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September | October 2020

nitrogen + syngas

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Ammonium nitrate markets

CO₂ as a feedstock

Solving nitric acid problems

MEG from methanol



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NITROGEN+SYNGAS
ISSUE 367
SEPTEMBER-OCTOBER 2020

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Cover: Ammonium nitrate storage silo, Austin Powder Company, Roseburg, Oregon, US. TFoxFoto/Shutterstock.com



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“Not again...”



It's not a very worthy thought, I'm afraid, but I must admit it was my first reaction on seeing the terrible pictures from Beirut on August 4th. The explosion that ripped through the centre of the historic and much troubled Mediterranean city was captured from many different smartphone cameras, and watching the expanding vapour cloud from the supersonic shockwave, and witnessing the sheer size of the explosion, it seemed immediately evident to me that it had to be a high explosive responsible, not the fireworks that could be glimpsed sparkling beforehand in the smoke from the burning warehouse. The rising cloud of orange-brown nitrogen dioxide that followed the blast was the clincher – it looked like it was ammonium nitrate yet again.

Tolstoy wrote in Anna Karenina that: “all happy families are alike, but every unhappy family is unhappy in its own way”. It seems to be a similar story for ammonium nitrate. Safe handling follows some simple basic rules and procedures which are the same everywhere: keep it dry and uncontaminated; don't store too much in one place, and separate the pallets/bins with an air gap where possible; avoid organic materials in direct contact with the AN; make sure there are adequate fire detection and prevention facilities; and above all make sure it is not stored too closely to densely populated areas. Via these means, millions of tonnes of AN are manufactured, traded, shipped and stored safely around the world every year.

Conversely, each accident reveals a different, seemingly implausible set of unusual circumstances, poor decisions and oversights which all combine to produce disaster. Consider the chain of events that led to the Beirut explosion: a Moldovan-flagged ship owned by a Russian living in Cyprus was chartered to carry ammonium nitrate from Georgia to Mozambique. It developed mechanical troubles that forced a stopover in Beirut for repairs. The ship was impounded for – ironically – safety and seaworthiness violations. The cargo was offloaded and stored in a port-side warehouse – so far, mere happenstance, but nothing out of the ordinary. But then there followed years of legal limbo as the owner abandoned interest in the vessel (which subsequently sank in the harbour), and the AN simply sat, forgotten, in the hot, humid warehouse, for seven long years, slowly degrading, while a dysfunctional government ignored messages from customs officials querying what to do with it, until a stray spark – possibly from welding – ignited flammable material that caused the ware-

house to burn down with 2,750 tonnes of by now probably unstable AN inside it.

It is impossible to legislate for every eventual-ity. In Tianjin in 2015, customs officials had been bribed to allow the illegal storage of 800 tonnes of AN in a port warehouse – amongst many other chemicals, some still unidentified, but, according to the official accident report, including nitrocellulose which auto-ignited and started the fire that eventually led to an explosion that killed 165 people. But often there are steps which could and should have been taken which would have prevented disaster. At West, Texas, where 240 tonnes of AN were stored legally but not safely, the US Chemical Safety Board investigation concluded that the explosion that killed 15 in 2013, including ten first responders: “resulted from the failure of a company to take the necessary steps to avert a preventable fire and explosion, and from the inability of federal, state and local regulatory agencies to identify a serious hazard and correct it.” At Beirut, all it would have taken is someone with the nous and authority to have ordered the AN to be moved to a safer location outside of the city. That oversight has cost at least 180 people their lives.

On the face of it, it may not appear as though Beirut has many lessons for the ammonium nitrate industry. It would be very easy to dismiss it as a consequence of a state on the brink of failure where corruption is endemic. But the letters published online after the event from customs officials to courts and judges show that it was also a consequence of a failure to listen to the well-founded concerns of those at the coalface who knew that this situation was dangerous, but who were powerless to do anything about it. All good organisations need to make sure that those kinds of warnings are not ignored. And when making risk assessments, it's worth remembering that ostensibly unlikely combinations of circumstances can and do happen, and that it is worth some thought as to how to guard against them doing so. ■

Richard Hands, Editor



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Price trends



MARKET INSIGHT

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

NITROGEN

Ammonia production has been reduced in Trinidad, Egypt, Indonesia and the Middle East over the past two months, with much of this capacity expected to stay offline in August and into September. This series of production cuts has balanced out the supply length that has dominated the market this year, pulling prices to lows not seen since mid-2016.

Tighter supply is being reported east of Suez until September. F.o.b. prices in the Middle East have gained \$7-8/t over the course of the past month, while southeast Asian f.o.b. prices firmed by \$14/t. But the options for buyers in east Asia from the Americas has kept prices not trending in any particular direction in delivered markets, and competition for September cargoes means that lower c.fr offers are emerging from Chinese buyers. Indian demand is steady and firm downstream prices will keep imports at 200,000-250,000 tonnes/month in the near term.

West of Suez, ammonia demand for August will remain depressed, reflecting the off-season and reduced industrial consumption. While the situation is starting to improve in Europe, import demand is unlikely to recover until at least September.

Urea prices bottomed out in May and have continued to rise since then, driven by record demand from India. India has ten-

dered to buy urea four times in the past two months due to a rise of 3.7 million tonnes in sales in the April-July period, an increase of 48%. The pull from India has singlehandedly lifted the urea market. Prices for granular urea from Egypt have risen from a low of \$205/t f.o.b. in May to \$280/t f.o.b. in early August. Middle East granular urea has moved up from about \$210/t f.o.b. to \$270/t f.o.b. in the same period. Chinese urea prices, which normally ease in Q3 at the end of the summer season, have instead increased to \$270/t f.o.b.

Other markets have also seen prices moving up. Brazil is the main focus in the western hemisphere, and buyers have seen increases of \$60-70/t since early June. The onset of the peak shipment period and competition for tonnage from India mean that buyers have little option but to pay up. Some buying has also taken place from Egypt and Algeria to cover short positions taken for July-September shipment to Europe, entailing significant losses for the traders concerned.

Indian demand will continue to support the urea market through September, but prices have risen rapidly and a correction is possible if Indian buying slackens in Q4. Buyers in other markets are also showing reluctance to accept continually rising prices – recent business has mainly involved traders taking long positions rather than making c.fr sales.

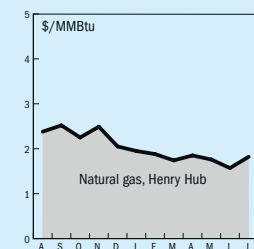
Table 1: Price indications

Cash equivalent	mid-Aug	mid-Jun	mid-Apr	mid-Feb
Ammonia (\$/t)				
f.o.b. Black Sea	178-205	180-200	210-225	220-223
f.o.b. Caribbean	160-175	175-190	200-215	215
f.o.b. Arab Gulf	230-260	180-200	200-220	215-250
c.fr N.W. Europe	210-250	220-245	250-281	250-285
Urea (\$/t)				
f.o.b. bulk Black Sea	230-253	195-215	215-228	212-215
f.o.b. bulk Arab Gulf*	264-285	219-245	226-245	222-235
f.o.b. NOLA barge (metric tonnes)	230-240	213-218	263	269
f.o.b. bagged China	275-295	242-263	250-283	240-245
DAP (\$/t)				
f.o.b. bulk US Gulf	353-390	293-304	297-323	300
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	157	163-165	172	146-148

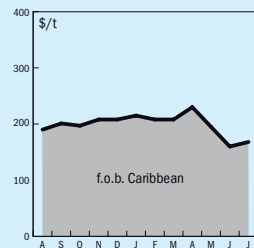
Notes: n.a. price not available at time of going to press. n.m. no market. * high-end granular.

END OF MONTH SPOT PRICES

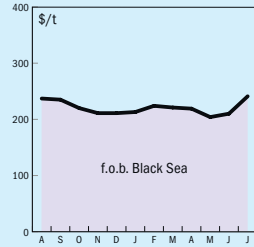
natural gas



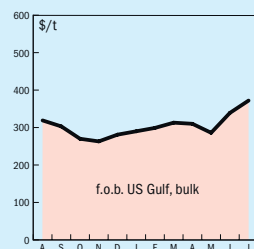
ammonia



urea

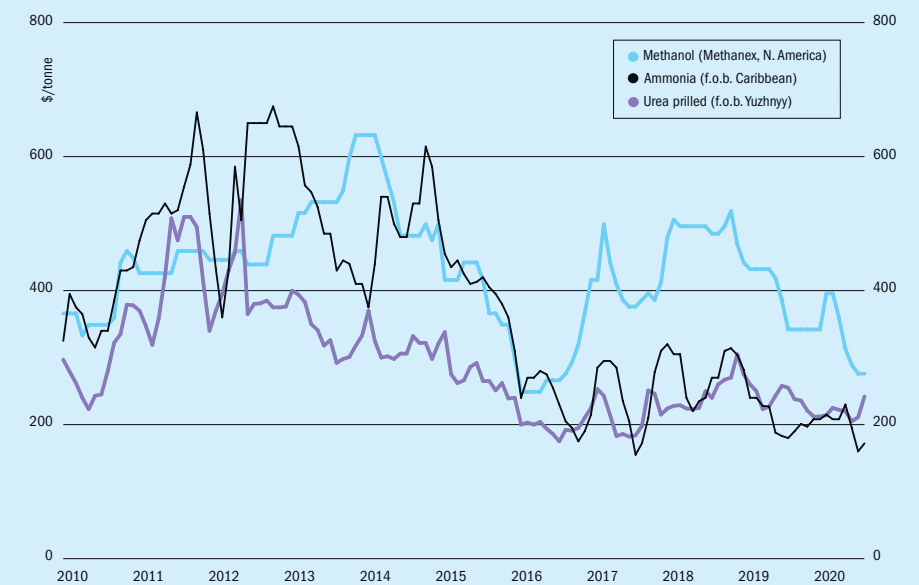


diammonium phosphate



Market Outlook

Historical price trends \$/tonne



Source: BCInsight

AMMONIA

- The ammonia market continues to be oversupplied, and prices have dropped to historically low levels. Yuzhnyy rates dropped to \$175/t f.o.b. in July. In spite of shutdowns in Trinidad and elsewhere, demand remains sluggish and recovery from the Covid epidemic is patchy, especially in the US.
- Industrial demand is picking up in Asia, but remains below normal values for the time of year.
- Although this is usually a slack period for US fertilizer ammonia demand, it is expected that the US will need to start buying ammonia again in September for the Fall application period, which may lead to a short-term deficit there.
- Likewise, many producers have stated that they will not bring plants back online until the market has staged a significant price recovery, so the potential for higher pricing is in place for the fourth quarter. But demand from the industrial market remains weak, and is unlikely to recover until 2021.

UREA

- The urea market has been lifted by a huge increase in buying by India, the world's largest importer. A good monsoon season has led to higher than expected consumption in India and could see record imports of urea in 2020. Indian domestic urea sales reached 5 million tonnes in July, and Nutrien reports that its sales from April to July 2020 into India were 50% up on the same period for 2019.
- MMTC's tender for 1.15 million tonnes went unfulfilled to the tune of 450,000 tonnes, and RCF tendered only 11 days later. More urea is expected to be purchased in September.
- Brazil has also been buying strongly, and together with India has lifted prices by more than \$30/t.
- However, there are some signs that the rally in urea prices may be peaking, with some resistance to higher prices in some markets. A slackening of Indian demand or an increase in Chinese sales into India could lead to a price correction during 4Q 2020.

METHANOL

- Methanol demand improved during 2Q 2020 in China, by about 4% on 1Q, with increased demand in both fuel and chemical applications as the country recovered from Covid. MTO demand was particularly strong. However, although China represents half of global methanol consumption, outside China demand was down 19% year on year, with MTBE hit by falling car use and chemical production reduced due to the pandemic.
- Production cuts by Methanex (in Chile, Trinidad and New Zealand) and others have reduced methanol supply by about 9%, which has helped the market find a balance point. In North America, production cuts have lifted prices from \$210/tonne to around \$236-243/tonne f.o.b. in recent weeks.
- The restart of the Brunei Methanol plants and Petronas at Labuan are likely to see prices stabilise or fall, barring an unexpected outage in the Middle East.

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Nitrogen Industry News

SPAIN

Fertiberia to make ammonia from 'green' hydrogen

Spanish fertilizer producer Fertiberia is teaming up with energy firm Iberdrola to build Europe's largest plant for generating green hydrogen for industrial use – in this case ammonia production. The 100MW solar plant and accompanying 20 MWh lithium-ion battery system and 20MW electrolytic hydrogen production system will be built at a cost of \$174 million, and electrolyse water to produce 720 t/a of hydrogen. When fed into Fertiberia's existing ammonia plant at Puertollano, 250km south of Madrid, the hydrogen will allow a 10% reduction in natural gas use by the plant, saving the company 39,000 t/a in annual CO₂ emissions. Start-up is planned for 2021. Fertiberia will also use electrolysis-generated oxygen as a raw material for nitric acid, which is used to produce ammonium nitrate at the site.

Iberdrola chairman Ignacio Galán said: "we are launching the first major green hydrogen project in Europe, demonstrating that thanks to renewables and technological innovation, it is possible to continue to meet the needs of the electrification and decarbon-

isation of our industry. The initiative shows the path and opportunities offered by the energy transition to develop innovative projects as the focus for industrialisation and employment in our country." Fertiberia president Javier Goñi added: "The partnership with Iberdrola allows Fertiberia to take a further step in its ambition to become a European reference for sustainable solutions for agriculture and to lead the paradigm shift required for the energy transition in the chemical sector, thanks to the manufacture of green ammonia from domestic renewable energy sources."

Annual hydrogen production in Spain is estimated at 500,000 t/a, mainly for use in the refining, chemical and fertilizer industries. Most of it is made from natural gas, and generates emissions of 5 million t/a of CO₂/year. Annual global hydrogen production of 70 million t/a generates 830 million t/a of CO₂, or around 2% of all global emissions. It is estimated that decarbonising global hydrogen production through the use of 100% renewable energy would increase global electricity demand by around 10%.

DENMARK

Topsoe extends scope of its ClearView online service

Haldor Topsoe and BASF have entered into an agreement to offer ammonia producers new optimisation possibilities via the inclusion of BASF's simulation tool, OASE² connect, in Topsoe's ClearView™ Ammonia connected service solution. The OASE connect simulation tool processes near real-time data from BASF CO₂ removal sections, allowing the ClearView Ammonia package to give customers greater insight into the status and optimisation potential of their ammonia plant operation.

OASE² white is an amine-based gas treatment technology for mixtures containing hydrogen and/or carbon monoxide. ClearView, launched last year, is a connected plant service that uses continuous upload of data to offer plant owners improved asset utilisation, energy savings, and less unplanned downtime. Based on a stream of comprehensive data from the plant, modelling and analytical software continually suggests optimisation opportunities and proactively alerts plant personnel of operational issues.

"This agreement is a great step forward for ClearView, enabling us to offer a complete connected services solution that adds even more value for ammonia producers. BASF has been our preferred supplier for CO₂ removal technology in our numerous ammonia projects over the years, and we have great trust in their expertise," says Michael Fjording, Connected Services Director, Haldor Topsoe.



Ammonia could power the vessels of the future.

Report on ammonia as a marine fuel

A consortium of companies including Alfa Laval, Haldor Topsoe, Vestas, and Siemens Gamesa have issued "Ammonium fuel – an industrial view of ammonia as a marine fuel" – a report intended to provide a comprehensive and up-to-date overview of the applicability, scalability, cost, and sustainability of ammonia as a marine fuel. The report describes ammonia as an attractive and low risk choice of marine fuel both in the transition phase towards a more sustainable shipping industry and as a long-term solution, based on the partners' industrial expertise and input from a list of competent industrial players. The report covers all aspects of the process of turning ammonia into marine fuel, including conventional and future green ammonia production, experience regarding safety with ammonia from other areas, the logistics of providing ammonia where it is needed, and the application on board the ship. It focuses on cost, availability, safety, technical readiness, emissions, and the elimination of risks related to future environmental regulations and requirements.

JAPAN

More interest in ammonia as a shipping fuel

Japanese shipping firm NYK Line, ship-builder Japan Marine United and classification society Nippon Kaiji Kyokai have signed a joint research and development agreement to build an ammonia-powered ammonia gas carrier and an ammonia floating storage and regasification barge (A-FSRB) for commercial use. The A-FSRB would be the world's first barge equipped with a floating storage and regasification facility exclusively for ammonia, according to NYK Line. The study will focus on developing a liquefied ammonia gas carrier, using ammonia as the main bunker fuel. The potential new vessel would ensure zero emissions, by using CO₂-free hydrogen as a raw material for ammonia production, in order to help meet International Maritime Organisation targets to reduce CO₂ emissions by at least 40% by 2030 and by 70% by 2050 compared with 2008 levels. The IMO is scheduled to finalise its GHG strategy in 2023.

The companies will also look at methods for the mass transportation and stable supply of ammonia, expecting demand growth from Japanese power firms to co-use the fuel at coal-fired power plants. The Japanese government is promoting the use of ammonia as a power generation fuel, saying a 10-20% mix at a coal-fired power plant would not require large-scale

NITROGEN INDUSTRY NEWS

refurbishment of the facility. Japan's Toyota Energy Solutions developed a 295KW ammonia-fired gas turbine unit in April last year.

RUSSIA

Dorogobuzh completes ammonia revamp

Acron's Dorogobuzh plant has completed a revamp of the site's ammonia plant, at a cost of 5 billion rubles (\$68 million). As a result of the work, plant capacity has been increased from 1,740 t/d to 2,100 t/d, generating an additional 130,000 t/a of ammonia, while lowering natural gas consumption by 7% per tonne of ammonia produced. The project was designed by LLC Novgorodsky GIAP, and the work was carried out by Dorogobuzh and Acron employees and 60 contractors from around the country, who brought in over 1,100 specialists and 50 pieces of equipment.

The Dorogobuzh ammonia plant in Russia's Smolensk region was originally commissioned in December 1979 with a design capacity of 450,000 t/a, and forms one of Acron Group's sites across Russia and beyond, including PJSC Acron at Veliky Novgorod and phosphate production at Murmansk (JSC NWPC). As well as these, Acron has interests in potash production, fertilizer transport and logistics, and the company also owns a minority 19.8% stake in Poland's Grupa Azoty, one of the biggest producers of chemicals in Europe.

Uralchem resumes production at Berezniki

Uralchem's Azot Branch at Berezniki says that it resumed full-scale production of nitrogen at the site on July 30th, following three weeks of shutdown. The company shut down all operations on July 7th following the detection of a "drastic" increase of chloride content in the Kama River, from which process feed water is taken. Uralchem says that the contamination threatened safe operation of the plant's process equipment. After 10 days, the content of chlorides dropped to acceptable levels at the intake point, allowing the company's management to make a decision to resume production. The re-start proceeded in stages, beginning with ammonia production at Unit 1 followed by downstream process units including granular ammonium nitrate and non-concentrated nitric acid production. Finally, Unit 2 producing ammonia, concentrated nitric acid, nitrite and nitrate salts, was restarted. Uralchem says lost production due to the unplanned shutdown amounted to about \$8 million, and the company has raised an urgent appeal to local environmental authorities to investigate and deal with the dumping of chemicals that caused the river pollution.

Meanwhile, Uralchem has launched a disclosure motion in a US court, allowing evidence to be taken in support of lawsuits relating to alleged theft of profits from Togliattiazot y former executives. Uralchem bought into Togliattiazot in 2008, later increasing its stake to 10%, but became suspicious of transactions involving Nitrochem Distribution AG. The case has been pursued through courts in Ireland, Cyprus and Russia, and has involved a protracted legal wrangle with Togliatti owner and former CEO Sergei Makhlai and his father Vladimir.

UKRAINE

OPZ extends gas tolling while seeking new tenders

Ukraine's Odessa Port Plant (OPZ) has extended its gas tolling arrangement with Agro Gas Trading (AGT) for two months from the 30th June, allowing the plant to remain operating during July and August. At the same time, it is in negotiations with a shortlist of three

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potential suppliers for the subsequent ten month period, including AGT, together with New York registered IBE Trade Corp and Geneva-based Maddox SA.

SAUDI ARABIA

Topsoe selected for green ammonia project

Haldor Topsoe's technology has been selected to form part of a \$5 billion green hydrogen project in Saudi Arabia's Neom 'smart city' development. Neom, a pet project of crown prince Mohammed bin Salman, is a \$500 billion development to build "a living laboratory and a hub for innovation" based on 5G technology, with an emphasis on high-tech and digital industries such as robotics and AI. Bechtel has been retained to design, build a project manage the construction of the city's transport, power and water infrastructure. Futuristic features for the city are said to include an entirely renewable energy supply using solar and wind power and power storage, an "artificial moon", phosphorescent beaches and "flying taxis". The city will be built in the Tabuk region, on the Red Sea near Saudi Arabia's border with Jordan.

