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September | October 2015

nitrogen + syngas

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Syngas in Southeast Asia

UAN's potential

Foil coated catalysts

CO₂ removal from syngas



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NITROGEN+SYNGAS
ISSUE 337
SEPTEMBER-OCTOBER 2015

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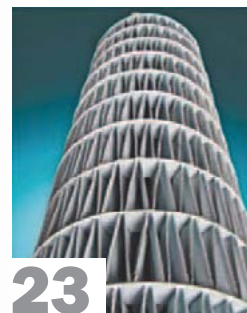
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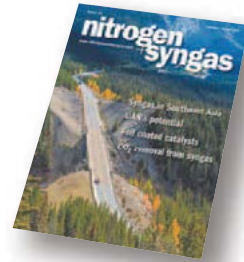
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A continuing problem



On August 12th, the port of Tianjin in China was rocked by two tremendous explosions. The first was reported to have the force of around three tonnes of TNT, the second of 21 tonnes. It was this second explosion which produced an explosive shockwave which devastated the local industrial estate, container port and nearby apartment blocks, killing nearly 150 people and injuring several hundred more.

The explosions took place at Ruihai International Logistics, a company specialising in transport and storage of chemicals. Numerous hazardous chemicals were reported to local authorities to be stored at the site, including sodium and potassium nitrates, and calcium carbide. However, it transpired that in addition to the reported chemicals, up to 700 tonnes of sodium cyanide were present at the site and scattered across the surrounding area by the blasts, which made rescue work and clean-up extremely hazardous for several days afterwards. More pertinently, however, the local Public Safety Bureau Fire Department told Chinese media that 800 tonnes of ammonium nitrate were being stored at the site. Many other chemicals seem to have been present - a full inventory may never be known.

The incident bears far too many similarities to the West, Texas disaster in April 2013, albeit on a much larger scale. The explosion followed a catastrophic fire, which appears to have caused the AN being stored to detonate, and as at West, firefighters and other first responders were among the casualties - 21 firefighters and 11 police are known to have perished at Tianjin. As at West, it appears that reporting of the storage of hazardous chemicals at the site was patchy at best and incomplete, and that the local fire department was not aware of the risk of explosion. Indeed, the actions of the fire department may have exacerbated matters by the action of water on the stored calcium carbide, generating acetylene gas which may have added to the combustible mix.

But most of all, as at West, it appears that housing developments had been allowed to take place far too close to a site storing potentially dangerous chemicals. At Tianjin, there were an estimated 5,600 people living within 1,000 metres

of the site of the explosion and 17,000 dwellings within 2,000 m, making the consequences all the more devastating. Chinese legislation in fact forbids siting of warehouses storing dangerous chemicals less than 1 km from "public buildings, major transport roads, railways and waterways, and industrial and mining enterprises", and it seems clear that this law has been ignored at Tianjin.

The Chinese government's reaction has been swift. Twelve employees and executives of Ruihai Logistics have been detained and eleven local government and port officials charged with negligence. A thorough survey of thousands of chemical producers and storage sites is under way to ascertain whether the law is being adhered to elsewhere. And, perhaps predictably, there has been a level of official secrecy thrown over developments, provoking unaccustomed criticism even in official state media.

The lessons are depressingly familiar, to do with better inspection and enforcement of safety standards, better communication between public safety bodies and emergency services, and above all in local planning and zoning decisions where people and hazardous chemicals may be in close proximity. At West, the issues seems to have been more to do with gaps in legislation and the coverage of different regulators, while at Tianjin it seems that there may have been deliberate collusion to circumvent regulations designed to prevent such a tragedy. Either way, as our planet grows more crowded, the issue of siting of chemical production and storage facilities and where developers are allowed to build housing becomes a daily more pertinent one. ■

Richard Hands, Editor

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MARKET INSIGHT

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

NITROGEN

The nitrogen market was awash with M&A activity during the summer months of 2015. The standout development was the merger between CF Industries and OCI in August, although industry consolidation had certainly been on the cards for a while before the deal between the two global producers was announced. The merger, which was confirmed on 6 August 2015, includes both companies' global assets excluding OCI's Egyptian and Algerian businesses and will create the world's largest publically traded nitrogen company, valued at \$8 billion. CF is no stranger to M&A activity; the company was of course the successful bidder in the acquisition of Terra Industries in 2010, which is the most recent transaction of comparable size to this year's CF and OCI merger.

The scale of the deal is of historic proportions, and yet the merger with OCI forms only part of CF's recent spree in M&A activity. The North American giant terminated discussions with Yara in 2014 over a merger of equals, and streamlined two of its previous joint ventures in 2015 by acquiring the remaining 50% interest in GrowHow from original partner Yara, and disposing of CF's 50% stake in Keytrade. And just days after it confirmed the merger with OCI, CF swiftly followed up with a second announcement that

it was entering into a strategic venture with the North American farm cooperative, CHS. The announcement has more than a touch of history-repeating-itself about it, bearing in mind that today's CF Industries was borne out of the farm cooperative business model, and ironically it was this time ten years ago that CHS received \$140 million from the initial public offering of CF Industries.

The impacts of CF's foray into a more global position in the nitrogen market will be widespread, both in its established North American territory, and in the wider global market. One area that will definitely be affected is the US UAN market. The consolidation of CF and OCI's UAN capacity in the US will give the newly formed company a majority market share – especially when we consider both companies' capacity investments that are under construction. The UAN market is under even greater speculation after there was a second industry acquisition in August that consolidates the UAN market further. Just a week after confirmation of the merger between CF and OCI, it was confirmed that CVR partners, which owns significant UAN capacity in the US, would buy Rentech Nitrogen for \$533 million excluding debt. The result of the recent consolidation in US UAN capacity is that the regional market will become more oligopolistic. Often people shy away from using the term oligop-

oly, but it simply refers to a market which is dominated by a small number of sellers, and there is no denying that in the US market, a UAN oligopoly will emerge in light of these recent mergers and acquisitions.

In the remaining months of 2015 there is likely to be a far more global spotlight on the nitrogen industry. At the end of August, the global economy was in the midst of a period of volatility as the slowdown in China prompted a downward spiral in stock markets around the world. At press time it was yet to be seen if the wavering global economy would see a correction relatively quickly or whether the effects will be longer-lasting.

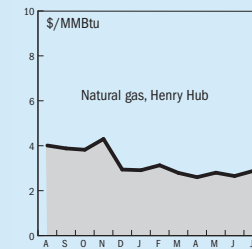
The immediate impact of currency devaluations in export-orientated markets such as China and Russia is that products traded in US dollars become more competitive – and so we would expect the depreciation in the yuan and the rouble to improve margins on nitrogen exports out of these regions. For Russian producers this is a phenomenon which has already benefited financial performance in 2015, following the continued depreciation of the rouble, while for Chinese producers a weaker yuan could incentivise further urea exports, the impact of which we know all too well – the influx of Chinese product would no doubt put further strain on the already oversupplied nitrogen market.

The longer-term impacts of the recent economic slowdown on the nitrogen market are harder to predict. The first uncertainty that would affect not just the nitrogen industry but all commodity markets, is the scale of impact on global financial markets. So far there has been a general consensus that we are not experiencing a re-run of the financial crisis of 2008, although if currencies and stocks continue to slide there is a chance we could see a sustained impact beyond 2015.

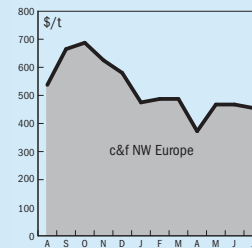
Perhaps the most long-term uncertainty that directly impacts the nitrogen market is the outlook for oil prices, and the onward impact on nitrogen feedstocks – namely gas and coal. After a modest recovery from the lows of early 2015, oil prices fell once again in August, driven by a combination of weak global markets and a continued abundance of oil production that has easily outpaced demand. The oil market will eventually recover to an extent, as there is a significant amount of global supply that cannot be sustained at current prices. Energy markets and the nitrogen market alike have a history of being self-correcting, but the uncertainty now is the timeline in which a correction will occur.

END OF MONTH SPOT PRICES

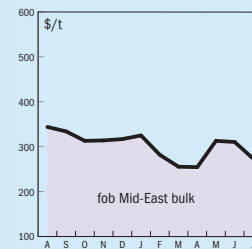
natural gas



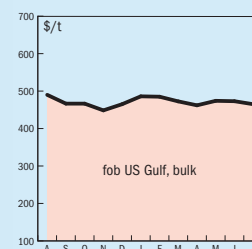
ammonia



urea



diammonium phosphate



MARKET INSIGHT

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

METHANOL

In North America, the June contract natural gas reference price was settled at \$2.86/MMBtu for Texas and \$2.88/MMBtu for Louisiana, up \$0.31/MMBtu from May. July's bid/offer range was fairly wide at \$1.02-1.09/gallon. August was in an even wider range at \$1.00-1.085/gallon, and September ranges from \$1.005-1.085/gallon. Overall demand was flat across most derivatives; including formaldehyde which has now peaked. Production at Methanex's unit in Canada has been constrained by a mechanical issue for much of the first half of the year; a major overhaul of that unit lasting 60 days will occur sometime this summer to resolve it.

In South America, Venezuela is estimated to be operating around 50% on average with economic and social issues believed to be affecting feedstock supply. Methanex's Chilean unit continues to operate at 35% capacity. In Trinidad, operations remain at the new 'normal' level – an industry average of 84%. Another large natural gas curtailment may occur in 2H 2015.

The European market was subdued, as the fall in China's stock market put pressure on liquidity in the Asian market and subsequently this impacted other regions. Prices in Europe were down, tracking falls in China. Demand was largely unchanged. Iranian plants are all running normally, while Sirte Oil in Libya is operating one line at low rates and the second line remains down. A restart has been targeted at EMethanex in Damietta, following an increase in gas supply to the region. Market values in Europe have fallen but this has been primarily driven by weakness in the Chinese stock market and methanol futures market. European traders are now reassessing the market following the crash in China. Spot methanol prices fell below €300/t ton to reach a discount of 22% to the 3Q 15 West European Contract Price, which was settled at a rollover of €359/t. Europe's demand profile remains unchanged, however. Acetic acid demand remains stable at healthy levels, supported by consistent offtake in the PTA and MCA markets. Operating rates in North Africa have been impacted by gas restrictions and technical issues over the summer.

In India, demand has come under seasonal pressure from the monsoon, when industry typically slows down. Iranian producers are offering large volumes of methanol to India through tenders. The latest tender was offered at a 2-2.5% premium but buyers were unwilling to pay this price, it is understood. Spot cargo availability is limited and few bids or offers were heard this week for fixed price cargoes. Liquidity is generally very thin.

Asian spot prices are posted in the range of \$280-330/t c.f.r. The Asian market sentiment was generally stable and healthy except for China. The Chinese market was very volatile, with a significant impact from the plunge in China's stock market. Demand is stable from conventional derivative sectors like formaldehyde and acetic acid. Demand into DME remains weak with a slight decline in the operating rate. Demand into MTO is stable. The new MTO unit in Shandong province is running well with a mid-to relatively high operating rate. Shenhua Xiwan (1.8 million t/a of methanol consumption) announced that its MTO unit is now mechanically complete.

On the production side, the average operating rate improved to 53% of nameplate capacity, or around 69% of effective capacity. Local supply in Shandong province recovered from the recent drought. The overall market trend was very mixed and showed significant fluctuations. In the spot market, mainstream discussions were generally in a range of \$300-310/t for import material. For discussions on a formula price basis, product was offered at a premium of about 2.0% for non-Iranian cargo and 1.0-1.5% for Iranian cargo.

In Southeast Asia, major methanol units are reported to be running well. The 45-day maintenance outage of Petronas's large unit is now targeted for the first half of August. In Indonesia, the annual turnaround of KMI's unit is planned for late October or early November. The market is running well with a good number of spot discussions and healthy market demand. The major pockets of spot buying activity are the main ports in Indonesia, the formaldehyde sector, and the biodiesel sector. However, driven by the weak China market, buyers adopted a cautious stance on the price level from the middle of the week. The selling idea is above \$325/t.

Table 1: Price indications

| Cash equivalent | mid-July | mid-May | mid-Mar | mid-Jan |
|----------------------------------|----------|---------|---------|---------|
| Ammonia (\$/t) | | | | |
| f.o.b. Caribbean | 420 | 425 | 435 | 440-505 |
| f.o.b. Arab Gulf | 380-400 | 350-405 | 400-430 | 470-490 |
| c.fr N.W. Europe | 455-480 | 460-480 | 473-510 | 480-535 |
| c.fr India | 420-455 | 410-450 | 490-500 | 530-570 |
| Urea (\$/t) | | | | |
| f.o.b. bulk Black Sea | 262-273 | 275-283 | 270-280 | 320-325 |
| f.o.b. bulk Arab Gulf* | 268-278 | 308-335 | 270-275 | 320-325 |
| f.o.b. bulk Caribbean (granular) | 280 | 295-305 | 290-300 | 325-335 |
| f.o.b. bagged China | 282-287 | 293-308 | 275-283 | 280-285 |
| DAP (\$/t) | | | | |
| f.o.b. bulk US Gulf | 470 | 468-472 | 485 | 485 |
| UAN (€/tonne) | | | | |
| f.o.t. ex-tank Rouen, 30%N | 195-197 | 185-190 | 231-235 | 200-227 |

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

Source: Fertilizer Week

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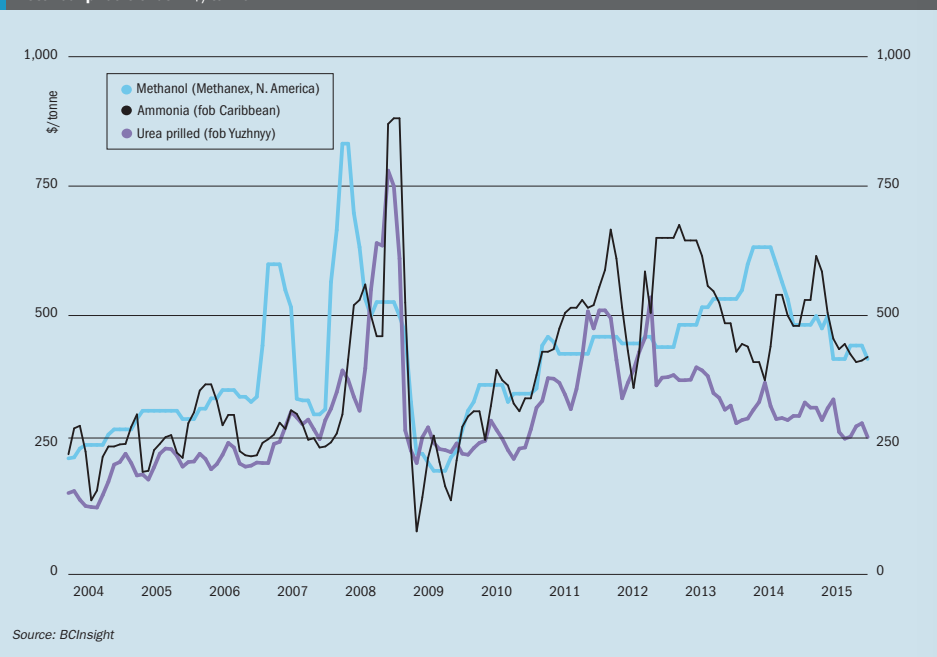
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Market outlook

Historical price trends \$/tonne



AMMONIA

- The ammonia market found some stability in August after the Tampa benchmark price was rolled over from July at \$460/tonne FOB. This followed a period of slow activity, although global supply is expected to tighten in the coming months as a result of scheduled plant turnarounds in various locations.
- In addition there have been several unplanned supply restrictions in key exporting regions such as North Africa and Trinidad.
- In Trinidad, natural gas curtailments continue to apply to nitrogen producers, and there are expectations that restrictions could be even greater in September, with cuts expected to reach up to 30-35%.
- Ukraine suspended Russian gas purchases in early July and has been sourcing natural gas from EU hubs via Slovakia since then. The next gas supply talks with Russia are due in September.

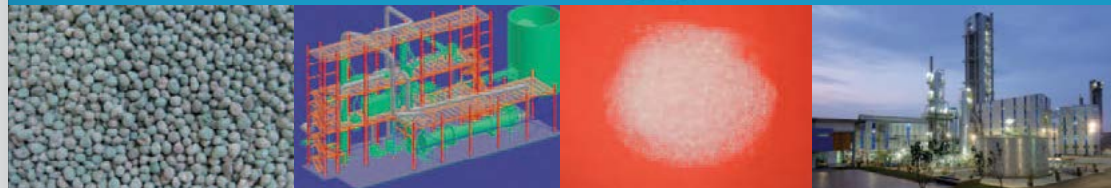
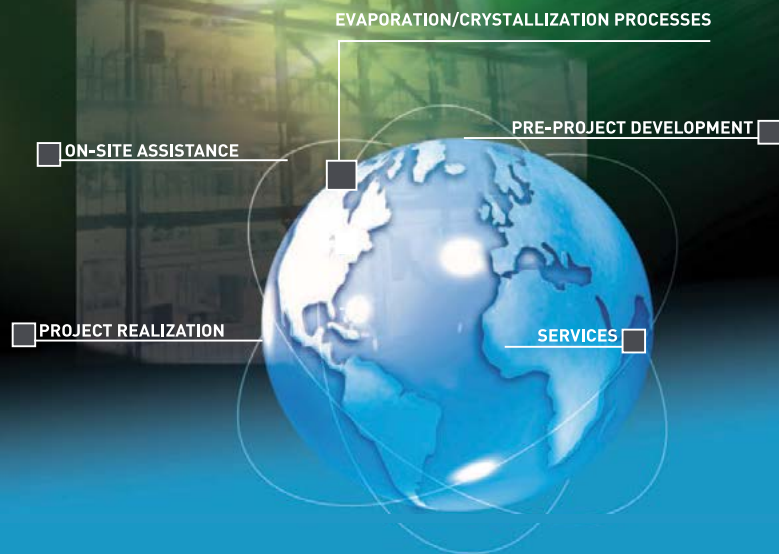
UREA

- Urea demand was slow in July and August, although import tenders from Pakistan in late August signalled a ramp up in buying interest and urea prices were expected to respond accordingly.
- Further tenders from India are also expected in September which would add some support to global urea price ideas, especially in the face of the recent oversupply.
- Egyptian urea producers remain severely impacted by a lack of natural gas supply, and this has halted product being shipped from the usually active exporter.
- The Chinese government announced it would reinstate VAT on fertilizer sales from 1 September.
- This move would require producers to bear the VAT cost and could impact unit costs, although the devaluation of the yuan is likely to boost export competitiveness.
- The current VAT rate stands at 13%.

METHANOL

- Gas curtailments continue to affect plants in South and Central America and North Africa. This is easing in Egypt and a restart at EMethanex is expected soon, but there are more gas curtailments expected in Trinidad later this year.
- The Chinese market has been volatile as economic news from the falling stock market has caused uncertainty about the level of future demand, and this has impacted upon other markets in the region. European demand is also uncertain going forward due to the ongoing economic issues there.
- North America has passed through the slacker summer demand season, but pricing looks relatively flat for the autumn.
- A full repeal of sanctions on Iran would open up the country's 5 million t/a of methanol capacity to global markets, reducing Iran's dependence on Chinese and Indian sales.

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UNITED STATES

CF and OCI in \$8 billion merger

CF Industries and OCI have announced that they have entered into a definitive agreement to merge CF Industries with OCI's European, North American and Global Distribution businesses in a transaction valued at approximately \$8 billion, including the assumption of approximately \$2 billion in net debt. The transaction, unanimously approved by the boards of directors of both companies, will create the world's largest publicly traded nitrogen company, to be called simply 'CF'. The deal includes OCI's nitrogen production facilities in Geleen, Netherlands, and its new plant under construction at Wever, Iowa, as well as the company's interest in the Beaumont ammonia and methanol plant in Texas and OCI's Dubai-based global distribution business. The combined entity will also purchase a 45% stake with the option to acquire the remainder of OCI's Natgasoline methanol project in Texas, due for completion in 2017. The merged company, to be operated by a UK-based holding company, will operate about 12 million tonnes N of global nitrogen capacity worldwide by 2016.

"This is a terrific opportunity for the shareholders of both companies, with mid- to high-teens cash flow accretion," said Tony Will, president and chief executive officer, CF Industries

Holdings, Inc. "This is also a great outcome for U.S. farmers as we have another supply point that will ensure our critical products are delivered reliably and in-time to meet our customers' needs."

