is the current transmission of the electricity grid and what is it forecast to be? What is the least cost investment for these countries in different geographies? What carbon taxes and technology advancements are needed to meet more aggressive targets?

Opportunities for small scale green ammonia in Saskatchewan

In Canada, the provincial government of Saskatchewan has a strategic desire to reduce GHG emissions through the development and identification of new and innovative technologies such as green ammonia production. The availability of waste feedstocks to produce green ammonia, expertise and leadership in CCS and CO₂/EOR, and a large agricultural sector which would use the ammonia as a fertilizer for plant growth, provide opportunities for small scale green ammonia production in Saskatchewan.

Green ammonia can be produced in Saskatchewan in three ways by using: flared and vented gas; carbon, capture and

storage; or biogas (e.g. from agricultural residues such as wheat straw and barley straw, municipal solid waste, food waste and animal residue).

Besides the environmental benefits of green ammonia (GHG reductions) there are many others.

- Small scale green ammonia plants can be produced closer to where the ammonia is being used, to avoid high transportation costs.
- Green ammonia is a viable solution to decreasing flaring and venting of associated gas in the Province.
- When green ammonia is produced through flared and vented gas as well as biogas it:
 - Provides a clean-tech solution to two key Saskatchewan sectors namely oil and gas and agriculture;
 - Benefits municipalities as a solution to their waste;
 - Can generate a revenue stream for farmers, industrial sectors and municipalities;
 - Provides rural economic development.
- Green ammonia production can be blended with existing operations, hence smaller footprints.
- If CCS technology is used to produce green ammonia the sale of CO₂ to an oil company provides a new revenue stream to the ammonia producer and additionally the CO₂/EOR unlocks incremental new oil production.

Electrolysers becoming competitive with SMR

Nel, a global leader in water electrolysis-based hydrogen production plants, has built some of the largest electrolyser plants in history and is currently constructing the world's largest electrolyser manufacturing plant with a nameplate capacity of 360 MW per year in Notodden, Norway. The aim is to achieve a system cost reduction of more than 40%. The manufacturing plant is scheduled to be operational in 1H 2020 with ramp-up aligned to customer requirements.

Driven by an increasing focus on decreasing electrolyser capex, Nel electrolysers are becoming an attractive and renewable cost effective alternative to steam methane reforming (SMR) of natural gas.

Nel and Yara have been awarded a grant from PILOTE scheme for developing next generation green (renewable) ammonia and fertilizer production. The target is to utilise Nel's next generation electrolyser technology currently under development tailored for large

scale hydrogen production from renewables. Development targets include: lower unit cost, higher level of flexibility, higher pressure, smaller footprint and high efficiency.

Decarbonising the nitrogen industry

Yara has set itself the target to become climate neutral by 2050. Over the past 15 years, Yara's greenhouse gas emissions have halved by almost eliminating N₂O. Now Yara is taking steps to further improve its performance by targeting CO₂ reduction and has ambitions to lead the decarbonisation of the nitrogen industry.

In January 2019 Yara created two new business units: Decarbonize and Circular Economy. The aims of Decarbonize are to reduce Yara's GHG emissions, produce zero carbon nitrogen (e.g. green ammonia), reduce infield agricultural GHG emissions and contribute to green energy carrier solutions and green food value chains. The aims of Circular Economy are to do more with less and to give value to waste.

According to Rob Stevens, VP Technology Scouting for Yara's new Decarbonize business unit, "Clean energy could double the demand for low-carbon ammonia".

The battolyser for decarbonisation of energy and industry

Dutch start-up company Battolyser BV is pilot testing a new technology at Nuon's Magnum power plant in Eemshaven in the Netherlands that combines the most durable alkaline Ni-Fe battery and the most durable alkaline electrolyser in one device, the so-called battolyser.

Renewable hydrogen for the process industry requires either electricity or hydrogen storage for steady-state operation. The battolyser integrates efficient electricity storage and controllable hydrogen output from intermittent renewable electricity sources for fuel and green chemical feedstock.

The battolyser stores electricity in the conventional galvanic manner until it is fully charged, at which point the device uses any additional electricity supplied for the electrolysis of water and evolution of hydrogen. If the device is integrated with hydrogen buffer storage and an ammonia production train, the result will be a versatile and highly scalable energy storage system that can provide responsive grid support on all time scales from seconds to months.

Charging the Fe-storage electrode together with oxygen production will be done while elec-

trical power, e.g. from renewables, is cheap and abundant. Generation of hydrogen when electricity is scarce, requires little energy. The process of charging the Fe storage electrode with delayed hydrogen release costs overall 3% extra energy input.

Casale's low carbon ammonia synthesis process

Ammonia production accounts for a significant share of global CO₂ emissions (approx. 1%). Demand for a low-carbon energy carrier, fostered by incentives and carbon taxation, can be achieved with existing and mature ammonia production technologies and energy storage.

Within this framework, Casale has developed a new, patented, low carbon ammonia synthesis process, A6000CC, to convert natural gas to ammonia with reduced CO₂ emissions to atmosphere, as low as <0.2 tonne CO₂/tonne NH₃ to the stack, i.e. about 80% lower than best available technologies.

This new process demonstrates low energy consumption compared to state of the art solutions while achieving carbon capture of more than 90%, considering both ammonia process and utilities, without the inclusion of a dedicated CDR unit for post-combustion carbon capture of flue gases. Decarbonisation targets are reached by using a pre-combustion strategy, where syngas is partially used as (syn)fuel. A pre-combustion carbon capture strategy increases efficiency and reduces cost compared to a post-combustion strategy.

Single-train plant production can achieve very high capacity allowing the use of low-carbon ammonia as a multipurpose energy carrier at large scale. Economy of scale and process optimisation, together with favourable business scenarios and market opportunities for captured concentrated CO₂ allow a low levelised cost of ammonia to be reached.

Ammonia combustion with lower NOx emissions

In recent years, Duiker Combustion Engineers has developed a stoichiometry controlled oxidation (SCO) concept to handle the ammonia-rich streams of refineries and other industrial processes. Several full-scale commercial SCO units have already been designed, delivered, installed and put in operation around the world in sulphur recovery units on refinery sites, firing pure ammonia or rich ammonia-containing flows. Field test measurements on the

CONTENTS

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England

Tel: +44 (0)20 7793 2567

Fax: +44 (0)20 7793 2577

Web: www.bcinsight.com
www.bcinsightsearch.com

full-scale commercial units have confirmed that NOx emission values of 40-80 ppmv can be reached, far below the emissions created with free ammonia combustion. This technology may also be highly suited for the direct conversion of ammonia into high-temperature heat (>1,600°C) with low NOx (without DeNOx) for applications such as fired heaters/ovens, industrial gas-fired furnaces, naphtha crackers, turbines and steam boilers.

As of July 25th Proton Ventures BV and Duiker Combustion Engineers B.V. started a strategic collaboration for, among other things, start-up of mini-ammonia plants in combination with the SCO technology.

Application of ammonia as a marine fuel

The use of ammonia as a fuel for marine shipping has strong potential to achieve significant reduction in greenhouse gas emissions and to enable ship owners to eventually phase them out entirely with renewable fuels. However, much is still unknown regarding application of ammonia as a marine fuel.

Maritime rules in terms of emission limits are becoming stricter and the use of an electrical motor has been recently proposed and tested. Due to the strict requirements in terms of energy densities, batteries are not a feasible solution. The use of renewable chemicals, the so-called solar fuels, are an innovative solution for this application. Ammonia guarantees high energy densities and no carbon emissions.

Ammonia can be converted back into power (ammonia to power) in internal combustion engines and in solid oxide fuel cells (SOFC). In the latter, the fuel reacts electrochemically avoiding typical combustion pollutants such as NOx. Real performances of ammonia fuelled SOFC and actual emissions are still to be investigated.

Ammonia from steel mill gases

Carbon2Chem® is a unique, large-scale project in which gases produced during steel-making, in particular CO₂, are no longer burned but transformed into valuable raw materials such as methanol or ammonia, thus achieving a circular carbon economy.

This four year project which started in June 2016 is coordinated by thyssenkrupp together with institutes of the Fraunhofer-Gesellschaft and the Max Planck Society and involving 15 other partners from research

and industry. It employs a cross-industry approach realising carbon capture and usage (CCU) using proven technologies. The biggest challenges are the gas treatment and the intermittent supply and fluctuating composition of the gases.

Large amounts of gases are produced during steel manufacturing. Currently these gases are used as a source of energy by burning them in power plants to generate electricity for steel production. However, steel mill gas comprising coke oven gas, converter gas and blast furnace gas contains 43% nitrogen, 25% carbon monoxide, 21% carbon dioxide, 8% hydrogen and 2% methane, which makes it suitable for the production of carbon- and hydrogen-containing synthesis gas, a precursor for various chemicals.

Since April 2018, a Carbon2Chem pilot plant has been in full operation, operating 24/7 at thyssenkrupp's steel making location in Duisburg, Germany. The pilot plant receives a slip stream of the steel mill gases.

The pilot plant has a 2 MW electrolysis plant that can produce 440 Nm³/h H₂. The gas cleaning plant has a capacity of approximately 240 Nm³/h (treating 100 Nm³/h coke oven gas, 70 Nm³/h converter gas and 70 Nm³/h blast furnace gas).

There are several options for making ammonia from the steel mill gases, for example, the steel mill gases can simply be used as a cheap feed to make ammonia without producing any CO₂. The blast furnace gas supplies nitrogen and hydrogen and the coke oven gas supplies additional hydrogen for the carbon-free ammonia synthesis. Carbon dioxide from the blast furnace gas can then be combined with the ammonia to produce 850 t/d urea (capacity is limited by the amount of hydrogen available).

To increase the production of urea to 3,500 t/d additional hydrogen could be supplied from the converter gas by CO shift but this has the drawback of producing additional CO₂.

Another alternative is to provide additional hydrogen from the electrolysis of water which would allow 40% of the CO₂ gas from the steel mill gases to be processed into urea (29,000 t/d).

Besides ammonia, the pilot plant is also being used to investigate the production of green methanol and higher alcohols for the fuel market.