As part of the project, 4 GW of renewable energy will be used to produce 650 t/d of hydrogen. This will then be converted into 3,500 t/d (1.2 million t/a) of ammonia using Topsoe technology. Topsoe partner Air Products will be the exclusive off-taker of the green ammonia, which will be transported "around the world" to be converted back into carbon-free hydrogen at local hydrogen refueling stations. Air Products' focus is to supply hydrogen fuel cell buses and trucks with carbon-free hydrogen by 2025, with distribution to end customers representing an additional investment of \$2 billion by Air Products. When implemented, the project will avoid emissions from over 700,000 cars, representing the equivalent of over 3 million t/a of CO₂.

"We are honoured to be part of this innovative world-scale project to reduce carbon emissions. Topsoe is focused on improving energy efficiency in today's technologies while developing the solutions of the future. This is a great step ahead," said Amy Hebert, Deputy CEO and EVP, Chemicals, Haldor Topsoe.

PAKISTAN

Restart for Agritech urea plant

Pakistan's Agritech Ltd, formerly known as Pak-American Fertilizers, says that it has

begun urea production at its Tara plant 100 km southwest of Islamabad in early August. The plant was forced to shut down on December 19th 2019 due to lack of availability of natural gas. It is now one of two plants that the government has given an allocation of regasified imported LNG at a subsidised tariff in order to increase domestic urea inventories. Local press reports that the 1,300 t/d urea plant is being supplied with 28.5 million scf/d of gas at a rate of \$4.48/MMBtu for three months. The other plant that is being supplied with gas at the concessionary rate is Fatima Fertilizers, with 300 t/d of urea capacity.

Pakistan's Ministry of Industries and Productino estimates that inventories of urea will fall below 200,000 tonnes during the period December 2020 – February 2021, as urea demand increases due to an agricultural subsidy increase for fertilizers, seeds, pesticides and tractors to boost domestic crop production.

AUSTRALIA

Incitec Pivot warns of threat from high gas prices

Australian explosives and fertilizer manufacturer Incitec Pivot has warned that its Gibson Island plant in Queensland remains under threat from high gas prices. The company says that it aims to find an additional A\$40 million in annual cost savings, but that the site's future is uncertain beyond 2022, when the current gas supply contract ends. In a briefing to investors, Incitec Pivot's fertilizers division Stephan Titze said: "Gibson Island continues to be challenged with high cost of gas on the east coast of Australia, lower global urea prices and reduced demand for our big end products as the drought in the cotton areas and low water levels in cotton dams continued in northern NSW and south east Queensland. We are working hard to secure economical gas to continue the operation of our Gibson Island plant post-2022. It's a great site with a very strategic location for imports and to serve adjacent markets, which gives us the option of importing nitrogen products in case we cannot secure economical gas."

In spite of plentiful gas on the west side of Australia, a lack of east-west pipeline capacity means that gas prices in Queensland remain high, as they are tied to the state's LNG exporters. Most of the gas produced in Queensland is exported to fulfil LNG contract requirements, and while the

remainder can be sold domestically, domestic consumers must therefore compete with global LNG prices, bringing Queensland gas prices to around US\$7.00/MMBtu for much of last year.

INDIA

Government seeks to speed up coal gasification project

Following a review of progress with the Talcher coal to urea project, Coal Minister Pralhad Joshi says that he has asked Talcher Fertilizers Ltd to "expedite" completion of the coal gasification plant. Talcher Fertilizers Ltd is a joint venture between state owned companies the Gas Association of India Ltd, Coal India Ltd, Rashtriya Chemicals and Fertilizers Ltd and the Fertilizer Corporation of India Ltd (FCIL). Based in India's coal-rich Odisha state, the coal gasification-based ammonia-urea project has a design capacity of 2,200 t/d of ammonia and 3,850 t/d of urea, using a mix of local coal and petroleum coke as feedstock. It will also recover 100 t/d of elemental sulphur as a by-product. Work is reportedly around 60% complete on construction of the plant, which is expected to come on-stream in 2023. Three other gas-based plants are also under construction or in commissioning, at Ramagundam in Telegana, Gorakhpur in Uttar Pradesh, and Sindri in Jharkhand state, which the government reports to be 99.6%, 88% and 78% complete, respectively. Although delayed by the Covid-19 outbreak, Ramagundam is still expected to commission this year, and Gorakhpur and Sindri in 2021.

NIGERIA

Dangote still aiming for start-up this year

Saipem says that the new Dangote urea plant is still likely to be commissioned this year. Saipem is the EPC contractor for the project, as well as supplying the urea technology for the plant, in the Lekki district of Nigeria's capital Lagos. The complex includes two ammonia-urea trains with a combined capacity of 3 million t/a. Saipem says that the plant is mechanically complete and test runs began in March, but were hampered by the Covid-19 outbreak, which prevented engineers flying from Italy to help with commissioning. The company says that it is now making special arrangements, including setting up dedicated flights for vendors and suppliers to enable it meet the completion deadline, and that the plant will be operating by the end of 2020.

CHINA

Contract awarded for melamine plant

Eurotecnica says that it has successfully concluded negotiations with the Chinese ShaanXi Qing Shui Yin Quan Coal Industry Development Co., Ltd. with the award of a license to build a *Euromel* technology melamine plant. The new plant will have a nameplate capacity of 180 t/d (60,000 t/a) and will be based on 4th generation *Euromel* technology, featuring a single-train arrangement as well as the traditional total-zero-pollution concept. The award marks the 23rd license for Eurotecnica of its *Euromel* process, and will bring total licensed nameplate capacity to more than 800,000 t/a, making it the only technology selected in the Middle-East and the leading technology in Asia and the Americas.

OMAN

Omifco signs three year offtake deal

Omani energy company OQ, via its commercial arm OQ Trading, has signed a three-year agreement with the Oman India Fertiliser Company (Omifco) to offtake and trade one million t/a of granular urea. OQ's supply and trading business will take the urea from Omifco's terminal in Sur in bulk carriers and deliver it to end-users in international markets such as India, Sri Lanka, Pakistan, the United States, Brazil, Vietnam, Thailand and China, according to OQ. The new agreement between the two companies began on August 1st, and the first vessel, with 49,500 tonnes of urea, departed for Brazil on August 2nd; the first ever shipment from Oman to Brazil. OQ has in turn struck a deal with Swiss-based agri-business trader Ameropa for a portion of the offtake, and the



The Omifco urea facility (left), next to the Oman LNG complex at Sur.

PHOTO: OMAN LNG

shipment to Brazil was via Ameropa.

The move comes as Omifco's original 15 year offtake deal, beginning in July 2005 when the plant first came on-stream, came to an end. Omifco, with capacity to produce 1.65 million t/a of urea and 350,000 t/a of excess ammonia, is 50% owned by the Omani government and 25% each by Indian state-owned fertilizer cooperatives the Krishak Bharati Cooperative and Indian Farmers Fertilisers Cooperative, and the original offtake agreement specified that the plant's output would go to India for sale by these two companies. It was founded as a way for India to take advantage of cheap natural gas in the Middle East for urea production.

"Omifco has positioned itself strategically in the urea and ammonia market globally, and we are quite proud of that. Now we have a great opportunity ahead of us; targeting new markets for the Omani urea," said Talal al Awfi, chief executive - commercial, OQ.

"We are pleased with the achievements that Omifco has accomplished during its first 15 years. Omifco has enhanced its mandate and enabled its growth; not just as a supplier for its founding companies, but also to offer high quality urea and

ammonia products to the rest of the world," said Hilal al Kharusi, chairman of Omifco.

SINGAPORE

BW LPG looking to ammonia as a shipping fuel

BW LPG, the largest supplier of LPG shipping vessels in the world, has told Lloyd's List that the company is looking to use ammonia as a pathway to carbon neutral and ultimately zero carbon fuels. In an interview, BW LPG chief executive Anders Onarheim said that while the company is currently converting its fleet to run on LPG as a fuel, to meet present IMO fuel quality regulations, the future conversion from LPG propulsion to ammonia would not require a large investment, although he also said that there was "still a long way to go" before it could be scaled up to commercial viability.

Mr Onarheim said the company is working with MAN Energy Solutions, which is also retrofitting its VLGCs with its two-stroke, dual-fuel engines, for ammonia-fuelled engines along with an internal team. Ammonia is regularly carried in LPG tankers and so such vessels would have access to a ready source of fuel.



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CHINA

Matthey to supply technology for world's largest single train methanol plant

Johnson Matthey (JM) has been selected by China's Ningxia Baofeng Energy Group as licensor for a third methanol synthesis plant at their coal to olefins complex near Yinchuan in Ningxia province. With a planned capacity of 7,200 t/d (2.4 million t/a), the unit will be the largest single train methanol plant in the world once completed.

Under the terms of the agreement, Johnson Matthey will be the licensor and supplier of associated engineering, technical review, commissioning assistance, catalyst and equipment supply. The methanol plant will take synthesis gas as a feed and utilise JM radial steam raising converters in a patented series loop to produce methanol for downstream olefins production. The plant will provide enhanced energy efficiency along with low opex, capex and emissions.

This is JM's 8th operating license in China and the third JM design licensed by Ningxia Baofeng Energy, following the recent successful commissioning of the 6,600 t/d Baofeng methanol synthesis unit in May 2020 and the original 4,450 t/d methanol synthesis unit, commissioned in 2014. Ningxia Baofeng Energy, founded in 2005, is the largest private coal to olefins producer in China. Its Ningdong chemical complex now produces 4 million t/a of methanol and 1.2 million t/a of polyolefins.

"We are very proud of our ongoing collaboration with Ningxia Baofeng Energy. It is testament to their confidence in JM's engineering expertise and ability to successfully design and help deliver their large-scale methanol plants", said John Gordon, Managing Director for Johnson Matthey. "In just over six years it has been exciting to see our strong partnership result in the commissioning of two large scale plants with increasing volumes and a third world-scale plant on the way. We are very much looking forward to this next ambitious phase of our journey and continuing to raise the bar of world-class project delivery."

ITALY

Agreement on 'syngas fermentation' technology

NextChem, Maire Tecnimont's subsidiary for 'Green Chemistry and Energy Transition' technologies, has signed an agreement with US-based LanzaTech to license the latter's 'Waste to Ethanol' process, expanding NextChem's technology portfolio in 'circular economy' and chemical recycling technologies, which currently include 'circular' hydrogen and methanol production technologies, based on the chemical recycling of plastic and dry waste via gasification. LanzaTech's adds a biological "syngas fermentation" technology, in which ethanol is produced by bacteria which operate on CO-rich feeds, transforming the syngas at low temperatures and pressure, improving the overall sustainability profile of the process. NextChem will exclusively license this technology in Italy and, on a project basis, in some foreign markets.

NextChem says that technological integration the most important aspect of the circular economy sector, as it allows the pro-

duction of chemical building blocks such as hydrogen, methanol, ethanol from currently non-recyclable waste, avoiding fossil sources and reducing climate-changing emissions while increasing the share of recycling.

"We are expanding our technology portfolio from a strategic perspective: our circular district model and our waste-to-chemicals technology platform are the answers both to the problem of reliance on foreign supplies of chemical products, and to the problem of recovery of currently non-recyclable waste fractions, and to the problem of decarbonisation", said Pierroberto Folgiero, CEO of NextChem and Maire Tecnimont. "NextChem aims to provide the market with technological solutions to completely replace traditional fossil-based chemistry with biochemistry and waste chemistry. We want to re-build coal chemistry, excluding coal entirely: an extremely ambitious goal, which today has become possible".

NextChem has also recently signed an agreement with Eni to build three waste gasification plants in Italy, to produce hydrogen, at Porto Marghera near Venice, a methanol plant at Livorno, and a syngas plant for Eni's Taranto refinery to generate

hydrogen for desulphurisation as well as carbon monoxide for direct iron reduction at the nearby steel mill.

GERMANY

Partnership for GTL technology commercialisation

Clariant has entered into a partnership with joined forces with Ineratec, a spin-off of the Karlsruhe Institute of Technology (KIT), to develop and commercialise novel technologies for the production of renewable fuels and chemicals. Clariant will provide its catalysis expertise and broad portfolio of syngas conditioning and upgrading catalysts to support Ineratec's novel gas-to-liquids (GTL) technology.

Stefan Heuser, senior vice president and general manager at Clariant Catalysts, said: "We are honoured to support Ineratec in their pioneering work in sustainable fuel production. Their state-of-the-art, containerized gas-to-liquid technology has great potential for the decentralized fuel market, and we are excited to contribute with our tailor-made syngas catalyst innovations."

Ineratec's process is a modular, containerised GTL technology which combines hydrogen, potentially generated from renewable power, with greenhouse gases such as CO₂ to form CO₂-neutral synthetic hydrocarbons and fuels. It uses reactors with a micro-structured core to provide a large surface area for heat and mass transfer, allowing highly exothermic reactions in a compact volume, with high conversion per reactor pass.

Hydrogen for electricity grid stabilisation

Thyssenkrupp's proprietary water electrolysis technology has been accepted by E.ON for participation in Germany's primary control reserve market. This means that thyssenkrupp's electrolysis plants will be able to act as large-scale buffers to stabilise the power grid and compensate fluctuations quickly and flexibly. Operators can now link their plants to the German electricity market via E.ON's virtual power plant.

thyssenkrupp and E.ON tested the technology at an existing water electrolysis plant operating as part of the Carbon2Chem® project in Duisburg. It was shown that thyssenkrupp's electrolyzers can increase and decrease their production at the speed required to participate in the premium primary reserve market, including being able to provide full supply within 30 seconds and maintain it for at least 15 minutes. The

electrolysis provides green hydrogen that can be stored for hours, days or months before being converted back into electricity or used as a clean, CO₂-free starting material in the mobility sector or for the production of sustainable chemicals.

UNITED STATES

Agreement for world-scale hydrogen plants

Air Products has signed a strategic cooperation agreement with thyssenkrupp Uhde Chlorine Engineers, under which the two companies will collaborate exclusively in key regions, using their complementary technology, engineering and project execution strengths to develop projects supplying green hydrogen.

thyssenkrupp will deliver its technology and supply specific engineering, equipment and technical services for water electrolysis plants to be built, owned and operated by Air Products, supporting Air Products' development of green hydrogen as an energy carrier for sustainable transportation, chemicals and power generation.

"The SCA with thyssenkrupp is an important element of our value chain in developing, building, owning and operating world-scale projects and supplying green hydrogen for mobility, energy and industrial applications. We look forward to applying our complementary strengths and delivering substantial sustainability benefits through transformational green hydrogen projects," said Dr. Samir J. Serhan, Chief Operating Officer at Air Products.

"We are proud to cooperate with Air Products in making value chains for fuels, chemicals, and industry feedstocks sus-

tainable. Large-scale electrolysis is the key technology to connect renewable power to the different sectors of mobility and industry. As a world market leader in electrolysis we bring in both: technology and production capacity at scale. Already today, we are set to supply one gigawatt for water electrolysis plants per year, and we are prepared to ramp up the capacity in this rapidly evolving market," said Denis Krude, CEO at thyssenkrupp Uhde Chlorine Engineers.

MALAYSIA

Samsung wins contract for Sarawak methanol plant

Samsung Engineering says it has received a \$55.5 million contract from Sarawak PetChem to conduct early works on the second phase of Sarawak's planned methanol facility in Malaysia. The move is seen as a likely precursor to Samsung being awarded the full \$1 billion EPC contract for the project. The 5,000 t/d methanol project, to be built in Bintulu, will be based on Air Liquide E&C's Lurgi MegaMethanol technology. Operations are planned to begin in 2023. Samsung and Air Liquide E&C jointly carried out the front-end engineering design (FEED) study for the project in April 2019.

AUSTRALIA

BHP to recycle tyres via waste gasification

BHP is partnering with Novum Energy in a project to recycle truck tyres from its facilities in Queensland. Novum will take used earth moving tyres from all seven BHP Mitsubishi Alliance (BMA) and BHP Mitsui Coal (BMC) sites in Queensland and convert

them into heavy and light oils, carbon black, syngas and steel at a processing plant which is being built in Nebo within the Isaac region. The company is aiming to process 19,000 t/a of rubber to produce about nine million litres of fuel oil, according to Novum managing director Rowan Kendall.

BMA asset resident James Palmer said that the tyre recycling program would not only create up to 30 jobs in the Bowen Basin but also reduce emissions across the company's operations. "We are constantly looking for ways to increase the sustainability of our operations, reduce emissions and contribute to regional communities and this new BHP-led initiative does just that," Palmer said. "New technology means rather than storing old tyres, which weigh around 4.9 tonnes each, they can now be recycled and turned into new products. This helps us create a circular economy in the region by repurposing waste locally and creating activity in the region."

DENMARK

Topsoe joins sustainable fuel project

Haldor Topsoe has joined a consortium of Danish companies to develop a hydrogen and sustainable fuel facility based on electrolysis in the greater Copenhagen area.

The project is expected to be executed by 2030 in three stages, achieving a capacity of 10 megawatts (MW) of electrolysis capacity in 2023, 250 MW in 2027, and 1.3 GW by 2030. With the large-scale supply of renewable electricity needed, the timing of phases two and three will depend on the execution of the offshore wind power project off the island of Bornholm in Denmark.



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People

SensoTech has announced a high level management restructuring which represents a generational change in leadership.

Robert Benecke and **Hannes Benecke**, sons of the founder Dr. Ingo Benecke have become the company's new managing directors with immediate effect, replacing Dr. Ingo Benecke and SensoTech co-founder **Mathias Bode**, who have run the company for 30 years, developing and producing sonic velocity measuring instruments for liquid analysis which can be found in numerous industrial plants around the globe.

Robert and Hannes Benecke said that they are looking forward to the new challenges and tasks: "In a way, we grew up in the company and know many employees for a very long time. SensoTech GmbH has very well-functioning structures and we look forward to further developing the company. We would like to thank the previous managing directors for their trust and look forward to the new tasks." The objectives of the new management are the further development of the individual company divisions and the expansion of the international sales network. In this way, the successful course of the past years is to be further pushed.

Retiring director Dr Ingo Benecke said: "We would like to thank our employees, customers and business partners for the good, long-term cooperation. We had both good time and difficult. But even the difficult times were mastered through active commitment. With the handover to Robert and Hannes Benecke, we are banking on the future. The new management will tackle the tasks ahead with high motivation and



Above (left to right): Hannes Benecke, Dr. Ingo Benecke, Mathias Bode, Robert Benecke.

determination and further develop SensoTech GmbH. We are convinced of this."

At its recent annual shareholders' meeting, **Nader I. Alwehbi** and **Thilo Manhardt** were elected as board members by a large majority of the votes cast, replacing **Khaled Homza A. Nahas** and **Carlo G. Soave** on the company's Board of Directors. The ten other members of the board were re-elected by a large majority, as was board's chairman, **Hariolf Kottmann**. The new board will serve until the company's next annual general meeting in 2021.

Sandvik Materials Technology has appointed **Jari Ponsiluoma** as Product Manager for Heat Exchangers and Fertilizer in Europe, the Middle East and Africa (EMEA). Ponsiluoma has 10 years' experience working at Sandvik Materials Technology after joining the company in 2008. In 2018, Ponsiluoma joined Ovako Group as a Product Line Manager for Powertrain (Automotive and Marine), but recently returned to Sandvik to develop Sandvik's position within premium segments.

"It is a great opportunity to be working with Sandvik again. I look forward to reconnecting with my contacts in the industry and developing new strategies to benefit our customers in the tube industry," he said.

Norwegian oil, gas and methanol producer Equinor, formerly Statoil, has appointed **Anders Opedal** as its new president and CEO from 2 November 2020. **Eidar Sætre** will retire after six years as CEO and more than 40 years in the company.

Opedal joined Equinor as a petroleum engineer in 1997, spent many years in Drilling and Well and served as Chief Procurement Officer. In 2011, he was chosen to lead Equinor's approximately 300 billion krone project portfolio. He later served as Executive Vice President and Chief Operating Officer before taking the role as Senior Vice President and country manager Brazil. Opedal holds a Master's degree in Engineering from The Norwegian Institute of Technology (NTNU) and an MBA from Heriot-Watt University in Edinburgh.

Calendar 2020/21

! The following events may be subject to postponement or cancellation due to the global coronavirus pandemic. Please check the status of individual events with organisers.