"Combining our businesses with CF builds upon the company's platform in Europe and expansive distribution network in North America, enhancing our collective scale and improving our ability to meet the needs of customers in the U.S. and around the world," said Nassef Sawiris, chief executive officer, OCI N.V. "As significant owners in the combined entity, our shareholders will benefit from the ongoing value creation of the business."

CF expects to achieve approximately \$500 million in rate synergies from optimisation of operations, capital and corporate structure. The transaction requires the approval of shareholders of both companies and is subject to the usual regulatory approvals. As part of the agreement, Nassef Sawiris and other members of the Sawiris family, OCI's founding and controlling stockholders, have agreed to vote their shares in favour of the transaction. They will together own approximately 15% of new CF's outstanding shares and have entered into a shareholder's agreement with new CF. The transaction is expected to close in 2016.

CVR buys Rentech Nitrogen

CVR Partners says that it intends to acquire all outstanding shares of Rentech Nitrogen Partners, by mutual agreement of the two companies. The buyout will exclude Rentech Nitrogen's Pasadena facility, which will be retained by Rentech's current owners. The total cost agreed for the deal is \$533 million, and will include CVR assuming or refinancing Rentech's net debts of \$30 million. Rentech decided to sell off its nitrogen business following a strategic business review completed in February. The merger of CVR and Rentech Nitrogen will create the second largest UAN producer in the United States (see our article on pp30-31 for more detail).

Jack Lipinski, executive chairman of CVR Partners, said; "the combination of our two strategically located fertilizer assets in Kansas and Illinois, a strong combined balance sheet and highly experienced management teams positions the merged companies to generate long-term value."

"The addition of Rentech Nitrogen's East Dubuque fertilizer facility increases our scale and diversifies our geography and raw material feedstock," added Mark Pytosh, CEO of CVR Partners. "Our customers will benefit from the expanded availability and variety of nitrogen fertilizer

products manufactured at the two facilities. The merger also expands our footprint into the upper Corn Belt region, which has the largest concentration of users in the US for the direct application of nitrogen fertilizer products."

Ground broken on new Yara/BASF ammonia plant

Construction work has begun at Freeport, Texas on the \$600 million joint world scale ammonia plant being built by Yara International and BASF. The project includes a new ammonia tank at the BASF facility, being overseen by Yara, and new terminal and pipeline assets for export of ammonia. The plant will produce 750,000 t/a of ammonia when it comes on-stream, projected to be in 2017. Ownership is 68% by Yara and 32% by BASF, with each company taking a proportional share of the off-take, although plant operation will be handled by BASF, which plans to produce caprolactam with its share of output, for downstream fibre production. Yara will meanwhile sell its off-take to industrial and agricultural users across North America.

Feedstock will come from hydrogen supplied over the fence by Praxair, dramatically reducing the capital cost of the facility. KBR has been awarded the fixed price turnkey contract for the engineering, procurement and construction (EPC).

LSB faces rising costs for nitrogen plants

LSB Industries says that construction costs for its new nitric acid and ammonia plant in El Dorado could be up to \$60 million higher than original estimates, although the company says that construction remains on schedule. The new nitric acid plant and concentrator will be operational by the end of 3Q 2015, according to LSB, with the 375,000 t/a ammonia plant on schedule to be completed and operational in 1Q 2016. Costs for the expansion have risen from the original estimate of \$495-520 million to \$560-575 million.

The construction work was made necessary by the May 15, 2012 explosion at El Dorado, which caused significant damage and injured four employees.

Agriculture may emit more nitrous oxide than believed

According to a recent study by the University of Minnesota, agricultural emissions of nitrous oxide (N₂O) might be up to 40% higher than previously believed. The study, published in the Proceedings of the National Academy of Sciences, tried to produce a better estimate for nitrous oxide emissions – N₂O has a global warming potential more than 300 times that of carbon dioxide on a tonne for tonne basis.

Nitrous oxide gas is emitted from rivers and streams that receive agricultural runoff, and the US Environmental Protection Agency (EPA) estimates that 75% of the country's N₂O emissions come from agricultural soil management. Researchers compared measurements of nitrous oxide across Minnesota, and found nitrous oxide emissions from rivers are nine times greater than estimates used by the Intergovernmental Panel on Climate Change (IPCC), the United Nations body which is seeking an international consensus on tackling the problem.

INDIA

Tata Chemicals considering \$1 billion sale of fertiliser business

Tata Group Chairman Cyrus Mistry has initiated a plan to hive off and sell the group's fertiliser business.

Tata Chemicals has reportedly asked Kotak Mahindra Bank to help find strategic buyers for the business at a valuation of close to a billion dollars to help the company trim debt and focus on the high-growth consumer and industrial chemicals businesses.

Tata Chemicals operates a urea plant at Babrala, Uttar Pradesh, as well as a phosphate fertiliser plant at Haldia, West Bengal, and also has a 33% stake in Moroccan joint venture phosphoric acid plant IMACID.

Move to recommission Sindri plant?

The Ministry of Chemicals and Fertilizers is reportedly close to asking for bids to revive the idled Fertilizer Corporation of India (FCI) urea plant at Sindri in Jharkhand. The 1950s vintage plant has been idle since 2002, and the cost of getting it operational again – or simply replacing it – has been put at \$870 million. Crucial to the enterprise will be a supply of gas feedstock, and it has been agreed with the Gas Association of India Ltd (GAIL) that a 60 km tie-on to the Jagdishpur-Haldia pipeline will be "expedited". However, gas costs could be as high as \$8-10/MMBtu, making the urea produced there more expensive than imports, and probably requiring further expensive government subsidy.

GSFC looking at urea, caprolactam

According to a filing with the Bombay Stock Exchange, state-run Gujarat State Fertilizers and Chemicals (GSFC) is planning to set up a nitrogen complex at Dahej with a total investment of up to \$1.25-1.55

billion. At the moment the project, which would involve a 1.3 million t/a ammonia-urea plant and 100,000 t/a of downstream caprolactam capacity, is at the feasibility study stage, although it has been approved in principle by the company's board. Land for the project has already been purchased. GSFC currently has four plants, two at Vadodara, and one each at Jamnagar and Kosamba.

Direct farm subsidy scheme proves to be a headache

India's projected switch to paying agricultural subsidies directly to farmers rather than fertilizer producers – the so-called Direct Benefit Transfer (DBT) scheme – is proving to be a headache to organise. There are disagreements at cabinet level about what the eligibility criteria should be for inclusion in the scheme. It has been suggested only those farmers that own land should be considered, but this would exclude the majority of India's farmers. The Department of Fertilizers and Chemicals has also told the Parliamentary Standing Committee on Chemicals and Fertilizers that its pilot project to capture the retail sales of fertiliser to farmers in six districts has failed to make any headway, and that the next stage of DBT implementation has been "put on hold" due to problems in targeting and determining entitlements and preparing a database of potential beneficiaries. A pilot project in two districts of Odisha remains only at the feasibility study stage with the state government.

AUSTRALIA

Orica to cut back on AN production

Orica says that it will scale back production of ammonium nitrate from its Yarwun plant in Queensland because of "challenging market conditions" and oversupply of AN in the Australian market, where it is primarily aimed at explosive use in the mining and quarrying industries. Orica says that it will scale back production from around 320,000 t/a to about 280,000 t/a, with the associated loss of 20-40 jobs. Production capacity at the site is 530,000 t/a, but the plant has not operated at full capacity for some time.

"While we remain confident in the long-term outlook for ammonium nitrate, there is a near-term oversupply in the market." Yarwun general manager Dave Buick said. "As a result, we have made a preliminary decision to adjust the capacity requirements...

Orica is operating in a highly competitive market, in which supply of ammonium nitrate is higher than demand levels, and we need to pursue strategies that secure the long-term viability of the business."

Incitec Pivot, meanwhile, is reportedly facing gas supply curtailments at its Moranbah ammonium nitrate plant in Queensland. The 330,000 t/a plant has been informed by Arrow Energy, operators of the Moranbah Gas Project, that gas supply restrictions of 10-20% are likely to extend into 2016, owing to lower than expected production volumes.

NETHERLANDS

New urea granulation unit for Yara

Yara has awarded Tecnimont subsidiary Stamicarbon the lump sum turnkey EPC contract to build a new urea granulation plant for Yara's Sluiskil facility in the Netherlands, with a value of approximately €125 million. The project's scope of work includes both the 2,000 t/d urea granulation plant, as well as utilities. The new granulation plant will also use proprietary technology developed and owned by Yara for the production of sulphur-enriched urea. The production of 660,000 t/a of sulphur-enhanced urea will replace the existing 400,000 t/a urea prilling unit at the site, and reduce UAN output by 230,000 t/a, but an additional 130,000 t/a of calcium ammonium nitrate (CAN) will be produced instead. The project is expected to be completed in 2017, 25 months from the signing date, and will be executed by an integrated team of Yara's and Tecnimont's specialists.

Pierroberto Folgiero, Maire Tecnimont CEO, commented: "We are really honoured to work again for Yara, the world's largest fertilizer producer. This contract consolidates a fruitful long-term industrial cooperation with such a prominent global player, developed through decades of technology supply carried out by our subsidiary Stamicarbon. Moreover, this project adds another prestigious reference to our fertilizer business experience as an EPC contractor, and offers sound evidence of the Group's leadership in the fertilizer sector, one of the strategic pillars of our core business."

Yara International president and CEO Torgeir Kvidal said: "In Europe and gradually also in other regions of the world, agricultural soils are lacking sulphur, which is an essential plant nutrient. With this investment we are able to serve a growing demand,

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helping farmers improve both yield and crop quality, while contributing to improved nitrogen efficiency."

SAUDI ARABIA

Safco V achieves commercial production

The Saudi Arabian Fertilizer Company (Safco) said that it began commercial operation on July 14th at its new 1.15 million t/a urea plant. Exports were expected to begin in August. Ammonia feedstock for the plant comes from other Safco plants at the massive al-Jubail complex, reducing the availability of merchant ammonia from the company by 600,000 t/a. The plant was originally projected to start up in the third quarter of 2014.

Sabic says that it is also planning to boost urea and methanol production at Jubail by the end of the year by recovering 1,500 t/d of carbon dioxide from its new 500,000 t/a ethylene glycol unit and feeding it into downstream chemical production. The glycol plant will come on-stream later this year. Some of the CO₂ will also be purified for food-grade use.

UKRAINE

Ukraine gas dispute rumbles on

Ukraine suspended purchases of natural gas from Russia on July 1st after a breakdown in price talks brokered by the European Commission. Gazprom has reduced the discount it offers to Ukraine state gas company Naftogaz, and has been seeking a price of \$8.75/MMBtu. Frayed relations between Russia and Ukraine, particularly over gas supplies, mean that for the past year supplies have been pre-paid and exist only in quarterly agreements which must be renegotiated afresh each time. The country's difficult gas situation (it imports 30 bcm per year, mainly from Russia) makes a restart of shuttered ammonia plants unlikely in the short term.

ARGENTINA

Profertil boosts efficiency after revamp

Profertil's ammonia and urea complex at Bahia Blanca has increased production by 11% at the urea plant and 9% on the ammonia side after a refit completed in May, the company has reported. Water consumption has also decreased by 6%. Much of the efficiency increase has been made possible by a highly efficient new

compressor, supplied by Siemens, an SGT-600 industrial gas turbine, a 1.3MW electrical generator, and a heat recovery steam generator supplied by NEM, which secures optimal steam generation for chemicals production from the gas turbine's exhaust heat. Profertil uses the generated electricity directly for chemicals production, reducing the amount of power which needs to be purchased. Siemens says the Haldor Topsoe ammonia process allows gas turbines to be used as an alternative to steam turbines for driving air compressors, allowing electricity generation at the same time.

UNITED KINGDOM

CF buys Yara's stake in GrowHow UK

Yara has agreed to sell its 50% stake in GrowHow UK to CF Industries for \$580 million, making GrowHow a wholly owned subsidiary of CF Industries. GrowHow was formed in 2007 when Terra Industries and Kemira GrowHow's operations in the UK were merged. CF Industries acquired Terra in 2007, along with the 50% stake in GrowHow UK, while Yara merged with Kemira in 2010 and inherited its share of the company.

GrowHow has two fertilizer sites in the UK, at Ince in Cheshire and Billingham, Teesside, with a total production capacity of 800,000 t/a of ammonia, 1.1 million t/a of ammonium nitrate, and 500,000 t/a of NPK compounds, all of it destined for the domestic market. Ince comprises one ammonia, three nitric acid, three NPK and one ammonium nitrate plants, and Billingham one ammonia, three nitric acid, one ammonium nitrate and one carbon dioxide plants.

CF Industries president and CEO Tony Will said: "We are pleased to welcome 550 new employees from GrowHow to CF Industries, and to add the production facilities in Ince and Billingham to our system of nitrogen complexes. Our UK operations are well-positioned in an import-dependent region to serve our customers' needs and to create value for shareholders."

The move came prior to the announced merger between CF Industries and OCI, above.

UZBEKISTAN

Contract awarded for ammonia-urea plant

Navoiyazot, the chemical production arm of state-owned Uzkimyosanoat, has awarded the engineering, procurement and construc-

tion (EPC) contract for its new gas-based ammonia-urea fertilizer plant at Navoiy to Mitsubishi Heavy Industries (MHI) and Mitsubishi Corporation. The plant will produce 2,000 t/d of ammonia and 1,750 t/d of granulated urea, with a surplus of around 1,000 t/d of ammonia. Plant design, manufacture and equipment procurement, on-site construction work and commissioning activities will be overseen by MHI, and Mitsubishi Corporation and Mitsubishi Corporation Machinery will jointly manage transportation of plant equipment.

INDONESIA

Work begins on new ammonia plant

Ground has been broken on a \$830 million ammonia plant in Sulawesi. The 700,000 t/a plant is being developed by gas producer Surya Esa Perkasa, and will be operated by Panca Amara Utama (PAU), which is 60% owned by Surya Esa Perkasa. Japan's Mitsubishi Corp. will be a minority shareholder in the facility, which will be built on a 192-hectare site near a gas field jointly operated by Pertamina and energy company Medco Energi International, which will supply natural gas feedstock. According to PAU, the plant will be completed in 2017, and will begin commercial operations in the fourth quarter of that year. Production will be sold both domestically and elsewhere in Asia. The size of the site means that the company has scope for further expansion, according to PAU president Garibaldi Thohir.

PAU has secured a \$509 million loan for the construction from the International Finance Corporation, with the remainder of the money coming from equity.

MALAYSIA

Korean investment in Malaysian AN plant

Fine chemical manufacturer Huchem, an affiliate of South Korea's Taekwang Group, has announced that it intends to invest \$865 million to build a nitrogen complex at Sarawak in Bintulu (Borneo), Malaysia. The complex will include 600,000 t/a of ammonia capacity, 400,000 t/a of nitric acid, and 200,000 t/a of ammonium nitrate. Huchem has said that it may eventually boost ammonia production to 1 million t/a in a second phase, with downstream production of polyurethane, caprolactam and synthetic nylon fibres and possibly fertilizer.

Commercial production for the AN facility is scheduled for 1H 2019, according to the firm. Excess ammonia will be exported to Korea – the country currently imports 1.4 million t/a of ammonia, and Huchem believes that this will give it better price control over its downstream polyurethane and nitric acid production – the latter is used in the Korean automotive and electronics industries as well as nitrogen fertilizer.

Commenting on the investment decision, Malaysian Investment Development Authority (MIDA) chief executive officer Datuk Azman Mahmud said: "the company's investment will bring positive economic benefits to the country in the coming years, particularly in Sarawak in the form of high income employment opportunities for Malaysian citizens as well as increased usage of local infrastructure, financial services, information technology, utilities and logistics services for local businesses among many others."

NEW ZEALAND

Tenders invited for Taranaki redevelopment

Following the completion of a year-long feasibility study, New Zealand fertilizer producer Ballance Agri-Nutrients has called for tenders for the replacement of its ammonia-urea unit. The existing plant, completed in 1982, produces around 260,000 t/a of urea, around one third of New Zealand's current consumption. Gas is supplied from the offshore Kapuni gas field, which has been producing since 1969. Three international companies have been selected as preferred bidders for the project, with the shortlisted companies expected to submit their proposals and costings by the end of the year, according to Ballance chief executive Mark Wynne, who did not disclose provisional capacity or cost for the new facility.

Speaking to local press, he said that the tender was an opportunity for the company to invest in new, more efficient technology to sustain globally competitive production into the future. "Technology has also advanced and we need to consider the benefits of a new state-of-the-art plant versus the cost of maintaining the current one," he said. However, he also cautioned that while it was an "exciting step", it was also just "the first one on a long journey which includes board and shareholder approvals. We won't be making any decisions before the year is out."

IRAN

Renewed interest in Indo-Iranian proposal

The nuclear accord agreed by Iran and the anticipated lifting of UN-mandated sanctions has revived interest in project proposals for Indo-Iranian joint venture urea plants. Such proposals have circulated for many years but none have ever quite materialised into a concrete project in the way the Oman-India Fertilizer Company (Omifco) plant did. Nevertheless, given India's continuing gas shortage, there is reportedly renewed interest in a proposal for a 1.3 million t/a urea plant in the Chahbahar petrochemical zone near the Pakistan border. Previous talks in 2013 about the project had involved three Indian companies; Rashtriya Chemicals and Fertilizers (RCF), Gujarat Narmada Valley Fertilizers & Chemicals (GNFC) and Gujarat State Fertilizers Corporation (GSFC) for the proposed joint venture plant, with gas price discussions – often the bane of previous project proposals – are said to be in the region of \$2.95/MMBtu, according to RCF.



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CHINA

New guidelines for coal gasification projects

China's energy regulator has released new draft guidelines for projects that convert coal to liquids or gas, and says that it aims to commit the sector to the strictest possible environmental standards. Coal to liquids (CTL) projects will be permitted to use a maximum of 3.7 tonnes of coal for every tonne of liquids produced, and coal to gas (CTG) projects a maximum of 2.3 tonnes of coal per thousand cubic metres of gas produced, according to the National Energy Administration. The NEA has further advised that in order to be considered for permitting, any new project

needs to be consistent with China's overall plans to control coal consumption, and would be encouraged to prioritise the use of low-quality coals with high sulphur and ash content, in order to reduce their use elsewhere.

China has been a pioneer of CTL and CTG developments in a bid to ease dependence on imported oil and gas, but the fall in global oil prices and use of scarce water resources in coal-rich regions like Ningxia and Inner Mongolia has cooled government enthusiasm for the technologies

UOP licenses MTO technology

Honeywell UOP says that China's Better Clean Energy will license its methanol-to-olefins (MTO) process for Better Clean Energy's new facility in Shandong province in Eastern China. The plant will convert coal to methanol and then into 300,000 t/a of downstream ethylene and propylene for processing into downstream polypropylene and polyethylene, helping meet growing demand for plastics and other key materials. In addition to technology licensing, Honeywell UOP will provide engineering, training, technical service and specialty equipment for the facility, which is expected to start up in 2016. The award is UOP's fifth Chinese license for its MTO process and comes after the successful start-up of its first commercial-scale MTO facility for China's Wison Clean Energy in September 2013. For Better Clean Energy Honeywell UOP will license its Advanced MTO process, which combines the UOP/Hydro MTO process and the Total/UOP Olefin Cracking process to significantly increase yields and feedstock efficiency, and which offers flexibility in the ratio of ethylene and propylene produced.

"MTO technology has revolutionized the modern petrochemicals industry by providing an economical way to turn low-cost coal and even natural gas into the chemicals needed to make plastics," said Mike Millard, vice president and general manager of Honeywell UOP's Process Technology and Equipment business. "Our first commercial MTO facility in China proved the viability of our technology, generating high yields of the compounds needed to meet the growing global demand for plastics."

In addition to Wison, UOP has licensed its technology to Shandong Yangmei Hengtong Chemicals Co. Ltd. to produce

295,000 t/a of ethylene and propylene, and Jiutai Energy (Zhungeer) Co. to produce 600,000 t/a of olefins. Jiangsu Sailboat Petrochemical Co. Ltd. also is building what is expected to be the largest single-train MTO unit in the world, producing 833,000 t/a of olefins.