The concept is expected to be ready for industrial scale use around 2030. This project brings thyssenkrupp closer to its goal of reducing emissions by 30% by 2030 and becoming climate-neutral by 2050. ■

IN BRIEF

Green ammonia and hydrogen

Green ammonia has the potential to lead to a future where farmers use fertilizers manufactured by sunlight, ammonia producers lead in the new energy market and ammonia capacity worldwide increases exponentially.

Key considerations:

- Ammonia has better power density than hydrogen and does not have to be kept at extremely low temperatures or under high pressure to be stored
- Ammonia is regarded as one of the more attractive options for zero emission shipping due to its energy density and ease of handling
- A premium price could be demanded for green ammonia products
- Ammonia as an energy carrier carries a high price relative to hydrogen fuel.
- Options for exporting renewable energy production include: electricity, green ammonia, green methanol and green hydrogen.

Ammonia as a fuel

Ammonia advantages as a green fuel:

- Zero carbon fuel
- Well established trade
- Can be produced 100% by electrical energy.
- Can be easily reformed to H₂ and N₂
- High energy density – can be stored with high energy density at <20 bar.
- Low opex and losses in storage.
- High hydrogen density.
- Low risk of fire – a relatively specific ratio of NH₃ and air (15-25%) is required to sustain combustion.

Its main weaknesses are:

- NOx emissions
- Odorous and toxic.
- Requires approval as a fuel in each country.

World hydrogen market

Most of the approximately 55 million t/a of hydrogen produced today is not CO₂-free.

Ammonia production accounts for >50% of the total hydrogen market which is currently >95% fossil fuel based (from gas, oil, coal).

Only 1% of hydrogen is currently produced from water electrolysis, the rest comes from steam methane reforming and gasification.

If produced from renewable power via electrolysis, hydrogen is fully renewable and CO₂-free.

Renewable hydrogen has the potential to decarbonise a large range of applications.

There is massive CO₂ reduction potential for power, gas, transport and industry. ■



espindesa

Your process licensor counterpart for nitric acid, ammonium nitrate and fertilizer technologies



Process Technology Licensor



Engineering and Design



EPC / EPCM Projects



Commissioning & Start-Up Assistance



Plant Operation Assistance

Arapiles, 13. Madrid
28015 - Spain
Tel.: (34) 914 483 100
Fax: (34) 914 480 456
www.espindesa.es



TECNICAS REUNIDAS



espindesa



CONTENTS

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Next generation catalyst gauzes for nitric acid plants

New designs of catalyst gauze packages and improved production technologies have been developed to meet the increasing demands from nitric acid producers. Tailor-made designs according to specific customer requirements have led to catalyst gauzes with improved overall performance and minimise the total cost of ownership for customers. New and improved catalyst gauze systems from Heraeus, Johnson Matthey and Sabin Metal Corporation are discussed.

Nowadays, more than ever, nitric acid producers are demanding the lowest overall costs for nitric acid production, targeting the most beneficial combination of highest ammonia conversion efficiency, lowest costs to recover the lost precious metals during the combustion process, as well as lower N_2O emissions. Fluctuating prices of platinum group metals (PGM) require catalyst suppliers to balance their catalytic gauze systems according to recent PGM price levels. New catalyst gauze packages and improved production technologies have been developed to meet these market requirements.

Heraeus' new FTCh catalyst gauze design

The heterogeneous oxidation reaction of ammonia in nitric acid plants takes place as ammonia is combusted across catalyst gauzes made from PGM. Heraeus has been a reliable gauze supplier to this market for more than 100 years.

In the 1990s Heraeus introduced the FTC System which consisted of a combination of dedicated catalyst alloys of different knitted gauze layers from top to bottom of the gauze pack.

This gauze technology took advantage of the idea of combining the ammonia oxidation catalyst with an integrated catchment function by using ternary PGM alloys. The FTC gauze family has been successfully used in nitric acid plants for almost 25 years.

Progress in scientific methods used for the investigation of surface reactions in the heterogeneous reaction mechanisms and

development of advanced 3D CFD simulation models combined with a deeper knowledge of surface reaction kinetics resulted in the development of a new high-performance catalyst type during recent years.

The resulting new catalyst gauze systems are tailor-made according to the specific plant operating conditions and consider the particular market requirements perceived by the customer.

The challenges according to the market requirements can be defined as follows:

- longer campaigns with increased conversion efficiency;
- further reduction of PGM losses;
- adaption of catalyst designs to changing prices of the PGM;
- environmental requirements on low N_2O emissions.

Integrated into this tailor-made approach, Heraeus introduced a new catalyst type called FTCh (high efficiency), which provides higher oxidation efficiency at lower installed catalyst weights with lower PGM losses during the gauze campaign.

Longer campaign length at high oxidation efficiency

Historic catalyst gauze types which were designed for long production campaigns resulted in high installation weights and/or a decreasing oxidation efficiency with increasing operation time of the nitric acid plants. In particular, in the second half of a production campaign the efficiency started to decline which resulted in fewer tonnes of nitric acid produced per tonne ammonia

consumed and hence higher costs for increased ammonia consumption.

The new FTCh catalyst type succeeded in overcoming the gradual decrease of efficiency of long term campaigns and has been successfully introduced in medium- and high-pressure plants, providing high oxidation efficiency over extended campaign lengths.

The challenges of the development of the new FTCh catalyst type with prolonged lifetime were solved by using scientific methods on analysis of changes of catalyst micro-surfaces of different gauze designs according to operating time in industrial plants.

The new catalyst gauze designs operate with reduced PGM losses and provide high long term stable surface areas by using special arrangements of PGM alloys and application of new gauze wire structures adapted to the hydrodynamic gas flow conditions from top to bottom of the gauze pack. After the introduction of the FTCh design to the nitric acid market several nitric acid plants were able to improve their production efficiency and take advantage of the improved long term performance.

Fig. 1 shows the process efficiency of nitric acid production in a medium pressure plant using the new FTCh gauze design at minimised precious metal inventory.

A further example, Fig. 2, shows the efficiency according to campaign length for a high-pressure plant. Using the new gauze design helped to increase the total production of nitric acid at relatively stable process efficiency thanks to approx. 30% longer

Fig. 1: Production efficiency of a MP plant with the new FTCh catalyst gauze design

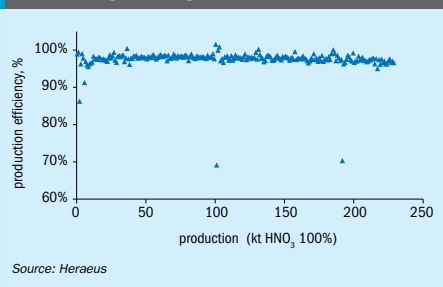


Fig. 3: N_2O emissions of a MP plant with FTCh catalyst gauze design and secondary catalyst

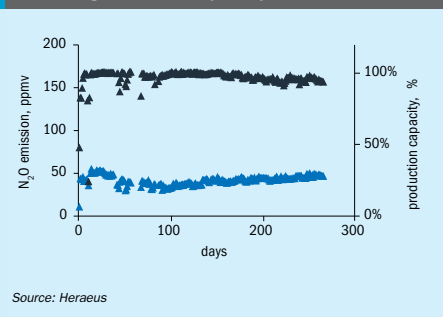


Fig. 2: Lifetime of gauze campaigns in HP plants

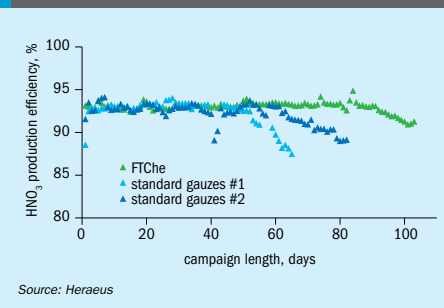
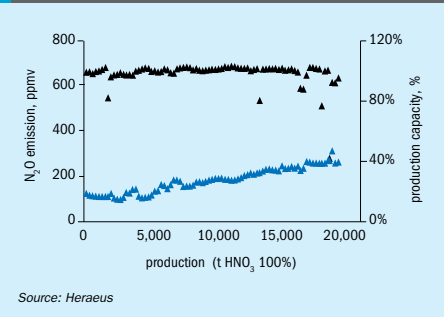


Fig. 4: Tailor-made FTCh-HR and secondary catalyst combination for HP plant at minimum ΔP



campaigns. This reduces the annual down time and saves costs by reducing wasted ammonia and requires less maintenance.

Catalyst gauze designs with low N_2O emissions

N_2O is generated in a side reaction to the ammonia oxidation process in nitric acid plants. When emitted to the atmosphere, N_2O has a global warming potential that is 310 times greater than that of CO_2 . Several countries have issued special environmental regulations. Europe, for example, has a cap and trade system called ETS, in which sites from 31 countries participate. In countries that participate in the ETS the costs of N_2O emission have been increased during recent years and are expected to increase further in the near future.

Nowadays N_2O generated at the primary catalyst can be effectively reduced to low N_2O levels using secondary or tertiary N_2O abatement solutions, but there is still room for further N_2O reduction, in particular for secondary abatement solutions.

Since N_2O is generated on the primary catalyst the most cost-effective solution will be a stronger reduction of the N_2O emission directly on this stage. In addition to performance parameters like high process efficiency and low PGM losses the N_2O emission is a further important parameter which has to be considered in the cost evaluation of nitric acid production.

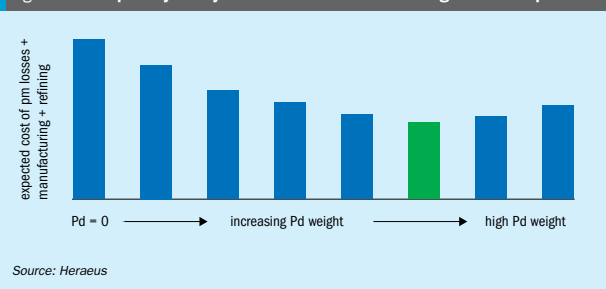
The Heraeus FTCh-HR (High Reduction) gauze system provides lower N_2O emissions than standard gauze systems. In medium-pressure plants the N_2O emission at FTCh-HR gauze systems can be reduced to about 250-350 ppmv in the beginning of the production campaign. Due to contamination and aging effects of the catalyst gauze surface the N_2O emissions increase during the campaign so that an average N_2O emission value of 400-700 ppmv can be achieved depending on specific plant parameters and the overall production of HNO_3 .