SEPTEMBER

23-24

Gasification Summit 2020, LYON, France
Contact: Avani Mehta, ACI
Tel: +91 9665011195
Email: avani@acieu.net
Web: www.wplgroup.com/aci/event/gasification/

27-2 OCT

POSTPONED TO 2021

Ammonium Nitrate/Nitric Acid Conference 2020, HOUSTON, Texas, USA
Contact: Hans Reuvers, BASF
Karl Hohenwarter, Borealis
Email: johannes.reuvers@basf.com
karl.hohenwarter@borealisgroup.com
annaconferencehelp@gmail.com
Web: an-na.org

OCTOBER

7-8

Syngas Nitrogen Russia and CIS, MOSCOW, Russia
Contact: Milana Stavnya, Programme producer, Vostock Capital
Tel: +7 499 505 1 505
Email: MStavnaya@vostockcapital.com

FEBRUARY 2021

16-18

Nitrogen+Syngas USA, TULSA, Oklahoma, USA
Contact: CRU Events
Tel: +44 (0) 20 7903 2444
Fax: +44 (0) 20 7903 2172
Email: conferences@crugroup.com

27-29

4th International Fertilizers Conference: Eastern Europe, Baltic States & Balkans, BUDAPEST, Hungary
Contact: WFM Chem-Courier agency
Tel: +38 056 370 12 04
Email: conf@wfmeasteurope.com

MARCH

1-3

Nitrogen+Syngas 2021, ROME, Italy
Contact: CRU Events, Chancery House, 53-64 Chancery Lane, London WC2A 1QS, UK
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Plant Manager+

Incident No. 2 Leak in weld overlay in urea reactor bottom

The following case study reports on a serious incident in a urea plant where a leak in the weld overlay in the urea reactor bottom resulted in a costly plant shutdown and near miss of rupture of the high pressure vessel. It is known that carbon steel can corrode with rates of 1.000 mm/year not taking into account erosion due to flashing. The impact of the NH₃/CO₂ ratio on the corrosion rate is questionable. The following prevention measures are suggested:

- Perform corrosion inspections during turnarounds (measure weld overlay thickness).
- Apply proper design of inlet nozzle devices to assure sufficient saturation of liquid with oxygen and avoid high velocities (erosion corrosion) and condensation corrosion (in case of 316L UG).
- Apply higher alloy materials for overlay welding such as 25-22-2 or (super) duplex.
- During operator plant tours look for potential leaks of overlay welding in HP equipment.

Event description

Operators noted a leak (first fumes, then large quantities of solution) in the bottom forged head of the urea reactor in a conventional technology 1,000 t/d urea plant from 1969. The incident happened four months after an inspection during a turnaround. The plant was running stable at 95% load. A hole of 38 mm X 6.4 mm was found with no signs of bulging or deformation visible on the outside. Four other corroded areas of 20 to 50mm in depth were also found.

Immediate response action

The plant was shut down when the leakage was identified. The reactor bottom forging was repaired (rewelded) and overlay welding was performed with Thermanit 19/15 H electrodes. A Japanese fabricator was involved in the repair and future corrosion inspections.

Causes

Since the weld overlay metal is less resistant to corrosion, the combination of heat of reaction and high flow velocity over the ten years of service, aside from any possible upset in the control of the residual O₂ and the NH₃/CO₂ ratio, must have resulted in a gradual thinning of the overlay until in some areas, it was gradually consumed making the carbon steel totally exposed, which then corroded at an accelerated speed in a very short period. The reactor was inspected every turnaround but it seems only visually. The carbamate and ammonia feed nozzles were replaced.

Consequence

Near miss of rupture of high pressure vessel and a shutdown of 18 days costing US\$ 1 million.

Urea reactor design

The urea reactor, from a Japanese manufacturer, is designed to operate at 280 kg/cm² and 204°C and was operating at 226 kg/cm² and 196°C. The plant operating data at the time of the incident was 219 kg/cm², 194°C, 1.7 ppm Fe and 2500 ppm O₂. The reactor has a diameter of 1.52 m and length of 27.43 m. The bottom forging is 83-94 mm thick – A212 Gr.B FBQ Class P 1 (ASME A-515, Gr.70, C = 0.31 max.). The stainless steel weld overlay was deposited using E-316L welding rods. The bottom forging has three 108 mm diameter nozzles located 60° apart feeding ammonia, carbon dioxide and carbamate respectively with a stainless steel baffle plate umbrella over the three nozzles.

Risk level

The likelihood of a major consequence was moderate but the risk level was high.

Prevention safeguards

Corrosion inspections should be carried out during turnarounds.

Mitigation safeguards

In case of a leak, confirm and locate the leak, shut down the plant and drain the synthesis section as soon as possible.

Possible causes

- 50 mm distance of deflector umbrella to overlay welding is too small risking erosion corrosion and/or condensation corrosion. Note that NH₃ and CO₂ form carbamate releasing a lot of heat. Typically a mixer is applied.
- E316L overlay welding.
- Influence of bottom flange weld.
- Besides visual inspections, were thickness measurements also performed during the turnaround?

Weld overlay thickness measurement

Weld overlay thickness measurement is performed with a Dualscope/Permascope using magnetic induction. It is only possible on Austenite materials (316L/25.22.2) with a ferrite content of less than 0.6%. However, it gives deviating readings when the overlay gets thinner (<6 mm) due to the presence of ferrite in first layer. The layer thickness reading does not define the layer of the real corrosion resistant part. The material used for the first layer is 309 type, with PWHT after the first layer.

When layer becomes thinner make use of a calibration block and use the ferriscope.

Drill a hole in the overlay and etch – the transition will be visible and the layer can be measured.

This case study report is one of many serious incident reports on UreaKnowHow.com's Fertilizer Industry Operational Risks Database, FIORDA, which has been created for collecting and sharing process safety and reliability information among participating companies in the fertilizer industry.



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Ammonium nitrate – still growing



PHOTO: THYSSENRUPP INDUSTRIAL SOLUTIONS

In spite of continuing safety concerns due to the Beirut explosion, and the rise of the use of urea as a nitrogen fertilizer, ammonium nitrate demand continues to increase in several key markets.

Ammonium nitrate's first major commercial use was as a component of blasting agents, and it remains the basis of most commercial explosives on the market, in particular as the mixture ammonium nitrate/fuel oil (ANFO). However, after WWII, it became popular as a fertilizer as well. The growing popularity of urea, which contains 42% nitrogen by weight compared to AN's average of 33-34%, has meant that, especially in the developing fertilizer markets of India, China and South America, urea has become preferred as a more efficient way of transporting nitrogen, and AN's share of the nitrogen fertilizer market has steadily dropped. Restrictions imposed following a series of accidents have also led some countries to ban the use of straight AN as a fertilizer. Nevertheless, its versatility and its rapid uptake by plants continues to ensure that it is preferred by farmers in some markets.

Manufacture

Ammonium nitrate is produced by the acid base neutralisation reaction of nitric acid with ammonia. As nitric acid is also made from ammonia oxidation, AN plants are typically co-located with ammonia and nitric

acid production. The ammonium nitrate is formed as a solution in water. For production of solid AN it is then typically concentrated in an evaporator or concentrator to a solution strength of 95-99% AN at high temperature (ca 150°C). This AN 'melt' is then passed to a prill tower or granulator to produce the solid AN prills.

Prill density can be varied by using different concentrations of ammonium nitrate melt. Low density prills, at a density of around 1.29, are formed from 95-97.5% AN melt, while high density prills, at a density of around 1.65, are formed from a 99.5-99.8% melt. Low density prills are more porous than high density prills and so absorb e.g. oil more easily. For this reason low density prills are used for making blasting agents – this is known as 'technical' or 'industrial' grade AN (TAN/IGAN). The high density prills are used as fertilizers (fertilizer grade AN or FGAN), with a typical nitrogen nutrient content of 33-34%. Because of the similarity in IGAN and FGAN production, both from an ammonium nitrate liquor, the IGAN industry originally evolved largely as an 'adjunct' to the production of FGAN. However, because of regulatory hurdles in storage and transport of AN, plants tend to be relatively close

to areas of end user demand, and as fertilizer and mining areas are often not the same, there has been a gradual polarisation of the industry into dedicated facilities producing one or the other.

The melt can also be mixed with other chemicals to produce other end products. One popular method is to mix the melt 75-25% with calcium carbonate (limestone) to produce calcium ammonium nitrate (CAN). Dolomite (calcium magnesium carbonate) can be substituted for calcium carbonate to produce magnesium ammonium carbonate (MAN).

Finally, the non-concentrated ammonium nitrate solution direct from the reactor can instead be mixed with a solution of urea to produce a solution called urea ammonium nitrate (UAN). UAN is typically available in three different concentrations: 28%, 30% and 32% nitrogen. The most popular form – 32% nitrogen – is a mixture of 45% ammonium nitrate, 35% urea and 20% water. Ammonia and nitric acid are used to adjust solution pH to close to 7.

Since ammonium nitrate is hygroscopic and therefore readily attracts moisture from air, in its solid form it is usually coated with an anti-caking compound, and is stored in air-conditioned warehouses or sealed bags. However, its high solubility does make it ideally suited for using solutions for fertigation or foliar sprays.

Agronomic benefits

Ammonium nitrate is popular as a fertilizer because its nitrogen is present in a form more readily available to the plant than urea, which must be oxidised to nitrate in the soil. The nitrate in AN moves readily with soil water to the roots, where it is immediately available for plant uptake, while the ammonium ion is taken up by roots or gradually converted to nitrate by soil microorganisms. Its rapid uptake means that it is less susceptible to volatilisation than urea, and if applied correctly leads to less leaching into ground water. It also makes it suited to areas with shorter growing seasons, such as in many northern latitudes in Canada, Europe and Russia. Ammonium nitrate generates 90% fewer ammonia emissions per unit of nitrogen than urea, which is a factor in many countries which are trying to reduce ammonia emissions, especially in Europe.

One of the interesting developments in recent years has been a significant switch in China from the use of straight urea as a fertilizer to an increasing reliance on NPK

blends as a way of increasing the efficiency of nutrient use in the country, especially now that the government has tried to cap overall use of nutrients to try and tackle environmental issues. This means that there is increasing need for AN and CAN as part of NPK blends. Although Chinese AN consumption is down from its peak year of 2014, it has nevertheless increased by 50% in the past decade.

Production

Total production of ammonium nitrate in terms of million tonnes N was about 21.1 million t/a in 2019. This figure has risen steadily if patchily this century, as Figure 1 shows, at an average annual growth rate of 4.4%. Of this total, about 34% was represented by straight AN fertilizer, 29% by technical/industrial grade ammonium nitrate, intended for commercial explosive use, 19% by calcium and magnesium ammonium nitrate (CAN/MAN – but mainly the former) and 17% by urea ammonium nitrate solutions (UAN). A small proportion is also used in the direct manufacture of ammonium sulphate nitrate and other derivatives. CAN and straight AN fertilizer is also often blended into various NPK fertilizers.

Table 1 breaks down production and consumption by region. However, note that the 'AN' figure in the first column also includes ammonium nitrate which is then used to make UAN, and that about half of the nitrogen content of the UAN figure comes from its urea component.

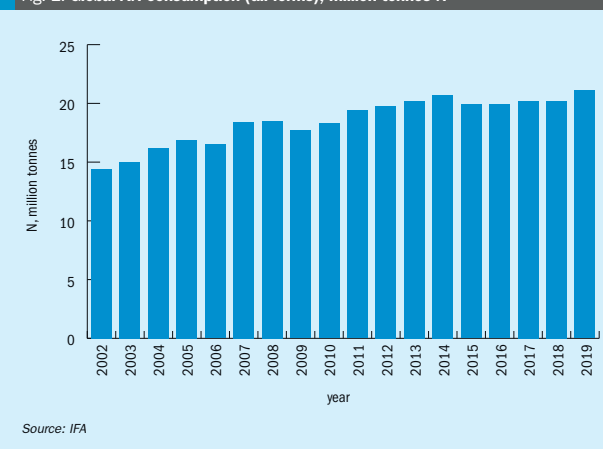
Demand

Demand for AN is concentrated in three main regions: Western Europe, North America, and Eastern Europe/Russia, which collectively account for two thirds of all consumption. However, each is quite different in terms of how that AN is used. In Western Europe, restrictions on the sale of straight AN fertilizer in countries such as Turkey, Germany, Ireland and parts of the UK due to its potential for misuse has led to substitution with calcium ammonium nitrate (CAN). Western Europe is the only significant market for CAN, responsible for three quarters of all demand.

In the US, conversely, a preference for fertilizer solutions but a corresponding tightening of regulations on the storage, transport and use of ammonia for direct application, on grounds of safety and security, has led to a rapid increase in demand for UAN solutions, and the North American market is heavily skewed towards UAN, with straight AN mostly used as a mining explosive.

Consumption in Eastern Europe and Russia has been rising rapidly. Russian consumption of AN has more than tripled since 2000. CAN and UAN are not major features of this market. The rise in domestic consumption in Russia has helped alleviate one issue that had bedevilled the global AN market – allegations of so-called 'dumping', or sale of product at below cost price in order to increase market share. Both the US and European

Fig. 1: Global AN consumption (all forms), million tonnes N



Above: The Vinacom low density ammonium nitrate (LDAN) plant in Vietnam.

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NITROGEN+SYNGAS
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Table 1: Ammonium nitrate statistics 2018, million tonnes N

Region	Production			Consumption			Balance		
	AN	CAN	UAN	AN	CAN	UAN	AN	CAN	UAN
Western Europe	2.69	3.17	0.90	2.67	2.87	1.67	+0.02	+0.30	-0.77
E. Europe/Russia	5.65	0.30	1.61	4.29	0.11	0.64	+1.36	+0.19	+0.97
North America	3.32	-	4.01	3.35	0.03	4.31	-0.03	-0.03	-0.30
South America	0.52	-	0.42	1.46	0.37	0.24	-0.94	-0.37	+0.18
Africa	0.98	0.01	0.04	1.23	0.15	0.01	-1.25	-0.14	+0.03
Middle East	0.22	0.27	-	0.21	0.19	-	+0.01	+0.08	-
South Asia	0.20	0.12	0.02	0.25	0.12	0.01	+0.05	-	+0.01
East Asia	2.06	0.09	0.01	2.08	0.09	0.01	-0.02	-	-
Oceania	0.65	-	-	0.74	-	0.11	-0.09	-	-0.11
Total	16.28	3.94	7.05	16.28	3.94	7.05			

Source: IFA

Union maintained anti-dumping tariffs on sales of Russian AN from most producers for many years following the breakup of the Soviet Union in the early 1990s, alleging that natural gas feedstock prices were being subsidised. The gradual spread of freer gas market pricing globally and the pickup in domestic demand in Russia has eased many of these concerns and in 2016 the US removed its tariffs and the EU reduced its tariffs in 2018. The situation is still not completely resolved however – in 2019 the EU imposed duties on UAN imports from Russia, although it also imposed duties on UAN from Trinidad and the US.

Looking to the future, UAN use continues to increase in the US, and AN compounds in NPKs and other fertilizers are likely to see continuing growth in Asia. On the explosives side, the main use for commercial explosives is in the mining and quarrying industries, and for large volumes of IGAN use is mainly confined to the coal, gold, iron ore and copper mining industries, which between them account for more than 70% of all IGAN consumption. Of these, coal is the largest share. Coal consumption is slowly falling from a 2013 peak, as Europe moves away from coal for environmental reasons and the US for economic ones. China, the largest consumer, is also trying to move its economy away from coal dependence and consumption has plateaued there. However, mining for copper and iron ore continues to increase, albeit at a slower rate than during the commodities boom of the first two decades of the century, driven by China's rapid industrialisation.

Covid has had a major impact on mining around the world. Orica, the world's largest supplier of IGAN, says that it currently anticipates a 10-15% drop in IGAN demand in 2020 as a result of Covid restrictions. However, the longer term growth prospects for the sector remain positive, at around 1.5% year on year, and Orica brought a new IGAN plant on-stream in Australia earlier this year.

Safety and security

The August 4th explosion in Beirut, believed to have been caused by 2,750 tonnes of AN being improperly stored at a warehouse in the port district, has once again reopened the question of ammonium nitrate's suitability as a fertilizer. Incidents around the world, both accidents and deliberate misuse have led to progressive tightening of regulations over the past few decades, usually on a national basis. Afghanistan, China, Colombia, the Philippines have all banned the sale of AN as a fertilizer because of security concerns, and most recently in Turkey, straight AN was banned as a fertilizer following a series of terrorist incidents in 2016. Brazil, the major user in South America, moved to a licensing system on AN purchase for importers and traders last year, which applies to all forms of AN. Russia maintains limits on warehousing and how long AN can be stored, and following the devastating explosion in Tianjin in China in 2015, many Chinese ports and railway authorities have introduced additional restrictions on import and storage of AN-

based compounds. India banned import of bulk, loose AN following the same incident, though it can still be imported in bagged form. In Europe, sale of any AN-based compound with a nitrogen content of more than 16% is prohibited to anyone not on an approved list of buyers.

All of these regulations place additional cost burdens on supply of AN, and the worry for the industry after any major incident is that there will be pressure on regulators to introduce tighter measures on the storage and transport of AN which progressively leads to the industry dying the 'death of 1,000 cuts' as each new regulation, perhaps not significant in itself, leads to increased costs which make it less competitive, or place such a burden on wholesalers and distributors that they can no longer be bothered to deal in it. So far the uniqueness of the situation in Beirut appears to have mitigated somewhat against that, but it has placed AN uncomfortably back in the spotlight again. It is certainly possible that there will be further substitution into forms perceived as less dangerous such as CAN, UAN or NPK blends over the coming years. However, the general utility of AN as a fertilizer as described in the 'agronomic benefits' section above, has so far managed to avoid any more general ban in spite of these concerns. Indeed, back in 1999 this magazine carried an article by a respected industry consultant predicting the eventual demise of AN as a fertilizer for precisely the reasons detailed above, yet here we are, 20 years later, and the market has instead grown. ■



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Carbon dioxide as a feedstock

Falling costs for production of hydrogen by electrolysis are encouraging more serious consideration of using recovered carbon dioxide as a feedstock for chemicals and even fuels production.

The cost of generating hydrogen by electrolysis of water and the cost of renewable wind or solar energy to drive that electrolysis has fallen dramatically over the past decade. The Hydrogen Council, an alliance of industry leading companies in hydrogen production, noted in its report earlier this year¹: “A Path to Hydrogen Competitiveness” that: “electrolysis fed with renewable electricity – the most common production method to produce ‘renewable hydrogen’ – has become 60% more affordable as low-carbon and renewable electricity prices have dropped and electrolysis capex has fallen. The cost of solar and wind power, the largest driver of renewable hydrogen production costs, has seen an 80% decrease over the past decade. Recent subsidy-free offshore wind auctions in Europe and bids close to or below \$20/MWh for solar photovoltaics (PV) and onshore wind plants have been seen. This downward cost trajectory for renewables should continue, with 14 times more solar capacity projected to become available in 2030 than was previously estimated. At the same time, electrolysis capacity has also started to accelerate, with at least 55 times more capacity expected by 2025 versus 2015, which will result in a similar cost drop in electrolysis capex.”

Two thirds of all new power generation capacity installed last year globally was represented by wind and solar power. As we have noted in articles this year, this potentially makes the production of ammonia and downstream nitrogen products from renewables a cost-competitive proposition, depending upon tax and other incentives. But while generating hydrogen from electrolysis avoids the emission of carbon dioxide from partial oxidation of natural gas, coal or other feedstocks to make syngas, it has also led to interest in whether carbon dioxide itself could become a feed for chemical production, generating ‘carbon negative’ or at least ‘carbon neutral’ chemicals.

Carbon recycling

Although research is ongoing into using polymer membranes or cryogenic separation methods, at the moment, on an industrial scale recovery of carbon dioxide is usually accomplished using solvents, including monoethanolamine or methyl-diethylamine (MEA/MDEA), methanol, such as in Linde and Air Liquide’s *Rectisol* process, methylpyrrolidone, and potassium carbonate (the Benfield process). These processes have all been demonstrated at large scales.

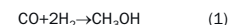
Once the CO₂ is captured, the question arises as to what to do with it. At present, there are essentially three options: pumping it into the ground in an existing oil and gas reservoir, either to achieve enhanced oil recovery (EOR), or to store it permanently (carbon capture and storage – CCS), with the final option being converting it into a more useful chemical form. To date, most large applications have been based around EOR, as – absent government incentives – there is no monetary return for CCS, and it would only be preferred where EOR is not possible or where a process can only meet environmental legislation by using CCS – a number of coal gasification project proposals tend to include a CCS component, for example, as it is unlikely that a coal gasification project in e.g., the US or Europe would be permitted without it. But if the chemical industry is to achieve its full ‘green’ potential, the best use would be to use the carbon dioxide as a feedstock for generating chemicals rather than oil, gas or coal, in effect ‘recycling’ the CO₂ into chemicals production.

A number of potential routes for this are available. On a large scale basis, chemicals such as formaldehyde and dimethyl carbonate can be produced from CO₂. But perhaps the two largest potential consumers of CO₂ are urea and methanol. Indeed, using carbon capture to boost urea production is already an established technology, for example as deployed by Mitsubishi Heavy Industries at the Ruwais urea plant in the UAE in 2007, which recovers 400 t/d of CO₂ to boost urea production².

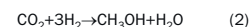
Methanol

While the global market for urea is over 180 million t/a, and that of methanol slightly smaller at around 100 million t/a, attention has focused particularly on methanol as an intermediate way of using CO₂, both because production of methanol opens the way to the manufacture of many other compounds, from formaldehyde, acetic acid and methyl methacrylate, to dimethyl ether, methyl t-butyl ether, olefins such as propylene and ethylene, and even gasoline, and because methanol can be used as a fuel directly, either on its own or in blends with more conventional fuels.