AZERBAIJAN

AzMeCo to receive Russian gas

The Azerbaijan Methanol Company (AzMeCo) is planning to import natural gas across the border from Russia's Gazprom after the State Oil Company of Azerbaijan Republic (SOCAR) said that it would be unable to provide gas feedstock for the plant. SOCAR president Rovnag Abdullayev said that AzMeCo had failed to sign a long-term gas supply contract with SOCAR in a sufficiently timely manner. However, SOCAR has now signed an agreement and undertaken commitments to supply Russian gas through its own pipelines. Gazprom currently purchases gas from

Azerbaijan under an agreement signed in 2009, but Gazprom chief Alexei Miller says that it can supply 1 bcm of gas per year to Azerbaijan if need be.

ICELAND

Chinese money for renewable methanol plant

China's Geely Holding Group, which is amongst other things the owner of Volvo, is planning to expand its methanol vehicle operations after making a commitment to invest \$45.5 million in Iceland's Carbon Recycling International Inc., which operates a methanol plant in Iceland based on hydrogen generated via renewable (geothermal) electricity. Geely's deal consists of an initial payment with additional purchases of CRI equity over a three-year period. The Chinese car manufacturer will then become a major CRI shareholder and join the company's board of directors, according to a CRI statement. Li Shufu, chairman of Zhejiang-based



Tanks of AZMECO methanol waiting for rail export.

PHOTO: AZMECO



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Geely, said the investment will build on its existing methanol technology, helping to speed up the development of methanol-powered vehicles in China. Geely says that it hopes that involvement in renewable methanol will allow it to promote methanol vehicle technology in Europe. The company has already deployed pilot fleets of methanol-fuelled taxis in China's Shanxi and Shaanxi provinces, and the city of Shanghai.

CRI has also teamed up recently with UK-based engineering firm Cofely Fabricom to develop and build a modular system for industrial installation to turn captured CO₂ into methanol. The partners say that the modules could be used by large industrial carbon emitters such as in the chemical, power and steel industries. Like CRI's 4,000 t/a methanol plant at Svartsengi, the modules would electrolyse water to produce hydrogen to combine with the captured CO₂ for methanol production via a low-temperature catalytic synthesis process.

NIGERIA

Exxon Mobil to up gas production

Exxon Mobil says that it is committing \$3 billion to gas resource development in Nigeria, helping to end gas flaring in the country and potentially providing feedstock for a plethora of downstream gas-based projects in the country, from fertilizers to methanol and power generation. Most of the natural gas produced in Nigeria is associated with crude oil production, and the Nigerian government has long sought to monetise and use the gas rather than wastefully flaring it. However, the failure of the government to pass the Petroleum Industry Bill has stalled local investment in the oil and gas industry, and ExxonMobil in particular has faced issues in dealing with the government over the ownership and taxation of gas finds. Among ExxonMobil's resources in Nigeria is the Erha field, with over 200 bcf of estimated gas reserves.

UNITED STATES

HEC gets six month stay of execution

Hydrogen Energy California, aiming to build a coal gasification plant with carbon capture, has managed to avoid cancellation after the Sierra Club filed a motion with the California Energy Commission to terminate the project. HEC aims to build a 390MW power plant based on coal gasification and capture 90% of the resultant CO₂.

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The project, sited at Kern County, was a Bush-era 'Clean Coal' initiative that has struggled on for several years, but cheap and plentiful shale gas has largely killed US interest in coal-based developments in recent years. HEC's main issue at the moment is finding somewhere to put the CO₂ that it will generate, having failed to reach agreement with local oil producer Occidental to use it for enhanced oil recovery (EOR) or to provide storage for the gas. Now HEC has until January 6th to execute a CO₂ purchase agreement, a carbon capture and storage (CCS), and transportation agreement, develop a list of commercial products to be produced and verify in writing that the intended products meet local county general plan and zoning requirements.

Air Liquide awarded detailed engineering contract for methanol complex

Yuhuang Chemical Inc has awarded Air Liquide Global E&C Solutions detailed engineering and procurement services for Yuhuang's 1.7 million t/a methanol plant, to be located in St. James Parish, Louisiana. Under this agreement, Air Liquide will also provide Yuhuang with procurement services for long lead and other equipment required for the \$1.85-billion world-scale methanol manufacturing complex.

"With an overall goal to complete this plant in early 2018, starting work on detailed engineering now is important and timely," said Jerry Oliver, Vice President of Manufacturing, Yuhuang Chemical Inc. "We are excited to work on this portion of the project with such a reputable US firm."

The project will entail three phases, with construction on the first phase projected to begin in 4Q 2015.

Northwest Innovation looking at low emission reforming

China's Northwest Innovation Works (NWI) has signed an agreement with Johnson Matthey Process Technologies Division to adopt a pioneering low carbon emissions reforming technology for its planned methanol plants in Washington and Oregon states. The baseline reforming technology being considered would have emitted 1.0-1.3 million t/a of CO₂ for each of the 5,000 t/a methanol plants, which have a estimated investment cost of \$5.4 billion. However, a preliminary analysis suggests that the Ultra Low Emissions (ULE) technology could reduce emissions by up to 75% at the three sites; Kalama and Tacoma, Washington, and Port Westward, Oregon.

Methanol produced at the facilities will be exported to Asia to manufacture olefins in MTO facilities. NWI also notes that using US natural gas to produce olefins is far more environmentally-friendly than the coal-based production typical in China.

The Kalama facility is currently in the permitting process, and a draft environmental impact statement is estimated to be completed by late autumn 2015.

Geoff Otterman, Divisional Director of Johnson Matthey's Process Technologies Division, noted, "Johnson Matthey is excited to be involved in such a prestigious project – which enables us to work closely with our partners to contribute world leading environmentally sustainable technologies to both the local and global economy."

IRAN

Ten million tonnes of methanol waiting in the wings

A report by IHS Inc suggests that 10 million t/a of new Iranian methanol capacity could be added by 2025 if UN sanctions on the country are lifted. Indeed, the report notes that Iran has proposed projects totalling more than 20 million t/a of new methanol capacity, but is of the view that a figure of approximately 10 million t/a is "more realistic". Iran is already a major producer of methanol, with 5 million t/a of current capacity, nearly 5% of total global methanol capacity. A full repeal of sanctions would also open up a large volume of methanol supply to global markets within the next five years, reducing the country's dependence on the Indian and Chinese markets for its exports, the report says. In 2015, total global methanol demand is expected to reach 70 million t/a, driven in large part by the resurgence of construction and automotive markets, and increased demand for cleaner energy.

Before the imposition of sanctions on Iran, the country tended to function as a classic swing producer, selling methanol on a spot basis to maximise short-term netbacks; this resulted in minimal regional price differentials. Iran was a major supplier of petrochemicals to Europe – primarily ethylene, polyethylene (PE) and methanol. However, after the imposition of the sanctions, business with Europe and several countries in Asia virtually disappeared and export volumes from Iran were redirected to China and India as well as a few other countries in Asia and Middle East. Iran was restricted to selling all of its

output to a limited number of markets, with regional spot prices much lower than in other countries. According to IHS Chemicals, in 2014, Iran exported 2.9 million t/a of methanol, with 60% of its exports going to China and 29% to India. IHS estimates that more than 100,000 t/a of methanol are currently imported into Europe from Iran.

"In the short-term, after the sanctions are lifted, Iran will likely re-ignite its relationships with Korea, Japan and Italy," said Mike Nash, global director of syngas chemicals at IHS Chemical. "And with the door to the West re-opened, Iranian producers can choose the highest-priced market to sell Iran's new methanol capacity, which will lead to a greater convergence of regional pricing."

A longer-term impact of any permanent lifting of sanctions to accelerate Iranian methanol capacity expansion plans would require access to feedstock, making it heavily dependent on the growth of the Iranian gas industry, and especially on supplies of natural gas from the South Pars gas field. The Iranian petrochemical industry, while quite diverse, is primarily focused on exploiting the country's vast resources of ethane-rich natural gas. The much larger impact of sanctions resulted from the inability of the country to maintain and invest sufficiently in its oil/gas and petrochemical feedstock and export infrastructure. This has led to chronically low capacity utilization rates; not least due to periodic shortages in ethane feedstock.

Methanol producers in Iran enjoy very advantageous production costs. The cost advantage of methanol production from Iranian natural gas is depicted on the adjacent cost curves for the years 2015 and 2019. IHS Chemical forecasts that the higher oil price forecasted for 2019 would further enhance Iran's position on the curve.

UNITED KINGDOM

Moratorium on unconventional gas may affect UCG project

Scotland's governing Scottish National Party (SNP) has already imposed a moratorium on unconventional gas production over concerns about hydraulic fracturing (fracking) as a technique, but it is now looking at widening this to cover underground coal gasification (UCG) projects. One of the projects is being developed offshore in the Firth of Forth by Cluff Natural Resources, whose founder Algy Cluff, argues that the closure of Scottish coal-fired power stations and declining North Sea conventional gas reserves mean that there will be acute demand for gas in Scotland, and says that he hopes "common sense" will prevail. Overall UK policy on gas extraction is currently reserved to the Westminster government, but the Scottish government's powers over planning mean its consent would be required for any project even before planned further devolution of powers from London over the next couple of years.

Cluff Natural Resources had previously abandoned a UCG project at the Point of Ayr on the northern coast of Wales in order to focus on the Scottish project. Cluff's chief operating officer (COO) Andrew Nunn, said: "We have screened a number of our licence areas...., in terms of their suitability to host a UCG demonstrator project at the earliest possible date. The outcome of that process is that we are focusing our efforts on getting our UCG project in Scotland up and running and currently we have no gasification activities planned in the Dee/Point of Ayr area until that demonstration project has been completed."

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People



Dominik Koechlin



Yvonne Harz-Pitre

Clariant has announced that **Dominik Koechlin**, non-executive member of the Board of Directors, died suddenly and unexpectedly on Sunday, July 12, 2015. Koechlin, who had a PhD in law, had joined the Board of Directors of Clariant in 2008. He was president of the compensation committee and member of the audit committee.

"All members of the Clariant Board of Directors as well as the Executive Committee, the employees and executives of Clariant, are deeply shocked to hear about Dominik Koechlin's death", said Rudolf Wehrli, Chairman of the Board of Directors of Clariant. "We mourn the loss of an adorable colleague and a passionate entrepreneur that Clariant has a lot to thank for."

The International Fertilizer Industry Association (IFA) has announced that **Yvonne Harz-Pitre** will join the organisation as IFA's new Director for Communications and Public Affairs in September. A German national by birth, Ms Harz-Pitre has also lived in France for many years and speaks excellent English. Her previous position was with Dow Agro Sciences in Paris, where she served as the Head of Global Communications for its AgroFresh Division.

GTL pioneer Velocys plc has suspended its CEO **Roy Lipski** pending an investigation into allegations of "serious misconduct." Lipski, who works from the company's commercial headquarters in Houston, has

been replaced during the investigation by CFO **Susan Robertson**.

"Mr. Lipski's suspension does not constitute disciplinary action and does not imply any assumption whatsoever that he is guilty of any misconduct," the board stated. "The board will keep his suspension under review and will aim to make the period of suspension no longer than is reasonably necessary. The allegations do not involve any element of fraud or financial impropriety."

Lipski, who has been at Velocys since March 2006, began his career working at Goldman Sachs International. The Houston headquarters employs nearly the entire workforce of about 100 people. Velocys also has technical facilities in Oxford, UK, and Columbus, OH.

Following the merger announcement between CF Industries and OCI NV (see Nitrogen Industry News, p10), the two companies say that the new merged corporation will operate under the name CF and be led by existing CF management. The initial board of the new corporation will have 10 directors, consisting of eight of CF's current directors, as well as **Greg Heckman**, former CEO of The Gavilon Group, LLC and current OCI N.V. board member, and **Alan Heuberger**, senior portfolio manager for Bill & Melinda Gates Investments (BMGI). The combined company will maintain its principal executive offices in Deerfield, Illinois. ■

Calendar 2015/2016

SEPTEMBER

21-23

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

OCTOBER

4-9

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

11-14

Gasification Technologies Conference, COLORADO SPRINGS, Colorado, USA
Contact: Gasification Technologies Council, 3030 Clarendon Blvd. Suite 330 Arlington, VA 22201 USA.

Tel: +1 703 276 0110
Fax: +1 703 276 0141
Email: info@gasification.org

26-28

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

NOVEMBER

10-12

World Methanol Conference, MUNICH, Germany
Contact: Lynn Urban, Sales Manager, IHS
Events. Tel: +1 303 397 2801
Email: Lynn.Urban@ihs.com

23-27

Training Programme for Urea Engineers, DOHA, Qatar
Contact: UreaKnowHow.com
Email: mark.brouwer@ureaknowhow.com

DECEMBER

10-11

International Fertiliser Society Agronomic Conference, CAMBRIDGE, UK
Contact: IFS Tel: +44 1206 851819
Email: secretary@fertiliser-society.org
Web: fertiliser-society.org

FEBRUARY 2016

29-3 March

Nitrogen+Syngas Conference, BERLIN, Germany
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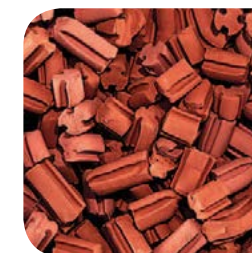
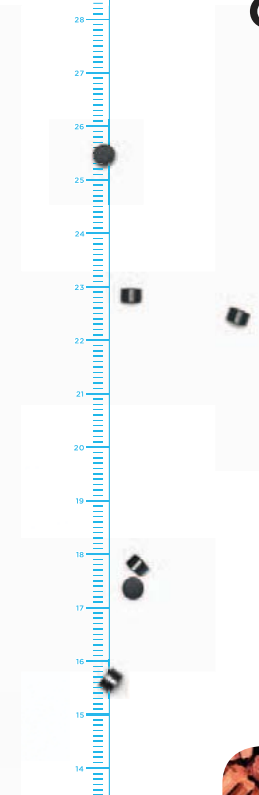
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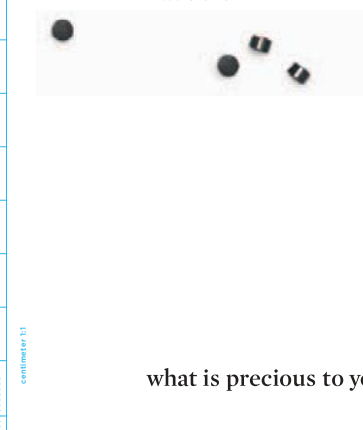
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Plant Manager+

Problem No. 32 Temperature drop at bottom outlet of HP stripper in a Saipem urea plant

The stripper in a urea plant is a key item of high pressure equipment affecting the overall performance of a urea plant. There is a significant difference between the Stamicarbon CO₂ HP stripper and the Saipem NH₃ HP stripper when judging its performance. The bottom outlet temperature of a Stamicarbon CO₂ stripper is normally relatively low (170-175°C) and when the performance of the HP stripper reduces (meaning lower stripping efficiency) this temperature will increase



indicating an increase in the ammonia content in the bottom outlet of the stripper. However, in a Saipem NH₃ stripper the situation is totally different. The stripper bottom outlet temperature increases with a higher stripper efficiency and an operator in a Saipem urea plant tries to operate the urea plant at the maximum bottom outlet temperature. The maximum value is determined by the acceptable corrosion rates, for example, 204°C for a bimetallic stripper.

Mr Ngateno Utomo of PKT, Indonesia starts this round table discussion with a practical problem: We operate a Saipem urea plant with a design capacity of 1,725 t/d. The plant is 13 years old. During start-up the temperature at the HP stripper outlet can reach 202°C at 100% plant load (flow of steam 38 t/h), but after a few days the temperature drops to 194°C (and flow of steam drops to 20 t/h). We have tried trimming all operating conditions but the temperature cannot be increased even when we reduce the plant load to only 50%. We tried to block in and restart the plant, but the condition reoccurred. Can anyone explain what the problem is with the stripper?

Mr Prem Baboo of National Fertilizers Ltd in India replies: The reduction in steam flow indicates restriction of the steam, for example due to one of the following reasons:

- Check the conductivity of the steam condensate for any leakage. If the conductivity has increased (200-1000 micro mho/cm) there is leakage in a tube or tube sheet and the shell might be pressurised with vapour causing restrictions of steam flow.
- Check the steam condensate drum level
- Check the stripper bottom level

I am fairly confident the first reason may be your problem. If a leakage is found, shut down immediately to avoid further damage/corrosion of the carbon steel shell side and the carbon steel tube sheet.

Ngateno responds: Thank you for your suggestions. We have checked and tried to increase and decrease the level in the stripper bottom and steam condensate drum level, but there is no effect on the temperature. The conductivity of the steam condensate is also normal.

Prem offers further advice: If the above points are fine, check the steam to the stripper control valve. Sometimes the internals are damaged and physically show normal opening but actual passage is blocked due to denting of the stem or foreign material blocking the control valve passage.

Ngateno replies: We have checked the steam control valve and then rechecked it by opening the bypass but it has no effect.

Mr Thai Son Phan of Phu My Fertilizer plant in Vietnam joins the discussion: Did you check the temperature into/out of the stripper steam condensate separator? I favour the temperature outlet. If it is not perfectly saturated (219°C at 22.5 bara) its heat exchange capacity decreases and the stripper bottom outlet temperature decreases gradually.

Mr Ali Salman Bokhari of Pak-American Fertilizers (Pvt.) Ltd. in Pakistan provides his support: In my view, you need to check the following:

- Do you have any vapour balance line installed between shell side of stripper and steam condensate (saturation) drum?
- Purge the shell side of stripper during normal operation and observe whether there is any positive change in stripper performance, more specifically steam consumption.
- Have you ever conducted a leak test of the stripper liquid distribution system and was it satisfactory?
- What type of ammonia feed pump is installed at your plant?
- Have you observed any coloration of product – yellowish or brownish?
- Have you observed some sort of oil layer or foam in the absorbers?
- What is the performance of other steam heaters at your plant?

Mr Umesh Kottara of Mangalore Chemicals and Fertilizers Ltd. in India contributes with his recommendations: Check that the HP stripper shell side vent is opened sufficiently to vent the inerts present in the steam. Check the quality of the steam introduced. We had a similar problem due to bubbling of the carbon dioxide feed (we have a CO₂ stripping process) into the urea solution at the stripper bottom due to a gasket leakage. We stopped the plant and found the gasket leaking as expected.

Fouling of stripper tubes may be another reason – adopt an appropriate chemical cleaning procedure for this, like EDTA.

Mr S.K. Gupta of IFFCO in India shares also his valuable experiences: I assume the stripper in your plant is bimetallic. What is the diameter of the tangential holes of the ferrule? In our experience a larger hole diameter solves the problem you indicated.

Ali returns: It is very interesting to know that you are increasing the hole size of the ferrule. What is the procedure?

SK replies: We have four urea strippers of the same heat duty in operation at our site. Initially we had two urea streams with titanium strippers. After an expansion of the site two more urea streams were added. The new urea streams have bimetallic strippers. We experienced the problem of temperature drop in the bimetallic strippers. We tried all the suggestions mentioned in this forum but to no avail. Saipem took notice and enlarged the ferrule hole diameter for their new bimetallic strippers. A few years back we replaced our aging two titanium strippers in the old urea streams with new bimetallic strippers. We have not experienced the problem in the new strippers. As per the advice of Saipem we are also planning to increase the ferrule hole diameter of the old strippers. Nowadays we are managing it by cutting off the feed for five minutes whenever there is problem in temperature drop.

Mr Pablo Gastón Schulz of Profertil in Argentina shares his experiences: We also operate a Saipem plant and have extensive experience with stripper heat transfer inefficiency. This year we had an abrupt trip due to a positioner failure in the stripper bottom level control valve. After this, the heat transfer efficiency in the stripper had a small step decrease, yet after each restart (we had two after this event) the problem got worse. Then, in just one week the stripper efficiency decreased in such a way that we were forced to shut down, since the plant could not be operated any more.

Analysing the DCS trends, we managed to identify the most probable cause: liquid maldistribution in the tubes. One key symptom was the noise in the MP steam flow, which got worse with time. The fact was that during this emergency trip, the ferrules became loose, due to the pressure buildup within the tubes. We performed a leak test during the turnaround and got an order of magnitude more leakage than allowable.

Since the male inserts of the ferrule were deformed (slightly, not visible), they could not be fixed in position by the metal grid. So we installed Teflon washers in between the ferrule and the tube, to tighten the ferrule. This allowed us the smallest leakage ever registered in our plant, and since then the stripper efficiency boomed up.