Combining it with the Heraeus secondary catalyst N_2O emission levels of 25-60 ppmv can be achieved for medium pressure

plants. Fig. 3 shows the N_2O emissions of a medium-pressure plant using FTCh gauzes and the Heraeus secondary catalyst. The gradual increase of N_2O emissions with production time can be attributed to the primary catalyst. The further development of lower N_2O emissions at the gauze catalyst stage is mainly focused on lowering the N_2O emissions at increasing production time.

The Heraeus FTCh-HR gauze system is also used to reduce N_2O emissions in high-pressure plants. Because high-pressure plants are very sensitive to additional pressure drop the application of additional secondary catalysts is limited to certain volumes which provide limited N_2O reduction. Heraeus developed a special PGM based secondary catalyst for this reactor type. Fig. 4 shows the N_2O emission of a high-pressure plant. Using a tailor-made combination of FTCh-HR and the secondary catalyst the N_2O emissions could be reduced far below the national N_2O emission limit.

Fig. 5: Cost of primary catalyst at different installed Pd weight for a MP plant



Influence of palladium prices on cost efficient gauze designs

The PGM are key constituents of the catalyst gauze systems. During the operation of the nitric acid plants PGM are mainly lost by evaporation and minor losses arise during the refining of the used catalyst systems. Reinvestment costs of PGM purchased to balance out the PGMs lost during a campaign is one of the major cost factors resulting from gauzes systems in nitric acid production. Unfortunately, the market prices of precious metals are always subject to change and a reliable forecast in which direction the prices will move is not possible.

According to recent price developments of precious metals, the palladium price has been rising and at time of writing this article was in the range between €1,150 and €1,400/toz. The platinum price is at a relatively low level and at the time of writing was in the range between €700 and €800/toz.

Platinum and palladium are the major components in catalyst gauzes systems. Rhodium and possible other metals make up a minor percentage and are typically below 5% of the total system.

Therefore, the total precious metal costs of the catalyst gauze systems are mainly determined by palladium and platinum prices though the others have to be considered for cost evaluations as well.

The high price level of palladium versus platinum results in requests from nitric acid producers to reduce the amount of palladium in catalyst gauze systems for economic reasons.

Palladium inventory has a strong influence on the total PGM losses occurring during the operation of the nitric acid plants.

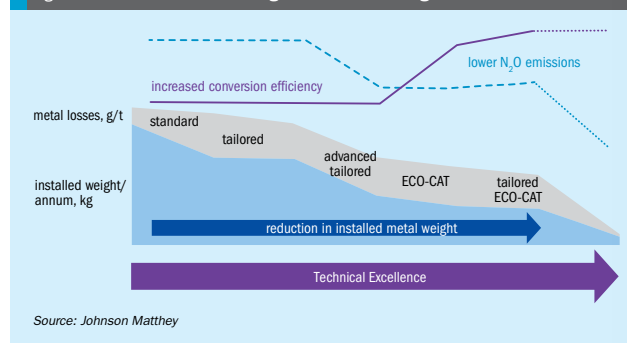
The weight of the PGMs used in the catalyst gauzes are always included in the overall cost evaluation which targets minimising the

costs according to the expected PGM losses, ammonia consumption and the financial cost of the PGM inventory. To determine the most cost-effective gauze system for each specific plant detailed information on the typical cost factors need to be included in the calculation of the catalyst gauze design.

Fig. 5 shows an example of the calculation of costs arising from different palladium weights in the catalyst gauze system for a typical medium-pressure plant at currently representative precious metal prices of €26/g Pt and €46/g Pd. The cost simulation included the expected net PGM losses which relate to the amount of PGMs which has to be reinvested, the cost of manufacturing the gauze system and the cost of refining the used catalyst gauzes after the production campaign.

The calculation shows that there is a cost optimum for installed palladium weight. It shows that installation of palladium in medium-pressure plants is still profitable but the weight for each plant has to be optimised carefully to minimise the total cost of ownership for customers.

Fig. 6: Technical Excellence: Progression of JM PGM gauzes



Johnson Matthey applies its Technical Excellence improvement program to gauze systems

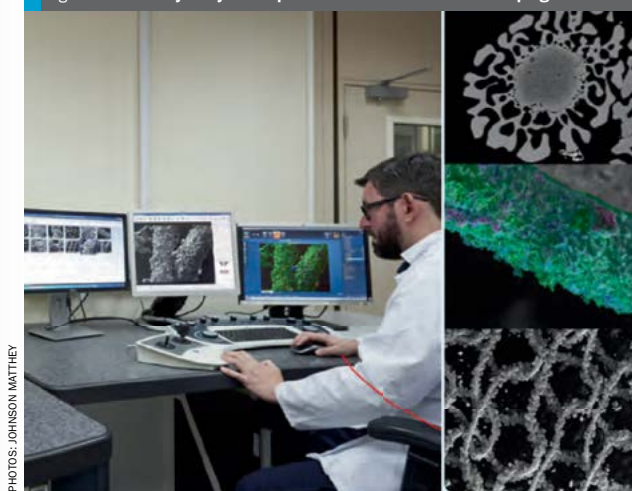
Johnson Matthey (JM) is a leading manufacturer of platinum-based catalytic gauzes for use in the production of nitric acid. Advances in catalyst gauze technology at Johnson Matthey are an on-going development which has resulted in a complex catalyst gauze system comprising a blend of binary and tertiary alloys of platinum, rhodium and palladium.

Technology is continually improving as JM develops bespoke gauze pack systems to meet customer demands for improved operational cost and environmental performance. Depending on customer drivers, each bespoke pack is made to meet specific requirements, providing excellent conversion efficiency and reduced pack weight whilst minimising N₂O emissions.

As depicted in Fig. 6, by using Technical Excellence to develop gauze pack systems it has been possible to reduce PGM metal weight, to lower N₂O emissions and to increase conversion efficiency – this allows customers to achieve and maintain high levels of efficiency thus helping to reduce production costs.

Johnson Matthey's ECO-CAT™ technology offering, which is recommended for the majority of nitric acid plants, uses palladium in a controlled manner to replace some of the platinum in the gauze. Exploiting its metal recovery properties, the palladium catches lost platinum without compromising the ammonia conversion. This increases the gauze performance and gives a sustainable and efficient system for nitric acid production

Fig. 7: Gauze analysis by JM as part of the Technical Excellence program



with the installation of palladium also reducing N₂O emissions.

ECO-CAT packs are tailored directly to each individual plant, utilising in-house modelling to select the most optimal blend of alloys and knit structures to suit both plant operating conditions and the prevailing PGM prices. A successful design combines the properties of platinum and palladium to maintain a high conversion efficiency and minimise N₂O emissions, with the prevailing PGM market conditions and N₂O emission legislation influencing the final installed weights.

The PGM metals are used in gauze pack systems that are made to meet specific customers' requirements, providing excellent conversion efficiency and optimum weight whilst minimising N₂O emissions and metal losses. The following case study describes the reduction in PGM content recently achieved for high pressure nitric acid plants.

Case study 1: JM gauze benefits in HP plants

The total installed PGM content in an ammonia oxidation catalyst is a key element of the overall cost of the system. Nitric acid plants operating at high pressures (>9 barg) and with a high nitrogen loading (>60 t N/m²/d) have high metal loadings in the range of 600-900 mg installed PGM content per tonne of acid produced in a campaign. Plants operating at a lower pressure and with a lower nitrogen load typically have

metal loadings in the range 200-500 mg/t installed PGM content.

ECO-CAT technology, which incorporates palladium rich alloys into the catalyst pack, is in widespread use and is the recommended technology for medium and dual pressure plants.

A nitric acid producer operating a high-pressure (HP) plant benefited from a 15% reduction in their catalyst system installed weight compared to standard technology. Additionally, the utilisation of recycled platinum within the pack resulted in a higher conversion efficiency towards the end of the campaign. Further optimisation of palladium placement within the pack resulted in a reduction in N₂O emissions from the system.

By applying ECO-CAT design principles to high pressure and high loading plants, the installed metal content can be significantly reduced, typically around 30-40% (Fig. 8). Additional benefits associated with ECO-CAT technology include reduced net PGM loss, lower N₂O emissions and improved campaign efficiency.

Case study 2: Improvement program optimising performance

By working on a technical excellence improvement program with customers JM uses operational feedback to develop ever higher performance gauze pack systems. JM identifies the target areas for development to improve the overall production efficiency and rate.

The typical development areas that can be addressed through improved gauze technology are:

- improved light off characteristics (time to peak efficiency);
- longer maintenance of peak efficiency (overall campaign efficiency and length);
- reduced pressure drop;
- improved metal recovery.

During execution of an improvement project which typically lasts over a number of gauze change cycles, incremental step changes are made to the gauze and catchment (getter) designs for each campaign to address the improvement areas.

Optimising designs

JM believes that only through careful data collection and analysis throughout the product life cycle, can it give customers the best possible products.

JM's highly trained technicians and scientists investigate weight loss, gas flow distribution and contamination sources of gauzes. These results are used to refine new gauze designs to reduce metal loss and enhance performance of future campaigns.

The dedicated Research and Development team has two ammonia oxidation test rigs, which are used to simulate plant conditions and to help understand the fundamental design basis of a successful gauze pack. This is complimented by a large range of analysis equipment, which can interrogate the top surface layers, as well as the bulk of the gauze, using electron dispersive x-ray analysis (EDXA) and scanning electron microscopy (SEM) for primary analysis, giving an overview on wire morphology, development and structure. Sufficient for most campaigns, these techniques provide elemental information to a depth of about 1µm.

Following such technical excellence programs nitric acid plant operators have been able to use tailored gauze packs where the gauze technology improvement has supported overall process improvements in the plant, meaning that the nitric acid plant has been able to run at record efficiencies and production rates, with the resultant cost per tonne of acid over the course of the program reducing by 20% (assumes constant metal price) and campaign lengths increasing by 40%, as shown in Fig. 9.