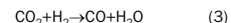
Methanol is normally conventionally produced from synthesis gas; a mixture of carbon monoxide and hydrogen, as follows:



However, using carbon dioxide as a feedstock requires the less exothermic CO₂ hydrogenation route to methanol:



This must also compete with the endothermic reverse water-gas shift reaction:



which can then supply CO for a conventional conversion for methanol via (1). Both (2) and (3) however generate water which can reduce the lifetime of conventional copper-zinc-alumina (CZA) methanol synthesis catalysts, and which must be separated from the methanol during a downstream purification step, increasing the cost³. This has led to experimentation with other catalyst systems to minimise water formation.

CRI

One company that has pioneered producing methanol from carbon dioxide and sustainable hydrogen is Carbon Recycling International (CRI). CRI was founded in Iceland in 2006 to explore the idea of recycling carbon dioxide emissions by using it to make useful products. Since 2012, the company has been using geothermal energy in Iceland from natural volcanic processes as a source of energy to heat steam in a turbine and generate electrical energy. This in turn is used to split water into hydrogen and oxygen, and the hydrogen is then combined with CO₂ in a process which CRI calls ‘Emissions to Liquids’ (ETL) to produce methanol. The CO₂ is captured from the Svartsengi geothermal

power station which also generates the power for electrolysis. Around 5,000 t/a of CO₂ is used to generate about 4,000 t/a of methanol, which is then blended into gasoline as a fuel additive for use locally. While burning the methanol releases the CO₂ back to atmosphere again, it is at least a carbon neutral fuel.

Horizon 2020

As part of the EU Horizon 2020 research programme⁴, CRI has also been awarded a €1.8 million grant to help scale its technology to larger scale production plants, a concept referred to as ‘CircolEnergy’, as the technology is designed to support and enable the transition to a ‘circular economy’. The technology has been used at a coal-fired power plant operated by RWE in Niederaussem, Germany, where carbon capture is used to gather CO₂ emissions from combustion of coal and combine it with hydrogen from electrolysis in the MefCO₂ project. MefCO₂, commissioned in 2019, produces only 1 t/d of methanol, but was designed as a test bed for the system’s capacity to react automatically to variations in hydrogen availability. The automated ETL process system was able to adjust rapidly to fluctuating electricity generation and the methanol synthesis system followed the changes in the availability of hydrogen. Results showed that conversion efficiency in the ETL reactor was not affected by these fluctuations and exceeded design criteria, presenting the opportunity for methanol production to be used in so-called ‘grid balancing’, storing excess energy generated from wind and solar at times when it exceeds demand for electricity, when marginal cost of electricity generation is effectively zero.

Now that this project is over, the process module is being transferred to another strand of Horizon 2020, where CRI is also working with Sweden’s Swerea MEFOS research centre facility in Luleå, Sweden. The module will be configured to convert residual blast furnace gases into methanol, using both hydrogen-rich off-gas and CO₂ from direct iron oxidation to make methanol for use as a shipping fuel for Swedish ferry operator Stena, which operates the world’s first methanol fuelled passenger ferry, the *Stena Germanica*.

Meanwhile, on a larger scale, CRI is working with Chinese chemicals corporation Henan Shuncheng Group to produce low carbon intensity methanol in China. The \$90 million project will involve building a plant at Anyang city in Henan province to

recycle about 150,000 t/a of CO₂, along with other waste gases to produce 180,000 t/a of methanol and LNG. Commissioning is expected by the end of 2021⁵.

Other projects

In Germany, bseEngineering and the Institute for Renewable Energy Systems at Stralsund University of Applied Sciences (IRES) have demonstrated the conversion of wind power into renewable methanol using CO₂ captured from flue gas. The technology is now being tested under ‘dynamic conditions’ of fluctuating power input over the course of a year-long programme. Basic production of methanol is 20 t/d (16,400 t/a) using one of bse’s modular reactors and a BASF catalyst, but the system has the flexibility to run at between 10 and 120% of design capacity according to bse⁶.

Clariant is providing its expertise in catalysis and syngas production in partnership with Air Liquide (who are licensing their Lurgi methanol process) and gas to liquids (GTL) technology company Ineratec – a spin-off from the Karlsruhe Institute of Technology – to develop a power to fuels and chemicals programme. Ineratec have their own modular containerised process for conversion of CO₂ to liquid fuels in a microchambered reactor. The technology relies on Clariant’s *HyProGen® R-70* catalyst to generate renewable syngas using recovered CO₂ and hydrogen from electrolysis via a reverse water-gas-shift reaction. Clariant’s *MegaMax* catalyst also powers the methanol synthesis reaction. Clariant said at a recent webinar organised by the Methanol Institute that it is looking at a three-stage methanol synthesis process



The MefCO₂ module on-site at Niederaussem, Germany.

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Computer rendering of one of Carbon Engineering's large scale air contactor systems.

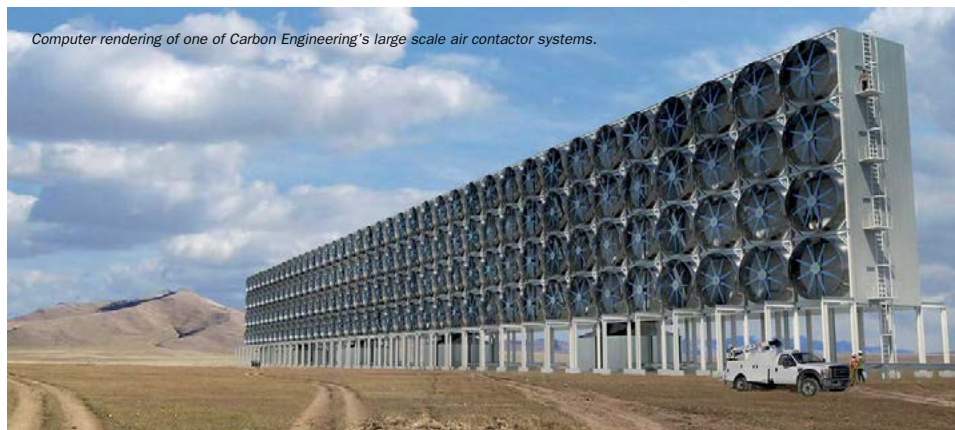


IMAGE: CARBON ENGINEERING

with inter-condensation of water and a recycle loop that leads to higher single pass conversion and less water flow on the catalyst. It also claimed that the process can achieve power to liquids economics competitive with current advanced biofuels⁷.

Haldor Topsoe meanwhile is part of a consortium called Liquid Wind with Siemens, Nel Hydrogen and Carbon Clean Solutions to develop a methanol plant based on hydrogen from wind energy. The company is aiming to build its first 'eMethanol' facility in northern Sweden, with initial operation slated for 2023. The company plans to develop five further facilities in Scandinavia before 2030, at which point the model will be replicated and licenced internationally. Topsoe is providing its new MK-317 Sustain methanol synthesis catalyst as part of the project⁸.

Direct air capture

Most CO₂ capture technology has concentrated on removal of carbon dioxide from industrial process streams or large scale combustion, where the CO₂ is already concentrated and in gaseous form. However, Carbon Engineering, a company based in Squamish, British Columbia which was founded in 2009 by Harvard professor David Keith, generated some headlines last year when they declared that they would be scaling up their technology for direct processing of carbon dioxide from air. Carbon Engineering calls this Direct Air Capture (DAC)⁹.

The process begins with an air contactor; a large structure modelled off industrial

cooling towers. A giant fan pulls air into the structure, where it passes over thin plastic surfaces which have potassium hydroxide solution flowing over them. This solution binds with the CO₂ molecules, removing them from the air and trapping them in the liquid solution as a carbonate salt.

The CO₂ contained in the carbonate solution is concentrated, via separating the salt out from the solution into small pellets in a structure called a pellet reactor. These pellets are then heated in the third step, a calciner, in order to release the CO₂ in pure gaseous form. This step also leaves behind processed pellets that are hydrated in a slaker and recycled back within the system to reproduce the original capture chemical.

Carbon Engineering announced in September 2019 that it was expanding the design for its first commercial DAC plant from a protected capacity of 500,000 t/a of CO₂ removal to 1.0 million t/a of CO₂. The planned facility, in the Permian Basin, is being built in partnership with Oxy Low Carbon Ventures, a clean technology subsidiary of oil major Occidental, and private equity firm Rusheen Capital Management. Front end engineering and design will begin in 1Q 2021 and construction for the plant is expected to begin in 2022, with the plant becoming operational within approximately two years.

Of course, the major issue with DAC is the relatively low concentration of CO₂ in atmospheric air. Even at the enhanced CO₂ levels that industrialisation has led to, CO₂ concentrations remain at only 400 parts per million (ppm), or 0.4%. This means that huge

volumes of air must be processed relatively efficiently in order to recover large volumes of CO₂. Nevertheless, by operating on such a scale, Carbon Engineering claim to be able to recover CO₂ at a cost of \$100/tonne. The company also argues that as the concentration of CO₂ is relatively constant globally, the technology is independent of location, and so could be constructed directly next to reservoirs suitable for carbon capture and storage (CCS), as in the Permian Basin plant, or plants capable of using the CO₂ for industrial processes.

And as far as the latter goes, Chevron is also investing in Carbon Engineering's DAC technology, though its interest is for synthetic fuel production – Chevron was involved in Fischer-Tropsch gas to liquids plants with Sasol in the 1990s, and developed a zeolite catalyst for F-T production, as well as providing isocracking and other technologies for product clean-up. In California, where Chevron and Carbon Engineering are developing CO₂ to fuel technologies using hydrogen from renewables, the state's Low Carbon Fuel Standard assesses a \$200/ton penalty on excess CO₂ in the fuel, so avoiding that penalty can make their synthetic fuel a the lower-cost option than conventional gasoline. That plant should be operational between 2022 and 2023.

Carbon Engineering argues that falling solar prices should enable them to bring "air-to-fuels" to market for about \$1/litre (around \$4/gallon) in the mid-2020s. This is equivalent to a methanol price of over \$1,300/tonne, although the company says that the price will continue to fall from there.

Practicalities

The issue that bedevils many green technologies is their cost compared to conventional production routes. The dominant cost factor has generally been that of electrolysis of hydrogen – the hydrogen oxygen bond in water is strong, and breaking it is thermodynamically costly. However, as noted above, the cost of generating the electricity to power the electrolysis continues to fall. Topsoe has pointed out that each doubling of capacity in wind or solar photovoltaic power generation reduces the cost per unit of energy by about 20%. A Nature Energy paper last year¹⁰ found that if market trends continue, green hydrogen could be economically competitive with natural gas on an industrial scale within a decade. Similarly, the International Energy Agency projects that the cost of clean hydrogen will fall 30% by 2030. Green hydrogen may already be nearly affordable in some places where periods of excess renewable generation drive down the costs of electricity to nearly zero. In a recent research note, Morgan Stanley analysts wrote that locating green hydrogen facilities next to major wind farms in the US Midwest and Texas could make the fuel cost competitive within two years.

However, a report last year in the Proceedings of the US National Academy of Sciences (PNAS)¹¹ has poured some cold water on the idea of a large scale move by the chemical industry to renewable feedstocks. The research team modelled the global chemical industry "to analyse the potential disruptive changes through large-scale CO₂ utilisation and resulting emission reductions." It found that, if rolled out across the petrochemical industry, while these technologies could reduce greenhouse gas levels in the atmosphere by 3.5 gigatonnes, this would require 18.1 petawatt hours of renewable electricity per year, far more than the total amount of renewable electricity available anywhere in 2030 even on the most optimistic projections. The thermodynamics of breaking the H-O bond are, as we noted earlier, fundamentally against you.

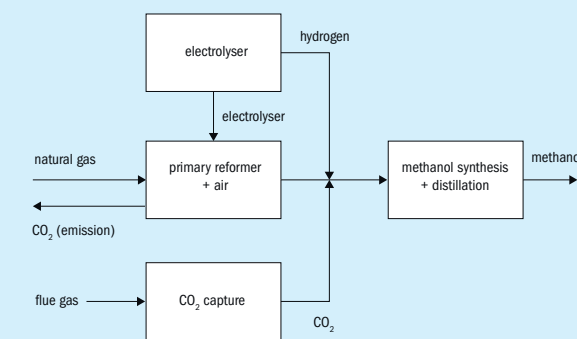
But this is to assume that a move to lower carbon chemical production is necessarily an 'all or nothing' affair. In fact it is possible to lower the CO₂ intensity of methanol production without moving completely to all-renewable operation. Andrew Fenwick of Johnson Matthey described a wide range of options for doing so in this magazine earlier in the year¹². And at the Methanol Institute webinar in August this

Table 1: Hybrid methanol plant concept

Case	Hybrid plant	eMethanol plant
Electrolyser	Same size	Same size
CO ₂ capture	Standard unit	Standard unit
Front end	Natural gas, 2 step	None
Output	1,000 t/d	280 t/d
CO ₂ emissions (t/tonne MeOH)	-0.1	-1.4
Breakeven price*	150	300

* compared to average methanol market price in Europe, June 2020 = 100 Source: Haldor Topsoe

Fig. 1: Case study: new hybrid plant



Source: Haldor Topsoe

year, Yawar Abbas Naqvi presented what he called a 'hybrid plant' concept⁸, as described in Figure 1. Table 1 shows the results of Topsoe's analysis, assuming an electricity cost of €29/MWh, and a realistic price for natural gas in Europe. It shows that even at today's prices, with the addition of the renewable hydrogen feed, a net negative carbon balance can still be achieved for a 1,000 t/d methanol plant which is largely working from natural gas, at a methanol price only a little way above current prevailing ones, and with the addition of environmental credits bringing it into the realms of commercial possibility. ■

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The Indorama Eleme urea plant in Nigeria, soon to double in capacity.

PHOTO: INDORAMA

Urea markets – Covid and beyond

Although the Covid-19 pandemic has been the big story in every market this year, the disruption and dislocations that this has caused have masked some of the bigger trends in the urea market, such as the revival of Chinese exports and India's push for self-sufficiency.

The urea market has had a turbulent year. At the start of the year, with only China seriously affected by the Covid pandemic, prices rose as the US found itself undersupplied, and South American buyers sought to increase inventories. Then, once the US application season was past, in May prices dropped to several year lows as buying dried up, with traders waiting to see what the impact of the Covid-19 pandemic would be as it began to seriously impact Europe and North America, and feedstock costs tumbled due to the crash in the oil and gas markets. However, a relatively benign monsoon season in India led to a scramble for more urea, with 5 million tonnes bought in July, and the market rallied again.

At the moment, governments have prioritised agricultural production, and any expected reduction in demand due to Covid seems not to have happened. That being the case, the pandemic has mainly

caused supply-side disruption, with some plants forced to close, at least for a few weeks, and in particular the lack of air travel has interrupted construction and commissioning of new plants.

It is still impossible to say how the rest of 2020 will play out, let alone 2021. Europe and North America fears a 'second wave' of Covid restrictions this winter, as falling temperatures force people back into closer proximity. In spite of the major international effort on producing a vaccine, it is likely one will not be widely available before next year. However, as countries become more practised at living with the virus, better treatments, more testing and widespread adoption of better practises may well mitigate the impact.

But while Covid may provide some short term disruption, over the longer term, there are other factors at work in the urea industry which are likely to have a more lasting effect on prices.

China

China continues to be the bellwether for the urea industry. In spite of a huge programme of plant closures over the past five years, the country remains far and away the world's largest producer and consumer of urea, and availability of Chinese export tonnage has been the key price determinant for the market for most of the past decade.

The large availability of Chinese urea was as a consequence of a self-sufficiency programme dating back to the Mao era and the so-called 'iron rice bowl' – a guarantee that the state would keep the nation fed. Rapid growth in demand for urea during the 1990s actually outstripped Chinese domestic production for a while, and the country became a major importer, but this was soon overtaken by a crash programme of building domestic capacity. By 2003 China was a net exporter of urea, and capacity continued to be over-built to stay ahead of demand into the 2010s. By 2015, domestic capacity reached 86 million t/a, far in excess of consumption (60 million t/a that year), and imports surged to 13.7 million t/a, swamping the international market.

That year was a turning point for China, however. The 13th Five Year Plan, which began in 2016, saw a concerted decision to move the Chinese economy from a primarily industrial focus to a more consumer-led economy. There was also a recognition of the environmental damage that China's rapid industrialisation had done, and a new 'green' focus for the economy. As well as a general attempt to move the Chinese economy from its reliance on coal, in the fertilizer sector, this led to a plan to cap fertilizer consumption at its 2020 value and try to achieve more balanced and less intensive agricultural production. It also led to a crackdown on air pollution in the major cities of the east coast, especially during winter months, and water pollution in the Yangtze River.

The environmental crackdown shut a good number of plants on a seasonal basis, but low prices and difficulty in renewing permits has also led to many closures of older, less efficient urea capacity in China. It is estimated that up to 20 million t/a of Chinese urea capacity may close in whole or in part between 2015 and 2020, and at least 13 million t/a of this will be permanent. For the most part this has been older plants whose gasification technology requires purer and more expensive anthracite coal. The new generation of more advanced gasifier plants are able to run on lower grade and cheaper bituminous coal. They are also larger and more energy efficient, and hence cheaper to operate. This was important, as similar crackdowns on Chinese coal capacity led to rising prices over the period 2015-2019, although during 2019 the government allowed some mines to reopen and output jumped nearly 10% year on year. Coupled with the Covid-19 outbreak, this has led to a collapse in Chinese coal prices this year – down by around 25% since January. Meanwhile, natural gas-based capacity continues to face shortages of gas and is often only seasonally active.

As capacity has closed, so has China's share of global urea capacity. In 2015 China represented 39% of all urea capacity worldwide, but by 2019 this had fallen to 32%. Chinese urea production has fallen with the closures in capacity, from 68 million t/a in 2015 to 52 million t/a in 2018, although this rose in 2019 to 54.9 million t/a as coal prices fell and the Yuan fell against the dollar.

As noted, agricultural consumption of urea continues to fall as farmers attempt to be more sophisticated in their applications and

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NITROGEN+SYNGAS
ISSUE 367
SEPTEMBER-OCTOBER 2020

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nutrient use efficiency increases. Industrial consumption is rising, especially for diesel exhaust treatment, and urea-formaldehyde and urea-melamine resins, but at present is not sufficient to balance falling agricultural use. Chinese urea consumption was 51 million t/a in 2018 and 50.2 million t/a in 2019, down from a peak near 57 million t/a in 2015.

This has meant that, although Chinese urea exports fell dramatically from 13.7 million t/a in 2015 to just 2.4 million tonnes in 2018, 2019 saw something of a bounce back, with exports rising to 4.7 million tonnes, contributing to weakness in the market. Looking forward, there is a continuing switch to more productive bituminous based urea capacity, with more new plants on the horizon, and a corresponding fall in anthracite capacity. This new cheaper and more efficient capacity may lead to a boost in exports and a lower floor price for urea.

India

India is the second largest consumer of urea in the world, reaching 32 million t/a in 2018-19. India, like China, had a policy of self-sufficiency in urea production, dating back to the 'Green Revolution' of the 1970s and 80s, but this lapsed in the mid-90s as naphtha and natural gas prices rose and availability tightened. Indian urea production plateaued at 20-22 million t/a, and since 1995 India has progressively become an increasingly large importer of urea; now the world's largest, at 7.5 million tonnes in 2019. Indian buying has come to dominate urea markets in much the same way that Chinese exports did.

The Modi government has set a return to domestic urea self-sufficiency as one of its major targets, and in 2017, it announced an ambitious \$8.7 billion plan to end imports of urea within five years, by rebuilding five closed down urea plants and setting up new facilities, bringing 6.4 million t/a of new urea capacity on-stream. It has also encouraged private developments, two of which are now complete. Chambal Fertilizers and Chemicals had closed its old urea plant at Kota near Gadepan in Rajasthan state in 2015 due to unfavourable economics, but has now built a new 1.27 million t/a replace-

ment plant, which was commissioned in January 2019. Meanwhile, Matix Fertilizers and Chemicals completed a new plant in West Bengal, also 1.27 million t/a, in 2017, but lack of coalbed methane availability prevented it from running at capacity, and it now awaits a link to the Dhamra LNG terminal.

Of the five government plants, also all 1.27 million t/a of urea capacity, the first, at Ramagundam, was due to start up earlier this year, but has been delayed by Covid and is now looking at beginning operations in October. The Gorakhpur, Barauni and Sindri plants were reported in August to be 80%, 74% and 73% complete, respectively, and are all looking at start-up in 2021. All three will be fed by LNG imported on the east coast at Haldia and supplied along the Jagdishpur-Haldia pipeline.

The final plant of the five government developments is at Talcher in Odisha State. Like the other projects, it is to have a final capacity of 1.27 million t/a of urea, although unlike the others the plan is to run it on coal as a feedstock. This is something of a radical development for India, which had an unhappy history with its first two coal-based urea plants, built in the 1970s, which suffered from all manner of production issues and which were finally closed down. The high ash content (35-45%) of Indian coal also means that certain types of gasifier are not suitable. However, the success of China in developing coal-based urea capacity has led to a re-think. The EPC contract for Talcher Fertilizers Ltd was awarded to Wuhan Engineering last year, but construction has made slow progress as Chinese engineers have been unable to travel due to Covid restrictions, and Indian-Chinese clashes over disputed territory in

Current likely completions will mean India adds 6.4 million t/a of domestic urea capacity.

the Himalayas have also complicated the political environment. Although completion is scheduled for 2023, this may be an optimistic date. A plan to build a new 1.27 million t/a urea plant at the Brahmaputra Valley Fertilizer Corp (BVFCL) site at Namrup in Assam, so-called Namrup-IV – was approved in October 2018, to replace the two older 220,000 t/a and 270,000 t/a units currently at the site, adding a net 780,000 t/a. However, an explosion at

the site in January shut down Namrup-II, and there is no progress reported as yet on the new plant. Even so, current likely completions will mean India adds 6.4 million t/a of domestic urea capacity in the period 2019-2021, provided that there are no further delays, and that gas supplies are available to operate the plants. In practise this may mean that the capacity addition is more staggered, out to 2023, say.