Yet for the sake of being sure before you shut down the plant, I suggest you take a systematic approach:

Steam side:

- Check for inerts in the shell. Open the vent.
- Check actual level in steam reservoir of the stripper (V109). If the shell is partially flooded you lose heat transfer area.
- Check the PV that controls the steam pressure, also the transmitter (in case the controller is failing)

Process side:

If you had a cold start up, if too much carbamate was present at the time of overflow of the reactor, a high pressure is built up within the tubes and despite the composition eventually becoming OK, this disruption in liquid distribution cannot be reversed by any load reduction. The only way we have found to reverse this is by stopping all flow (we have a procedure for this). The key is that when having a hot restart the composition is OK from the very beginning so there is no disruption. You only have to be very careful to keep the NH₃/CO₂ ratio in the normal range.

Also make sure that the problem is not coming from another area. Check the delta T of the reactor, and sample the outlet to verify conversion and N/C ratio. Check the actual N/C ratio by having an instrument specialist verify CO₂ and NH₃ measurements. When we had this problem typically there is more water in the pro-

cess since the decomposition is shifted to the MP and LP sections.

Be careful not to allow the PV020 (MP steam to stripper steam drum) to be saturated to 10%, along with the MP decomposer TIC. We made this mistake and overloaded the LP decomposer, and this led to E08 (CW condenser) eventually plugging, leading to a shut down. This was because the proportion of gases from the LP decomposer and gases from waste water treatment column was distorted, making the solution less aqueous. During shutdown, check that the distributor toroid weld is not damaged, also check the serrated overflow. This could also lead to maldistribution of liquid.

We also had the gas orifice of the ferrules enlarged by Saipem along with moving the tangential holes so that the liquid level increases. You are definitely facing the same problem we had.

Ali replies: I agree with your comments. Actually uneven opening of the hand control valve controlling the reactor level (due to any reason - instrument malfunction or mis-operation) causes a hammering impact on the liquid distribution system resulting in displacement of ferrules. We have also faced this problem in our TEC plant during early years of operation.

You must be familiar with ferrule and swirl operation. Actually stripper efficiency is based on the film uniformity of the urea solution in terms of the thickness in the falling film heater and film thickness is dictated by the velocity of the urea solution through the tubes, which in turn is dictated by the liquid head and swirls hole size. That is why hydrolysis occurs in the stripper and fluctuates with fluctuations in plant load. In extreme conditions it may lead to dry run operation, which is a nightmare situation.

Mr Akash Deep Mawkin of National Fertilizers Limited in India shares his suggestions: Probable causes for not achieving the stripper outlet temperature:

- stripper level is actually running very high (touching the tube sheet and restricting the vapour passage through tubes);
- steam condensate separator level is very low (no saturated steam is going to stripper);
- restriction in steam inlet to stripper;
- reactor outlet pipe having leakage (inside the reactor);
- poor stripper liquid distribution (may be due to the ferrule tangential portion being damaged due to thinning);
- temperature and flow indicators are malfunctioning (this can be checked if there adverse effect on MP section).

Mr Zeeshan Shoab of Fauji Fertilizer Company Limited in Pakistan provides his input: After reading all of the above discussions, in my opinion the condition of the ferrules needs to be checked. Improper film generation may cause poor thermal efficiency of the stripper. Sometimes the ferrules nozzle holes are blocked or ferrules were out of place causing gas bypassing, indicated by a high top stripper temperature. In addition, it is important to maintain the proper NC ratio in the system.

During start-up, don't let the stripper temperature exceed 198 to 200°C at 60 to 70% plant load. Raise the temperature of the stripper bottom gradually. If high temperature MS steam is given too quickly hot spots may appear on the inner wall of the stripper tube and cause channeling.

This problem may occur due to poor indication of the level transmitter that misleads the stripper bottom holder level controller. A high level may cause channeling. ■

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Syngas industries in southeast Asia

Southeast Asia is continuing to see steady growth in both nitrogen capacity and demand. Reform in Myanmar and new energy developments in Vietnam and Malaysia have the potential to continue this.

The Association of South-East Asian Nations (ASEAN) includes 10 member states with a combined population of 625 million people and an economy roughly the size of France or the UK, but growing at an average of 5.8% per year over the past five years. Indeed, the region taken as a whole has been the second fastest economy in Asia, after China, tripling in size from 2001-2013. Perhaps unsurprisingly, growth has been fastest (albeit from a low base) in the relatively less developed economies of Laos, Cambodia and Myanmar, while it has been slower in the more developed economies of Singapore and Brunei.

While the region has perhaps been overshadowed, especially in the area of foreign direct investment by the rapid growth of China to the north, it remains relatively resource rich in terms of gas and coal reserves, and the region's geography; split up by islands and mountain chains, means that gas infrastructure in particular has been slow to develop. Initially this meant a large amount of 'stranded' natural gas, with development of major liquefied natural gas (LNG) export projects or the production of syngas-based chemicals

such as methanol, ammonia or urea which can be more readily transported. But rapid industrialisation and increasing populations are leading to greater demands for power production, and the power industry is driving the connection of the region via pipeline and growing competition between power and chemical industries for gas resources.

As Table 1 shows, natural gas reserves are concentrated in two states, Malaysia and Indonesia.

However, there are also significant reserves in Brunei, Burma, Papua New Guinea, Thailand and Vietnam.

Burma/Myanmar

Until relatively recently, Burma was a pariah state run by a military government which had been in power since 1962 and which had annulled the only free elections ever held, in 1990, and imprisoned the National League for Democracy (NLD) leader Aung San Suu Kyi. However, from 2008 the regime has begun to unbend, leading to the freeing of Aung San Suu Kyi and the NLD winning parliamentary representation in the 2012 by-elections.

The military junta formally stood down in 2011 and the new government, although still heavily backed by the military, has sought to end long-running ethnic guerrilla conflicts in the north of the country. Myanmar has been rewarded for this transition to democratic rule with a lifting of international sanctions and trade restrictions, but the country's long years of isolation have left it relatively poor and undeveloped, with a creaking national infrastructure often still reliant on e.g. railways dating back to British rule in the 1940s.

Nevertheless, the government has been relatively successful in attracting foreign investment, and GDP has risen by 7-8% per year over the past four years. Natural gas production has increased steadily, from 12.4 bcm in 2008 to 16.8 bcm in 2014. The country's current natural gas output mostly (ca 70%) comes from the offshore Yadana and Yetagun fields, but the government held a licensing round in 2011-12 and gas production is now forecast to rise as a result of new projects coming online, for example at Zawtika. Some of this gas – around 25% from all new projects – has been earmarked for domestic power, fertilizer and transportation use.

Burma exports natural gas to Thailand and, more recently China, now that the security situation in the north of the country is more settled and the Shwe project has begun production and a pipeline from Kyaukphyu to Kunming in southwestern China has been completed.

Fertilizer industry

The long years of sanctions have stunted Myanmar's industrial and agricultural development. Agriculture employs 60% of the workforce and accounted for 33% of GDP and 32% of export earnings in 2013. Fertilizer consumption fell after domestic

Nitric acid catalysts and process plants ...

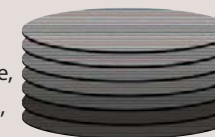
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Table 1: Gas reserves and production in Southeast Asia, 2014 billion cubic metres

| | Production | Exports | Reserves |
|------------------|------------|---------|----------|
| Burma | 16.8 | 12.7 | 280 |
| Brunei | 11.9 | 8.3 | 270 |
| Indonesia | 73.4 | 31.2 | 2,820 |
| Malaysia | 66.4 | 38.9 | 1,060 |
| Papua New Guinea | 5.0 | 4.7 | 150 |
| Thailand | 42.1 | - | 230 |
| Vietnam | 10.2 | - | 610 |

Source: BP

prices were fully decontrolled in 2003, and total consumption of fertilizer averages only around 800,000 tonnes per year, of which just 80-120,000 t/a is produced domestically, from a clutch of small state-owned urea plants. Urea consumption was 225,000 t/a in 2013, according to IFA, with about half of that coming from domestic production. There are five ammonia-urea plants with a total capacity of around 650,000 t/a, two of which have long been closed down, and the others operate at drastically reduced capacities due to gas shortages and maintenance issues. Nevertheless, in spite of this the country is more than self-sufficient in rice production, and exports to its neighbours. The potential is thus there for Myanmar to become a major regional food producer and exporter, on a par with Vietnam or Thailand. Fertilizer use per hectare in Myanmar is less than one tenth of that in Vietnam.

There were abortive attempts around the time of the Yadana gas project in 2002 to piggy-back new ammonia and urea capacity onto the development, but this eventually fell by the wayside. However, the lifting of sanctions has been seen as a renewed opportunity for Myanmar to develop more of a domestic fertilizer industry, and Japanese companies have been in discussions about new plants. Earlier this year, Myanmar's Ministry of Energy also invited expressions of for a joint venture with Myanmar Petrochemical Enterprise, the state-owned producer, to rehabilitate the MPE No 3 factory at Kyawzwa, which has 360 t/d of ammonia and 600 t/d of urea capacity, and which has been idled since 2010.

Brunei

The small Sultanate of Brunei on the northern coast of Borneo was at the forefront of gas discovery and development in the ASEAN region, with large oil and gas reserves discovered in the 1960s and LNG exports beginning in 1972 from the Lumut LNG plant. The five trains there have the capacity to produce 9.5 bcm per year, with 8.3 bcm exported in 2014, mostly to Japan and Korea under long term contracts. Brunei's oil production peaked in 1979, but gas production has been relatively constant, and well within the country's significant reserves (see Table 1). Domestic gas consumption has been rising, although at present around 75% of production is still available for export. Nevertheless, in recent years the

government has licensed deep water exploration to find new reserves and has targeted downstream petrochemicals as another potential way of diversifying the economy. French major Total made significant gas and condensate discoveries in Block B in 2010 which could bolster gas reserves and sustain LNG exports as well as providing gas for other uses. Total plans to add 1 bcm per year of production from its second phase of production from the Maharaja Lela field development starting in 2015.

Downstream developments began with the \$600m Brunei Methanol Co. 850,000 t/a methanol plant at Sungai Liang Industrial Park in 2010. BMC is a joint venture between Brunei's state-owned Petroleum Brunei (50%) and Japan's Mitsubishi Gas Chemical Co. (25%) and Itochu (25%). The Brunei Economic Development Board has also been seeking to build a nitrogen fertilizer complex at the site, with proposals and feasibility studies going back to 2004, and most recently (2012) for a 500,000 t/a ammonia plant, with several Japanese companies involved in discussions. Urea, melamine, diammonium phosphate, ammonium sulphate and caprolactam have all been discussed, but so far no contracts have been awarded.

Indonesia

With a population estimated at 250 million, Indonesia is the fourth largest nation in the world, sprawling across an archipelago of thousands of islands across 5,000 km. Its diverse population means that Indonesia has had to cope with religious tensions and separatist struggles in recent years, but in 2005 a peace deal was signed with the Free Aceh movement, leading to democratic elections in the province in 2006. Indonesia's population continues to expand rapidly. Increasing industrialisation is also altering patterns of demand. An oil exporter for many decades, the country became a net importer for the first time in 2004.

Indonesia also has the largest gas reserves in the region, put at just under 3 trillion cubic metres in 2014 according to BP, about 70% of those offshore, and the country remains a major exporter of natural gas, by both pipeline (to Singapore and Malaysia) and especially via LNG. However, domestic gas production peaked in 2010 at 77 bcm and since then has fallen back to 66bcm, while gas consumption has risen over the past decade, albeit

from a low rate, as the government has tried to encourage use and move the country's energy balance away from expensive oil, including in the transport sector. This in turn has impacted upon Indonesia's exports of LNG – until 2005 the country was the world's largest LNG exporter, but exports have fallen at the same time that other producers such as Qatar and Australia and even Malaysia have overtaken it.

With pipeline infrastructure across the archipelago relatively undeveloped, Indonesia has looked to use LNG as a way of transferring gas internally, from gas-producing regions around Borneo and Sulawesi to the booming cities of Java and southern Sumatra, and including the use of floating LNG regasification plants to avoid the high costs of building regasification plants. The 2 million t/a Donggi-Senoro LNG terminal on Sulawesi shipped its first LNG cargo to Arun in northern Sumatra recently, where the LNG export terminal has been re-purposed as a receiving terminal since February 2015. But low coal prices and the boost in LNG demand provided by Japan's shutdown of its nuclear plants have meant that Indonesian gas demand in the past couple of years has not expanded as quickly as expected. The 82,000 tonne Lampung floating regasification unit has remained idle off the coast of Sumatra since January, according to state gas company Perusahaan Gas Negara (PGN). Even so, the government of Indonesia believes that the country will have become a net gas importer by 2025.

The country also has huge coal reserves, mostly in Sumatra and eastern and southern Borneo, and with it considerable volumes of coalbed methane. Indonesia's coal production has more than tripled over the past decade, rising from 81 million tonnes of oil equivalent in 2004 to 280 mtoe in 2014, placing Indonesia third in global coal production, after the US and China. While most of this coal (75%) is exported to China, Japan, Taiwan and India, amongst others, and making Indonesia second only to Australia as a coal exporter, domestic consumption has also risen, reaching 60 mtoe in 2014.

Downstream industry

Indonesia has several ammonia and urea manufacturers, mostly based in Sumatra, Java, and on the east coast of Kalimantan (Borneo). Fertilizer production is almost entirely a state industry in Indonesia where



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state-owned ammonia/urea manufacturer PT Pupuk Sriwidjaja (Pusri) also acts as the government's holding company for the four other state-owned fertilizer manufacturers. Pusri was the first manufacturer, established in 1959 at Palembang in South Sumatra. At the start of 2015 the site comprised four trains with a combined capacity of 2.26m t/a of urea and 1.5m t/a of ammonia.

The government established three further fertilizer companies in the 1970s: PT Petrokimia Gresik in East Java in 1972, using fuel oil feedstock initially until piped gas supplies became available in East Java; PT Pupuk Kujang in 1975 at Cikampek in West Java; and PT Pupuk Kalimantan Timur (Kaltim) in 1977 at Bontang in East Kalimantan. A fifth state-owned ammonia/urea producer, PT Pupuk Iskandar Muda (PIM), began production in 1982 at Lhokseumawe near the Arun gas field in Aceh, North Sumatra, PIM has the capacity to produce 1.17m t/a of urea and 750,000 t/a of ammonia following the completion of a second plant in 2004, and the PT Asean Aceh Fertilizer (AAF) plant was also established at Lhokseumawe in 1981 as a joint venture by the Association of South East Asian Nations (Asean), but was idled due to lack of gas supplies, which have also affected the PIM complex. Kaltim also operates a 660,000 t/a methanol unit at Bontang, and Pertamina a smaller 330,000 t/a plant at Bunyu. Pusri's small, first plant was replaced in 1981 with Pusri IB, and a replacement for the second plant, Pusri IIB, is currently under construction and is scheduled to begin operations in November this year. Pusri IIB has a capacity of 660,000 t/a of ammonia and 900,000 t/a of urea, replacing the smaller Pusri II 360,000 t/a ammonia-urea plant.

A further expansion to Indonesia's urea capacity came earlier this year with the start-up of Kaltim V. Designed to produce 1.15 million t/a of urea and 600,000 t/a of ammonia, Kaltim V replaces the ageing Kaltim I plant, again with a net increase in production. Indonesia's urea capacity stood at about 7.9 million t/a at the start of 2015, with demand running ahead of this at almost 9 million t/a, but Pusri IIB and Kaltim V will increase domestic capacity to 8.7 million t/a of urea capacity, and there are plans for more developments now in train.

Petrokimia Gresik is developing a second urea plant, Amurea 2, with 660,000 t/a of ammonia and 570,000

Table 2: Urea production and demand, ASEAN countries, 2013, million t/a

| | Production | Consumption | Imports | Exports |
|--------------|-------------|-------------|------------|------------|
| Indonesia | 6.7 | 5.5 | 0.1 | 1.3 |
| Malaysia | 1.4 | 0.8 | 0.4 | 0.9 |
| Myanmar | 0.2 | 0.2 | 0 | 0 |
| Philippines | 0 | 0.9 | 0.9 | 0 |
| Thailand | 0 | 2.4 | 2.4 | 0 |
| Vietnam | 2.1 | 2.6 | 0.6 | 0.2 |
| Total | 10.4 | 12.4 | 4.4 | 2.4 |

Source: IFA

t/a of urea capacity. Site preparation and engineering is already under way, and the new unit is due to start up in late 2017. PT Pupuk Kujang IC, provisionally scheduled for 2019, would add 660,000 t/a of ammonia and 1.15 million t/a of urea capacity. And Pusri is also developing a new project at Bintuni Bay in West Papua in collaboration with Ferrostaal AG and LG International, once a supply of gas has been confirmed.

Indonesia's burgeoning mining industry, meanwhile, is a major consumer of ammonium nitrate, which has led to the development of considerable new AN capacity in the country in recent years to supply coal, copper, gold and other mining operations. Multi Nitrotama Kimia expanded its complex at Cikampek, West Java from 39,000 t/a to 140,000 t/a via the addition of a second train in 2011, and two new AN plants were completed at Bontang in 2012: PT Black Bear Resources Indonesia (BBRI), in which South Africa's AECI is a major shareholder, which uses ammonia sourced from Kaltim to produce 92,000 t/a of AN; and PT Kaltim Nitrate Indonesia, a joint venture with Australia's Orica, which has 300,000 t/a of capacity.

Malaysia

Malaysia has large natural gas reserves; more than 1 trillion cubic metres, but with a much smaller population than Indonesia – 30 million compared to 250 million. This has given it more gas availability for power, chemical production and export as LNG. Under the auspices of state-owned oil and gas firm Petronas, Malaysia operates 400,000 t/a of ammonia and 540,000 t/a of urea capacity at Bintulu on the northwest of Borneo, in a plant developed by the Association of South-East Asian Nations (Asean) in similar fashion to the unit at Aceh in Indonesia. Urea capacity increased

in 1999 with the opening of a new 595,000 t/a ammonia-urea facility by Petronas, at Kedah. Petronas also completed a 450,000 t/a stand-alone ammonia plant at Keroh in Terengganu province on the east coast of the Malay peninsula in 2002.

More recently, Petronas has developed a new \$1.5 billion large-scale ammonia/urea fertilizer plant at Sipitang in Sabah State on the island of Borneo. Based on natural gas feedstock, the SAMUR plant has a capacity of 2,100 t/d (690,000 t/a) of ammonia and 3,850 t/d (1.27 million t/a) of urea.

A 600,000 t/a methanol facility was constructed at Labuan in 1993 using Lurgi technology, and the facility was expanded more recently, with the addition of a 1.7 million t/a mega-methanol plant at the site, also using Lurgi technology.

Papua New Guinea

Papua New Guinea occupies the eastern part of New Guinea, the world's second largest island. Much of the country is rural, especially in the tribal societies of the interior, which are dependent on subsistence agriculture. Mineral deposits are extensive, and there are significant reserves of oil and natural gas. The relative lack of infrastructure and an insurgency which ended only in 2005 have slowed development in Papua New Guinea, but in recent years the pace has begun to pick up.

The first development, a twin-train LNG export plant with a total capacity of 6.6 million t/a, started up in 2014. Now there are two proposals for gas-based chemical plants which the government says it is considering: a proposal from Mitsubishi Chemical and Itochu for a \$2 billion methanol and dimethyl ether plant, and a methanol and urea proposal from Japan's Sojitz Corporation. No firm decision has been taken as yet, however.

Vietnam

Our article elsewhere in this issue (pages 28-29) discusses the fertilizer situation in Vietnam in much more depth, but briefly, there are now three major nitrogen complexes in the country. An older, coal gasification-based plant in the north of the country is operated by Vinachem, recently revamped and expanded to 500,000 t/a of urea production. In the south there are two gas-based plants using gas from the Nam Con Son basin, developed by BP, PetroVietnam and Conoco, which comes ashore at Phu My, where a fertilizer and power plant complex was built from 2001-2004. A second, identical plant was completed further south at Ca Mau in 2012.

Regional supply/demand

Almost all of the ammonia produced in the region goes to produce urea – Indonesia's recent foray into ammonium nitrate being the most significant exception. Table 2 gives a breakdown of urea production and consumption across Southeast Asia. Only the major producers and consumers are listed – volumes used in Cambodia, Laos, Brunei, Singapore and New Guinea are less than 50,000 t/a each.