Immediately beyond the gauze a further area of focus for nitric acid producers remains nitrous oxide (N₂O) abatement

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Fig. 8: Installed metal content ranges for HP nitric acid plants

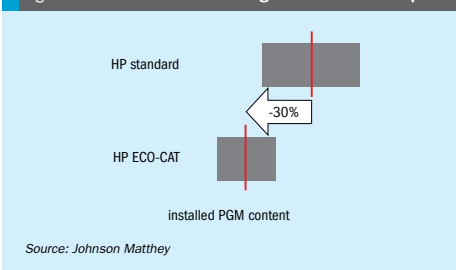


Fig. 10: Yara 58-Y1 secondary abatement catalyst



catalyst. Through its co-operation with Yara International ASA, JM supplies the leading high performance secondary nitrous oxide abatement catalyst and supports customers with expertise on containment baskets that are specifically designed for their plant and the use of Yara's abatement catalyst.

Case study 3: N₂O abatement in MP plants

A medium-pressure plant in Europe was looking for an abatement system to reduce its emissions. JM assessed their operating parameters and sent an Engineering team to the customer site to inspect the condition of the burner basket, with the aim to tailor a secondary abatement solution to the plant's specific requirements.

The Yara 58-Y1 secondary abatement catalyst (Fig. 10) is the proven N₂O emissions reduction technology exclusively marketed by JM. Key characteristics of this product are:

- intrinsically capable of achieving high N₂O abatement;
- mechanically and thermally stable, with limited attrition and reduced tendency to doming and bypass;
- high geometric surface area and subsequent high activity yet low pressure drop, and;

- no impact on oxidation reaction or contamination downstream of the burner. It was identified that, together with a new containment system, modifications would need to be made to the existing beams for the structure to support the combined weight of the catalyst and containment under the gauzes, (Fig. 11). JM worked closely with the plant stakeholders to deliver its proprietary containment design and to determine an abatement capacity that was both financially sound and able to meet applicable environmental regulations.

Once implemented, the combined effect of the containment system and catalyst bed of Yara 58-Y1 pellets allowed for an emissions abatement level of over 95%. This containment system and catalyst bed have been in operation for over a decade now at the customer plant and have consistently achieved a stable and seamless N₂O reduction throughout this period.

JM are experienced in successfully designing robust, stable containment baskets specifically customised for the burner in conjunction with the N₂O catalyst. This avoids preferential flow, which improves the performance of the abatement catalyst, helping to increase the conversion efficiency and minimise operational costs.

Fig. 9: Benefits achieved from JM gauze technical excellence improvement program

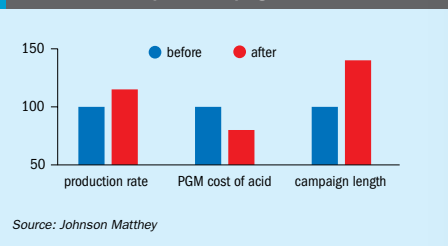
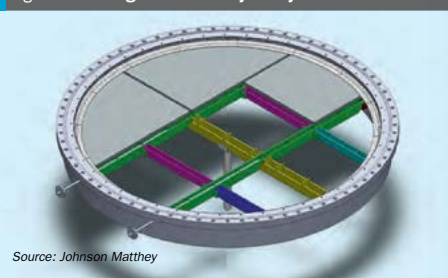


Fig. 11: JM design for secondary catalyst containment



Sabin's new customisable catalyst systems

With the implementation of its manufactured catalyst systems for nitric acid production, Sabin Metal Corp. have now created the missing piece of the puzzle, seamlessly fitting into Sabin's existing portfolio of products and services for the nitric acid industry. The move to begin the design and production of catalyst systems was obvious to Sabin. After so many years of platinum recovery gauze production, vast experience in plant cleaning (destructive and non-destructive), and decades of precious metals refining and recovery, Sabin had already covered the majority portion of the precious metals cycle in the nitric acid industry. Sabin has now seamlessly closed the loop with the manufacture of catalyst gauzes.

Sabin can create client-specific advantages through "one-off production" in manufacturing catalyst gauzes; using state-of-the-art computer design programs to configure the catalyst systems to the individual client's needs and goals, with the optimum number of catalyst gauze layers and minimum precious metal installation weight.

Fig. 12: Sabin's catalyst gauze



Sabin's efforts to optimise the catalyst system pay off not only in the form of significantly reduced precious metal losses but also bring a distinctly longer catalyst life. Sabin's clients experience the full, comprehensive service package: from the consultation on new catalyst optimisation at start-up, through the continuous analysis and assessment of the ongoing operation, all the way to the monitoring and adjustment of all related plant conditions, all designed to ensure maximised performance.

Focus on high pressure plants

Sabin's getter systems for platinum recovery focus primarily on plants of high pressure, temperatures and ammonia plant load. The development of the Sabin proprietary catalyst systems was therefore a logical progression to meet the specific needs and demanding requirements of the high pressure process.

Through its activities in platinum recovery and plant cleaning, Sabin has long been aware of the high losses of precious metals from the catalysts, especially in high-pressure plants. In addition to the purely economic impact based on the high price of precious metals, these losses also cause the catalyst to age at an early stage of the campaign, and thus cause a disproportionate increase in ammonia consumption resulting in a premature end to service life.

Even today, the usual practice is to compensate for the precious metal losses in high pressure plants by installing a higher number of gauze layers within the catalyst package. But even if ammonia is no longer present in the process gas, the catalyst gauzes continue to lose precious metal due to the remaining relatively

high oxygen partial pressure and the high process gas temperature. This traditional approach thus leads not only to an excessive use of precious metals in the catalyst pack, but also to excessive precious metal loss, often up to twice the expected value.

Sabin's catalyst gauze technology

In order to develop alternative catalyst systems that aim at both a reduction of the overall amount of precious metals used (reducing the number of gauze layers in the catalyst pack) and an extension of the service life of the catalyst, it is necessary to know the optimum number of gauzes and to employ a manufacturing technology that allows a flexible adaptation of the gauze configuration to the individual requirements of a plant.

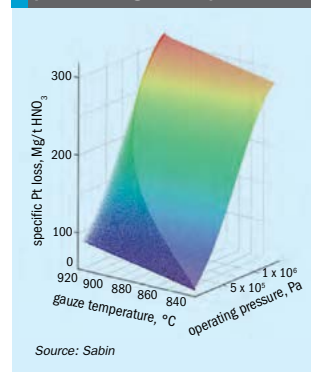
The flat-bed knitting technology used by Sabin meets these criteria in many respects. The custom manufacturing provides for a considerable range of variation in alloy, structure and specific weight of the single catalyst gauze. Sabin's technology makes it possible to manufacture the gauzes in a round shape to fit the corresponding reactor diameter. Therefore the machine is only equipped with the minimum, nominal precious metals weight and expensive cuttings in the end processing are avoided.

For the individual design of the catalyst system, Sabin makes use of state-of-the-art simulation software based on kinetic and thermodynamic principles, which indicates the progress for the mass transfer limited reaction in the catalyst package. Depending on the specific NH₃ load, the optimum number of gauzes which guarantees a 100% conversion of the ammonia used is determined from the operating pressure and the control temperature of the process. At the same time, the spe-

Fig. 13: Detail of knitting process in catalyst gauze manufacturing



Fig. 14: Specific Pt losses [mg/t(HNO₃)] as a function of operating pressure and gauze temperature



cific losses of the alloy components are calculated from the pressure and temperature dependence of their losses. The more precise the process data specified by the plant operator, the more precisely can the catalyst system be adapted to the specific process conditions.

In the final step, the total precious metals installation weight is adjusted to the targeted campaign length respectively the production volume of nitric acid. The application possibilities of the combination of state-of-the-art simulation programs and flexible manufacturing technology are manifold. Particular attention is paid to reducing the use of precious metals and especially the losses thereof in the ammonia oxidation process; however, the application can just as well be utilised to obtain a reliable prediction on extending catalyst service life or in order to plan plant capacity expansion.

CONTENTS

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

A unique alternative to RCF is born

When it comes to lining fired heaters in the petrochemical industry, refractory ceramic fibre (RCF) has been the go-to material, but it has its drawbacks. **Steve Chernack** of Morgan Advanced Materials' Thermal Ceramics business looks at how these can be mitigated and discusses a new alternative material that meets stringent health and safety requirements.

In the petrochemical world, RCF, also known as aluminosilicate wool (ASW), has long ruled as the material for lining fired heaters. It's not hard to understand why, the material possesses several attributes that ensure it performs well in the harsh environment. This includes having a low thermal conductivity and heat capacity, superior thermal shock resistance and the ability to withstand extreme temperatures. On the operation side, it is renowned for its excellent handling, longevity in service and good resistance to pollutants.

These characteristics mean RCF can extend the life of fired heaters, increase their energy efficiency and ultimately the furnace's reliability. However, despite its benefits, RCF does come with its drawbacks. Notably, the material produces crystalline silica as a by-product when fired, which can have an adverse effect on health when overexposure occurs. European Union (EU) regulations are now in place to address the health concerns of RCF and crystalline silica, requiring materials manufacturers to search for innovative solutions to protect workers and introduce furnace linings fit for the future. Under the EU Carcinogen Directive, businesses are required to use substitutes to RCF where it is technically and economically feasible to do so. However, these requirements are open to interpretation and, until recently, no material has been able to match the superior insulating performance and high melting point of RCF for use in units such as reformers and cracking heaters.

Economics, ethics and compliance

For many oil refinery operators, replacing RCF with other alternatives will increase furnace downtime, making it an unpopular

and costly option. A typical large furnace can generate product revenues of £100,000 or more per day. Clearly, many operators are having to weigh up the pros and cons between putting furnaces into extended periods of downtime that affects their bottom line and complying with EU regulations designed to further protect worker's safety.

On the other hand, operators do value their ethical approach. In a number of cases, RCF linings have been maintained beyond their expected lifespan, rather than replacing them. This is both for monetary reasons and in the hope that a viable alternative will be made available, as once replaced, the lining will typically be in use for another 15-20 years. However, this conscious decision may be taken at the expense of an efficient and high performing furnace.

Additionally, from 2020 onwards, producers and users of RCF in Europe will have to keep the amount of fibres in the workplace at <0.3 fibres/ml. Many other countries around the world have also imposed similar stringent controls. Such controls make using RCF difficult and expensive. Disposal of RCF is also costly, requiring special landfill sites due to its classification as hazardous waste.