Even so, in theory this should reduce Indian urea imports by a similar amount, although this year, like 2019, has seen exceptional demand in India. India imported 9.7 million tonnes of urea in 2019, and has seen record buying in the first half of this year. Indian demand for urea is projected to increase by about 3.5% year on year, which could see it add 4 million t/a of demand over the next five years.

Brazil

Brazil is another major importer of urea, and this figure has been growing due to shutdowns of domestic capacity. Brazilian demand for urea was 6.3 million t/a in 2019, the same as for 2018, but domestic production declined to 0.9 million t/a, and will be lower still this year, as 2019 saw the closure of two urea plants at Camacari and Laranjeiras, with a combined capacity of 1.0 million t/a of urea. The only remaining plant in Brazil is now the 660,000 t/a Araucaria plant, and state owned operator Petrobras has also suggested that that could face closure as well. As a result, Brazil's expanding agricultural economy, which is seeing nitrogen demand rise at about 4% year on year, could be importing record amounts of urea this year. Brazilian imports of urea stood at 5.5 million t/a last year, but are forecast to rise to 6.8 million t/a by 2023, which would – assuming the completion of domestic Indian urea capacity – make Brazil the world's largest urea import market.

Iran

Iran remains another wild card in the international urea market. Iran has long sought to monetise its huge natural gas reserves via downstream chemical production, with urea and methanol among the major products. However, the Trump administration the US has pulled out of an international deal over Iran's nuclear programme and re-imposed sanctions on the country, making

exports of urea from Iran's continuing pipeline of new urea plant completions more difficult. Iran produced 6.1 million tonnes of urea in 2018, of which it exported 4.2 million tonnes, mostly to India. However, exports for 2019 dropped to 2.6 million tonnes, with India essentially out of the market, and Iran forced to rely on swap deals with Turkey and Brazil. The start-up of the 1.1 million t/a Lordegan urea plant in Iran this year makes Iran's export dilemma all the more acute.

Rising capacity

In addition to new capacity in China and India, there are a number of new urea plants, many of the export-oriented, in other parts of the world. Nigeria has seen considerable new project development, with Indorama Eleme constructing a second 4,000 t/d (1.3 million t/a) urea plant due to come onstream in 2021-22, and Dangote adding 2.5 million t/a of urea capacity in two trains at its Lekki site near Lagos. The first of the two urea trains is currently in commissioning, and the second is expected to be operational early next year.

Russia and central Asia are also seeing new urea plant construction. In Russia, methanol producer Metafrax is building a new 570,000 t/a urea plant at the company's Gubakhi site, using CO₂ from the methanol plant as part of the feed. TogliattiAzot is constructing a third, new 726,000 t/a urea plant at Perm, and KuibyshevAzot is adding a new 540,000 t/a urea plant at Togliatti. EuroChem has announced plans for a 1.32 million t/a urea plant at Kingisepp near St Petersburg, and Shchekinoazot is building a new 660,000 t/a plant in the Tula region. These five will add another 3.8 million t/a of urea capacity by 2023.

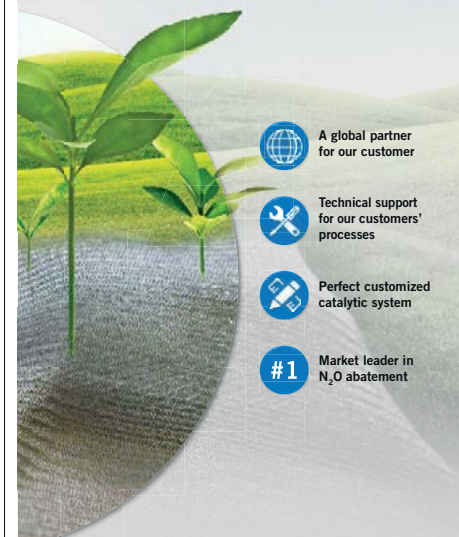
Elsewhere in the CIS, the gas-rich countries in Central Asia are also looking to monetise gas via petrochemicals, especially where gas export pipeline options are limited, or subject to Gasprom tariffs. Uzbekistan's new 580,000 t/a urea plant at Navoi is due on-stream in 2021, and the country is now looking at another new fertilizer complex at Samarkand, while Azerbaijan's SOCAR is planning to build a second 660,000 t/a urea train at its existing site.

Outside of Asia, Brunei Fertilizer Industries is also due to complete a new 1.3 million t/a urea plant next year, and there are some other capacity increments at places like Koch's Enid plant in the US. In total, somewhere around 17 million t/a of new urea capacity is due to come on stream between 2019 and 2023, even excluding China, where new capacity is likely to outpace closures.

Demand is expected to rise by 10 million t/a over the same period, with India, Africa and South America (especially Brazil) projected to be the fastest growing areas. This leaves a considerable excess of new capacity. Covid has delayed many new projects, and caused some production dislocation, which may mitigate against this in the short term, but in the longer term it is likely to mean low prices – with Chinese bituminous plants the floor price setters – and probably some shutdowns of marginal capacity. Indian imports will fall as domestic capacity comes on-stream, but perhaps not to the extent that the government hopes, as demand continues to rise. Brazil, meanwhile, is likely to become an even more important buyer. The restriction of Iranian capacity by sanctions may help the market for now, but that could also be another major bearish factor should a new US administration take a different tack from 2021.

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MEG from methanol and syngas

PHOTO: JOHNSON MATTHEY

MEG Mini plant.

New technology makes it possible for methanol producers to diversify their product portfolio and participate in the high growth mono ethylene glycol market. **A. Shah** of Johnson Matthey reports on the development of the new technology and its commercialisation.

Mono ethylene glycol (MEG) is the most common industrial diol and is used in the manufacture of polyester fibre, fabrics and polyethylene terephthalate (PET) resin used for production of plastic bottles. Other industrial uses are as a coolant, heat transfer agent, antifreeze and a hydrate inhibitor in gas pipelines.

New process technology using a proprietary catalyst developed by Johnson Matthey Davy Technologies Limited (a fully owned subsidiary of Johnson Matthey Plc) and Eastman Chemical Company (Eastman) enables the production of MEG from methanol and syngas. This offers a unique and exciting opportunity for methanol producers who are interested in diversifying their product slate.

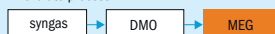
Fig. 1: Main production routes for MEG

Conventional route (naphtha/ethane-based)

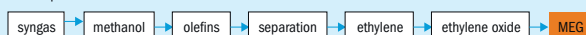


Coal routes (syngas-based)

1. Oxalate process



2. MTO process



3. JM and Eastman MEG process



Source: Johnson Matthey

First licence for new MEG technology

The first licence for this new MEG technology was granted in September 2018 to Inner Mongolia Jiutai New Material Company who are building a major coal to MEG complex in Inner Mongolia, China which will use the new MEG technology to produce 1,000,000 t/a of MEG. This will be the first commercial plant using the new technology and is a result of development by Johnson Matthey (JM) and Eastman which started in 2006.

Market opportunity and production routes

Current worldwide consumption of MEG is approximately 30 million t/a and has grown by over 5% per year over the last decade. With a growing middle class, particularly in Asia, over ten million t/a of new MEG capacity will be required over the next ten years.

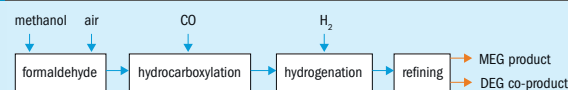
Fig. 1 shows the main production routes for MEG. Until 2012, nearly all the MEG in the world was produced by the conventional route from ethylene, which is produced by cracking natural gas or naphtha. In Asia, ethylene is produced mainly from naphtha and the increase in the oil price in the 2000s encouraged the development of the Oxalate process in China, using syngas produced from coal as the feedstock and several plants in China use this technology today. This route has an explosive intermediate and there have been reported issues with product quality where the MEG quality deteriorates within a few days of production. Another syngas-based route is the production of methanol from syngas followed by conversion of methanol to ethylene in a methanol to olefins (MTO) plant. MEG is then produced by the conventional process making it a long process.

Finally, there is the JM and Eastman process where methanol and syngas are converted to MEG. The process uses well proven unit operations with new proprietary catalyst technology with high conversion and selectivity enabling efficient use of raw materials. This process is more economic compared to the conventional ethylene-based route when the oil price is above \$55 per barrel.

The novel MEG process

A simplified block diagram of the novel process is shown in Fig. 2. The key feedstocks are methanol, carbon monoxide and hydrogen and besides MEG, the

Fig. 2: Block diagram of the MEG process



Source: Johnson Matthey

Table 1: Key performance data

Feedstock consumption per tonne of MEG	Unit
Methanol	0.64 t/t
Hydrogen	0.8 kNm ³ /t
Carbon monoxide	0.40 kNm ³ /te
Typical consumption of main utilities per tonne of MEG	Unit
Steam (all levels)	6.5 t/t
Cooling water	210 m ³ /t
Electricity	385 kWh/t

Source: Johnson Matthey

process produces a small amount of valuable diethylene glycol (DEG). If required, the formaldehyde plant can be designed to also provide an export formaldehyde stream.

In the formaldehyde plant, methanol from battery limit reacts with air over a catalyst to produce formaldehyde. The first MEG plant reaction stage is hydrocarboxylation, where aqueous formaldehyde reacts with carbon monoxide to produce glycolic acid. The glycolic acid is then reacted with an alcohol to form esters, which are then hydrogenated to form mono ethylene glycol and diethylene glycol.

Feed and product specifications

The feedstock specifications are AA grade methanol, high purity carbon monoxide (99 vol-% min) and hydrogen (99.9 vol-% min).

The MEG product specification meets ASTM E2470-09 and the new Chinese National Standard GB/T 4649/2018. The key parameter for purity of the product is ultra violet (UV) transmittance and the MEG produced by the JM and Eastman process has been demonstrated to meet the specification in all UV transmittance wavelengths. The DEG product purity meets the ASTM D2694-05 specification.

Performance data

The key performance data is summarised in Table 1. DEG is a valuable by-product and approximately 19 kg of DEG is produced per tonne of MEG. The process has low waste

water emissions and there are no hazardous intermediate products or by-products.

Technology development

JM has used the mini plant concept to develop and commercialise new DAVY™ technologies for nearly 50 years. It started with oxo alcohols in the 1970s.

Some of the new technologies commercialised over the last 50 years include the following:

- oxo alcohols – since 1970s;
- butanediol – since 1980s;
- tetrahydrofuran – since 1990s;
- ethyl acetate – 2000;
- detergent alcohols – 2002;
- octanol – 2007;
- 2-propyl heptanol – 2014;
- hexanediol – 2018.

Efforts are now focused on MEG technology.

The development of new technologies is undertaken at the state-of-the-art technology centre in Stockton, UK. The mini plants are designed, built and operated by teams of chemists, chemical engineers and specialists working together combining their respective expertise to develop the optimum process flowsheet by selection of appropriate catalysts in conjunction with optimum reaction systems. The mini plants are designed to ensure all the fundamental design parameters can be scaled to commercial size. Besides mini plants extensive use is also made of other tools such vapour/liquid equilibria testing equipment, hydraulic rigs, and simulation and plant modelling tools.

Every part of the MEG flowsheet was replicated in the several mini plants which were operated over several thousands of hours to generate comprehensive data covering reaction kinetics, catalyst performance, separation equilibria and where appropriate the recycle streams were closed.

The mini plants were also used to produce the final product MEG and DEG. Using comprehensive data collected from long term operation of the mini plants, designs have been developed for commercial scale plants with MEG capacity ranging from 200,000 to 500,000 t/a.

JM and Eastman collaboration

Another key aspect in the MEG development has been the benefit of the collaboration with Eastman who have a strong background in coal gasification, syngas chemistry and derivatives. Eastman operates the USA's first coal gasification plant and produce a range of high value chemicals. Eastman has expertise in material testing, product quality analysis and significant operating experience. A dedicated team of highly experienced chemists, scientists and engineers from both JM and Eastman worked together for over ten years during the development of the new MEG technology. Between JM and Eastman, a process design package and support during detailed engineering, plant start-up and post plant start-up can be provided.

Integration with methanol plant

JM can also offer designs which would integrate the methanol and MEG plants. Such a complex would benefit from common syngas production based on either coal gasification or steam reforming of natural gas with sharing of offsites and utilities. Such a facility would also offer the opportunity to produce methanol and formaldehyde as export streams.

Summary

The novel MEG technology from JM and Eastman enables production of MEG using methanol and syngas as feedstocks and has the following attributes:

- a competitive investment and operating cost;
- economies of scale with single train capacities up to 500,000 t/a;
- Demonstrated MEG product quality meeting the fibre grade application requirements.

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Lowering CO₂ emissions with EARTH[®] technology

TechnipFMC's EARTH[®] technology, with its structured catalyst jointly developed by TechnipFMC and Clariant, has been proven to be a cost effective way to drastically improve productivity and energy efficiency of the steam reforming process, while reducing the CO₂ footprint per unit hydrogen and syngas product. The technology can be applied in projects to increase the capacity of ammonia and methanol plants and allows significant reduction of greenhouse gas emissions. **S. Walspurger** of Technip Benelux B.V. and **S. Gebert** of Clariant GmbH report on the EARTH[®] technology and its applications.

Syngas and hydrogen are the most widely used industrial gases in the bulk chemical, refining and petrochemical industries. Syngas is an essential primary building block to produce ammonia, methanol, oxo alcohols and synthetic fuels via Fischer Tropsch synthesis. Nearly half of global hydrogen generation is used to produce ammonia, which is then used either directly or indirectly as fertilizer (>75%) and as a building block in the chemical industry. Another significant share of the hydrogen generation finds application in the refining sector, for clean upgraded fuels production.

With increasing worldwide population, and increasing demand from the agricultural and chemical sectors, worldwide ammonia production capacity continues to grow. However, market overcapacity combined with a strong trend towards higher efficiency application of fertilizers (e.g. via digitalisation), currently limits capacity growth to a relative low level (approx. 1% p.a.). Furthermore, persistently low ammonia prices put considerable pressure on producers' margins.

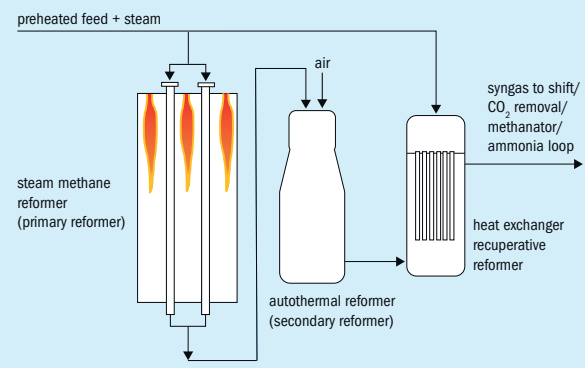
In refining, hydrogen consumption increases as the requirements for upgrade of fuel quality drives the demand for deeper hydrotreatment and hydrocracking processes. In addition, the recent acceleration of the demand for refined biofuels also contributes to the growth of hydrogen needs.

Among commercially available hydrogen and syngas production technologies,

steam reforming of natural gas is usually the most cost effective means to ensure profitable hydrogen, syngas and ammonia industrial scale production. The reforming process comprises catalytic conversion of natural gas and/or higher hydrocarbons with steam at high reactor outlet temperature (between 750°C and 950°C), and at moderate pressure (20-40 bar). Steam reforming is an endothermic reaction that requires significant heat input usually obtained by burning waste gas and make-up fuel (additional natural gas in most cases).

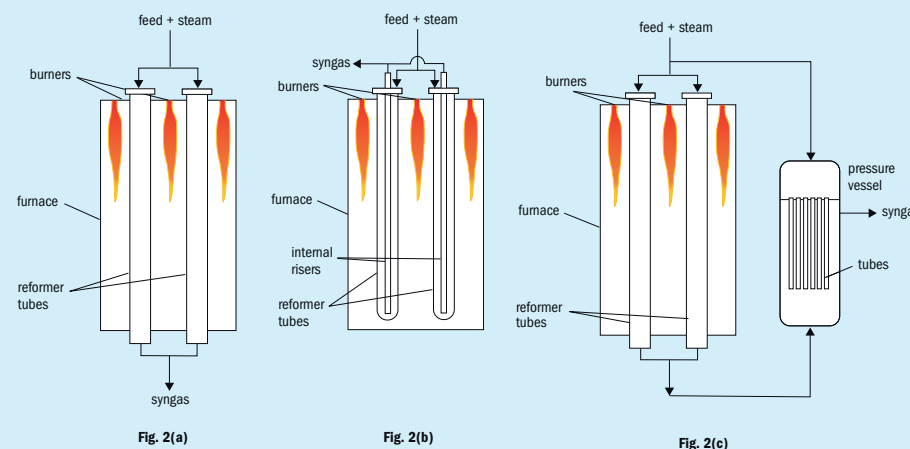
The steam reforming process is therefore carried out in a fired heater, whereby a multitude of parallel tubular reactors are provided with the necessary heat of reaction via burners disposed around the reactor tubes. Only part of the fired heat is directly absorbed by the reactive medium in the tubular reactors. Residual heat not absorbed by the tubes is recovered from the combustion products (flue gas). To this end, a so-called convection section, or heat recovery section, is located next to the reformer and enables residual heat recovery for process use,

Fig. 1: Simplified flowsheet of a state-of-the-art recuperative reformer in parallel to primary and secondary reformers



Source: TechnipFMC and Clariant

Fig. 2: 2(a) conventional reformer tubes, 2(b) U-shaped reformer tubes having an internal riser allowing for internal counter current heat exchange, 2(c) heat-exchanger reformer connected in parallel to the conventional reformer. Figs 2(b) and 2(c) are known as recuperative reforming.



Source: TechnipFMC and Clariant

for combustion air preheating, and for raising steam that is typically used for the process itself (process steam), for driving machinery (compressors and pumps) and for export to neighbouring units when advantageous.

Depending on the quality of the feedstock, one tonne of hydrogen produces typically between 9 and 12 tonnes of CO₂, bringing the steam reformer to the top of the list of single point CO₂ emitters, for instance in large refineries and petrochemical complexes. In ammonia synthesis, carbon dioxide is rejected before the ammonia synthesis loop, usually by CO₂ absorption in a suitable solvent such as carbonates or amines, and is also emitted from the steam reformer stack. Typically the CO₂ footprint of ammonia production is between 1.8 and 2.2 tonnes of CO₂ per tonne ammonia (without accounting for CO₂ capture and use in urea production).

Over the past decade, alternative technologies to produce steam at attractive cost and with reduced (or even no) net CO₂ emissions have been adopted rapidly and widely. In parallel, over the last two decades steam reforming technology licensors have shifted the efficiency and heat integration paradigm, and deployed advanced

technologies capable of reutilising the heat contained in the hot process gas exiting the reformer as a heat source to drive the reforming reaction itself. Such technologies are commonly called "recuperative reforming" (Fig. 1) and mostly consist of either a heat-exchanger recuperative tubular reactor that is placed in parallel to the primary and/or secondary reformers, or a heat-exchanger recuperative reformer placed in the convection section of a fired heater.

Recuperative reforming

In Fig. 2(a), a conventional top-fired reformer is shown, with inlet and outlet situated at opposite ends of each reforming tube. The mixture of steam and feed is converted to syngas (CO+H₂) by absorbing roughly half of the energy released in the reformer firebox through the catalyst tube walls. The syngas temperature at the outlet of the tubes is typically in the range of 750°C to 950°C, depending upon the desired conversion, hydrogen and CO yield.

Fig. 2(b) depicts recuperative reforming technology, whereby a tube is inserted in a U-shaped reformer reactor, creating an

annular counterflow arrangement to enable high grade heat recovery within the tube itself. In this layout the highest temperature is obtained at the end of the catalyst bed located at the U end of the tube, while the syngas exiting at the (top) outlet of the tube is partially cooled by counter-current heat transfer.

Fig. 2(c) shows an alternative design whereby the heat recuperation is carried out in a separate, external heat-exchanger recuperative tubular reactor, placed in parallel to the fired steam reformer. In this configuration, syngas exiting the fired reformer is routed to the parallel reactor as the heat source, while additional fresh feed + steam is converted on the tube side (cold side) of the reactor against the provision of this heat. This latter process integration option has gained interest in the context of syngas production capacity increase for ammonia and methanol plants as well as the recent wave of refinery revamps supporting the clean fuels market. For grassroots units, the heat exchanger recuperative reformer is also an attractive option since it improves the energetic performance of the plant and decreases the CO₂ footprint per syngas unit production.