As can be seen, Indonesia, and to a lesser extent Malaysia and Vietnam are the major producers, and of those, only Indonesia and Malaysia are major exporters. Vietnam, although it technically has a surplus of urea production, has remained a slight net importer in recent years because of domestic costs of production, as our article elsewhere discusses.

Indonesia is also the largest consumer, with Thailand and Vietnam also large users of urea, with Malaysia and Philippines more moderate consumers. As non-producers, Thailand and Philippines must of course source all of their urea from imports. Although there is intra-regional trade, with Indonesia supplying to Vietnam, for example, it can also be seen that the region as a whole was a net importer of urea in 2013, with most imports coming from China, and to a lesser extent the Middle East.

On the methanol side, Malaysia is the largest producer, with Indonesia and Brunei also significant producers. Volumes are almost entirely destined for export, mainly to East Asia, especially China.

Looking forward

The main developments in the region, as we have discussed above, are new ammonia/urea capacity building in Indonesia and the SAMUR plant in Malaysia. Pusri II, Kaltim V and SAMUR will add between them a net increase of 2.7 million t/a (once older trains are retired) of urea capacity, more than enough to take up the net regional deficit, and possibly pushing it slightly into surplus. Further capacity in Indonesia will add to that surplus in 2017 with Gresik 2, even before the projects at Kujang and Bintuni are considered. However,

Indonesia's natural gas situation remains precarious as consumption continues to increase, and with the possibility of becoming a net importer over the next decade, and it may be that Indonesia joins the list of countries constrained by gas availability at times of peak power demand.

Brunei, Papua New Guinea and Myanmar all have gas availability and potential projects on the table, should there be any slackening in the pace of developments in Indonesia, although at present, in an oversupplied urea market, those projects look marginal at the moment. ■



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NITROGEN+SYNGAS
ISSUE 337
SEPTEMBER-OCTOBER 2015

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Vietnam looks to increase urea exports

David Hayes reports from Vietnam, where local producers are looking to find new export markets, with increasing competition from low-priced imports and slowing domestic demand as a result of drought.

Vietnam's urea producers are looking to increase export sales in the face of strong price competition from low-priced imports and a slow down in domestic fertilizer demand last year caused by a drought affecting most parts of the country and other areas of Southeast Asia. Following large investment by state-owned enterprises in building urea production facilities to support the government's agricultural sector development programme, Vietnam now faces an oversupply of urea due to the availability of low cost imports from neighbouring China.

The oversupply has placed the government in a quandary: raising import duties to protect the state-owned urea producers has caused widespread complaints among the nation's large numbers of small farmers who rely on low-priced imported fertilizer and reduce their usage if prices rise. On the other hand, Vietnam's urea producers want import tariffs to protect their

investments and to help increase sales and domestic market share.

After import prices rose early in 2015, the Ministry of Agriculture and Rural Development (MARD) requested the Ministry of Finance to abolish the current 5% import tax on urea following a further surge in the price of imported urea in the second quarter of this year that has already caused a sharp fall in fertilizer imports due to lower overall purchases by the nation's farmers.

Although the drop in imports has been welcomed by Vietnam's urea producers, which originally expected to have the domestic market largely to themselves, rising import prices have provoked widespread complaints from farmers who rely on cheap imports to supply their urea needs. According to local news reports published by Vietnam Chamber of Commerce, prices of imported urea reached a record high of around \$332/t in late May, registering a 10% increase or \$32/t com-

pared with urea import prices in early April 2015. Domestic wholesale prices for urea soared to around VND 5,400 to 5,500/kg, while the retail price index in northern Vietnam reached VND 6,000/kg in mid-July.

In the first four months of 2015 Vietnam imported around 286,000 tonnes of urea worth about \$70 million, the chamber of commerce reported, representing a 61.5% decrease in volume year-on-year and a 50.2% fall in value year-on-year. MARD has forecast that Vietnam will need about 500,000 tonnes of urea for this year's summer-autumn crop season, while urea stockpiles are reported to be running low.

Increased imports

In spite of the nation's urea self sufficiency, urea was the largest product among Vietnam's overall fertilizer imports in the first four months this year, which totalled 756,000 tonnes worth US\$159 million, registering a 45.7% fall in volume and a 34.4% drop in value respectively year-on-year.

MARD's request for the Ministry of Finance to zero-rate urea imports to assist poorer farmers reliant on low-cost urea imports seeks to reverse last year's increase in the urea import tariff. The import duty was raised to 5% from the 3% previously set at the end of 2013, largely in response to urging from urea producer Ninh Binh Nitrogen Fertilizers Ltd, which uses a coal-gasification process and which has relatively high coal feedstock costs, for protection against low cost Chinese imports.

The call to abolish urea import duty marks the latest round in competition between Vietnam's urea manufacturers and low price Chinese imports for Vietnam's growing fertilizer market. Previously reliant on imports for a substantial portion of its urea requirements until a

few years ago, Vietnam reached self sufficiency in urea in 2012 for the first time, when work constructing Ca Mau urea plant in the south of the country and Ninh Binh urea plant in the north were both completed that year. However, the availability of cheap urea imports continues to pose problems for Vietnam's urea industry as supplies from China arrive across the northern land border by truck and by ship through various coastal ports.

"Vietnam lies just next to China and it's easy to get Chinese products with low quality and at a cheap price. Many farmers still prefer cheaper products as they are not well educated," commented a source at Japan Vietnam Fertilizer Co Ltd (JVF), one of the country's major NPK fertilizer producers.

According to a report by Vietnam National Chemical Group (Vinachem), which owns two urea plants in the north that use the coal-gasification production process, Vietnam's total supply of urea in 2013 was 3.25 million metric tonnes, around 45% more than actual demand. This figure includes more than 2 million tonnes produced by the country's four urea plants, along with 1.2 million tonnes imported from China, much higher than total domestic urea demand of 2.2 million t/a that year.

According to government figures total chemical fertilizer demand in Vietnam currently is about 1.1 million t/a. Of this urea demand is about 2.5 million t/a, while demand for DAP, MOP and ammonia sulphate is almost 1 million t/a for each. Government figures show current demand for NPK at 3.5-4.0 million t/a. However, about 50% of this figure is thought to consist of low quality bulk blended NPK made using low cost imported materials.

Demand increasing

Fertilizer demand is growing throughout Vietnam, contributing to the country's rising crop production.

"Total fertilizer demand is growing but not so quickly, it's about 5% to 7% annually. It's growing as the farm land area is growing and farmers' incomes are a bit better," the source said. "In 2013 and last year Vietnam's rice exports overtook Thailand's. Farmers want to increase their yields so they increase fertilizer use. That's one reason for the increase in demand."

To what extent fertilizer consumption will grow this year is in doubt, however, as Vietnam, along with a number of other

countries in Asia, is currently suffering from a drought that has affected production of rice and other crops. Farmer purchases and use of urea along with other chemical fertilizers have fallen as a result, putting Vietnam's urea producers under additional pressure this year.

The country's two producers of coal-based urea products appear to be hardest hit, as their production costs are higher than Vietnam's natural gas-based urea production. This is due to higher cost of local coal supplies as feedstock, which are controlled by Vietnam's national coal and mineral industries controlling corporation, Vinacomin, compared to natural gas which is subsidised by the government at about 50% of the market price.

In addition to facing domestic competition from gas-based urea, the two plants using coal feedstocks also are more vulnerable to competition from low priced urea imports.

"This year the situation has changed as there is a drought in Southeast Asia affecting Vietnam, Thailand, the Philippines and other countries. There is a serious drought in the whole of Vietnam, especially the central region," the source said. "The Mekong River is in the south and in the north there is the Hon River, but in the central region there are not so many rivers. In the north and south they can get water from the rivers for irrigation but because there has been no rain and high temperatures this has affected paddy production. Rice cannot grow because of the high temperatures and in areas where there are no irrigation systems there is little water, so those areas need less fertilizer as well."

Urea capacity

Vietnam's current installed urea production capacity is 2.35 million t/a, of which about two thirds of the production capacity is installed in the south and one third in northern Vietnam. Both urea plants in the north under Vinachem use the coal gasification process.

Ha Bac Nitrogen Fertilizers & Chemicals Ltd is Vietnam's oldest urea plant being originally established in 1960 with assistance from China. The plant is Vietnam's smallest urea facility with an output capacity of 190,000 t/a.

Ninh Binh Nitrogen Fertilizers Ltd is Vietnam's newest urea plant to use the coal gasification process and also has been built with assistance from China. Designed to produce 320,000 t/a of ammonia and

560,000 t/a of urea, the plant is located in Bac Giang Province.

Elsewhere, state-run PetroVietnam Fertilizer & Chemicals Corporation, a member of the Vietnam National Oil and Gas Group, owns two urea plants in southern Vietnam. Both of the plants use natural gas from off-shore gas fields as feedstock, buying their supplies from Vietnam National Oil and Gas Group member, PetroVietnam Gas.

Built at a total estimated cost of \$700 million, PetroVietnam Ca Mau Fertilizer Co Ltd's 800,000 t/a plant located in Ca Mau province is PetroVietnam's newest urea plant. Completed in 2012, the Ca Mau plant is part of the \$1.4 billion Ca Mau gas-electricity-urea complex designed to use 2 billion cubic metres (bcm) of gas per year from the offshore PM3 gas field to produce urea and generate electricity. Gas is supplied from the PM3 field through a 325 km transmission pipeline including a 298 km submarine pipeline section to landfall and a 27 km land line to the Ca Mau complex.

Ca Mau requires about 500 million cubic metres per year of gas to run its granular urea production facilities at full capacity. Haldor Topsoe supplied the ammonia synthesis technology while the urea synthesis technology is from SAIPEM. In addition, Toyo Engineering licensed its spout fluid bed granulation technology for urea pelletising. In addition to the ammonia-urea plant, the Ca Mau complex includes Ca Mau gas-fired power plants No1 and No2 which total 1,500 megawatts installed generating capacity. According to the company, the urea plant produced over 1.7 million tons of granular urea during the first two years of operation worth VND 13.8 billion.

Apart from Ca Mau plant which exports urea to neighbouring Cambodia in addition to supplying the domestic market, PetroVietnam also owns the 800,000 t/a Phu My urea plant that forms part of the Phu My gas-electricity-urea complex in Ba Ria-Vung Tau province which formed the basic design concept for the Ca Mau complex to follow. Phu My receives gas from the off-shore Cuu Long and Nam Con Son gas fields. The plant produces 1,350 t/d of ammonia based on Haldor Topsoe technology and 2,200 t/d of urea based on Snampgetti technology.

Meanwhile, according to PetroVietnam a gas price increase to \$7.40/MMBtu on April 1, 2014, up from \$6.56/MMBtu previously has hit the company's profits as gas accounts for 70% of the Phu My urea plant's total input costs. ■



PHOTO: PETROVIETNAM
Vietnam's Phu My urea plant.

UAN's changing dynamics

US consumption of urea ammonium nitrate continues to grow, but new shale gas-based plants may soon shut out imports from large scale producers in Europe and Trinidad.

Table 1: New, recent and planned UAN capacity

| Company | Location | Capacity | On-stream |
|--------------------------|--------------------------------|---------------|-----------|
| MHTL | Point Lisas, Trinidad | 1,480,000 t/a | 2010 |
| Zakłady Azotowe Pulawy | Pulawy, Poland | 500,000 t/a | 2010 |
| Acron | Novgorod, Russia | +500,000 t/a | 2012-14 |
| CVR Partners | Coffeyville, Kansas, USA | +300,000 t/a | 2013 |
| OCI | Wever, Iowa, USA | 1,420,000 t/a | 2015 |
| CF Industries | Donaldsonville, Louisiana, USA | 1,420,000 t/a | 2015 |
| Grodno Azot | Grodno, Belarus | +470,000 t/a | 2016 |
| Midwest Fertilizer | Posey City, Indiana, USA | 1,420,000 t/a | 2018 |
| Ohio Valley Fertilizers | Rockport, Indiana, USA | 900,000 t/a | 2018? |
| Northern Plains Nitrogen | North Dakota, USA | 600,000 t/a | 2018? |

Use of urea ammonium nitrate (UAN) is growing worldwide, but for the moment remains largely a North American phenomenon (about four fifths of demand), where the market has long been used to liquid fertilizers. To some extent UAN has prospered at the expense of two other fertilizers; solid fertilizer grade ammonium nitrate (FGAN), which faces increasing scrutiny over safety and the potential for deliberate criminal misuse, and direct application liquid ammonia, which has likewise been stolen for misuse in the US, in this case for drugs manufacture, and which also has health

and safety questions about its storage and transport.

UAN is in essence a simple mixture of urea and ammonium nitrate in a liquid solution, with an overall nitrogen content of 28-32% by weight; lower than both solid urea (42% nitrogen) or solid AN (typically 33-34% nitrogen). A typical UAN solution (of 28-32% N) contains 38-48% AN, 30-35% urea and 20-30% water (again by weight). Ammonia and nitric acid are used to adjust solution pH to close to 7 (usually between 6.8 and 7.5) and a small amount of corrosion inhibitor (about 0.15%) is also added for ease of storage and transport.

Although the low nitrogen content makes it slightly less efficient in transport terms on a tonne for tonne basis, leading to the price discount seen in Figure 1, it does have some compensating advantages to farmers – as a liquid it is easy to spray in an even fashion, or use in a fertigation system, and can be used with controlled dosing or distribution systems. It can also be easily mixed with other liquid fertilizers or herbicides, pesticides and micronutrients. In addition there are agronomic benefits; UAN is – in part – more quickly available to a growing plant than urea, which has first to be hydrolysed to ammonium. UAN's nitrogen content includes both 25% ammonium and 25% nitrate, both of which are readily available in the soil. It also contains 50% urea, which requires several days to convert to the ammonium form before it is available to plants. UAN also volatilises less than urea after warm weather application. The ammonium and nitrate in UAN do not volatilise, while urea does. It therefore has some of the advantages of ammonium nitrate in cooler climates with shorter growing seasons without the storage and handling difficulties of solid AN.

However, liquid fertilizers require farmers to be set up to deal with them, and this tends to restrict the potential market for UAN to more developed countries. UAN consumption peaked at just over 18 million t/a in 2008, but dropped sharply after the global financial crisis to 14 million t/a in 2009. Since then it has however rebounded significantly, and stood at just

under 20 million t/a in 2013. This still represents only about 5.5% of all nitrogen consumption worldwide, and has become increasingly concentrated in North America, which is responsible for 80% of all UAN consumption, and where it represents more than 30% of nitrogen demand. Another 15% is represented by consumption in Europe, particularly France, Germany and the UK, with Australia and Argentina also significant consumers. In the US, consumption is centred particularly upon the corn-growing states of the north and mid-west, particularly North and South Dakota, Kansas, Nebraska, Minnesota and Iowa, where it has steadily displaced liquid ammonia as a nitrogen source. The US consumed an estimated 15.7 million t/a of UAN in 2013.

Shifting production

Production of UAN is obviously predicated on production of ammonium nitrate and urea. Although there are some smaller plants which buy in these chemicals and merely mix them, in recent years production has steadily begun to focus more and more on large, integrated complexes which produce ammonia, urea, nitric acid and ammonium nitrate as well as downstream UAN.

High natural gas costs in both the US and Europe, the major consuming regions, had led to UAN production devolving elsewhere. While the US had still retained a sizeable share of UAN production – around 45% in 2007 – Russia and Ukraine and some eastern European countries, especially Poland and Romania, were also large producers, as well as the Netherlands, and in 2009-10 these were joined by Trinidadian-based Methanol Holdings Trinidad Ltd (MHTL), with a huge 1.5 million t/a plant geared at export to the US.

However, changing natural gas markets now look set to change the UAN market considerably. Cheap shale gas in the US has made production there, close to the source of demand, much more profitable, and in the past couple of years company mergers and the emergence of new large-scale UAN projects in the US have combined to radically shift the global market balance.

Consolidation

The dominant market player in UAN is CF Industries, which consolidated its position in 2010 via a merger with Terra Industries, claiming between the two merged companies a total capacity of 5.9 million t/a of UAN, all of it North American based, representing at the time around half of regional capacity and one third of world capacity. Now, the company's new merger with OCI has the potential to extend that reach still further, particularly since both companies are in the process of developing major new UAN complexes in North America, as shown in Table 1. The move will also take CF into the European market, where OCI runs 200,000 t/a of UAN capacity at Geleen in the Netherlands courtesy of its own earlier purchase of DSM Agro.

However, even more recently announced, the proposed buyout by CVR Partners, which operates the petroleum coke-based nitrogen plant at Coffeyville, of Rentech Nitrogen at East Dubuque, will create North America's second largest UAN producer, with 1.2 million t/a of capacity, placing it just ahead of Koch, Agrium and PCS Nitrogen, and leaving the region with just five main domestic suppliers.

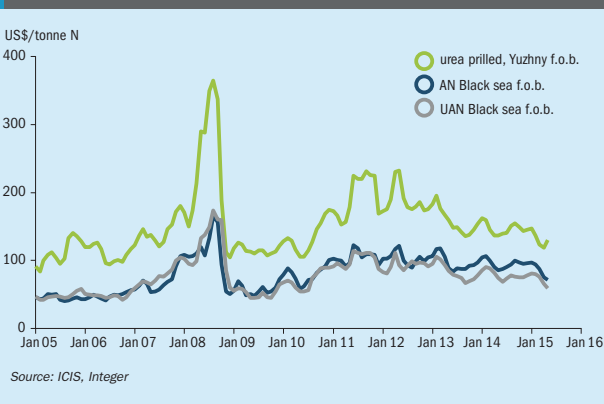
The consolidation of CF and OCI's US capacity in the US will give the newly formed company a majority market share when the new capacity investments that are currently being completed are taken into account; the combined capacity of 8.7 million t/a or around 60% of US capacity.

Too much capacity?

So where does this leave other producers? The additional 2.9 million t/a of capacity represented by the new Donaldsonville and Wever plants represent over 80% of current US imports of UAN, and as Table 1 shows – in spite of the cancellation of the CHS Spiritwood plant, there are still several large US UAN plants under development. The two plants now completing will presumably displace US imports from Trinidad, Russia and Europe, and although the shutdown of capacity in Ukraine offers some market relief, east European producers have recently added and are still adding new capacity. Although the US market has grown by 3 million t/a over the past five years, it may not be able to absorb all of the new capacity, and it seems a fair bet that at least one and probably two of the other US-based plants may not come to fruition because of the glut of new UAN production.

UAN producers, especially those who are part of a large, integrated complex, are uniquely fortunate in that they can shut down the downstream UAN solutions plant and instead simply produce urea and ammonium nitrate (or calcium ammonium nitrate in some cases). The US is still a major importer of urea and will continue to be so after Wever and Donaldsonville are on-stream, and there are some indications that CF Industries may switch some of the Donaldsonville capacity to urea rather than UAN production. However, there is also a lot of new urea capacity under development in the US, with Agrium, Koch and CF Industries all having new plants or expansions under construction and EuroChem and Cronus among others also developing new plants, and this escape route may not stay open for long.

Fig 1: Urea nitrates price developments



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Sixty years of ammonia safety

Venkat Pattabathula of Incitec Pivot Ltd. and **Jim Richardson** of Clariant (Singapore) Pte. Ltd. Trace the history of the AIChE Ammonia Safety Symposium from its beginnings in 1956 as part of the Boston AIChE National Meeting. Since then, the Symposium has been held annually; a tribute to its effectiveness in reporting accidents, safety developments and technology improvements.

It has been 102 years since the first ammonia plant based on the Haber-Bosch process started production at BASF's site in Oppau, Germany, and 60 years since the first ammonia plant safety symposium was held as a session of the 1956 American Institute of Chemical Engineers (AIChE) annual meeting in Boston, Massachusetts. During this time, tremendous advances have been made in process technology, safety and related facilities. Unlike other chemical and refining industries which are slow to share information, the sharing of safety incidents and lessons learned by ammonia producers and technology suppliers at Ammonia Safety Symposia has made the production of ammonia and urea two of the safest chemical processing industries.