All of this is compounded by the increasing commitment of major industrial companies and trade associations to improve 'green' standards and places the onus on the fibre industry to find viable alternatives that match or possibly exceed the performance of RCF. For example, the fibre has been more resistant to attack by alkali-based pollutants than the existing low biopersistence fibre compositions. This has prevented the replacement of RCF in many applications.

The case for operational improvement

Clearly, replacing RCF is easier said than done, and as stated earlier, there is a fine balancing act between economics, ethics and compliance. However, switching out RCF does have benefits that can be easily overlooked.

The first benefit that operators could realise is minimised downtime. When furnaces are scheduled for downtime, it usually takes at least 24 hours before the furnace is cool enough for engineers to even go in to inspect the furnace.

Then, due to the crystalline silica in RCF, before any work in or around a fired heater with an RCF lining can happen, workers must ensure that they wear a full set of appropriate personal protective equipment (PPE). This is to meet guidelines on occupational exposure limits (OELs), but also to protect against other hazards.

Just putting on and taking off the PPE alone can take quite some time, plus when undertaking bigger jobs, like repairing linings or metal tubes in the furnace, there can be additional complications. Due to OEL restrictions and the need for extra PPE, engineers cannot work for extended periods of time in the furnace. Especially in warmer climates, engineers must stop and vacate the furnace at set intervals.

Finally, if any emergency repairs are needed, operators need to call in specialists and order materials to repair the lining. Quite quickly, what looked like one day for planned downtime can spiral into days or even weeks of unplanned extended downtime where the furnace and revenue generating abilities are out of action.

Catalyst and Getter Systems As Unique as Your Plant

Your Single Source for SCS Catalyst and SRS Getter Systems Filter, Cleaning and Destructive Precious Metal Recovery

- Multi-dimensional catalyst systems, highly customizable for each plant
- Getter systems designed for high efficiency and low pressure drop
- Precious metal recovery from filters, sludges, sweeps and vacuum cleaners
- Non-destructive cleaning of plants and components including metal refining
- Destructive recovery of precious metals from redundant or decommissioned plant equipment

Related topics?

Scan Here.



Contact us for a free consultation:

evaluation@sabinmetalscorp.com



METAL CORPORATION
Nitric Acid Group

Scottsville, NY 14546 USA
Telephone: 585-538-2194

CONTENTS

What's in issue 361

COVER FEATURE 1

Combatting AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England

Tel: +44 (0)20 7793 2567

Fax: +44 (0)20 7793 2577

Web: www.bcinsight.com
www.bcinsightsearch.com

Arguably, low biopersistence linings would, to an extent, prevent these scenarios from happening for operators.

The issue of hazardous waste

RCF linings don't just pose operational problems during their working life. When decommissioned, they also require specialist disposal that adds extra costs.

For example, in Europe, disposal of waste materials in EU member states is controlled by the implementation of a number of directives. Wastes containing more than 0.1 wt-% of RCF are classified hazardous under Directive 91/689/EC. RCF wastes from manufacture and use are required to be handled and disposed of by a licensed waste contractor in an appropriately licensed hazardous waste landfill.

In practice, many RCF users have experienced significantly increased costs because local waste disposal sites are not licensed or prepared to accept hazardous wastes.

A unique alternative to RCF

While there are plenty of reasons to switch from RCF linings to a low biopersistence alternative, existing low biopersistence fibre compositions do not perform as well from a thermal perspective, nor do they resist pollutants as well in comparison.

To solve this challenge, Morgan Advanced Materials has been using its Fibre Centre of Excellence in Bromborough, UK to conduct research into RCF alternatives. Instead of attempting to make marginal gains in low biopersistence performance, Morgan has taken a different approach and revisited RCF itself.

The purpose has been to produce a new fibre with all the performance attributes of RCF but with low biopersistence and that does not form crystalline silica during use.

The result of this research and development is Superwool® XTRA™, a fibre that uniquely does not form crystalline silica. Crucially, in terms of its effect on environmental, health and safety (EHS) risks, Morgan's breakthrough material is exonerated from any carcinogenic classification under Nota Q of Directive 97/69EC.

The new insulating fibre was the culmination of almost a decade of research and development, plus almost four years of stringent testing in specified critical applications with customers.

Petrochemical operators have the reassurance that Superwool® XTRA™ meets the American Petroleum Institute's (API) standards, which guides the industry. The API's

classification temperature which is to be used for insulation outlines an obligatory 150°C (302°F) overtemperature capability on the fibre within furnaces.

Critical furnaces within the oil refinery and petrochemicals industry run between 1,200°C and 1,250°C (2,192°F and 2,282°F) and therefore require materials with a 1,400°C (2,552°F) minimum classification rating. With a classification rating of 1,450°C (2,642°F), Superwool® XTRA™ offers a performance equal, and in many cases superior to RCF.

Making the switch

For operators looking to switch away from RCF, it is important that due consideration is given.

Identifying the need for a new furnace lining is not an easy task as testing and trialling new materials can be costly per trial, not to mention furnace downtime. Ensuring lining quality is essential for protecting personnel, minimising heat loss and maintaining operational reliability.

Furnace linings which may have developed breaches over time are prone to increased thermal loss; some of which may not be visible from the outside. To minimise costs, it is recommended that testing coincides with the scheduled downtime, so fabricators can swap-out and install the new lining.

One technique for identifying thermal losses lies in the use of infrared (IR) thermography scans. By using these IR scans, engineers can keep the furnace in operation while conducting an analysis. If a hotspot is found, if possible, it is always faster and more cost-effective for the repair to be done on-line to reduce business revenue impact.

Consider engineering design carefully

To achieve maximum efficiency and longevity for the materials specified during the furnace relining process, it is critical to ensure the engineering design is appropriate.

Not only must the materials have enough studs to hold them in place, they also require sufficient joints for expansion or shrinkage. If a brick lining is installed without adequate expansion joints, the brick can grow so large that it pushes the entire lining off the furnace wall. This will lead to further inefficiency, requiring the entire process to be repeated.

Over long periods of time at temperature, fibre modules degrade resulting in

shrinkage gaps between the modules. These normally need filling with more fibre during scheduled maintenance shutdown periods. With Morgan's Superwool® XTRA™, the fibre is innovative in that it expands when heated to high temperatures, which has several benefits.

First, potential shrinkage gaps possibly visible at cool-down will close up during operation. Second, expansion properties allow Superwool® XTRA™ to be used in critical applications when mating dissimilar lining materials. These unique properties and design considerations can result in reduced downtime, minimising labour costs and maximising operational revenues.

Trust the professionals

A new furnace lining which uses the right materials, is designed to requirements and installed correctly, can last for as long as 20 years. With a vast range of furnace lining products available on the market, each requires unique installation methods, so it is important that the personnel employed to carry out the work are highly skilled and experienced.

Failing to do so can lead to complications, and ultimately result in large sums of money being lost.

Additionally, degradation of furnace insulation can result in development of hot spots on the casing that can damage equipment and cause an unsafe condition for personnel. It can also disrupt the process as operators compensate for the higher heat loss.

In turn, if these hotspots are located near the tubes within the furnace, they can be extremely dangerous, as the typical hydrocarbon process materials in these tubes are highly flammable. If the tubes break, there is a significantly heightened risk of an explosion.

Tested and proven

Superwool® XTRA™ has proven itself through considerable testing and real-world applications to be a viable alternative to RCF. In addition to its efficiency credentials, the product's improved EHS performance and lack of crystalline silica as a by-product have alleviated the worries of operators and installers at petrochemical sites.

It is available in various forms and able to provide low-biopersistence thermal insulation not just to the oil refining and petrochemical industries, but also to the iron and steel, and incineration industries. ■



Ammonia plant in Togliatti, Russia.

A flexible concept for ammonia production

PHOTO: LINDE

K. Wawrzinek and C. Brunazzi of Linde describe the benefits and features of the Linde Ammonia Concept for large-scale and small-scale ammonia production. Recent ammonia plants built by Linde demonstrate the flexibility of the concept, which can be adapted for different feedstocks, to produce co-products such as industrial gases and methanol or for small-scale modular plants.

LAC™ overview

The Linde Ammonia Concept (LAC™) is based on an inert-free ammonia synthesis loop, which reduces loop size and eliminates the need for purge gas cleaning and recovery. In principle the ammonia loop is fed with a gas mixture of clean hydrogen and nitrogen. The N₂ is produced in a standard nitrogen production unit (air separation unit). The H₂ is generated in a state-of-the-art hydrogen production unit based e.g. on the steam reforming of natural gas. The concept is very flexible, as the hydrogen can also be produced from heavy feedstocks via gasification (LAC.H) and, if CO₂ is required as an additional product, e.g. for downstream urea production, the process can be easily adapted to match the required NH₃ to CO₂ ratio.

Production of ammonia from hydrogen-rich off gas streams (LAC.L3) originating e.g. from chemical plants is the most direct route to ammonia by applying and adapting some of the core process blocks of the

LAC™ product family. This concept has been implemented successfully and achieves the lowest production cost, as no dedicated syngas generation unit is required.

Fig. 1 shows a simplified comparison of the major process steps of the Linde Ammonia Concept for light feedstocks with the process set-up of a conventional ammonia plant.

The Linde Ammonia Concept for light hydrocarbons (LAC.L1), consists essentially of a hydrogen plant with a single stage isothermal shift reactor (ISR), pressure swing adsorption (PSA), standard nitrogen unit, and a high efficiency ammonia synthesis loop as shown in Fig. 1. After the feed treatment a Linde high efficiency top-fired primary reformer is applied for the conversion of hydrocarbons into syngas containing mainly H₂ and CO. The concept avoids introducing air to the process, which keeps the inert level at a minimum, depending on the feedstock composition only, and reduces

the size of the syngas cooling chain compared to a conventional ammonia process. Pure nitrogen from the N₂ generation unit is introduced directly upstream of the ammonia syngas loop, thereby avoiding loading the syngas generation plant.

In order to increase the hydrogen yield, the CO of the syngas is isothermally shifted in a single step reactor, Linde's coil wound isothermal reactor, minimising the catalyst volume. The heat produced during the shift reaction is used to vaporise the recycled process condensate, avoiding the need for a process condensate treatment unit see also Fig. 4).

The oxygen containing components and CH₄ are removed from the system with the help of a pressure swing adsorption system, eliminating the need for energy intensive CO₂ removal and catalytic methanation. The pure H₂ is then mixed with pure N₂ upstream of the ammonia synthesis loop. The purity is adjusted so that a purge free loop can be applied, and hence a dedicated purge gas separation unit for recovery of H₂ becomes obsolete.