Fig. 3: Sketch of EARTH® tube detailing the internal flow recirculation



EARTH® technology

TechnipFMC and Clariant are introducing a new steam reforming product to the market to drastically improve both the energy efficiency and productivity of reformer tubes. TechnipFMC developed and patented a new recuperative tubular technology called EARTH®, for Enhanced Annular Reforming Tube for Hydrogen.

EARTH® is a drop-in insert comprising a concentric tubular assembly combined with a structured reforming catalyst in the outer annular space, which may be installed both in existing and new reformer tubes, to simultaneously achieve heat recuperation and higher throughput in steam reforming process (Fig. 3).

TechnipFMC and Clariant have joined their collective expertise in process, heat transfer and catalysis to develop and deliver EARTH® technology to the hydrogen and syngas market. The proprietary geometric layout in combination with the highly active, stable and mechanically robust catalyst coated on a tailor-made structured component promotes efficient and optimised heat transfer as well as low pressure drop. The development of the catalyst has been based on Clariant's extensive multi-faceted know-how on

structured catalysts for fuel cell applications and for mini hydrogen plants.

Technical and economic advantages

The EARTH® reactor technology has the advantage of being highly compatible with most existing commercial steam reformer units, which typically have inlet and outlet ends located at opposite sides of the furnace. Unlike first generation technologies using mostly U-shaped tubes with an internal riser, EARTH® enables easy, drop-in revamp of most existing reforming units. The geometry of the internal concentric tube assembly can be customised to meet the desired hydrogen output and steam production.

Stress and lifetime

Thanks to the internal heat recovery pass, the external heat flux demand is reduced, allowing for less intense firing and improved usage of the reformer tube material. Additionally, the outlet system, which is a critical mechanical item on modern steam reformer units, is exposed to much less severe conditions than the conventional technology, and is therefore subjected to less mechanical stress.

Efficiency and intensification

The significant improvements of EARTH include reducing firing, thus lowering the operating cost and/or enabling higher plant throughput, (i.e. the increased productivity and yield of the reformer tubes at equivalent firing). The technology is advantageous for achieving a capacity increase of up to +20%, at otherwise constant reforming conditions, with no or minor modifications on the steam reformer and heat recovery system. Moreover, EARTH® enables improved energy efficiency from the introduction of feedstock to the production of hydrogen or syngas, and carbon footprint values correspond to alternative recuperation technologies.

Catalyst performance

EARTH® technology uses a low pressure drop structured catalyst designed by TechnipFMC and Clariant to achieve highest activity and heat transfer combined with outstanding stability and mechanical robustness. The catalyst is suited to operate in the annular space between reformer tube and the outer concentric inner tube,

coping advantageously with the mechanical stress attributable to thermal cycling and high temperatures, and the strongly reduced volume of the catalyst bed.

As a result, the gas throughput (gas hourly space velocity) in the catalyst tube can be increased significantly compared to conventional ceramic pellet technology while remaining within the desired pressure drop envelope. Concomitantly, the surface to volume ratio of the structure, as well as the geometrical design, allows for a step increase in activity and heat transfer properties compared to the random packed bed solution with traditional ceramic pellets. Overall the benefit of the intensified catalyst structure, in combination with the tailored internal heat recuperation facility, translates into an increase in syngas production of +20% per catalyst tube.

Carbon footprint

The EARTH® internal heat recovery enables the firing duty per unit syngas produced to be decreased, allowing for up to 10% CO₂ emissions reduction per unit of value product, thereby achieving lower carbon footprint compared to conventional steam reforming technologies. In view of the lower reformer tube outlet temperature, due to the internal heat recovery, and the fact that the reformer outlet system normally constrains the severity of reforming, EARTH® paves the way to high conversion and low steam to carbon ratio that are key parameters to decrease the operating cost and to increase the overall energy performance of the steam reforming process.

Steam production

An implication of the EARTH® technology is a moderation of the steam production, very similar to other recuperative technologies. Although steam co-production has been used for decades as a practical and cost-effective method to recover high grade heat from the process and to valorise it by steam export to neighbouring consumers in the refinery or industrial complex, a trend observed in many integrated petrochemical platforms and refineries is to minimise steam export (even to zero steam export). In ammonia and methanol plants where steam is typically needed to drive compressors and other units (e.g. methanol distillation section), EARTH® is a promising technology to significantly reduce greenhouse gas

emissions and to increase profitability by widening the operability envelope for consideration of alternative energy sources such as green electricity.

The implementation of EARTH® can be customised according to the targets and operation strategies of the hydrogen and syngas producers. An example of how EARTH® technology can deliver advantages according to operation objectives is shown in Table 1. These figures are indicative and case specific.

EARTH® technology has the advantage of being a drop-in technology that can fit in existing as well as new reformer tubes. It is therefore merely a catalyst changeout that is typically completed during a planned turnaround. Moreover, the implementation of EARTH® technology does not induce plot space issues. In case the EARTH® technology is supplied together with new tubes the end user may choose for catalyst pre-loading off-site.

The return on investment for the EARTH® technology depends obviously on site specific valorisation of utilities such as high pressure steam, the applicable CO₂ emission regulations, the valorisation of the additional hydrogen generated compared to installation of new equipment. For all scenarios, TechnipFMC investigates closely with the end user the performance target and adapts the design of the EARTH® technology to achieve the best possible compromise.

EARTH® Implementation with Ak-Kim

Akkim Kimya Sanayi ve Ticaret A.S. (Ak-Kim) is a subsidiary of Akkök Holding and is one of the fastest growing leading chemicals manufacturers in Turkey. Among other products, Ak-Kim produces hydrogen peroxide by mostly using the hydrogen product of the chlor-alkali process. To achieve cost effective hydrogen peroxide production, hydrogen from a small syngas plant is used to complement the primary hydrogen source. The CO product obtained from the syngas plant enters in an on-site solvent production plant. The small syngas reformer had been in operation for 20 years, at which point Ak-Kim decided to implement EARTH® to achieve fuel savings and to increase steam reformer efficiency in comparison to the conventional random packed ceramic catalyst tube technology.

The design of the EARTH® inserts was chosen to decrease steam export to a large extent and to maximise internal heat recov-

Table 1: Indicative comparison of EARTH® with the conventional technology

	Conventional	EARTH®	
Capacity	base	same	+20%
Efficiency feed + fuel to H ₂	base	~+10%	~+10%
CO ₂ footprint per Nm ₃ of H ₂	base	~-10%	~-10%
Steam export	base	up to -50%	~same

Source: Clariant

Table 2: Comparison of EARTH® with the conventional technology for Ak-Kim case

	Conventional	EARTH® tubes	Variation
Syngas throughput	100%	100%	0%
Radiant efficiency, %	54.9	66.7	+ 21%
Export steam flowrate, kg/h	1195	509	- 57%
Make-up fuel flowrate, kg/h	125.4	78.1	- 38%

Source: Clariant

er, therefore reaching a maximum reduction of feedstock consumption. TechnipFMC took advantage of the end-of-life of existing tubes to propose a pre-packed delivery on site. The installation of the tubes was performed within one day, which is on a par with any tube replacement activity for such scale. Under the supervision of TechnipFMC and Clariant the plant was started-up very smoothly one week after the EARTH® tube installation, with an immediate observed step change performance of the steam reformer, in terms of both fuel consumption and steam export.

A performance test of the EARTH® tubes was completed successfully three weeks after the start-up, in early 2019. During this period the plant achieved stable operation at the nominal design plant capacity. The DCS recordings and the samples analysed by gas chromatography during the performance test have been used for reconciliation of the heat and mass balance of the complete plant, and for the EARTH® tubes themselves.

The conversion observed in the EARTH® tubes corresponded to an equilibrium temperature of 853°C and process gas temperature of 855°C, confirming that the catalyst performed very close to the equilibrium conversion, with the expected performance for the start of run. Furthermore, the measured pressure drop over the reformer tubes was less than 1 bar, well below the original pressure drop specifications corresponding to the conventional tubes loaded with ceramic pellets.

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Solving problems in nitric acid plants

Troubleshooting and root cause analysis help to identify and solve problems in the operation of nitric acid plants and to prevent future reoccurrences. Johnson Matthey, Casale and Sabin Metal Corporation discuss their approach to solving problems in nitric acid plants to improve plant reliability and efficiency and to avoid unplanned shutdowns, costly replacement of equipment and loss of production.

JOHNSON MATTHEY

Root cause analysis of poor performance in nitric acid plants

J. Ashcroft, R. Lopez-Garcia and I. Hepplewhite

Johnson Matthey (JM) has assisted in root cause analysis for several customers in recent years, working in conjunction with the plant engineers to improve nitric acid plant performance. JM was supplying the primary platinum group metal (PGM) ammonia oxidation gauze for these plants, when they began to experience performance issues, typically seeing a reduction in both conversion efficiency and increase in N_2O emissions. In most of these cases, the initial conversion efficiency started high before rapidly dropping several percent during the campaign.

In all these cases, a combined team of engineers, from JM and the customer plant, proceeded with a detailed root cause analysis (RCA) to identify the possible causes of the problem and to prepare and implement the corrective actions to solve this issue. By following the RCA process, a fault tree analysis was developed from an identification exercise, which highlighted potential cause factors to the problem. A range of root causes have been identified in different plants over the last few years, including catalyst contamination from poor gas filtration and boiler leaks. The most common cause, typically resulting in the worst drop in performance, has been a structural problem with the basket within the burner, resulting in ammonia by-passing the catalyst.

Symptoms of poor performance

JM supplies ammonia oxidation catalyst in the form of knitted PGM gauzes to a range of nitric acid plants. These plants operate across a wide range of operating pressures and nitrogen loadings, and different design principles are applied to the catalyst design for each category of plant. Catalyst packs are also designed and manufactured to allow for ease of installation, which can reduce any potential downtime.

This optimised design approach results in JM catalysts achieving high performance, often increasing conversion efficiencies by over 1% compared to competitor product performance. End of campaign catalyst analysis and further optimisation of the design can result in greater increases in both performance and campaign lengths achieved.

However, there have been occasions where the plant performance has been reduced, with plants experiencing a sudden drop in conversion efficiency and a corresponding increase in N_2O emissions. The magnitude of the reduction in performance can vary depending of the plant pressure and loading, and the root cause of the poor performance. Reductions in conversion efficiencies of up to 5% and a three-fold increase in N_2O emissions have been observed, which raises concern about both the plant and catalyst performance.

Following notice from the customer on any poor performance, JM begins discussions both internally and with plant engineers to determine the cause of the reduction in performance.

Identification of potential causes

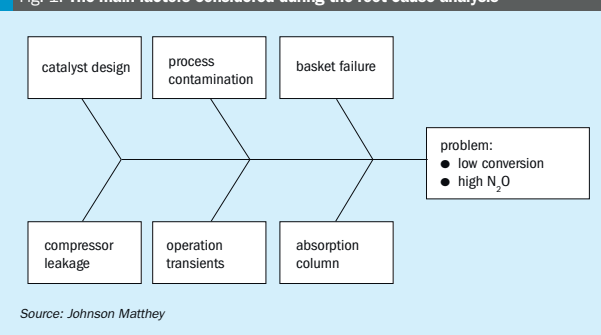
As the cause of the poor performance is often not immediately clear, the first stage in identifying the cause is to proceed with a detailed root cause analysis (RCA) to identify all possible causes of the problem, identify all probable causes and, when identified, prepare and implement the corrective actions required to solve the problem. Well-structured RCA processes can greatly reduce or eliminate costly problems and minimise the impact to the producer.

There are a number of methods available to carry out root cause analysis. A common method is to use the A3 problem solving method, along with additional tools including a fishbone cause and effect diagram. This allows for all potential root causes to be systematically identified, and the likelihood of each cause can then be assessed. The root causes deemed most probable are then investigated further by engineers from the customer plant and JM.

The root cause analysis consists of several steps:

- Identification and description of the problem, asking the following questions:
 - What deviation was observed?
 - Which object had the deviation?
 - When did the deviation occur?
 - Where did the deviation occur?
 - How much of a consequence did it have?
- Selection of the team in charge of the RCA
- Identification of the potential hypotheses and reasons that have caused the problem
- Establish a workplan and strategy to rule out hypotheses
- Definition of steps to solve the problem with minimum impact

Fig. 1: The main factors considered during the root cause analysis



The A3 methodology followed an 8-stage process to identify and correct the root cause of the reduction in performance.

1. **Define the problem:** Clarify the problem using data and quantify the impact of the problem.
2. **Break down the problem:** Generate current process data to understand the entire process; collect information to visualise the current situation; break the problem into parts that can be solved separately; prioritise parts of the problem with the greatest impact.
3. **Define objectives:** Define the desired outcome based on the specific problem identified; decide what specific results are required; state the goals using SMART criteria (Simple, Measurable, Achievable, Relevant and Time).
4. **Identify potential direct causes:** Establish hypotheses of direct causes using fishbone diagram or brainstorming sessions; validate or discard the hypotheses using data, field observation and/or expert judgement.
5. **Identify root cause:** Find the root causes of the direct causes validated in step 4.
6. **Define action plan:** Identify actions required to tackle the root causes identified; prioritise the actions according to their impact and feasibility.
7. **Follow up action plan:** Assign responsibility for executing actions and track progress; check the effectiveness of the actions.
8. **Standardise successful process:** Extend solutions to other processes if they encounter similar problems or common root causes.

The team that carried out the root cause analysis was a team of engineers from

both the customer plant and JM. Initially, an exhaustive list of potential factors that could have an impact on plant efficiency were listed. This list was then reviewed by the team of engineers and several factors could be ruled out. The main factors considered for the majority of these case studies are summarised in Fig. 1. The team at the customer plant and at JM were then both given tasks to rule out certain hypotheses.

Process contamination

A potential root cause for reduction in performance was identified as high levels of contamination on the gauze surface resulting in lower selectivity to nitric oxide. There are many sources of contamination, with iron contamination the most damaging as it both blocks the platinum catalytic sites and oxidises ammonia with a greater selectivity to nitrogen and nitrous oxide.

Depending on the severity, surface contamination is often visible on the gauze surface in the form of dark patches. In these cases, JM recommends plant engineers observe the gauze surface for signs of obvious contamination, as well as any physical damage (e.g. tearing) to the gauze surface.

It is also recommended that plant engineers check the pressure drop over the mixed gas filter. If the filter material has been lost or damaged there will be a change in pressure drop over the filter. A review of the ammonia quality certificates can also be carried out to review if levels of iron contamination sourced from the ammonia feed have increased during the campaign.

Although these checks reduce the likelihood of contamination as a root cause, it is often not sufficient to completely rule it out,

and contamination or damage to the catalyst often remain as an active hypothesis.

Basket failure

Basket failure is very difficult to rule out as a hypothesis. A visual inspection through the burner sight glass can be carried out, however often nothing unusual will be observed. This is because basket failure often occurs in the form of cracks along welds which would only be visible during a full inspection of the open basket during a shutdown. Basket failure often remains a probable hypothesis for the reduction in performance.

In the event of a basket failure resulting in significant by-pass of the catalyst, the ammonia oxidation reaction may begin to take place on the surface of the burner. This results in the burner material reaching high temperatures, and the resultant heating can often be observed through hot spots on the burner surface. In this case, basket failure would become a very probable root cause. Further heating of the burner can result in early aging, and plant engineers who observed this symptom would often choose to shut down the plant to carry out a full inspection of the basket and burner.

Compressor leakage

JM has worked with many plants historically to determine the root cause of performance problems and, depending on the plant configuration, it can be possible for a compressor leak to result in tails gas being introduced upstream of the gauzes, introducing nitric oxide which could react to form additional nitrogen and nitrous oxide. Plant engineers are advised to check the configuration of the compressor and

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expander and if the set up does not result in mixing of inlet and tail gas streams in the event of a leak, this hypothesis can be ruled out.

Operation transients

During a root cause analysis, detailed process data is requested from the customer and sent through and reviewed by JM. The outcome of this review is highly dependent on the data received, however several common themes have been observed in multiple plants, including the nature and magnitude of the increase in N₂O emissions. For example, when poor performance is linked to the PGM catalyst, the increase in emissions and corresponding drop in efficiency is gradual as the reaction moves too far into the catalyst pack too early in the campaign.

Often, plant data will show a sudden spike in N₂O emissions, rather than a gradual increase. Step changes in emissions can be linked to catalyst performance if they are following a compressor trip: often the force on the gauze results in a loss of the high surface area growth (cauliflowers), resulting in a temporary and sudden reduction in available catalytic sites for the oxidation reaction. The performance would be expected to improve as the gauze begins to restructure again, however if the damage is great enough then the previous levels of performance may not be reached again. In some cases, the sudden reduction in performance in the plant is not preceded by a plant trip. In these cases, ammonia by-pass becomes a probable root cause.

Plant temperatures are reviewed in the days leading up to and following the reduction in performance. Several cases have reported uneven temperature distribution across the gauze, with one thermocouple reading significantly higher or lower temperatures than other thermocouples. Higher temperatures can indicate uneven flow patterns and a higher loading in one section of the gauze. It could also indicate a higher selectivity to nitrogen and nitrous oxide in this area of the basket, as these reactions are more exothermic than the production of nitric oxide.

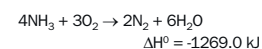
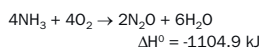
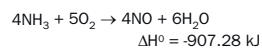
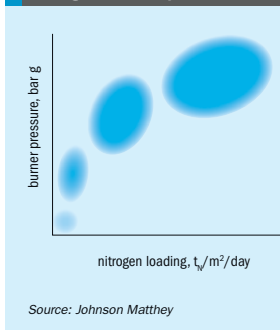


Fig. 2: Four plant operating ranges demonstrated in terms of nitrogen loading and burner pressure



Absorption column

Poor performance in the absorption column can result in reduced plant efficiency. To rule out this hypothesis, the NOx emissions in the tail gas are plotted against time and if they show a decreasing trend as the nitrogen loading is decreased this would suggest normal operation within the column.

Poor performance in the column would have no effect on N₂O emissions, which are only generated or abated within the ammonia oxidation burner and tertiary tail gas systems. If the reduction in conversion efficiency is accompanied by a corresponding increase in nitrous oxide emissions, this suggests the absorption column is not a probable root cause.

Impact of catalyst design

While plant engineers investigate process conditions and unit operations that have been identified as potential root causes, JM reviews the catalyst design using proprietary kinetic models to simulate the performance of the catalyst at the appropriate point in the campaign to determine the reaction profile within the catalyst packs.

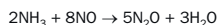
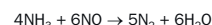
In some cases, the reduction in performance has coincided with a new catalyst design being installed. The new design will typically have changed the alloys and knit structure used within the pack and will have been optimised for the plant operating conditions. However, due to the design being new, customers are often understandably concerned that the catalyst pack could be the root cause of the poor performance.

Catalyst design principles

When designing catalyst packs, JM considers the plant operating conditions and campaign requirements to design a pack with a competitive PGM weight that will deliver high performance throughout the campaign. The design rules applicable vary depending on the plant type, with four plant categories covering almost all operating conditions (see Fig. 2).

For medium pressure plants, operating around 2-6 bar g and with a nitrogen loading of less than 20 tonne N/m²/day, JM designs the catalyst pack using proprietary design tools to generate a highly efficient design whilst minimising the installed metal content. This design utilises high surface area gauze structures in the top layers of the pack, providing sufficient platinum sites to complete the majority of the reaction at the beginning of the campaign in the top two layers of the pack.

The kinetics relating to ammonia oxidation have favourable selectivity to nitric oxide when the reaction path length is short. If the path length increases, and more gauze layers are used before the ammonia is all converted, the likelihood of nitric oxide reacting with ammonia increases, and reduces the overall efficiency of the pack.



In addition to minimising the reaction path length with high density knit structures, the design rationale for medium pressure plants will often utilise high palladium alloys in the bottom part of the pack. The system gives greater average conversion efficiency and lower N₂O emissions for medium pressure plants than standard technology. A catchment system is often installed below the catalyst gauzes and will be designed for optimal recovery given the prevailing PGM market conditions at the time, and to minimise the pressure drop.

Modelling the reaction profile through the catalyst

To ensure that the gauze design could not be a contributing factor to any sudden decrease in efficiency, a simulation of the catalyst pack is often run using the ammonia oxidation kinetic model to verify that the ammonia oxidation reaction is completed at the appropriate point within the pack. The case study below was carried out to illustrate the expected reaction

profile of a medium pressure plant gauze design at various points within the campaign. The reaction profile modelling carried out during a root cause analysis will vary depending on the category of nitric acid plant and the issues faced by the customer.

During start-up, the gauze wires are flat and have limited surface area, and the reaction is completed within the 6-layer pack. Immediately following a successful light off, the wire surface begins to restructure to form high surface area growth, termed "cauliflowers", and the bulk of the reaction is expected to complete within the top two layers for a plant with this pressure and nitrogen loading.