The beginning

Sixty years ago, a small group of engineers, chemists, technicians and plant operators came together at the Boston, Massachusetts AIChE annual meeting to discuss safety in ammonia and air separation units. In his paper presented at the 2005 Ammonia Safety Symposium in Toronto, Canada¹, Gerry Williams from Plant Surveys International, Inc. summed up the first three years of the meetings as follows: "In December 1956, the first Air and Ammonia Plants Safety Symposium was a part of the AIChE Boston Annual Meeting. The program chairman was Norton H. Walton from the Atlantic Refining Co. (ARCO), Philadelphia, PA. This meeting focused on air separation plants. Frank G. Kerry of American Air Liquide, New York presented a paper on the safe design and operation of low temperature plants. Clyde McKinley and Frank Himmelberger,

both from Air Products, Allentown, PA presented a paper on oxygen plant air contaminant safety principles. Ernst Karwat of Linde Eismaschinen Co., Munich, Germany presented Linde's view on air separation plant safety.

"In addition to the paper presentations, an Oxygen Plant Safety Conference was held to 'discuss factors which contribute to the safety of air separation plants.' The conference (or round table) was attended by air separation plant operators and engineering contractors/designers. Earl C. Clark of Air Reduction Sales Co. moderated the session. A transcription of the roundtable was made to preserve what was said so others not in attendance could benefit from the discussion.

"The second and third annual Ammonia Symposia were in Baltimore, Maryland in September of 1957 and at Salt Lake City, Utah in 1958 respectively. Norton Walton (ARCO) chaired both meetings. Again, roundtable sessions (sometimes referred to as 'off-the-cuff' sessions) were held at both meetings. Topics included metal inspection of ammonia plant vessels, Piping, exchangers, and miscellaneous equipment; air separation plant air intake location, combustible gas analysers, etc. Transcripts of these roundtable sessions were published in several editions of CEP."

"Even though the above topics were discussed, most of the papers and discussions were related to air separation units (ASUs). One might ask why so much emphasis was placed on ASU safety during the first three years of the Ammonia Safety Symposium, which was originally called the "Air and NH₃ Plant Safety Symposium of AIChE". During the 1950s, gasification of coal, petroleum coke and other hydro-

carbons to produce synthesis gas was quite important for the chemical process industry, including the ammonia industry. Steam reforming was not as prevalent as today, so production of H₂ and CO by gasification was quite important. Since oxygen was needed for gasification, prevention of explosions due to hydrocarbon accumulation, especially acetylene, in the low temperature fractionation units of ASU's was critical. Accumulation from sources such as acetylene in ambient air surrounding the plant or decomposition of compressor lubricating oil was a common thread discussed by many companies. Findings such as explosions occurring when ozone contacted ethylene or acetylene at low temperatures, led to safer operation of ASUs. Companies such as Air Products, Air Liquide and Linde developed and presented many solutions to control and manage the risk of hydrocarbon accumulation.

"With the progress made in process safety, plant technology, plant operating safety and improvements in air, ground and water emissions during the last 60 years, ASU problems experienced during the 1950s have essentially disappeared. Some still occur, but with much less frequency. Much of the improvement can be attributed to the presentations and discussions and sharing of experiences during the early days of the Air and Ammonia Plant Safety symposiums."

Proceedings and committee

After the third symposium (1958), the AIChE felt that it should continue on an annual basis and that a dedicated subcommittee should be established to provide leadership for the meeting. They asked

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Norton Walton from ARCO to set up this subcommittee, and he subsequently chose 14 other individuals. William A. Mason from Dow became the first chairman of the Safety in Air and Ammonia Plants committee. In 1967, the committee produced its first "Subcommittee Rules and Policies" or bylaws. As written by Gerry Williams in his 50th anniversary paper¹:

"The purpose of this subcommittee is to make plants which manufacture oxygen, nitrogen, ammonia and related chemicals as safe as possible. This is to be done through the vigilance of its members with the objective of presenting at an annual symposium, reports on accidents, safety developments and other technical improvements relating to safety that are of interest and, therefore, assistance to the industry." In a 1983 version of the bylaws, the scope was changed to include plants which manufacture ammonia and related chemicals such as urea, nitric acid, ammonium nitrate and methanol. The purpose has remained unchanged since then.

In late 1959, the first Technical Manual of the Air and Ammonia Plant Safety Symposia was published. The first manual, Volume 1, contained all of the papers and round table sessions from the first three symposiums. Since then, papers and Q&A sessions have been published in different volumes. This ceased with the 2002 manual due to the difficulty and time required to accurately transcribe and correspond with the attendees asking and answering the questions. Instead written questions and answers are now posted on the AIChE website by the program chair at the end of the symposium.

During the first few years of the symposium, meetings were chaired by volunteers from the industry. By 1967, the ammonia committee consisted of 16 people from around the world to organize and coordinate yearly meetings at one of the AIChE national meetings. Due to the success of the meetings, the ammonia safety symposium separated from the AIChE annual meetings and has been held as a separate stand-alone meeting since 1992, still with the help of the AIChE.

The Ammonia Safety Committee currently consists of 16 members representing operating plants and technology suppliers from around the world. Officers consist of the committee chairman, committee secretary, program chairman and program vice-chairman. The program chairman usually chooses the vice-chairman

and submits to the entire committee for approval. The vice-chairman progresses through the different positions until he becomes committee chairman.

Attendance at the first few symposia consisted of personnel from operating plants and technology suppliers mainly from North America. To illustrate how international the meeting has become, roughly 50% of the more than 400 attendees at the 2012 Chicago symposium were from outside North America. Clearly, interest in the symposium topics and information obtained from networking with other plant operators have been the main drivers for perpetuating the symposium.

Symposium milestones - 1960s

During the 1960s, when large tonnage ammonia plants became much more common, presentations at the symposium began to concentrate on safety issues and technology improvements in ammonia and urea plants. Whereas a few papers discussing ammonia plants were included in the 1959 symposium, most of the papers in the 1967 symposium dealt with safety and technology in the ammonia and urea industries. Topics such as failure of reformer outlet piping and catalyst reductions were included in the 1963 symposium. Authors of the outlet piping paper² concluded that Type 304 stainless steel suffered high temperature stress rupture when used for process lines downstream of the reformer. Based on their experience with Incoloy 800 reformer tubes, they recommended the same metal for reformer outlet piping. Topics related to control systems³ were introduced in 1964. A presentation on three fatalities⁴ that occurred at the Asahi Chemical Industries Plant in Japan in a shift converter in December 1960 was presented at the 1964 symposium. The root cause was not following safety rules when working in a nitrogen environment. The result, by publication and discussion of the incident, was more awareness of the dangers and following procedures when working in confined spaces. Papers on hydrogen attack of carbon and low-alloy steels were being presented by 1965. Papers on noise levels in ammonia plants, safe handling of UAN solutions and safety problems in urea plants were well documented by 1966. Brittle fractures caused by lack of or poor post weld heat treating (PWHT) were discussed during the 1966 symposium.

By 1967 when many large tonnage sin-

gle-train plants were operating around the world, the symposium had become much more international, with many ammonia producers and technology providers outside of North America attending and presenting at the symposium. For example, Power-Gas Corporation from England⁵ presented a paper on brittle fracture of centrifugally cast stainless steels. A status report on ammonia storage⁶ and a Q&A session⁷ regarding the design, fabrication and testing of vessels for high pressure service was presented and held respectively at the 1967 symposium. Presentations ranging from silica migration from refractory in high pressure/high steam environments⁸ and catalyst experiences⁹ in large tonnage plants that had come online during the 1960s were made. The paper regarding testing catalyst experiences was the first to discuss loading, start-up and operation of LTS catalyst, which had become widely used by 1967. Presentations regarding HK-40 reformer tubes, material costs of accidents and plant control systems were included in this meeting. Problems with nickel carbonyl, Ni(CO)₄, were first mentioned during the 1967 symposium.

During the 1969 symposium, presentations regarding the cost of injuries to plant personnel were made. Failure of waste heat boilers¹⁰ which still affect the operation of modern ammonia plants was discussed during the 1969 symposium. Even with all of the information available to attendees at these symposiums, there were at least 42 significant incidents in the ammonia industry and related facilities such as urea and nitric acid during the 1960s.

1970s

Because the production of ammonia increased dramatically during the 1960s, handling and transportation was a major topic of the 1970 symposium. When plants were small, most end-users were located close to the production facility. However, as plant capacity increased, shipping distances became longer with international trading done at a much higher level. This necessitated a much higher level of safety during on and off loading as well as understanding of how ammonia can affect storage tanks and shipping containers.

Discussions on the types of reforming catalysts available for high pressure reformers and their effect on performance were well represented at the 1970 symposium, as well as corrosion problems in acid gas

removal systems such as MEA, hot potassium carbonate and sulfinol. Environmental issues such as air, water, land and noise pollution also became topics of discussion at the symposium. Because of continuing issues with urea plant corrosion leading to plant incidents, corrosion was a significant topic. By 1970 when new and larger plants had been operating for a few years, topics regarding trip systems used during start-up and shutdown cycles were a topic of interest. Presentations on new, high strength and high activity reforming catalysts for new high flux reformers were made.

New converter designs by M.W. Kellogg, ICI and Haldor Topsøe were introduced at the 1971 symposium. Of significance was Topsøe's paper on radial flow converters for new plant installations and also revamp installations. The first report on the causes of plant shutdowns¹¹ was presented at the 1971 symposium separating pre-1968 designs and 1968 and later designs. This was followed by updates in 1973, 1977, 1982, 1986, 1998, 2000, 2003 and 2008. Stress corrosion cracking in ammonia storage tanks was a major topic during the 1971 symposium. The recommendations to maintain 0.2% water in a storage tank along with keeping O₂ out of the tank was made at this symposium. Because most new plants being built at this time were built with centrifugal steam turbines and compressors, vibration monitoring became a popular topic. Measuring and monitoring during start-ups and operation was a good way to ensure good operation.

By 1972, the supply and price of natural gas in North America was becoming critical for the ammonia industry. Many plants built before 1970 were still operating on gas with a price of less than \$0.20/MMBtu. By the early 1970s with an impending supply crunch, and facing curtailments or higher prices, many plants started looking at alternatives. These included converting existing plants to SNG using the CRG process, producing syngas via gasification and converting reforming firing to fuel oil. One paper¹² by Felmont Oil Corporation clearly rung a bell for future plant closures based on either the lack of gas supplies or the high price in the future.

Because of the need for better energy efficiency due to high cost gas, many papers presented during 1973 and 1974 dealt with process control using computers. Prior to this time, most plant management thought that a 'good' operator could operate the plant efficiently using pneumatic controllers

that were commonly used at that time. This attitude changed dramatically when plants were able to increase production by 5-7% by simply installing a computer to control the H/N ratio exit the secondary reformer. Companies like Fisher Controls and Honeywell made a number of presentations during the mid-1970s outlining the benefits of computer control; leading to the dynamic control systems used today.

Another topic during the mid-1970 was testing of reformer tubes. Tube failures were more common in plants built during the late 1960s and early 1970s due to high heat flux rates. Techniques such as eddy current, creep stress analysis and ultrasonic testing became much more common at this time to help predict tube failures so that they could be replaced before they failed, thus preventing unscheduled shutdowns.

Many topics on energy efficiency improvements were discussed due to the pending energy shortage and high feedstock prices. New reforming tube metallurgies were also introduced at this time which eventually led to the replacement of HK-40 tubes. Newer alloys such as HP and eventually microalloy HP types were introduced in later years leading to lower pressure drop and cooler tube wall temperatures in reformers due to thinner walls. Papers on fuel oil firing for reformers were presented based on experiences in a few plants. By the late 1970s, efficiency topics such as H₂ recovery, LTS guard vessels and other energy efficiency papers were being presented at the symposium.

In addition to mechanical and process control upgrades and energy efficiency improvements, occupational hazards for plant personnel and the community became much more important during the 1970s. Many papers on what is now called responsible care were presented, along with presentations on the cost of equipment failure and occupational injuries. Public communication in case of emergencies was first discussed during the 1976 symposium. Occupational exposure to ammonia was a topic of importance by the late 1970s.

Even with so many presentations on improved plant monitoring, operator training, equipment inspections and improved technology, there were 66 papers regarding plant incidents presented at the symposiums during the 1970s. Fortunately, root cause analysis was applied to most of the incidents so that lessons learned could be shared with other producers.

The energy crisis

The bitterly cold winter of 1976/77 in North America, during which many plants had to shutdown due to natural gas shortages, sowed the seed for the demise of many older high energy ammonia plants. By the early 1980s, more than half of the plants operating in North America in 1975 had been shut down. Most were small capacity plants, so the impact on the total production of North American ammonia was not so great. However, the increasing cost of energy in the US during the 1970s and early 1980s resulted in no new plants being built in the US for more than 30 years.

In addition to an energy shortage in the US during the late 1970s and early 1980s, the price of ammonia was also very near the variable cost of production for many years, and did not respond to growing worldwide demand until the middle 1990s. Ammonia prices were quite stable for about 20 years, leading to a tremendous increase in energy efficiency and capacity upgrades. This led to a number of technological improvements that were introduced to the industry during the 1980s. Implementation of capacity and efficiency revamps also became a very popular topic of discussion during the 1980s.

Even though no new plants were being built in North America for many years after the 1970s energy crunch, new plant construction occurred around the world in low energy cost countries. Production increased substantially in the Middle East and Asia during this time. Many of the problems that had been experienced by North American and Western European producers during the 1970s began to be seen by newer plant operators. Consequently, the Ammonia Symposium became much more international as producers from around the world started attending to present papers regarding their experiences and to network with other producers.

1980s

During the 1980s, revamping of plants in high energy cost countries became very common. With more movement of ammonia from low cost producing countries to North America and Western Europe, the structural integrity of transportation and storage vessels was discussed in many presentations at the ammonia symposium. Stress corrosion cracking of ammonia storage and transportation tanks was

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discussed extensively. Acoustic emission inspections for H₂ induced cracking for ammonia storage and transportation vessels was also discussed. A presentation on the first 25 years of the ammonia symposium¹³ was presented by John Lawrence of CF Industries at the 1980 symposium.

Energy efficiency and increased capacity of existing ammonia plants was the subject of many papers at symposia during the 1980s. Two changes on the process side resulted in catalyst developments that are still on-going today. As existing plants increased their operating rate by 30-50% above the design rate, pressure drop across the reformer led to further developments in tube metallurgy and catalysts. As mentioned earlier, new reformer tube alloys allowed plants to replace HK-40 tubes with larger inside diameter tubes. This either reduced pressure drop across an existing plant at constant production rates, or maintained pressure drop across the reformer at higher operating rates. Catalyst manufacturers responded to the need for higher activity/lower pressure drop reforming catalysts by introducing multi-pass shapes such as UCI's 'Wagon Wheel' reforming catalyst. To further reduce front-end pressure drop in ammonia plants, operators also lowered the S/G ratio to the reformer. Unfortunately, this resulted in other issues such as a higher likelihood of carbon formation in the top of reformers, issues with metal dusting in WHB's, Fischer-Tropsch reactions across the HTS reactor and additional by-product make across both shift reactors.

Once again, catalyst manufacturers responded to the need of the industry. For example, most catalyst manufacturers were supplying alkalis reforming catalysts for the top of the reformer, leading to better coking resistance and longer lives by the mid-1980. Widespread use of hydrogen recovery systems allowed plant operators to increase the methane leakage at the exit of primary reformers, leading to lower secondary reformer exit temperatures. This lowered the amount of CO exit the secondary reformer which reduced the potential for metal dusting. To eliminate FT synthesis over HTS catalyst, copper promoted HTS catalyst was being provided by most catalyst manufacturers by the late 1980s. Because copper promoted catalyst was more active, the inlet temperature to HTS catalyst was lowered from traditional values of 360-380°C to 320-340°C. This lowered the overall CO leakage from the shift reac-

tors, and allowed plants to produce more process steam. All operating changes and technology improvements were well documented by plant operators and technology providers throughout the 1980s.

Alternative ammonia plant designs and equipment to improve efficiency and foster revamps were discussed throughout the 1980s. For example, ICI introduced their AMV process in 1982. Kellogg introduced their horizontal ammonia converter the same year. Gas heated reformers were discussed by Chiyoda at the 1986 symposium.

Corrosion in CO₂ removal systems was discussed quite extensively during the 1980s. The first paper on conversion of an MEA system to amDEA to reduce corrosion was presented at the 1987 symposium. This was followed by other papers on the same topic in later years. Also in 1987, a panel discussion was held regarding stress corrosion cracking of condensing turbine rotors. M.W. Kellogg presented a report on nitriding in ammonia loops. Modernisation of existing plants by installation of distributive control systems (DCS's) and computerized ammonia plant trip systems was discussed in many papers during the 1980s. Installation of co-gen systems in a number of plants was discussed. Noise control for plant personnel safety was a recurring topic during this decade.

Revamp of ammonia converters from axial flow, quench type converters to more efficient designs were well underway by the end of the 1980s. As can be seen in many of the presentations, more conversion per pass in radial flow and horizontal type converters led to higher operating rates and better efficiency at minimal cost. The conversion of four converters by CF Industries during the mid-1980s (presentation at 1988 symposium) into more efficient designs convinced the industry of the technology such that almost all plants operating today operate with some type of radial or horizontal design.

Throughout the 1980s, topics on energy efficiency and plant revamps in North American and Western Europe were thoroughly represented at the ammonia symposium. Even with these improvements, the worldwide percentage of ammonia produced in Western Europe and North America continued to decline due to no new plants being constructed in these high energy cost regions. By 1990, less than 15% of ammonia produced in the world was being produced in Western Europe while less than 25% of the world's ammo-

nia was being produced in North America. Clearly, the industry was getting more international leading to more and more attendees at the ammonia symposium from outside traditional attendee regions.

As many of the single train high pressure plants built during the late 1960s reached 20 years of operation, incidents with plant and equipment controls, valves and operating procedures were quite common. The incident, root cause and lessons learned were frequently shared with the international community at the Ammonia Safety Symposium. At total of 69 papers regarding incidents were presented during the 1980s.

1990s

The worldwide production of ammonia, urea and ammonium nitrate increased dramatically during the 1990s to satisfy the growing demand for fertilizers. Most of the increase came from new plant construction in low energy cost regions, but North America and Western Europe also increased production through upgrades to existing plants. Producers in high energy cost regions during the early 90s continued to operate on very slim profit margins until about 1994, when the price of ammonia and urea finally started increasing. Unfortunately, higher prices were short-lived, with ammonia prices again approaching \$100/t by 1999. Prices didn't improve on a sustained basis until the early 2000s.

Safety and health issues remained major topics of presentations during the 1990s. For example, the first paper on responsible care covering the entire life cycle of a chemical process was presented at the 1990 symposium. Issues regarding mercury in natural gas used in the production of NH₃ were discussed at the 1990 symposium. An explosion of a multiwall ammonia separator due to the presence of mercury was the reason for the presentation. Work related to this presentation was quite valuable for the ammonia, LNG and ethylene industries.

Post weld heat treatment (PWHT) and WHB failures remained a common topic throughout the 1990s. Evaluation topics such as fault tree and HAZOP analysis were discussed in many papers. Even though discussions on safety when working in N₂ environments was discussed during the 1960s, the first paper dedicated to confined space entry was presented at the 1990 symposium. Papers on by-product

formation across shift converters and why methanol production across LTS catalyst impacts plant production and efficiency were presented by Haldor Topsøe. A paper on high temperature operation of HDS catalyst and a paper on the cause of an uncontrolled reduction of LTS catalyst due to a temperature run-a-way were presented by United Catalysts.

API's claim in the early 1990s that C-1/2Mo steels were no more resistant to hydrogen attack than carbon steels resulted in many plant metallurgical inspections with results reported throughout the 1990s. A paper showing H₂ attack of 2.25Cr-Mo steel below the Nelson curves received a lot of attention.

In addition, many papers on risk management and responsible care were presented during the 1990s which included: quantified and quantitative risk analysis; the health effects of ammonia; safety management during turnarounds; training workers to comply with OSHA regulations; electronic document management; EPA's RM regulation; online inspection of valves using radiotracers; lessons learned with EPA's risk management programs; risk management for location of control rooms and risk management plan for ammonia retailing; online examination of high pressure vessels; and safety management systems for cost savings in addition to helping prevent accidents.

The International Fertilizer Industry Association presented a paper¹⁴ at the 1995 symposium which stated that since 1980, the production of ammonia and nitrogen fertilizers had shifted from industrial regions such as North America and Europe to gas-rich and large fertilizer consuming areas such as Southeast Asia, the Middle East and Caribbean. The shift in production led to additional globalisation of the ammonia symposium. For example, only 20% of the papers presented at the 1999 symposium were presented by North American companies. S. Nand from The Fertilizer Association of India presented a paper¹⁵ on down time in Indian ammonia and urea plants. He followed this with a presentation on their safety and reliability in operation in 2009.