The ammonia synthesis loop requires only pure hydrogen and nitrogen and hence is easily adaptable to different feedstocks, depending on what is available at the given site. Inert-free gas generation allows additional products to be derived from the syngas, i.e. polygeneration schemes are inherently easy to realise. Compared with the conventional ammonia process route, the LAC.L1 process has the following features:

CONTENTS

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

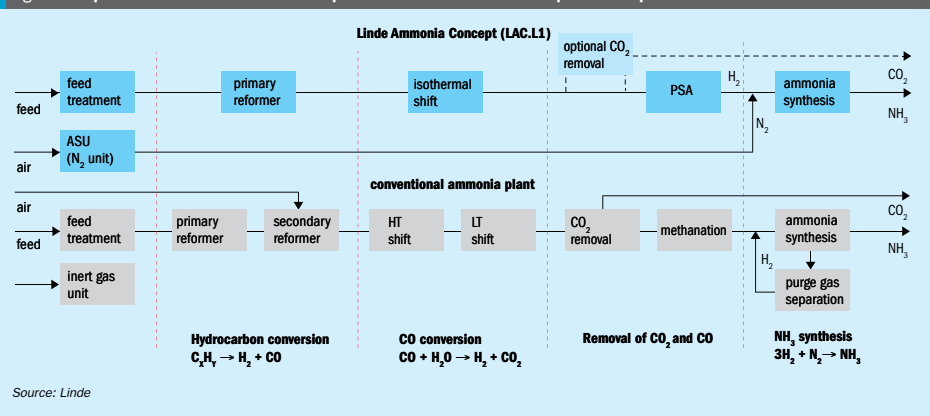
Southbank House, Black Prince Road
London SE1 7SJ, England

Tel: +44 (0)20 7793 2567

Fax: +44 (0)20 7793 2577

Web: www.bcinsight.com
www.bcinsightsearch.com

Fig. 1: Comparison of Linde Ammonia Concept with conventional ammonia production process



- generation of inert free synthesis gas gives important savings in the synthesis loop and avoids a purge gas purification step;
- elimination of three catalytic process steps (secondary reforming, HT shift conversion and methanation), reducing the total catalyst volume to approx. 50% of that in a conventional plant;
- inert-free syngas loop allows smaller reactor size;
- CO_2 removal is not required for NH_3 production, but may be optionally applied, if useful;
- elimination of a syngas drying system (ASU and PSA deliver dry products);
- process condensate treatment is eliminated by routing the condensate directly back to the isothermal shift reactor producing process steam (Fig. 4);
- inert-free syngas can be extracted to serve other co-products such as CO or methanol;

- pure hydrogen can be extracted directly;
- the LAC is a very direct route to ammonia resulting in a reduced start-up time and substantial savings in lifecycle costs;
- reduced equipment and line sizes leverage modularisation potential for small and medium size plants.

Linde has proven experience in the design and operation of the Linde Ammonia Concept and can deliver both the design and full EPC of large-scale facilities. The execution of modularised units e.g. for hydrogen plants and nitrogen generation units is also proven at multiple sites, an experience which can be extended to modularised small-scale ammonia plants.

Recent projects

Table 1 provides an overview of Linde plants based on the Linde Ammonia Concept. Flexibility in feedstock and co-product

generation are valuable attributes which are frequently and readily applied.

Polygeneration in Al Jubail

The first in a series of recent Linde Ammonia plants was built in Al Jubail, Saudi Arabia, a polygeneration plant serving the chemical complex of Sadara with NH_3 , CO, and H_2 (see Fig. 2).

The flexibility of supplying these three products with one syngas generation unit is only possible if an inert-free syngas is produced such as that realised in the Linde Ammonia Concept.

Due to the high demand of CO, no shift conversion has been installed. The CO is purified in a cryogenic methane wash unit, which also delivers raw H_2 for the final purification in the PSA. Hydrogen can also be imported under certain conditions. Due to the highly integrated scheme, internal product balancing is possible providing flexibility resulting in more efficient and economic plant operation.

Fig. 2: Plant configuration for polygeneration of NH_3 , CO, and H_2 , in Al Jubail at Sadara, start-up 2016

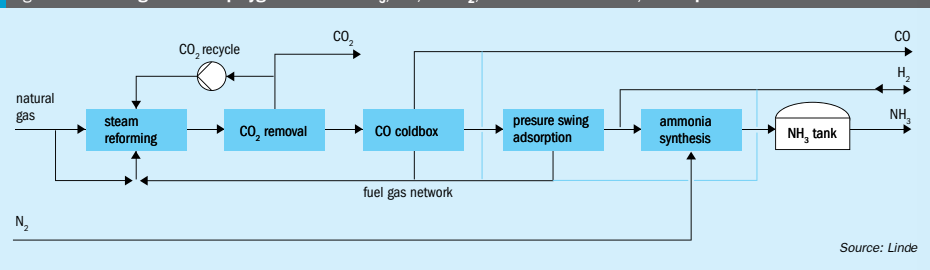
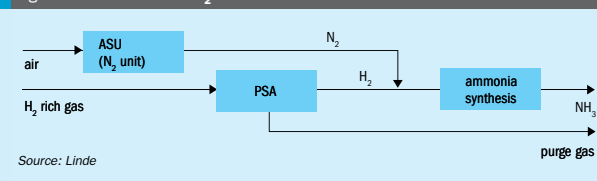


Table 1: An overview of Linde plants based on the Linde Ammonia Concept

Project	Country	Capacity (t/d)	Year of start-up	Feedstock	Co-products	Concept
Bharuch	India	1,350 (revamped 2000)	1981	oil	CO, methanol	LAC.H for heavy feedstock
Dalian	China	1,000	1996	oil	-	LAC.H for heavy feedstock
Vadodara	India	1,350	1998	NG + naphtha	-	LAC.L1 for light feedstock
Moura	Australia	230	1999	NG	-	LAC.L1 for light feedstock
Phosphate Hill	Australia	600	1999	NG	-	LAC.L1 for light feedstock
Jilin	China	1,000	2003	Oil	-	LAC.H for heavy feedstock
Daqing	China	250	2005	NG	-	LAC.L1 for light feedstock
Al Jubail	Saudi Arabia	615	2016	NG	CO, H_2	No iso-shift due to CO product
Togliatti	Russia	1,340	2017	NG	H_2	LAC.L1, H_2 extraction
Rock Springs	USA	confidential	2017	NG	-	LAC.L1 for light feedstock
Salalah	Oman	1,000	2020	MeOH purge gas	-	LAC.L3, no syngas generation due to H_2 -rich feedstock

Source: Linde

Fig. 3: LAC.L3 based on H_2 -rich feedstock



Ammonia based on H_2 -rich feed gas in Salalah

The simplicity and adaptability of the Linde Ammonia Concept is demonstrated by the Salalah plant which uses methanol off-gas as feed (see Fig. 3). Because the methanol off-gas is already rich in hydrogen, no syngas generation unit is required.

This type of plant – LAC.L3 – is by far the most economical way of producing

ammonia, because of the low capex as it eliminates the most energy consuming step in ammonia production – syngas production from a hydrocarbon.

Operational experience in Togliatti

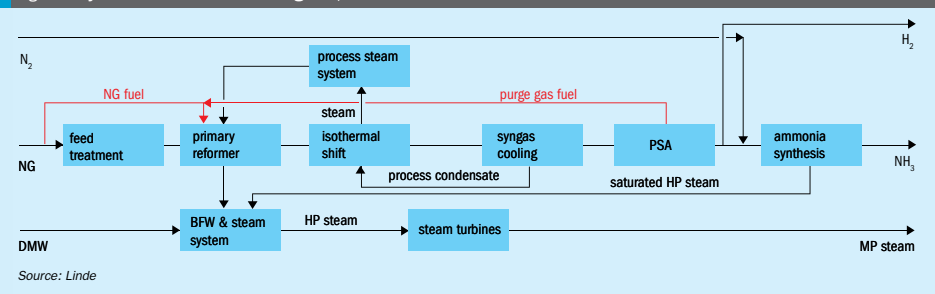
The Linde ammonia plant in Togliatti, Russia, started up in 2017 and is operated by Linde Azot Togliatti, a joint venture of Kuibyshev Azot with Linde Gas. It is designed

based on the process scheme for the LAC.L1 as shown in Fig. 1. One additional feature is the direct extraction of very pure hydrogen upstream of the ammonia synthesis loop. This simple feature enables the plant to produce both hydrogen and ammonia (see Fig. 4). During normal operation a small amount of hydrogen is exported in addition to the ammonia, but the plant has the flexibility to provide a higher hydrogen export flow. In addition, excess steam is exported to the client's steam system. Nitrogen is supplied from an OSBL source.

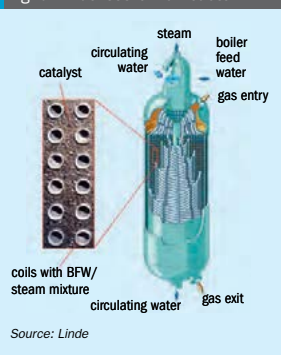
Iso-shift reduction and operation

Before bringing the iso-shift-reactor into operation, the catalyst must first be reduced to make it active and selective for the CO shift conversion reaction. Typically, the reduction of copper catalysts is a critical process, as it is an exothermic reaction and the maximum allowable temperature

Fig. 4: Major blocks of LAC Plant in Togliatti, Russia

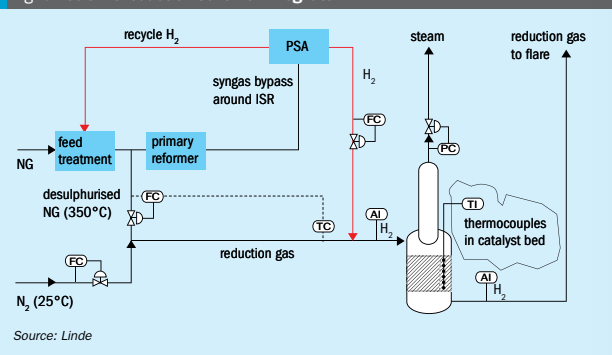


5 Fig. 5: Linde isothermal reactor



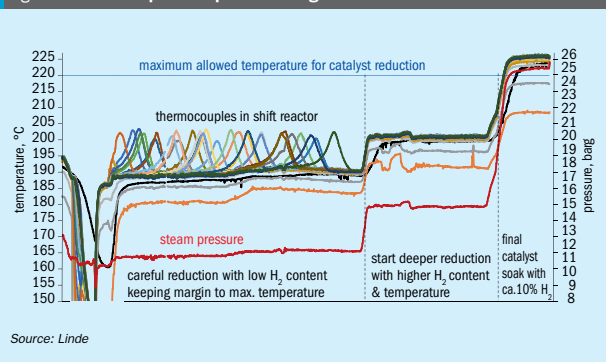
Source: Linde

6 Fig. 6: Iso-shift reduction scheme in Togliatti



Source: Linde

7 Fig. 7: Iso-shift temperature profiles during reduction



Source: Linde

is limited to values well below those during normal operation. However, an isothermal reactor makes the process safer, protecting against overheating simply due to the cooling effect of the steam. The principle design of the Linde isothermal reactor is shown in Fig. 5. Cooling of the catalyst takes place with boiling water inside the tubes of a coil wound bundle.