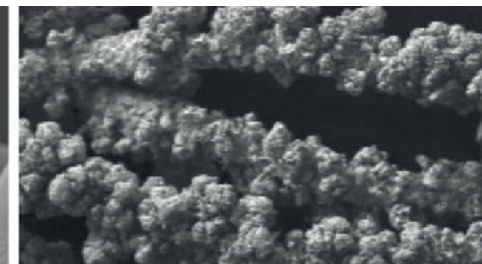
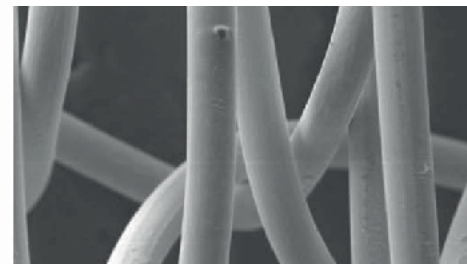
The results showed that within one week of operating, over 99% of ammonia had been converted after the second layer of the gauze design. Towards the end of the campaign the top layers would be expected to deactivate as they lose platinum throughout the campaign and the reaction profile would be expected to move further through the pack. By this stage that palladium-based alloys lower in the pack will have collected sufficient platinum to provide catalytic sites to continue providing a high level of performance.

If the kinetic modelling of the catalyst does not support the theory that the PGM catalyst design was not fit for purpose, then this result, along with the process data analysis, will allow the hypothesis of catalyst design causing poor performance to be ruled out.

Outcome of root cause analysis and mitigating actions

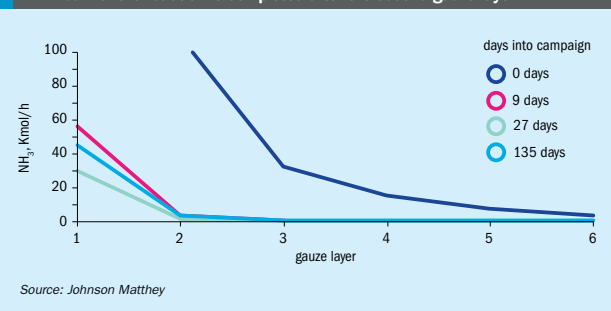
Following the elimination of many potential root causes for the reduction in plant performance, the three potential root causes most often found are:

- high levels of contamination on the surface of the catalyst;
- physical damage (e.g. tearing) to the gauze surface;



Wire surface as manufactured (left) and after cauliflower formation (right). The significant increase in surface area can be observed.

Fig. 3: Reaction profile of the catalyst after various days of operation showing the bulk of the reaction is completed after the second gauze layer



Source: Johnson Matthey

- damage to the basket resulting in ammonia by-passing the ammonia oxidation catalyst.

It is often not possible to further narrow down the root cause of the problem without a visual inspection of the gauzes and the basket containment system. The affected plant will often schedule a shutdown to carry out a full visual inspection of the basket. If contamination or physical damage to the gauze have remained as probable root causes, JM will often manufacture an additional gauze layer(s) that can be installed over the existing gauzes if required, often manufacturing with a reduced lead time due to the significant negative impact that low performance can have on a plant.

Common root causes that have been found in recent years include:

- cracks in baskets formed from weld failure and thermal cycling, resulting in ammonia by-pass;
- cracks in baskets formed due to using an abatement catalyst with an extremely high pressure drop, resulting in either ammonia by-pass of the oxidation catalyst,

- nitrous oxide by-pass of the abatement catalyst, or both;
- severe contamination on the gauze surface resulting from a boiler leak;
- severe contamination on the gauze surface resulting from damage to the upstream gas filtration system.

Conclusion

The use of root cause analysis in this scenario results in an in-depth and prompt review of potential causes of the reduction in performance. Through working together and using established problem-solving methodologies, customer plant engineers and JM engineers can reduce the large number of potential causes to a small number of probable root causes. This knowledge allows plant engineers to prepare and arrange for potential basket repairs in the case of basket failure, and to make the informed decision to order any additional gauze layers in the case that the gauze system is contaminated or damaged. As a result, the time spent shut down is often minimised and the impact from further production losses is reduced.

CASALE SA

Solving operational and design problems in nitric acid plants

J.F. Granger, I. Cerea, J. Goicochea and A. Guarino

Casale's nitric acid technology, includes process and mechanical knowhow as well as experience in operation and troubleshooting, strengthened by almost six decades of experience of GP in operating nitric acid plants. As a result, Casale's clients can take advantage not only of its strong engineering and technology capabilities but also its experience of plant operation which gives Casale a unique position in the fields related to the design, reliability, and troubleshooting of these plants.

Furthermore, the implementation of remote plant monitoring provides a new opportunity that enables Casale to further support customers to predict and solve plant issues, combining long-term troubleshooting experience with an accurate and constant analysis of the plant data.

Fundamentals of reliability

The reliability of a plant is linked to many factors such as the quality of the equipment, plant maintenance and the way the plant is operated.

The quality of the equipment is important but it is not always easy to make the proper choice between a very expensive item of equipment and a cheaper one with a shorter lifetime. For example, should a tantalum cooler condenser be installed instead of a stainless steel one, if the latter has a lifetime of more than ten years?

Maintenance is also crucial. Very often, a lot of pressure is put on the shoulders of the people in charge of maintenance to minimise the duration of any shutdowns. There are many examples showing that it is crucial for the future of the plant that these turnarounds should be prepared and performed in a professional way. The fact that the catalytic gauzes must be changed on a regular basis provides opportunities to carry out maintenance activities. Since the gauze changes are always planned, there is no excuse for not taking the opportunity to perform some maintenance at that time.

Reliability is also linked to operation. It is obvious that, in any plant, respecting the operating instructions is fundamental for the reliability of the plant and directly impacts its safety.

At the same time, the reliability of the plant is driven by the design choices originally made. Take, for example, the cooler condensers, where the process gas can be either on the shell side or the tube side of the equipment. The main issue with cooler condensers is corrosion by condensation and re-boiling of nitric acid. If the condensation happens when the process gas is in the tubes, it is quite easy to forecast and determine, but when it is on the shell side it is not so easy.

A bad approach to solve an issue

When a problem appears in a nitric acid plant or any other fertilizer plant, the first people to face it are the operational team and later the maintenance people. Leaving aside the fact that quite often operations blame maintenance and vice versa, the natural tendency is to modify the equipment to solve the issue. However, this approach is quite dangerous since it generally does not solve the root cause and could potentially generate additional issues.

Another response is to change some operating instructions to solve the problem, but again this is not the best way forward. The correct approach would be to carry out a deep analysis of the problem to clearly identify the issue. This implies involving people who have experience in both process and operation. Maintenance or equipment specialists are also useful at this stage to confirm the options considered by the team.

In this scenario, the operational analysis becomes a fundamental part of a more extensive analysis that not only supports the diagnostics of failures but also helps to understand the root causes during mechanical inspections.

Casale approach to troubleshooting

Casale's approach to troubleshooting includes the following steps:

- safety first;
- data collection;
- identify technical elements;
- recognise faulty measurements;
- adopt a simpler process analysis;

- multidisciplinary root cause analysis;
- digital opportunity.

Safety first: All HSE general aspects and specific safety constraints should be checked before acting. Rushing to implement a solution can expose to safety hazard.

Data collection: First, the team collects all available data which can contribute to solve the issue. To succeed on this, an open and frank communication between the different people involved is established. This prevents certain elements from being omitted or hidden.

Identify technical elements: In some cases, it could be possible to identify the problem by a quick analysis of the collected data. In particular, if the data is not in agreement with the normal and expected operation of the plant.

Recognise faulty measurements: Measurement errors and faulty instruments are often the root cause of operational problems.

For example, a few years ago, when lightning up the gauzes of a nitric acid plant, a red plume was emitted to the stack within a couple of minutes. Despite the different checks to the plant instruments, the problem was not solved. This led the operational team to elaborate a sophisticated explanation of the observed phenomena. However, when the process team arrived, they identified the lack of air as a root cause. After insisting that the air flow meter be rechecked, it was found that one flowmeter was inaccurate. After correction, the plant was restarted without any problems.

Adopt a simpler process analysis: The production of nitric acid is a well-known process. Hence all observed plant behaviour can be easily explained with standard concepts.

Plant operators should therefore avoid creating new theories or elaborate explanations to describe observed plant phenomena. This could be an indication of lack of training or understanding of these concepts. Casale with its strong operation and design background can quickly identify the root cause and propose a robust solution to the identified problem.

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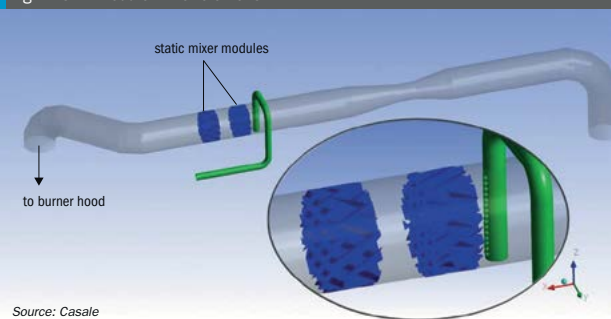
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Fig. 1: CFD Module mixer element



purpose to minimise the intervention and reduce the plant shutdown time and the intervention cost.

This activity required a detailed analysis of plant data and vendor documentation together with a computational fluid dynamic analysis of the air ammonia mixer along with the entire burner and feeding gas geometry.

The mixing elements and the relevant ammonia sparger have been simulated through a CFD tool to evaluate the contribution of each single element to the ammonia distribution over the gauzes (Fig. 1).

As shown in Fig. 2, the CFD analysis resulted in a proper mixing capacity of the inline mixing elements but highlighted poor ammonia distribution by the ammonia sparger over the mixing element, causing a high distribution ammonia spread over the gauzes and higher temperature operating span.

A new ammonia sparger design (Fig. 3) was developed to improve the ammonia distribution upstream of the existing mixing elements and to reduce the temperature spread over the gauzes.

Thanks to the proper identification of the root cause, with the replacement of the ammonia sparger, the temperature span over the gauzes has been solved. This was accomplished by replacing only a small element of the mixer device and without affecting the integrity of the overall mixer internals.

This in situ replacement had the added benefits of reducing plant downtime and cost savings by avoiding the expense of replacing the entire mixer.

Digital opportunity: While the classical approach to troubleshooting will remain a valid solution in the years to come, modern technologies and digitalisation efforts, already being used in different industries,

condenser equipment is back to its original design.

Multidisciplinary root cause analysis: In some cases, the solution to a technical issue, requires the contribution of different engineering competences that are not normally available as part of the plant staff.

For instance, during the commissioning of a new nitric acid plant, a high temperature spread on the thermocouple located underneath the catalyst gauzes of the ammonia burner was reported. This temperature spread was leading to difficult operating control and poor efficiency. Furthermore, the temperature difference was exposing the catalyst to an uneven PMG loss over the catalyst surface and therefore to a potentially shorter campaign length.

After excluded other causes and validating through a pyrometer the presence of the temperature span over the gauzes, the issue was found in the air-ammonia mixer.

A more detailed check of the entire air-ammonia feeding line was then carried out to precisely identify the root cause with the

Fig. 2: CFD study of existing mixer element and resulting uneven distribution over gauze surface

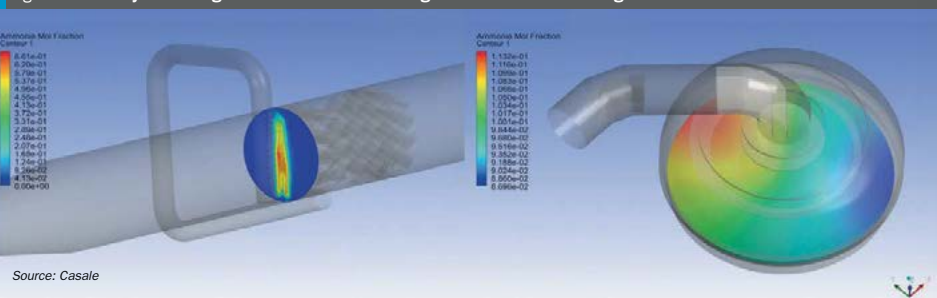
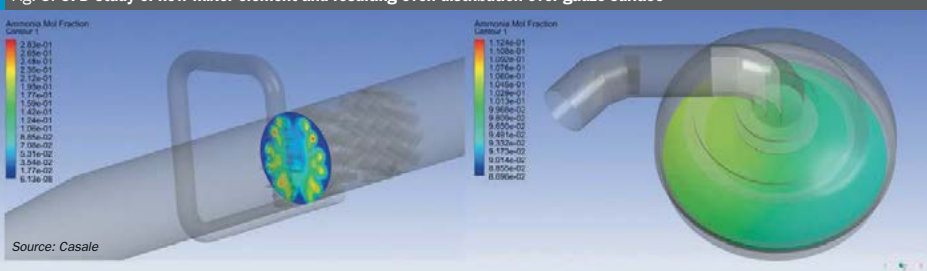


Fig. 3: CFD study of new mixer element and resulting even distribution over gauze surface



are gaining popularity due to their cost saving advantages and short execution times.

In this changing scenario, the operational data becomes fundamental for the development of maintenance programs aimed at improving reliability.

Casale's view is that, thanks to modern technologies, troubleshooting needs should be anticipated and likely avoided. In fact, most of the time the solution to a problem is found through analysis of historical data, meaning that it could be prevented through predictive analysis of data.

Casale has developed and is continuing to work on systems that provide greater insight and a more detailed analysis of DCS plant data through customised software tools and remote monitoring.

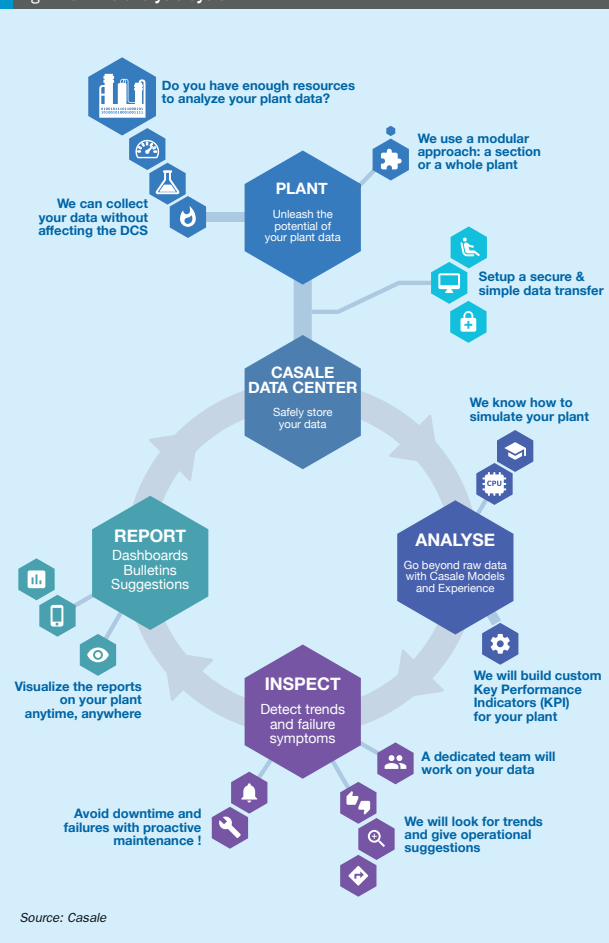
Plants generate a huge amount of data on a daily basis, but data is mostly used for DCS visualisation and archival purposes, and for helping field operations and control. Unfortunately, due to the lack of resources and time, prominent trends and data correlations are seldom analysed thoroughly, leading to suboptimal operation.

To help plant operations, support maintenance and improve mechanical reliability, Casale has created a portfolio of digital products that takes full advantage of existing plant data infrastructure and allows the remote analysis of plant conditions to help clients to improve the reliability of their nitric acid plants.

Casale Remote Engineering Service (CARES)

Casale's remote plant monitor service (CARES), has been designed to directly connect Casale's experts (ranging from process to mechanical engineers) with plant operators and managers to support daily operations and assist troubleshooting following a multidisciplinary approach,

Fig. 4: CARES analysis cycle



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as described. The service is like having a team of experts looking after the plant to anticipate operational problems. Fig. 4 shows the CARES analysis cycle.

At the core of remote engineering services, Casale uses an automatic data reconciliation algorithm to convert measured data from the plant into physically consistent values that respect global and local mass and energy conservation around units of operation, sections of the plant or the whole plant.

The data reconciliation is much more than a process simulation, it is a tailor-made process model built up to reveal the real-time performance of the plant, including full information of the critical process streams, which cannot be directly measured in the field. Thus, calculated key performance indicators (KPIs) based on reconciled data offer great value to clients, providing an effective way to identify critical aspects of the plant operation and their temporal behaviour.

Data reconciliation also allows the identification of faulty readings and anomalies in the field instrumentation used to guide the process operation. Thanks to the power of the data reconciliation, abnormal deviations among reconciled quantities and field

measurements are promptly detected and thus used to alert critical conditions into the plant. Essentially the identification of erratic readings of the instrumentation may suggest the underperformance of a plant section or the drift of parameters towards critical operating conditions and constraints.

How does CARES help clients?

Using a combination of advanced analytics and expert advice provided by the customer care team, plant behaviour is analysed, focusing on the aspects that are most relevant to the client:

- Boost plant productivity: CARES provides continuous support to utilise the plant capabilities at its best and to achieve maximum production and efficiency.
- Troubleshooting: CARES offers support in identifying the root cause of plant upsets and unexpected shutdowns, providing solutions to improve reliability and increase the on-stream factor.
- Improve understanding and confidence in plant operation: Take the right action at the right moment. Feel confident and conscious of the plant behaviour. This is not an easy task. CARES provides valuable advice which allows improved

knowledge and confidence of the plant operation and production process.

- Identify plant limitations: Identify equipment bottlenecks and operating procedures that are hindering plant performance.
- Supporting pro-active maintenance and inspection programs.

Expert advice is communicated to clients via a web dashboard available anywhere, anytime via a secure web page. The aim of the web dashboard is to provide a clear view of the plant and equipment performance using simple visual indicators (widgets) for the key performance indicators.

The dashboard service is completely customised according to customer needs. It is provided with a chat interface to maintain a direct link with the Casale customer care team and is complemented by periodic conference calls and written reports. The customer care team is also ready to support clients when problems occur.

Adopting the latest digital technologies has opened the door to new ways to merge Casale's operational and plant competences to provide more predictive and customised plant troubleshooting

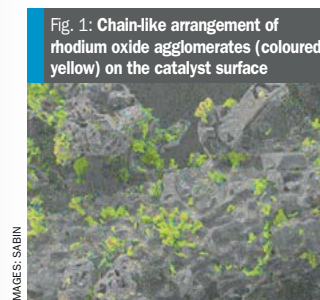


Fig. 1: Chain-like arrangement of rhodium oxide agglomerates (coloured yellow) on the catalyst surface

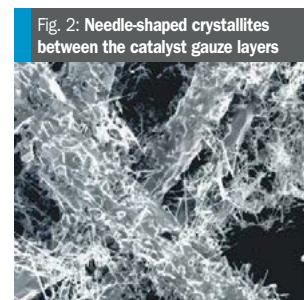


Fig. 2: Needle-shaped crystallites between the catalyst gauze layers

perceived visually as a glowing section of the catalyst package and instrumentally as an increase in the catalyst temperature.

However, this perception only describes the process of kinetic self-acceleration of the exothermic reaction, not the ignition itself. The actual ignition takes place at an earlier point in time, but the released heat of reaction is withdrawn from the self-acceleration of the reaction and instead heats the catalyst and the immediate internals of the reactor, so that the ignition process is hardly noticeable.

Another problem is that the thermocouples are typically arranged below the catalyst and hence a significant delay occurs in the measured temperature signal. This effect results in the signal showing a considerably higher temperature increase than actually occurs. As a result of this apparent extreme rise in temperature, due to the self-acceleration of the reaction, the ammonia ratio in the mixed gas is often increased very slowly. The catalyst thus remains in this phase over a longer period of time in a temperature range which causes an accumulation of rhodium oxide on its surface and thus it is irreversible damaged.

Such an accumulation of rhodium oxide in the starting phase of the catalyst can be demonstrated by means of scanning electron microscopic analysis of samples of the used catalyst. The degree of damage ranges from agglomerates arranged in chains on the catalyst surface (Fig. 1) to the extreme case of needle-shaped crystallites between the catalyst gauze layers (Fig. 2).

Ultimately, the effects can be seen in the fact that the HNO_3 yield increase is delayed and the maximum yield is never reached. The aging of the catalyst starts earlier in the campaign and the increase in ammonia consumption develops faster. The cause, however, is the incorrect start-up procedure.

Process simulation is the only way to find this specific cause and optimise the start-up process. To simulate the start-up process, the heat capacities of the catalyst and the immediate reactor built-in components are required. These heat capacities can be determined from the cooling curves after the ammonia supply is interrupted. Taking into account the kinetic parameters of the reaction as well as the process parameters of the plant and its

thermodynamic principles, a simulation model is developed based on the current start-up procedure, which is then applied in the process simulation for optimisation.