As the ammonia industry continued to expand, so did the urea industry. Thielsch Engineering presented a paper at the 1995 symposium on failures in urea reactor vessels. Additional papers regarding new plants and larger plant designs were common during the late 1990s. Papers

on the re-location of shutdown ammonia plants to gas rich regions were also common, as well as updates on production and energy efficiencies of new plants, revamped plants and reactor technologies.

Even after 40+ years of sharing of safety incidents and their root cause at the Ammonia Safety Symposium, incidents continued. During the 1990s, a total of 87 incidents were reported during the Ammonia Safety Symposium. More than likely, a large number of these were the results of skilled worker turnover due to aging of the operator pool trained during the development of the modern ammonia plant during the 1960s and 1970s.

2000s

Technology improvements such as larger and more efficient compressors, improved plant designs, metallurgy, control systems and catalysts led to the construction of larger and more efficient ammonia and urea plants during the early 2000s. Improvements in revamp capabilities also led to much higher operating capacities for existing ammonia plants. This led to a tremendous increase in global ammonia production between 2000 and 2009.

Technology improvements such as KBR's KRES for new and revamped plants was reviewed in a number of papers. A paper on construction and commissioning of the worlds largest purifier ammonia plant at BFPL was presented at the 2006 symposium. The Uhde dual pressure ammonia process was introduced at the 2003 symposium, with a follow-up paper on the commissioning of the first 3,300 t/d plant at QAFCO. Construction and commissioning of the first large scale ammonia/urea complex in Vietnam was presented by Haldor Topsøe.

Safety topics such as risk-based inspection prioritisation, a system (Tripod-Beta) to discover the causes why people make mistakes, fertilizer plant security, corrosion under insulation, application of safety instrumented systems, safety and reliability in NH₃ synthesis converters, plant safety audits and operator training simulators

There were quite a few incidents related to materials degradation in ammonia and urea plants. A reduction in ammonia emissions in urea plants was discussed in a number of papers. Ammonia from coal and new ammonia to coal processes were presented by a number of companies.

Incidents involving catastrophic failure of reformer tubes continue happening even today. Finally, new catalysts leading to better conversion, life and energy efficiency such as AmoMax ammonia synthesis and low methanol make LTS catalysts were introduced during the period.

Ammonia plant incidents

Overall, about 1500 papers were presented from 1956-2014 and among them, 400 were related to safety incidents. Some of the most significant incidents and lessons learned during the last ten (2004-14) years are as follows:

Syngas start-up heater failure¹⁷

During February 2005, a fire occurred in a synthesis loop start up heater that resulted from a rupture in one of the four coils. This led to a major back end outage at Incitec Pivot's ammonia plant in Brisbane, Australia. The failure was due to localised overheating of a coil section caused by inadequate flow of syngas. The failure occurred during the restart following a back end trip.

The coil failure resulted in a major fire and explosion in the heater, resulting in serious damage to the heater, instrumentation, control valves and piping. This resulted in a major outage of the plant. An investigation of this incident identified the root cause as override of the critical equipment trip system (CETS) which is now part of plant SIS. The pilot burners in the start-up heater had issues in lighting up caused by poor performance of the flame scanners. Hence, the operating practice was to establish the pilot burners forcing a flow signal on the fail safe controller that defeats the low syngas flow trip. Although the flame scanners were attended, the override practice had continued. The post incident remedial actions included the following:

- a new procedure for the bypassing of the trip system that includes a rigorous risk assessment;
- updated operating procedures for the start-up heater with all current alarm and set points. Also, the operating instructions were revised to reinforce that low syngas flow trip on main burners should never be overridden during start-up;
- additional improvements such as differential pressure measurement across the coils, thermocouples on each coil to measure tube wall temperatures and alarms were also taken.

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Ammonia tank failure¹⁸

While re-commissioning a repaired atmospheric ammonia storage tank, overpressure ruptured the tank during the cool-down step. The ammonia release caused injuries and a fatality. The tank was being re-commissioned after a drain valve had been replaced. The tank had been drained and purged. The incident occurred in 2005 at Yara's Rostock plant in Germany.

Yara followed the European Fertilizer Manufacturers Association (EFMA) guidelines for de-commissioning and re-commissioning atmospheric ammonia storage tanks. The EFMA guidelines, Appendix 9, in Recommendations for the Safe and Reliable Inspection of Atmospheric, Refrigerated Ammonia Storage Tanks, state that a sufficient volume of an ammonia water (aqua) mixture (20% ammonia) should be placed in the tank to entirely cover the bottom before introducing liquid ammonia for cool-down. The purpose of the water is to prevent liquid ammonia from impinging on the floor plates and causing them to cool rapidly in the presence of oxygen, resulting in SCC.

After cooling the tank, Yara began draining the aqua and the tank failed. The failure occurred on the floor at the outer tank seam and allowed liquid ammonia to escape. Yara had introduced enough aqua to fill the tank to 25 cm to ensure covering the entire bottom regardless of slope. However, a layer of oil had floated to the top of the aqua. The draining disrupted the oil film, allowing liquid ammonia to mix with the aqua and to generate enough heat to rapidly boil off liquid ammonia. The ammonia vapour overwhelmed the pressure relief system and caused the floor-to-outer-cup seam to fail. An investigation found that the pressure in the tank had possibly reached two barg.

Explosion in Benfield storage tank¹⁹

The former AMI Agrolinz Melamine International had become 100% of the Borealis Group as of 2007. The ammonia plants are old; plant 1 is an Uhde design from 1974 with a capacity of 859 t/d, currently debottlenecked to 1000 t/d. Plant 2 is a Humphreys & Glasgow reforming design of 1968 vintage, with an Uhde synthesis loop (1991) and a capacity of 550 t/d. CO₂ removal in Plant 1 is with a Benfield solution, whereas CO₂ removal in Plant 2 is with Selexol.

The incident occurred in Plant 1 in December 2006. The Benfield storage tank was at the centre of the incident. The stor-

age tank was being used to boil off excess water that had accumulated in the tank from the collection drains of the Benfield system. Questions were raised if the existing atmospheric vent [200 mm diameter] was large enough to handle the significant quantities of steam without overpressuring the tank. A decision was made where an additional vent of 300 mm was needed.

It was during the installation of the additional 300 mm vent at the top of the tank when an explosion occurred which resulted in two fatalities to contract workers attempting to install the new vent and one severely injured employee. Sparks from a grinder entered the tank and was the ignition source. The entire tank roof [weight 2600 kg] was displaced 10-15 m vertically and 50-60 m horizontally.

Many investigations were carried out, and the explosion was considered to have occurred due to the accumulation of hydrogen from corrosion of the carbon steel in the apex of the roof where the new vent was to be installed. Gas checks were not possible at this location.

The conclusion was that although corrosion of CO₂/carbonate solutions is very complex, corrosion can occur and significant amounts of hydrogen can be generated even under very alkaline conditions. Making the tank from stainless steel is an option, but a nitrogen purge is the best solution to avoid hydrogen accumulation.

Explosion in primary reformer furnace²⁰

Yara's Tetre Belgium ammonia plant was built in 1968. The reformer is a top-fired design. The plant has an auxiliary boiler sharing the convection zone and primary reformer arch burners, but also has tunnel burners exit the primary reformer and steam superheat burners below the steam superheat coil. All the burners have pressure controllers. Isolation in the event of a trip is carried out by shutting the pressure controllers in the control room followed by isolation of individual burners by outside operators.

On a Friday night in June 2009, a lightning strike on power lines resulted in a total site shutdown. Night shift restarted the boiler before they went home. The first job for day shift was to start the superheat burners. They lined the gas up and put in the igniter which triggered an enormous explosion. The two operators involved were both seriously injured with broken bones and burns.

The tubes and the roof collapsed onto the tube tops. The primary reformer walls

were stopped by the secondary on one side, convection zone on another, and the pipe rack and control room on another.

The cause was identified as the night shift had isolated the gas in the field to the tunnel and superheat burners, but not to the reformer arch burners and the pressure controller to the reformer was still in auto. The day shift found the tunnel burners were isolated and assumed that the arch burners were also isolated, but they weren't. Hence, when they lined up the gas to the superheater burners, gas started going into the reformer box via the pressure controller. It mixed with the air and just needed an ignition source.

The control room which was near the furnace and although not blast proofed, was minimally damaged. It appeared that there was an inherent weakness in the process safety system, no operational discipline [check list was not followed on start-up], no inter lock system, and lack of experience on part of on-shift operators for start-up procedures. The plant was out of operation for a total of 11 months – 2 months for demolition and 9 months for reconstruction. A new automated burner management system proposed by KBR was accepted and installed before restarting.

Conclusions

Sixty years have passed since a small group of engineers, chemists and plant operators came together in Boston, Massachusetts to discuss safety in ammonia and air separation plants. During this time, production of ammonia has increased from about 10 million t/a to more than 180 million t/a. Many of the companies associated with advances in technology and production during the early years of the ammonia symposium have either gone out of business or been merged through consolidation of the industry. At the same time, many new faces have appeared around the world producing ammonia and urea utilizing the latest technological advances.

Production of ammonia, which occurred mainly in the industrialised world during the 1960s slowly moved to gas-rich areas like China, Southeast Asia, the Middle East and Caribbean during the 1980s-2000s. The industry continues to evolve, however, with many new ammonia and urea plants currently under construction in North America due to a plentiful supply of shale gas.

Energy efficiency, driven by the need to lower the cost of production has improved

by 50% or more since the first symposium was held due to advances in technology and plant design. Whereas plants with a capacity of 500 t/d were rare when the first symposium was held, single train ammonia plants of 2,500 t/d or larger are quite common today. Consequently, plant outages have become much more costly, while the logistics of product placement has placed more responsibility for safe handling of products once they have left the production site. Incident lessons learned and shared through the Ammonia Safety Symposium are as valuable today as they were years ago when they occurred. They will become even more valuable during the next decade as existing plants age. As the last 60 years have shown, technological improvements will continue to lead the way to lower cost and higher production of ammonia. ■

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COMPLETE PLANTS FOR SALE

250 TPD NITRIC ACID PLANT

- Name Plate: 250 TPD
(has produced up to 300 TPD) at 63% concentration
- Shut down in 2010 – Documentation available as well as a spare motor, and both a spare high and low stage rotor.

600 TPD UREA PLANT

This urea plant was designed and built using Stamicarbon conventional urea technology with CO₂ stripper and high pressure condenser. The plant had a number of modifications over the years including:

- 1996: New stripper (E-103)
- 1997: High pressure condenser (E-104)
- 1997: New reactor (R-101)
- 1999: Low pressure condenser, new inner tube bundle (E-202)

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NITROGEN+SYNGAS
ISSUE 337
 SEPTEMBER-OCTOBER 2015

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High-alloy stainless steels for longer equipment life

Materials for nitric acid service must evolve to meet rising efficiency targets and corrosion challenges. In response to this, Sandvik Materials Technology develops and manufactures advanced stainless steels and special alloys that are helping its customers to achieve better corrosion protection and higher ammonia conversion efficiencies.

Ammonia plants are expensive and high-on-stream factors are crucial to achieve optimal ammonia conversion efficiencies. Longer equipment lifecycles are integral to this in order to recuperate the investment costs, and to reassure investors as to the long-term prospects and risks of the operations.

Achieving these longer and uninterrupted processes requires equipment with greater reliability and maintainability, without adding to the initial construction costs. The answer for this lies in selecting more corrosion resistant materials capable of withstanding the harsh/corrosive environments that are typical of nitric acid (HNO₃) service.

Nitric acid typically involves two stages. Firstly, the oxidation of ammonia to nitrogen monoxide (nitric oxide) which takes place in environments characterised by high pressure, excess oxygen and high temperatures (typically of 1,200°C) with an alloy of platinum and rhodium as catalyst.

Secondly, absorption of the nitrogen oxides requires that gases are cooled to below 315°C, compressed and reheated to 435°C, and cooled to about 310°C. While the compression and cooling aids the reactions, oxidation of the nitrogen monoxide and absorption occurs with the formation of nitric acid.

Use of materials with effective corrosion resistance properties is essential to these processes; especially during the instances of high pressure synthesis which occur at the intermediate production stage.

Traditional materials

When assessing the capabilities of a steel, consideration should be given to the oxygen requirements for passivation, resistance to stress corrosion cracking (SCC) caused by chlorides and resistance

to erosion. While nitric acid is a strong acid, it is also a powerful oxidiser and helps form a protective, 'passive' oxide layer on stainless steel. Yet this acid in high concentrations and/or at high temperature is also highly corrosive. What is needed is an advanced material which offers superior corrosion properties than standard grades.

It is first useful to understand why standard steels often underperform, such as austenitic type 304L that is used extensively in fertilizer manufacturing plants where nitric acid is present. Different corrosion issues may arise in different areas of the plant, and ASTM 304L is not suitable in some parts, particularly at high pressures and elevated temperatures.

Depending on its concentration and temperature, nitric acid may require special stainless steel grades with low molybdenum (Mo) contents. Whereas Mo is effective-yet-costly as an anti-corrosion element in other applications, it can negatively affect a material's corrosion properties in nitric acid (although this does not apply in all cases and Mo can have other effects that are important for this application).

Conventional austenitic stainless steels like 304L have been favoured for concentrated nitric acid solutions due to the addition of 4% silicon which enhances the resistance to intergranular corrosion.

The chromium (Cr) content of a stainless steel generally determines its corrosion resistance; the greater the Cr content, the higher its resistance to corrosion. This was discovered in the 1960s when new-developed fully ferritic alloys with a higher Cr content of around 26% were found to provide encouraging results. Nevertheless, these materials suffered from the kinds of welding problems typically associated with ferritic grades and their use was deemed impractical.

High chromium grades obtain the best results in boiling nitric acid solutions, such as 310L NAG (Nitric Acid modified Grade) that contains 25% Cr and is shown in Huey Tests (ASTM A262 practice C) to outperform 304L in boiling 65% acid. The grade is also characterized by low carbon and phosphorous and < 0.3% silicon content to improve its corrosion-resistance and phase stability, and an increased in nickel to around 20% to maintain the austenitic structure.

In other circumstances, a very low carbon content combined with low impurities – non-metallic defects within steels that negatively affect the mechanical integrity – is important to obtaining the best corrosion resistance.

While these elements imbue the grades with improved corrosion resistance and better austenitic stability, they have also exhibited performance shortcomings. These arise due to the fact that the material requires large amounts of air (oxygen) to ensure efficient passivation which can limit operability of the synthesis and recycle sections of the plant.

In these instances, a replacement material is required that can operate more effectively in limited oxygen, corrosive environments. When assessing such a grade, due consideration should be given to the oxygen requirements for passivation, resistance to SCC caused by chloride and resistance to erosion.

Development of Sandvik 2RE10

Further developments saw the introduction to the market of an austenitic stainless steel known as Sandvik 2RE10 with

extremely low carbon and impurity contents. The grade was developed to combat corrosion problems in nitric acid service. High levels of chromium and few impurities give the grade considerably better resistance to nitric acid than steels of type ASTM 304L.

This is shown in the isocorrosion diagram in Fig.1, alongside Sandvik 3R12 which is the Sandvik version of ASTM 304L.

The high chromium content (24.5% Cr) of Sandvik 2RE10 helps the material to form a dense and more stable passive chromium oxide layer. The nickel (Ni) content was also increased in order to lower the ferrite content and ensure good corrosion resistance. The material's chemical composition conforms to EN no. 1.4335 which allows for considerably higher maximum levels of carbon (C), silicon (Si), phosphorus (P), sulphur (S) and molybdenum (Mo). High levels of these elements increase the potential for corrosion, therefore they have been kept as low as possible in Sandvik 2RE10. The chemical composition (nominal %) of Sandvik 2RE10 is: ≤0.015% C, ≤0.15% Si, 1.8% Mn, ≤0.020% P, ≤0.005% S, 24.5%Cr, 20% Ni, ≤0.10% Mo.

Stress corrosion cracking (SCC)

The higher nickel content makes Sandvik 2RE10 slightly more resistant to stress corrosion cracking than conventional austenitic stainless steels like ASTM 304L. Sandvik 2RE10 has considerably higher pitting corrosion resistance than ASTM 304L and is also superior to ASTM 329, one of the earliest duplex steel which is

reflected in its higher permitted carbon content, as illustrated by Fig. 2.

Tests in nitric acid

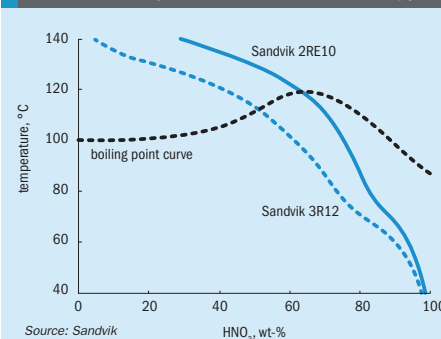
Certain tests are recommended in order to assess how well a material will perform in nitric acid. One is the Huey test which is used to assess the intergranular corrosion properties of a material. Figure 3 shows the results of Huey testing which is performed by boiling a sample in 65% HNO₃ for five periods, each lasting 48 hours, in this case using sensitized specimens of Sandvik 2RE10 and steel type ASTM 304L. The low tendency for sensitisation is an advantage in complicated welding operations.

The Huey test is more frequently used as a delivery test to check that annealing has been performed effectively, or to check for Cr depletion as well as intermetallic precipitation in the material. Here, we can surmise that the guaranteed maximum corrosion rate for Sandvik 2RE10 is 0.12 mm/year (5 mpy) in the solution annealed condition, and 0.20 mm/year (8 mpy) after sensitisation at 675°C. Even lower values can be guaranteed by agreement in certain cases.

Fig. 3 demonstrates that sensitisation does not increase the corrosion rate greatly in Huey testing, whereas the corrosion rate for ASTM 304L increases significantly.

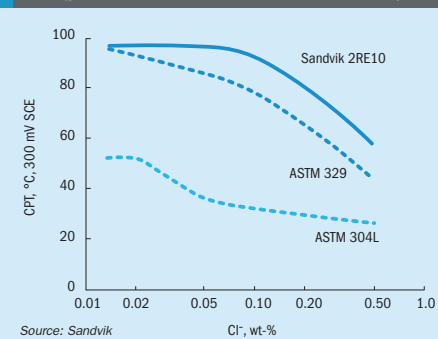
The generation of isocorrosion curves is another useful test by which it is possible to predict the performance of different steel grades. The curves are produced using data from general corrosion testing

Fig 1: Isocorrosion diagram for Sandvik 2RE10 and 3R12 (ASTM 304L) in a naturally aerated, stagnant solution of nitric acid. The curves represent a corrosion rate of 0.1 mm/year



Source: Sandvik

Fig 2: Critical pitting temperature (CPT) for Sandvik 2RE10, ASTM 304L and ASTM 329 in neutral chloride solution (potentiostatic determination at +300 mV SCE)



Source: Sandvik

Fig 3: Corrosion curves for Sandvik 2RE10 and ASTM 304L obtained from Huey testing after sensitisation at 675°C

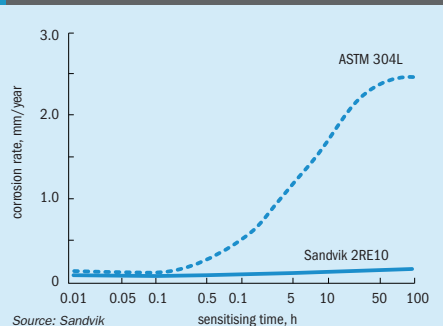
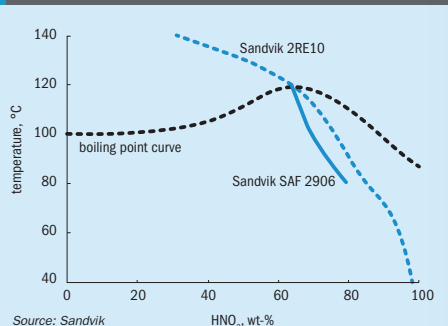


Fig 4: Isocorrosion diagram for Sandvik SAF 2906 and Sandvik 2RE10 in a naturally aerated, stagnant solution of nitric acid. The curves represent a corrosion rate of 0.1mm/year



whereby a sample is exposed at a certain temperature and concentration.