The temperature is largely controlled by the temperature of the boiling BFW, and hence can be adjusted via the pressure control on top of the integrated steam drum. For catalyst reduction the pressure needs to be decreased to control the temperature peaks, which occur during the reduction process. As can be seen in the schematic in Fig. 5, the cooling density in the reactor is very high, and the greatest distance between a catalyst pellet and the wall of a cooling tube is less than the tube diameter. This results in good cooling throughout the

entire catalyst bed, reducing the risk of hot spots and premature aging of the catalyst.

Fig. 6 shows the catalyst reduction procedure carried out in Togliatti. The reduction is carried out using low pressure for both the reducing gas and the steam pressure, the latter to assure the correct cooling temperature level.

The inlet temperature of the reducing gas is adjusted by mixing hot natural gas with low H₂ content with cold nitrogen from battery limits. At the start the hydrogen content must be kept very low to avoid strong temperature peaks, and hence the concentration must be monitored thoroughly throughout the full reduction sequence.

Fig. 7 shows the temperature peaks due to reduction and the steam pressure. The total reduction took some 60 hours. Afterwards, the temperature and steam pressure could be adjusted slowly according to the needs of production.

During the test run the temperatures in the reactor were beneficially low due to the good cooling and the low pressure drop over the syngas production allowing a lower steam pressure. This is useful, because with lower temperature the CO slip is reduced and therefore the hydrogen yield is increased. Furthermore, the lifetime of the catalyst is increased, because sintering (the main aging mechanism) is reduced at low temperatures.

Once the steam pressure control was in automatic mode, the operation of the shift reactor ran smoothly and did not require attention. The temperatures were stable irrespective of any load changes. This makes operation of the plant with a high hydrogen yield easy and safe.

The PSA system is designed such that operation is possible without iso-shift, i.e. with higher CO content in the PSA feed gas. On the one hand this is required for the reduction procedure, because the PSA must work under these conditions without the shift reactor. On the other hand, it also makes the operation of the plant easier, even if the CO slip increases with ageing of the shift catalyst.

Steam and turbine system

Typically, the large compressors are turbine driven with HP steam, which is generated from the steam reformer and the syngas cooler in the ammonia synthesis loop. This is also the case for the plant in Togliatti. There are two major compressors in the plant in Togliatti, i.e. the syngas compressor and the refrigeration compressor.

Fig. 8 shows an overview of the steam system, indicating four different steam levels: 112 barg, 50 barg, 5 barg and 0.2 barg. HHP with approx. 112 barg is used to drive the syngas compressor turbine and an



Bringing Life To Your Fertilizer With Colours



ANTICAKING AGENT



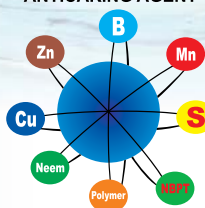
DUST SUPPRESSOR



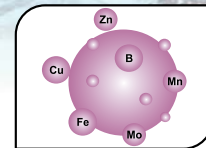
COLOURING AGENT



DIATOMACEOUS EARTH / REACTIVE SILICA



Micronutrient Coating Technology



MICRONUTRIENT/TRACE ELEMENT FIXER



ANTIFOAM FOR PHOSPHORIC ACID



FROTH FLOTATION AGENT



HARDENING AGENT

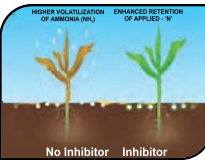


NEEM CAKE



NEEM OIL

FREE FLOWING AND DUST FREE FERTILIZERS



**Urease Inhibitor (NBPT)
Nitrification Inhibitor (DMPP)
Neem Oil**

BRIGHT Coloured Fertilizers

GLOBAL PRODUCTION FACILITIES



INDIA • UAE
BRAZIL • SPAIN



NEELAM AQUA & SPECIALITY CHEM (P) LTD.

701, North Avenue, Road No. 9A, V.K.I. Area, Sikar Road, Jaipur-302013 (INDIA)
Ph. : +91-141-2333718, 2333418 • Fax : +91-141-2331102 • Mobile : +91-9829069545
Email : mkmathur@neelamaqua.com, support@neelamaqua.com,
www.neelamaqua.com

- CONTENTS
- What's in issue 361
- COVER FEATURE 1
- Combating AN misuse
- COVER FEATURE 2
- High temperature hydrogen attack
- COVER FEATURE 3
- Green ammonia
- COVER FEATURE 4
- Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019



Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

HP pressure of 50 barg pressure is required for process steam. The major part of the process steam is produced from process condensate in the iso-shift reactor and the cold part of the syngas cooler downstream of the steam reformer. The required make-up to HP level is provided by extraction from the syngas compressor turbine. The rest is used in the condensing stage.

Furthermore, the HP level serves the refrigeration compressor driver, which also has an extraction at MP level (27 barg) for export to battery limits, representing the balance of the steam system. The LP users are served from the HP level via a let-down station.

The described set-up requires stable steam production and an HHP level prior to start-up of the syngas turbine. The start-up trends of the syngas turbine are shown in Fig. 9.

It can be seen that the turbine start-up is a fast procedure, with only about 20 min warm up idling, and then fast ramp up through the critical frequencies to minimum operating speed (MOS) must be assured. Having reached this speed, extraction is automatically opened slowly and the pressure control can be used. After less than four hours from cold condition, speed control and suction pressure control of the compressors are enabled. Operational experience with this system is very good and it can be seen that the control is comfortably faster than required for load changes. The limiting factor is clearly the ramp rate of the catalytic processes, i.e. the steam reformer and ammonia synthesis loop.

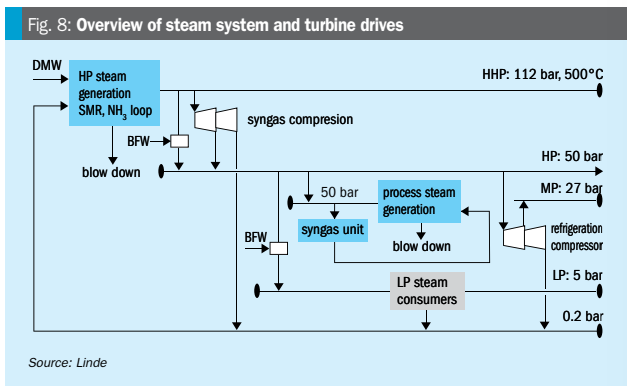
Firing flexibility

During normal operation PSA purge gas is the main fuel and natural gas is used as trim fuel to adjust the temperature at the steam reformer outlet. This is the typical usage of the fuels. It is important to have a reliable and flexible design for the firing system of the steam methane reformer which is at the heart of the syngas generation.

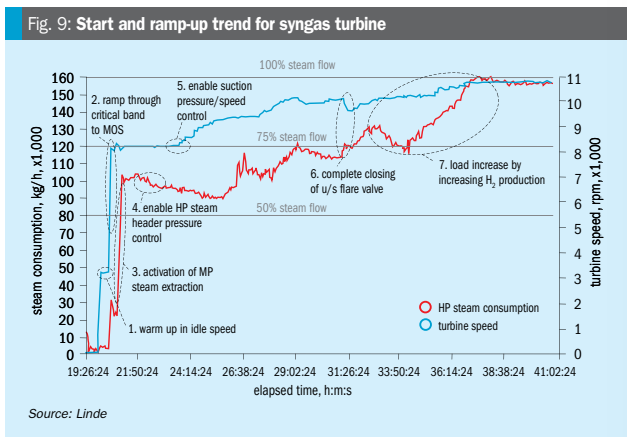
There are two categories of operational scenarios for which additional effort for the firing system can be advantageous for the plant economics:

- plant start-up;
- upset cases.

During the start-up sequence of the different process units and when all units are in operation until the products are on specification different gases are sent to flare. This period has to be kept as short as



Source: Linde



Source: Linde

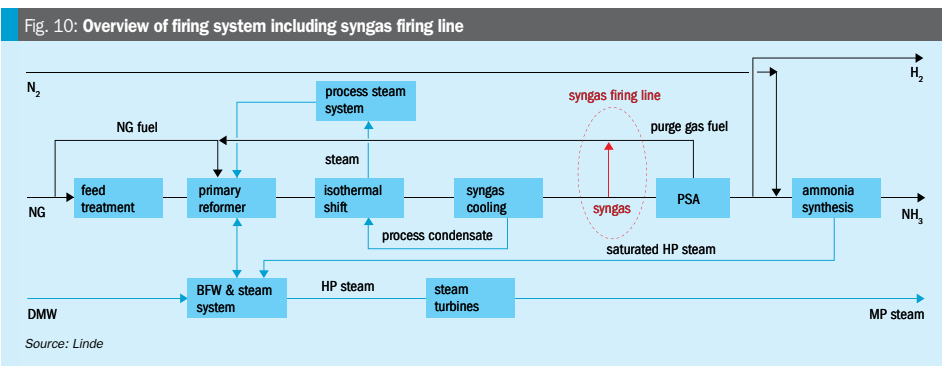
possible as it consumes utilities, but does not produce revenues. For example, during start-up the PSA requires a minimum feed gas flow and quality before it can be taken into operation. At that time the steam reformer is already running at significant load consuming natural gas feed and fuel. However, flexibility in the fuel system can contribute to a reduction in cost during that period. This flexibility is added as indicated in Fig. 10.