By means of such a process simulation, the necessary information about the temporal course of ignition and self-acceleration of the reaction is obtained. Calculations in the context of a case study show that when the reaction ignites, the amount of heat released is almost completely withdrawn from the self-acceleration of the reaction to heat the catalyst and the immediate reactor built-in components. With the rise in temperature of the catalyst and the immediate reactor built-in components, their heat capacity progressively decreases, so that an ever greater temperature increase is achieved with the corresponding amount of heat. The self-acceleration of the reaction starts from the first minimum of the heat capacity curve and only from that point onwards can the temperature measurement show that the reaction has ignited.

Fig. 3 and Fig. 4 show the corresponding calculations. Fig. 3 shows the course of the heat capacities over temperature. The graph shows the extreme gradient between the temperature at which the NH_3 admixture begins (blue point) and the temperature at which the self-acceleration of the reaction starts (green point). Fig. 4 shows the corresponding heat flow rates. Initially, almost all of the reaction heat released (gray curve) flows into the heating of the catalyst and built-in components (blue curve). With decreasing heat capacity, this heat flow passes through a maximum, whereupon more heat is available for the self-acceleration of the reaction. With the onset of the increased self-acceleration of the reaction, the heat of reaction is increasingly discharged with the process gas (red

SABIN METAL CORPORATION

A three-pronged approach to solving problems with ammonia oxidation catalyst

B. Cook and Dr Jürgen Neumann

There are a wide variety of problems encountered when it comes to ammonia oxidation catalysts within nitric acid plants. The spectrum extends from the ignition of the reaction on the catalyst to the way it ages, and from possible contaminations to mechanical damage to the catalyst package itself. It is not always easy to distinguish between cause and effect, which is why "band-aid" measures are so often applied; ones that cover and somewhat mitigate the undesired effect, but do not actually solve the causal problem.

There are essentially three tools available to the catalyst manufacturer to support the nitric acid producer in his process optimisation efforts: process modelling and simulation, CFD flow simulation and the analysis of the spent

catalyst pack using scanning electron microscopy.

What all three tools have in common is that they create a visualisation of the problem(s) and can thus make a clear statement about cause and effect. Understanding the root cause(s) provides the possibility of defining clear measures to optimise the process or, in the event of deviations, to return the process to the normal state.

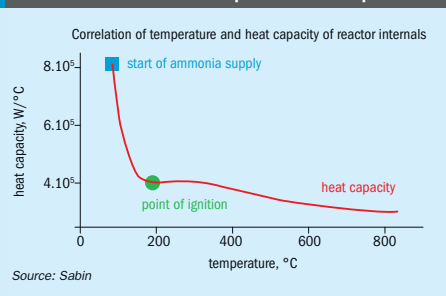
In this article Sabin presents three methods on the basis of two distinct problems: 1) the ignition of ammonia oxidation on a new catalyst, and 2) the influence of the flow characteristic on the performance of the catalyst. Customer-provided case studies are used to illustrate these two commonly confronted problems in nitric acid plant efficiency.

Impact of first ignition

The first ignition of a new catalyst has a dramatic effect on the development of its lifetime activity and the extent of its precious metal losses, and thus ultimately for its overall service life and achievable HNO_3 product yield. The problem lies in the fact that at the first start-up, ammonia oxidation must be ignited. The brand new, and almost completely inactive catalyst, is therefore introduced at temperatures that are far below the ignition temperature of ammonia.

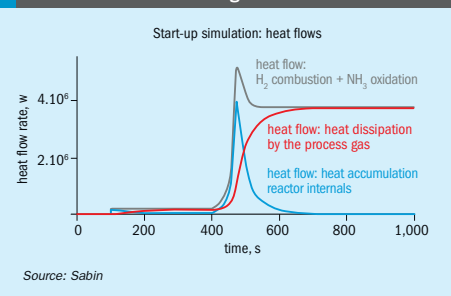
In order to ignite the initial reaction, hydrogen combustion is used to create an ignitable region on the catalyst surface. The more intensely and homogeneously the hydrogen flame can be applied to the catalyst package, the easier this is to accomplish. The ignition of the reaction is initially

Fig. 3: Course of the heat capacities of the catalyst and the immediate reactor built-in components over temperature



Source: Sabin

Fig. 4: Simulation of the progress of the start-up process by means of the occurring heat flows



Source: Sabin

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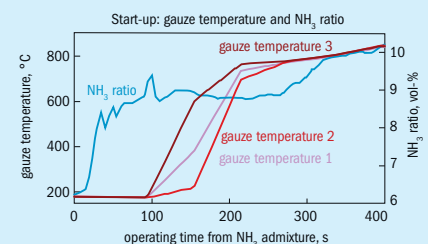
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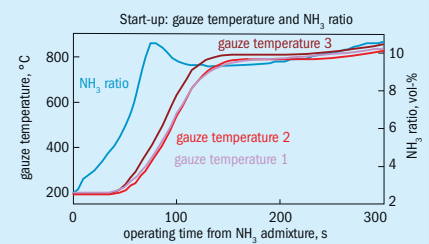
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Fig. 5: Temperature profiles (red) and development of the ammonia ratio (blue) of the original procedure; example from a case study



Source: Sabin

Fig. 6: Temperature profiles (red) and development of the ammonia ratio (blue) of the optimised procedure; example from a case study



Source: Sabin

curve). When the steady state is reached, the heat output by the process gas is equal to the heat input by the reaction.

At the end of such a study there is an optimised start-up procedure calculated from the simulation, which is then implemented accordingly by the operators. It specifies in detail the preheating by means of hydrogen combustion as well as the point in time for the addition of ammonia and the temporal increase in its ratio in the mixed gas. Fig. 5 and Fig. 6 show the time course of the temperatures at the three thermocouples (red) of the reactor as well as the temporal increase in the ammonia ratio in the mixed gas (blue), with Fig. 5 showing the original and Fig. 6 the procedure optimised by means of process simulation.

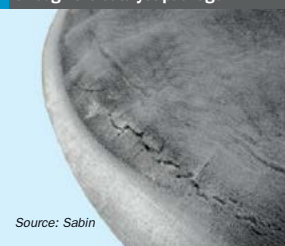
In addition to the start-up simulation, all conceivable operating states can generally be represented by means of modelling and process simulation and examined with regard to a wide variety of issues.

Impact of gas flow characteristic

An uneven gas flow characteristic in the reactor can have very different effects. Such an inhomogeneous characteristic is made visually recognisable by shadows that move in a recurring sequence over the catalyst surface or, in extreme cases, by regions that appear permanently darker on the catalyst package than the rest of the surface.

A different coloration of the catalyst surface ultimately testifies to a different surface temperature, which results from different loads caused by the flow and in particular a different ratio of axial to radial flow components. A high axial proportion allows the reaction to penetrate deeper into the catalyst package; the reaction is distributed

Fig. 7: The most common sign of inhomogeneous gas flow: a crack through the catalyst package



Source: Sabin

over a larger number of catalyst gauze layers, which means that such a characteristic causes a lower temperature on the surface of the catalyst package. When the plant is shut down, such regions will cool down more quickly than the rest of the catalyst package, so that longitudinal stresses occur which can lead to cracks in the catalyst pack, especially in the edge area. Fig. 7 shows an extreme expansion of a crack through the entire catalyst package, which can be attributed to such a flow condition.

At the other extreme are flow characteristics with a high radial flow component. The reaction in this case does not penetrate far into the catalyst package and almost the entire amount of ammonia is converted at just a few of the uppermost gauze layers of the catalyst package. The consequence is an early onset of the aging of the catalyst due to high platinum losses in these regions.

The most common causes for the occurrence of such inhomogeneous flow characteristics are the elbow flow characteristic and the separation of the flow from the reactor wall at the transition from the elbow to the

reactor. Other upstream units can also create a twist that propagates to the catalyst level.

The only way to visualise the flow characteristics is to simulate those using computational fluid dynamics (CFD). At the beginning of every project there is the transfer of the technical drawings into a three-dimensional computer graphic. Fig. 8 shows such an implementation using the example of a Weatherly high pressure reactor. The interface of the elbow, reactor, its built-in components and the catalyst package are provided with a structured surface grid which form the boundary surfaces of the calculation. The solution area is divided into a finite number of control volumes by construction lines. On the surfaces formed by the construction lines the grid is generated, which constitutes a three-dimensional framework for the final volume lattice (see Fig. 9).

By means of the CFD flow simulation, the influence of all aggregates and internals of the flow characteristics can now be determined and the flow in the reactor can be visualised using flow threads (Fig. 10). Furthermore, the direction of flow of the individual flow threads into the catalyst packet and thus their radial portion can be determined by means of the vector representation (Fig. 11). The implementation of the reaction finally enables the linkage of flow and reaction, whereby the flow influence on the reaction behaviour in the catalyst package can be examined separately (Fig. 12).

Using the findings of the flow simulation of the current state, combined with the problem of the catalyst damage, solutions can now be developed that bring about more uniformity of the flow and thus a more homogeneous load on the catalyst pack.

In the associated case study, there was a preferential flow caused by the elbow

Fig. 8: 3D computational graphic of a Weatherly high pressure reactor

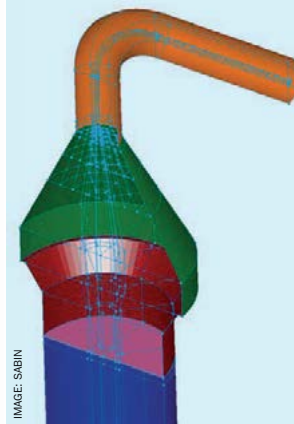
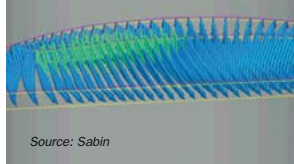


IMAGE: SABIN

Fig. 11: Vector representation of the flow into the catalyst



Source: Sabin

Fig. 13: CFD simulation with additional distribution plate



IMAGE: SABIN

Fig. 9: 3D orthogonality of the volumetric calculation mesh

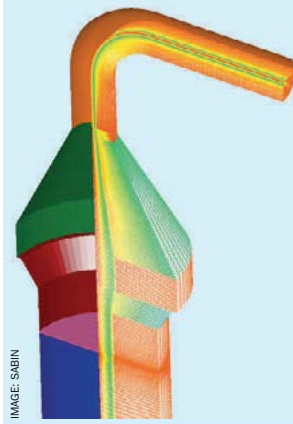
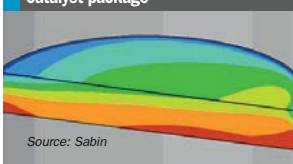


IMAGE: SABIN

Fig. 12: Linking flow characteristic and reaction; temperature profile in the catalyst package



Source: Sabin

Fig. 14: CFD simulation with additional concentrically arranged truncated cones

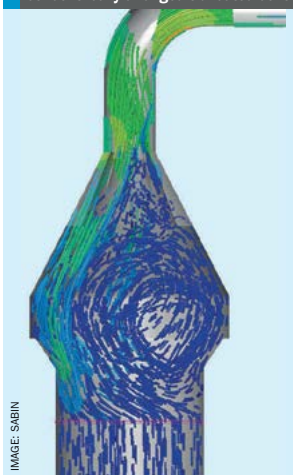


IMAGE: SABIN

Fig. 10: Visualisation of the flow characteristic

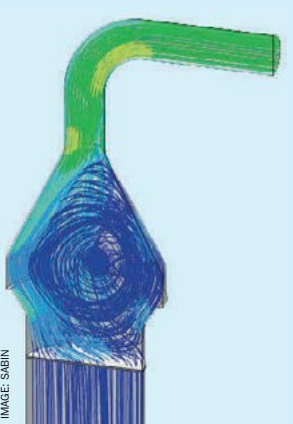


IMAGE: SABIN

which led to a flow separation on the right-hand side at the inlet into the reactor. As a result, this flow caused a radial proportion of the flow increasing to the left when it entered the catalyst package and thus a corresponding temperature gradient over the entire catalyst pack. The crack in the catalyst package occurred exactly in the region of the calculated highest temperature. This finding meant that the damage was not due to thermal stress but to material fatigue.

There were two possible solutions. One related to an additional installation of a distributor plate, which by generating an additional pressure drop, could bring about flow equalisation (Fig. 13); the other would be the installation of concentrically arranged truncated cones, which would generate a reduction in the inlet angle and thus prevent flow separation (Fig. 14).

The comparison of both flow patterns made it clear that only the distributor plate produced significant improvement in the flow characteristics. Using concentrically arranged truncated cones, the flow conditions were shown to be insufficient to prevent the flow from separating at the transition from the elbow to the reactor.

This case study shows that the CFD simulation is a powerful tool for studying the influence of flow characteristics on the performance of the process of catalytic ammonia oxidation. Another area of application of CFD simulation is the investigation of the feeding of ammonia and the quality of its mixing with the air flow in adjacent mixers. ■

Improving nitric acid plant performance

N. Temnaya and S. Suvorkin of NIIK report on the modernisation of monopressure (UKL-7) and dual pressure (AK-72) nitric acid plants in Russia and the CIS.

The main nitric acid manufacturing facilities in Russia and the CIS are based on large scale UKL-7 and AK-72 process units that are in need of upgrading.

Besides producing nitric acid, existing UKL-7 and AK-72 units generate thermal energy in the form of superheated steam which is fed into the plant's network and mechanical energy which is generated in high-temperature gas turbines and is used for process air compression.

The main modernisation targets for existing UKL-7 and AK-72 units are to:

- switch to a selective catalytic tail gas reduction system;
- enhance unit capacity by reducing air consumption;
- reduce/eliminate natural gas consumption;
- switch existing gas turbines to lower operating temperatures to increase their performance.

Research and Design Institute of Urea and Organic Synthesis Products (NIIK) is a leading design and technology company for chemical plants in Russia and the CIS. In co-operation with engineering and technical centre Khimazot-SPb LLC, NIIK is actively engaged in various projects for the modernisation projects of existing mono and dual pressure nitric acid units.

Currently NIIK is implementing two UKL-7 units modernisation designs which differ in the following ways:

- gas turbine equipment available in the market;
- process equipment design;
- steam generation system used.

The first design is a new modernised UKL-7-76M unit equipped with a GTT-3M gas turbine offering improved technical and economic performance (Fig. 1). The nominal capacity of the unit is 16.5 t/h nitric acid (HNO₃ monohydrate).

Table 1: Comparison of the main features of UKL-7 units with different gas turbines

Key performance indicators	UKL-7	Existing modernised units		Using alternative turbocompressor or TKT-88/7.6
		with GTT-3M	with GTU-8	
Nitric acid capacity, t/h	14.8	16.5	16.5	20.0
Natural gas, '000 m ³ /t	0.120	0.060	0.050	0.040
Power, '000 kWh/t	0.040	0.040	0.010	0.010
Steam removal P 1.6 (1.8) MPa, Gcal/t	1.2	1.1	1.3	0.7

Source: NIIK

Table 2: The main parameters of the improved AK-72 unit

Key performance indicators	Basic	Improved
Nitric acid production capacity, t/h	50.0	60.0
Natural gas consumption, '000 m ³ /t	0.085	0.045
Temperature of exhaust gas before HP gas turbine, °C	760	560-590

Source: NIIK

The second UKL-7 process design, currently in operation, uses a GTU-8 gas turbine unit, which is characterised by its smaller size and requires no intermediate air coolers or compensatory capacity of the drive. This scheme offers a quick return on capital investment and a compact and simpler plant arrangement (see Fig. 2).

The improvement of the existing monopressure UKL-7 unit benefits from:

- 20% nitric acid capacity increase;
- 30% reduction in natural gas consumption,
- 15% increase of steam removal.

Going forward, a new single stage turbo-compressor unit TKT-88/7.6 will be introduced to the market as the latest NIIK \ REP Holding (Saint-Petersburg) development.

The TKT-88/7.6 turbo-compressor unit for new nitric acid plants is supplied as a single unit with a starting device, combustion chamber and aggregate equipment located in a noise-insulating casing on the support frame.

A distinctive feature of the TKT-88/7.6 gas turbine unit is the increased air capacity which has an output of 20 t/h min nitric acid (HNO₃ monohydrate).

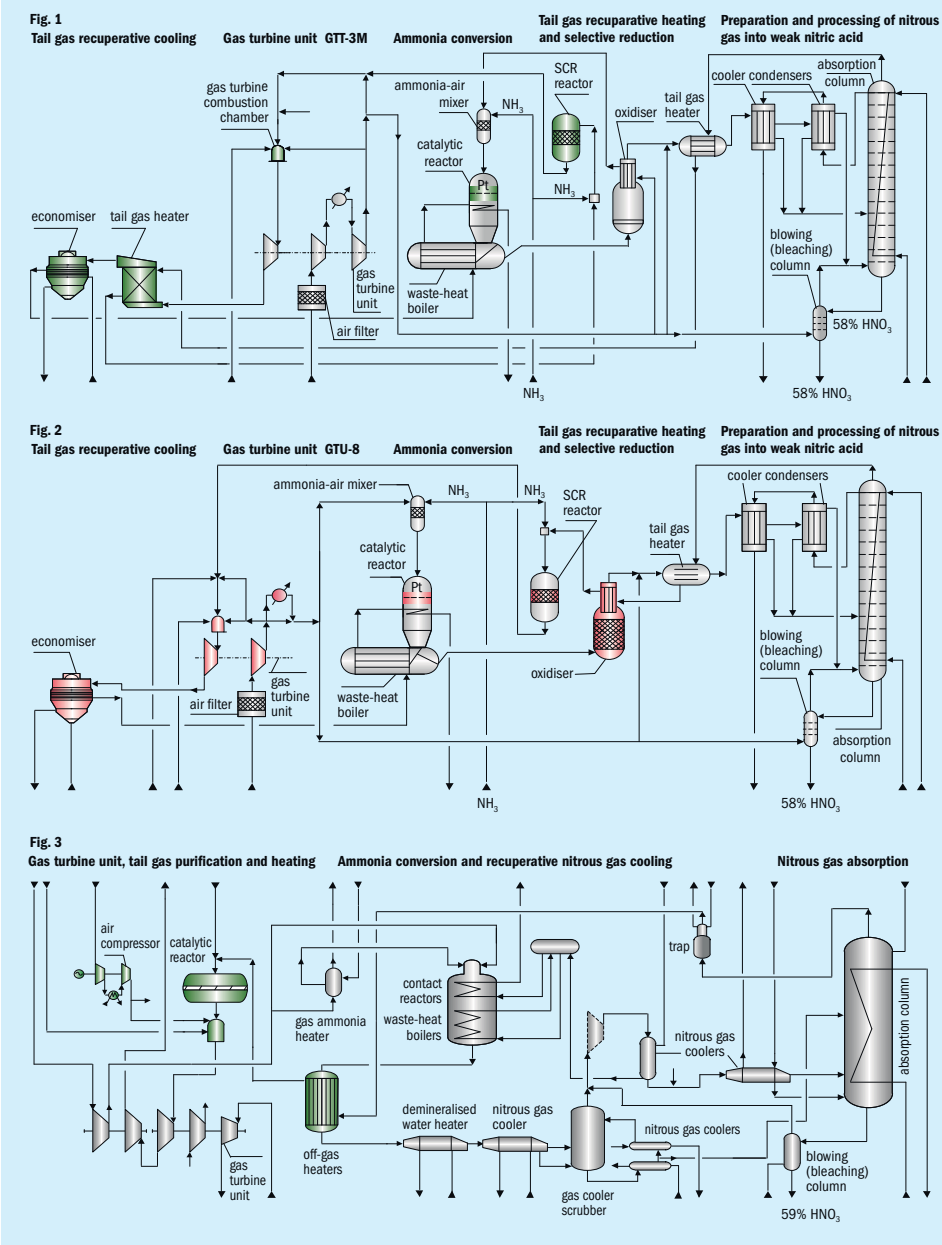
The new TKT-88/7.6 unit increases nitric acid output to 20 t/h min and reduces natural gas consumption (Table 1).

NIIK in cooperation with KhimAzot-SPb are also currently implementing the modernisation of a large scale AK-72 dual pressure unit with selective catalytic tail gas reduction. In the proposed design, the gas turbine unit will be switched to low temperature conditions (550-590°C).

At the same time the capacity of the modernised AK-72 plant will be increased to 60 t/h nitric acid (HNO₃ monohydrate) and the natural gas consumption will be reduced by 50%.

The main parameters of the improved AK-72 unit are specified in Table 2.

Figs 1, 2 & 3: Nitric acid plant modernisation



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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.

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ISSN: 1750-6891
Design and production:
JOHN CREEK, DANI HART



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

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Published by: BCInsight Ltd
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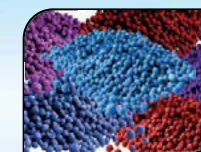
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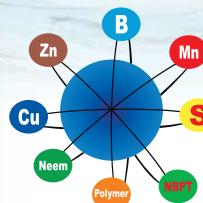
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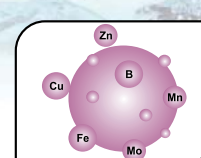
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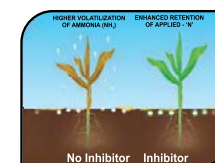
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NITROGEN+SYNGAS
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SEPTEMBER-OCTOBER 2020

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