In the Linde Ammonia Concept the syngas upstream of the PSA can easily be introduced as make-up fuel instead of natural gas, because the characteristics of the syngas are similar to the ones of the PSA purge gas. Only one additional line with a fuel valve and meter is required and the respective implementation for burner design and control logics.

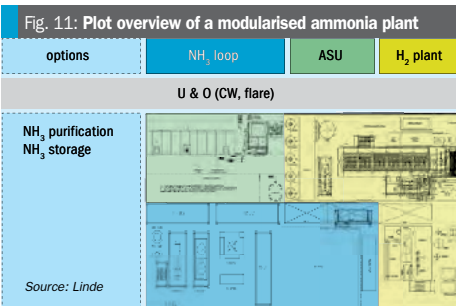
Besides start-up, this feature can also be used during the following situations:

- PSA trip;
- catalyst reduction of ammonia synthesis catalyst (only limited H₂ from PSA is required, but the SMR must run at significant load to serve the compressor turbines);
- ammonia plant trip;
- NG/PSA purge gas fuel problem

During all of these situations, syngas firing can be used to save on fuel costs. Furthermore, the stability of the SMR firing system is improved. Avoiding a SMR trip, which results in a longer downtime for production of ammonia and hydrogen and also contributes to ageing of catalyst and reformer tubes is therefore highly beneficial.



Source: Linde



For these reasons, it is advisable to install such a feature to the fuel system to improve economics during start-up and upset conditions.

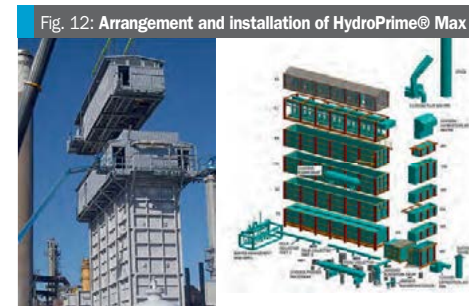
Plant performance

Plant performance was proven in a 72-hour performance test run. The product quality (99.9 wt-% NH₃ and 99.9 vol-% H₂) and the respective capacities were met or even exceeded. Furthermore, all emission values have been met reliably.

The energy consumption achieved during the test run was slightly better than expected due to a higher steam export and lower power consumption, in summary, below 6.9 Gcal/t NH₃, i.e. approx. 1% below the calculated value. This figure was also maintained in operation after the test run.

Modularisation for small-scale ammonia plants

The ammonia market shows increased interest not only in large-scale production facilities, but also in smaller plants for production close to the application. This is triggered by



several factors, amongst others by regionally available feedstocks and increasing transport cost due to rising insurance premiums.

To address requests for small-scale plants, Linde has developed a modular design for ammonia plants smaller than 300 t/d. The design criteria for small plants is different to those for mega facilities. For small plants the capital cost is even more critical, whereas the operational cost is not as important as for larger plants. This is reflected in Linde's process design which:

- adapt the process concept to minimise the number of equipment items;
- apply standardised plant components;
- design modules to minimise construction work and time on site

The core components of the ammonia plant are shown on the coloured plot in Fig. 11. Hydrogen is generated in a modularised hydrogen plant using Linde's HydroPrime® steam reformer, which is already under execution in four projects in Sweden, Russia, USA, and Asia. In the hydrogen unit modularised Linde products are combined: steam reformer, pressure swing adsorption and cooling chain modules. A modularised

unit is also applied for nitrogen generation. The ammonia synthesis loop is designed with less equipment than the typical LAC to minimise costs and plot space. The LAC is beneficial for modularisation, because the inert-free design keeps equipment and line sizing at a minimum. If required, the three core units can be supplemented by modular units for utilities, cooling water, ammonia purification, and ammonia storage.

By simplifying the process, applying modularised standard units with maximum prefabrication, the installed cost per tonne of ammonia is not significantly higher than for large-scale plants. However, the energy efficiency of large-scale plants cannot be matched because there is less heat integration due to the lower equipment count.

Fig. 12 shows the module arrangement and installation of the HydroPrime® Max steam reformer. Due to the high degree of modularisation site work can be reduced.

The experience gained from the modularisation of the ASU, HydroPrime® Max and PSA has been transferred to the concept for small-scale ammonia synthesis loops which apply the Linde Ammonia Concept. ■

CONTENTS

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Advertisers' index

Editor: RICHARD HANDS
richard.hands@bcinsight.com

Technical Editor: LISA CONNOCK
lisa.connock@bcinsight.com

Contributors:
ALISTAIR WALLACE
alistair.wallace@argusmedia.com

MIKE NASH
mike.nash@ihs.com

Publishing Director: TINA FIRMAN
tina.firman@bcinsight.com

Subscription rates:
GBP 425; USD 850; EUR 655

Subscription claims:
Claims for non receipt of issues must be made within 3 months of the issue publication date.

Sales/Marketing/Subscriptions:
MARLENE VAZ

Tel: +44 (0)20 7793 2569
Fax: +44 (0)20 7793 2577
marlene.vaz@bcinsight.com
Cheques payable to BCInsight Ltd

Advertising enquiries:
TINA FIRMAN
tina.firman@bcinsight.com
Tel: +44 (0)20 7793 2567

Agents:
Japan: (also subscription enquiries)
KOICHI OGAWA

O.T.O. Research Corporation
Takeuchi Building
1-34-12 Takadanobaba
Shinjuku-Ku, Tokyo 169, Japan
Tel: +81 3 3208 7821
Fax: +81 3 3200 2889

Previous articles from Nitrogen+Syngas and Nitrogen & Methanol from 1996 to the present are available digitally in PDF format. To make a purchase, or for a list of available articles, please see: www.bcinsight.com

Copyright: Issued six times per year, or bi-monthly. All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means – electronic, mechanical, photocopying, recording or otherwise – without the prior written permission of the Copyright owner.

ISSN: 1750-6891

Design and production:
JOHN CREEK, DANI HART



Printed in England by:
Buxton Press Ltd
Palace Road, Buxton, Derbyshire, SK17 6AE

© 2019 – BCInsight Ltd

BCInsight

Published by: BCInsight Ltd
China Works, Unit 102,
100 Black Prince Road,
London SE1 7SJ, UK
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

Advertiser	Page	Website
Casale	9	casale.ch
Casale	25	casale.ch
Eurotecnica Contractors and Engineers	5	eurotecnica.it
Eurotecnica Contractors and Engineers	OBC	eurotecnica.it
Heraeus	13	heraeus.com
Integer Research Ltd / Argus Media Co	11	argusmedia.com
IPCO Germany GmbH	29	ipco.com
Johnson Matthey	IFC	matthey.com
Nitrogen+Syngas 2020 Conference	IBC	crugroup.com/events
Neelam Aqua & Speciality Chem (P) Ltd	51	neelamaqua.com
Sabin Metal Corporation	45	sabinmetal.com
Tecnicas Reunidas Espindesa	37	espindesa.es
Tecnimont Group	33	mairetecnimont.com
Ventilatorenfabrik Oelde GmbH	15	venti-oelde.com

Next issue: November/December 2019

- Online urea process control and analysis
- Stabilised urea fertilizers
- Carbon pricing and the siting of future syngas capacity
- The global market for urea – will oversupply continue
- Chemicals as energy carriers

Closing date for advertisement space booking is 25 October 2019
For further information and to book advertisement space contact:
Tina Firman, Publishing Director: tina.firman@bcinsight.com
Tel: +44 (0)20 7793 2567 Fax: +44 (0)20 7793 2577

33rd

Syngas | Ammonia | Urea | Nitrates | Methanol | GTL | Hydrogen



Nitrogen + Syngas 2020

17-19 February 2020 • World Forum, The Hague, The Netherlands

Maximising efficiency through innovation and knowledge sharing

“ Nitrogen + Syngas is the conference for future business. ”
Omar Takrouni, President, Jubail Fertilizer Company (Al Bayroni)

About this Event:

CRU's Nitrogen + Syngas conference is a respected technical event for the global community. For 33 years it has provided a platform for technical professionals across the industries to meet, network, and learn about the latest developments in operations, technology, process and equipment.

Every year, hundreds of producers, licensors, and materials and equipment providers attend to ensure they have knowledge, understanding and professional connections required to improve their production, maximise profitability, and maintain safe, reliable, and environmentally responsible plant operations.

Whether you are investing in a new plant, revamping an existing plant, or maintaining your plant to achieve optimal production, safety and environmental performance, Nitrogen + Syngas is a 'must-attend' event.

Event Highlights:

50+ technical papers and presentations

Operators – Pay just €700 (+VAT)

2019 attendance: 750+ professionals representing

12+ hours of certified technical training

80+ world-class exhibitors

290+ companies and

50+ countries

Sponsors:



Official publications:



Supporters:



For more information and to book your place, visit www.nitrogensyngas.com

CONTENTS

What's in issue 361

COVER FEATURE 1

Combating AN misuse

COVER FEATURE 2

High temperature hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com

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



Melamine...

is a key presence in our lives!

Euromel® Melamine is extensively used in the new convention centres for its superior performance. Sound absorption panels, doors and sidewalls rely on melamine for insulation, fire resistance and low weight.

Euromel® is the trademark for melamine produced at plants licensed, engineered and implemented by Proman Group's Eurotecnica Company, the leading melamine technology provider since 1978.

Contact us to find out more.

www.euromel.com



Don't forget the next
issue of **Nitrogen+Syngas**
November/December 2019



CONTENTS

What's in issue 361

COVER FEATURE 1

Combatting
AN misuse

COVER FEATURE 2

High temperature
hydrogen attack

COVER FEATURE 3

Green ammonia

COVER FEATURE 4

Nitric acid
catalyst gauzes

NITROGEN+SYNGAS
ISSUE 361
SEPTEMBER-OCTOBER 2019

BCInsight

Southbank House, Black Prince Road
London SE1 7SJ, England
Tel: +44 (0)20 7793 2567
Fax: +44 (0)20 7793 2577
Web: www.bcinsight.com
www.bcinsightsearch.com