Each sample is exposed in three periods (24h+72h+72h) and is carefully weighed before and in between the periods. The corrosion rate is then calculated in the same way as for the Huey test, with an average value from the second and third period used as the corrosion rate at the specific concentration and temperature. Curves are then produced corresponding to a specific corrosion rate, normally 0.1 mm/year, see Fig. 1.

Good corrosion resistance is required to ensure equipment reliability when reducing requirements for passivation air, particularly in synthesis equipment. The data in Fig. 1 confirms that Sandvik 2RE10 exhibits considerably better resistance to nitric acid than steels of type ASTM 304L due to its high chromium and low impurity contents.

Pitting and crevice corrosion

Problems of corrosion in fertilizer plants can vary considerably because of local service conditions. Therefore steel materials continue to evolve in order that ammonia plant operators can achieve optimal conversion efficiencies with equipment that lasts longer and offers design advantages. The result is more cost-effective and risk averse nitric acid operations across the plant.

As mentioned above, Mo can have other important effects in nitric acid applications as evidenced in the high-alloy duplex (austenitic-ferritic) stainless steel Sandvik SAF 2906 which exhibits good resistance to nitric acid due to its balance of chromium

and molybdenum. The isocorrosion diagram in Fig. 4 shows the performance of the grade alongside Sandvik 2RE10.

The chemical composition of Sandvik SAF 2906 is carefully balanced with a high content of chromium and nitrogen and a moderate amount of molybdenum. This gives the material a high resistance to localised corrosion caused by chlorides. One way of comparing the pitting corrosion resistance of different grades is with the pitting resistant equivalent (PRE) number – generally speaking, the higher the PRE number of a stainless steel the higher the pitting resistance.

The PRE number pertains specifically to the levels of chromium, nitrogen and molybdenum defined as, in weight-PRE = %Cr + 3.3 x %Mo + 16 x %N. The PRE value for Sandvik SAF 2906 is 41.5 compared to ASTM 316L which is 26.

Furthermore, the grade's austenitic-ferritic microstructure imbues it with a proof strength that is about three times as high as for conventional austenitic stainless steels. Because of this, Sandvik SAF 2906 has a coefficient of thermal expansion close to that of carbon steel for definite design advantages over austenitic stainless steels.

Further developments

Over the decades, materials for nitric acid applications continue to evolve in order to satisfy changing demands. For instance, for plants experiencing high levels of chlorides and nitric acid, then the strong recommendation would be to specify Sanicro 28. The material is a high-alloy multi-purpose austenitic stainless steel for service in highly

corrosive conditions, and also performs very well in nitric acid. In test according to the Huey Test corrosion rates lower than 0.15 mm/year (6 mpy) are obtained.

The high alloying contents of chromium and nickel give Sanicro 28 considerably better resistance to sodium hydroxide than standard stainless steels of the type ASTM 304 and ASTM 316. At moderate temperatures and concentrations, Sanicro 28 is a suitable alternative to pure nickel, which may be attacked by erosion corrosion. Other developments have seen a growing move towards duplex grades which, compared with austenitic stainless steels, have a higher proof and tensile strength due to their more stable metallurgy.

Conclusions

In response to mounting performance demands placed on equipment and materials, Sandvik 2RE10 has excellent resistance to corrosion in nitric acid and good weldability. With these properties, the grade is very suitable for heat exchanger tube and pipe in processes that treat nitric acid – e.g. in the manufacture of nitric acid, acrylic fibres, ammonium nitrate and the reprocessing of nuclear reactor fuel. Extensive practical experience in such applications has confirmed the superiority of Sandvik 2RE10 over standard steels such as ASTM 304L.

Further to this, grades Sanicro 28 or even Sandvik SAF 2906 are the best options for increased operational dependability should a plant experience high levels of chlorides and nitric acid. ■

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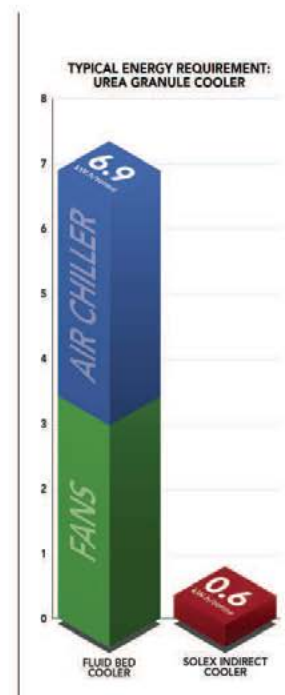
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Foil supported catalysts in steam reformers

W Whittenberger and **P W Farnell** of Johnson Matthey report on a foil supported steam reforming catalyst system, CATACEL™ SSR™, which has been developed and is delivering significant performance benefits in several commercial steam reformers in Europe and the Americas.

Johnson Matthey has been at the forefront of the development of steam reforming catalysts for many decades, being the first supplier to bring to the market features such as alkalis catalysts that have now been adopted industry wide. Continued innovation resulting in KATALCO™ QUADRALOB™ steam reforming catalysts has enabled the company to remain as the market leader in steam reforming catalyst supply. Johnson Matthey continues to invest in developing its range of reforming catalysts and technologies in order to remain at the forefront of this challenging technology.

This article outlines some of the latest advances which are helping the development of the next generation of steam reforming catalysts. For many years, catalyst-impregnated ceramic pellet media have driven steam methane reforming reactions in hydrogen, methanol, and ammonia plants. CATACEL™ SSR is a coated foil-based alternative to pellets that has been in development for some years.

Steam reforming catalyst design is a balance between many competing requirements and catalyst features, such as strength, heat transfer, activity, pressure drop, and avoidance of unwanted side reactions such as carbon formation. By adopting a foil-based structure, CATACEL™ SSR can break away from many of the limitations imposed by the use of ceramic pellets. CATACEL™ SSR offers a catalyst system that exhibits a higher activity, improved

heat transfer, lower pressure drop and improved resistance all at the same time. Performance of this technology has been proven in the hydrogen market since May 2012. Johnson Matthey has been working for several years on the development and testing of this catalyst with the Catacel Corporation and acquired CATACEL™ SSR technology in September 2014.

What is it?

At the core of the patent protected CATACEL™ SSR technology is the ability to coat catalyst materials onto the surface of thin metal foils. The proprietary coating process ensures that the catalyst remains attached to the surface of the foil during the catalyst lifetime. This coating process is a core technology that has been leveraged from many years of experience using

coated foils in the emission control and combustion fields. Most of these coated foil applications, including CATACEL™ SSR, use special high temperature alloys as a substrate material.

In the CATACEL™ SSR application, alloy strip is formed into engineered foil supports called fans (Fig. 1). The fans are coated with a nickel based steam reforming catalyst using the processes mentioned above. The fans are quite “springy” and can easily be pulled or pushed into different diameters or shapes.

The fans are stacked one upon another in the reforming tube, separated by thin metal washers (Fig. 2). The outer edges of the fans are located close to, but not touching, the internal surface of the tube.

The stacked fans deliver superior heat transfer by impinging gas on the internal surface of the reforming tube, rather than

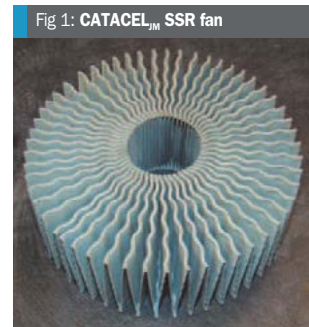


Fig 1: CATACEL™ SSR fan



Fig 2: CATACEL™ SSR stack

Fig 3: Gas forced out of triangular ducts



relying on convective heat transfer mechanisms. This results in about 20-30% more heat transfer for the same (or lower) pressure drop when compared to traditional catalyst pellets. In addition, the fans offer 1.5 to 2 times more geometric surface area than conventional pellets.

How it works

The stacked fans and impingement mechanism work as follows. Gas flowing down the tube encounters the first fan structure. It cannot move through the fan (the centre is blocked as discussed below). It is therefore forced out of the triangular ducts, impinging directly on the internal surface of the reformer tube, where it gathers heat (Fig. 3). Having nowhere else to go the gas flows around the edges of the fan and back into the triangular duct on the underside of

Fig 4: Gas flowing over the edges



the fan (Fig. 4). The washers that separate the fans from one another facilitate this flow back into the fan. Once inside the fan, the gas is free to move to the next fan in the stack and repeat the process.

The gas moving in and out of fans is continuously flowing over all of the surfaces of the fans, where the reforming reaction takes place. However, in practice, not all of the gas moves back into the fan and some slips over the outer edge of the washer to the fan below. When this gas reaches the next fan, it encounters turbulence and is mixed back into the bulk flow, ensuring that all gas has multiple chances to react on a fan surface.

The impingement heat transfer mechanism results in a significant performance benefit when compared to pellets. This is measured in the laboratory by flowing air through a CATACEL™ SSR stack installed

Fig 5: Pressure drop versus flow

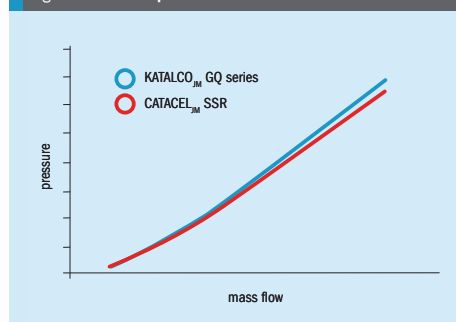
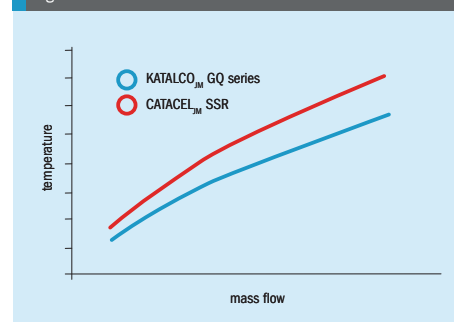


Fig 6: Heat transfer versus flow

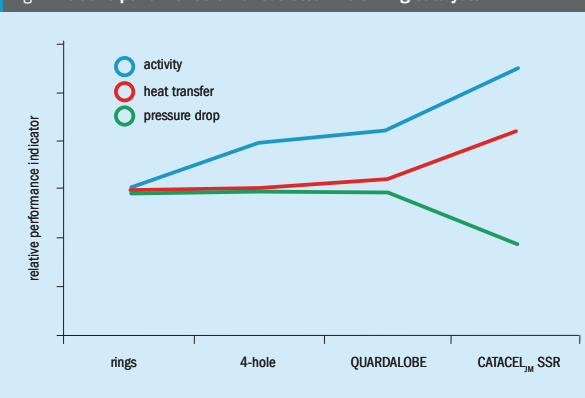


in a specially designed heat transfer and pressure drop measurement rig. Results from this testing are shown in Figs 5 and 6. A CATACEL™ SSR design was selected that gave a pressure drop very similar to that of KATALCO™ GQ size QUADRALOB™ reforming catalyst pellets, as shown in Fig. 5. The improved heat transfer achieved by the CATACEL™ SSR design is shown in Fig. 6, which illustrates an improvement of approximately 30%.

The key performance indicators for the CATACEL™ SSR catalyst set on a timeline of the various Johnson Matthey steam reforming catalysts is shown in Fig. 7. This shows how the activity, heat transfer and pressure drop of steam reforming catalysts have developed over the past three decades. The development of the KATALCO™ 4-hole steam reforming catalyst resulted in a significant increase in catalyst activity and this was accompanied by a noticeable increase in heat transfer performance. This development had a significant impact on the performance of steam reformers that adopted this catalyst. The further development of the KATALCO™ QUADRALOB™ steam reforming catalyst generated a further boost in activity, but more importantly generated a significant increase in catalyst heat transfer whilst reducing the pressure drop and this generated further benefits for operators of steam reformers.

Set against this, the performance improvements of the CATACEL™ SSR catalyst are substantially larger than those that can be obtained by further development of ceramic based pellets and are larger than any previous ceramic-based improvements seen. The development of the CATACEL™ SSR catalyst with Catacel Corporation provides the latest development in Johnson

Fig 7: Relative performance of various steam reforming catalysts



Matthey's steam reforming offer, demonstrating its continued leadership in this difficult and challenging technology.

Any of the improvements in performance parameters taken on its own would generate substantial benefits for operators of steam reformers. However, as the activity and heat transfer can both be markedly improved whilst at the same time reducing the pressure drop, it generates the potential for noticeable improvements in steam reformer operation. The heat transfer benefit of CATACEL_M SSR will generate reductions in tube wall temperature, increasing the heat transfer efficiency of the furnace. The increased activity will further reduce the tube wall temperature and reduce the approach to equilibrium, reducing the methane slip at a given outlet temperature. Additionally, the extra activity and cooler tube wall temperatures will reduce the risk of carbon formation and increase both catalyst and tube lives. The lower reformer pressure drop will reduce the load on compressors, allowing improved plant efficiency or the potential for slight increases in throughput. In a new reformer that has been designed to take advantage of the benefits offered by CATACEL_M SSR, considerable capital can be saved.

Deployment

In order to deliver performance benefits the stacked fans must be properly deployed in the reformer tubes. The fans are pre-assembled into stacks (Fig. 2), with the fans mounted on a support structure that sits within the central space of the fans.

Fig 8: Install tool



Fig 9: Install tool in use



This aids in the speed and accuracy of the catalyst installation by avoiding the need to install the fans individually. The outer edges of each fan must be located close to but not touching the inside tube surface and each stack must rest directly over the stack below (and remain there during any thermal expansion or contraction events) without any gaps that could create hot spots. Fan positioning is managed using patent protected deployment technology that forms part of the support structure along with patent protected installation tools and methodologies.

The internal surfaces of reformer tubes can be quite irregular, especially on plants that have been in service for some time. New tubes can exhibit weld protrusion into the tube as well as asymmetry from the boring process. Older tubes will exhibit increased internal diameter due to creep growth during service and can have areas with bulges where they have been overheated. The CATACEL_M SSR stacks must be installed through an inlet flange that is typically at nominal dimension. This means that the CATACEL_M SSR fans must be inserted in a slightly compressed configuration and engage with the stack (or support) below. It must then be expanded to bring the fan edges into the correct position versus the tube wall.

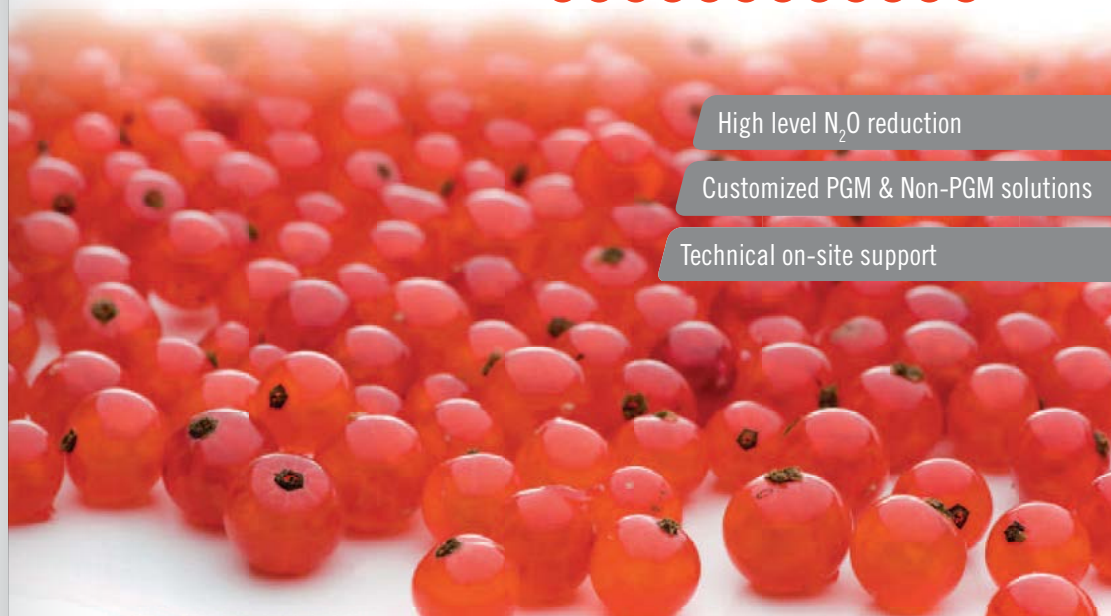
CATACEL_M SSR installation

Special patent-protected tools are used to manage the installation of the CATACEL_M SSR catalyst. These tools lower the catalyst safely into the tube in the compressed configuration and manage the expansion of the fans to match the local tube shape. Additionally they are robust, capable of handling at least one reformer installation, relatively lightweight and are safe to use in a typical syngas environment. Electricity has been avoided in these tools for safety reasons, and all functions are operated either by compressed air or gravity. Compressed air functions are managed by control boxes that are placed on the reformer mezzanine and connect to the tool through umbilicals. Fig. 8 shows one such tool and Fig. 9 shows the tool in use at one such installation.

CATACEL_M SSR removal

The strategy for removing spent CATACEL_M SSR stacks is similar to the catalyst installation, and uses a special removal tool to

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Foil coated catalysts

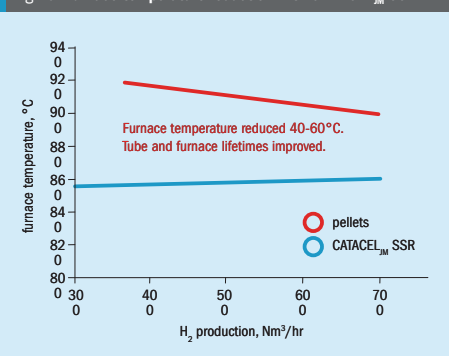
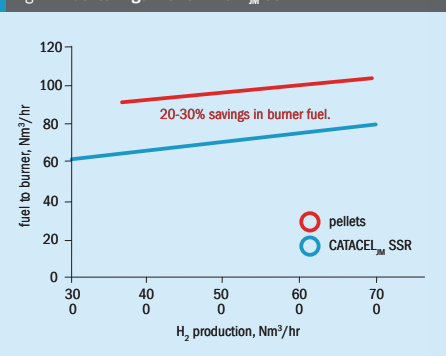
COVER FEATURE 4

CO₂ removal from syngas

NITROGEN+SYNGAS
ISSUE 337
 SEPTEMBER-OCTOBER 2015

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Fig 10: Furnace temperature reduction with CATACEL_{SM} SSRFig 11: Fuel savings with CATACEL_{SM} SSR

grasp the central support structure to allow the stack to be lifted from the tube. A modest lifting force is needed to remove the CATACEL_{SM} SSR stacks. The central support structure of the CATACEL_{SM} SSR stack is designed to accommodate these loads, and has been proven to do so without failure. As with the installation tool, compressed air is used to actuate the removal tool.

Original CATACEL_{SM} SSR installation in Turkey

In August 2008, an early version of CATACEL_{SM} SSR was installed in a small can reformer in Turkey. The plant ran well for four years in spite of numerous upsets unrelated to the CATACEL_{SM} SSR catalyst. Even though it was still performing well, that catalyst was removed in January 2013 at a scheduled turnaround and replaced with the current version of CATACEL_{SM} SSR. The removal and reinstallation process was accomplished without major incident. The coated foils removed had maintained their original integrity in spite of the process upsets and significant contamination from boiler feed water, indicating that coated foil materials can survive and thrive in a reforming environment. The new charge started up well and has operated without issue since installation.

Second installation in Mexico

In May 2012, a CATACEL_{SM} SSR loading was installed in a small can reformer in Mexico. This customer sought to obtain natural gas savings by reducing fuel consumption, while having the option to increase throughput beyond the design

capacity, and attain a longer operational lifetime for both the catalysts and reforming tubes. The reformer configuration at the plant consisted of reformer tubes of varying ages, several of which had been recharged with ceramic pellet catalyst as recently as January 2012. After thorough study and analysis, the plant management decided to replace the ceramic catalyst media in all reformer tubes with CATACEL_{SM} SSR catalysts. The change-out was completed with minimal downtime in May 2012 by plant staff under expert supervision.

After installation, the plant restarted without incident, and immediately demonstrated a 13.5% reduction in burner make-up fuel consumption. Over the following weeks, the plant operating conditions were optimized to take advantage of the CATACEL_{SM} SSR. Figs 10 and 11 show furnace temperature reduction (40-60°C) and fuel savings (25-30%) realized at various plant rates with the plant optimized for CATACEL_{SM} SSR.

The customer is delighted with their CATACEL_{SM} SSR catalyst installation. The plant continues to perform at the optimum levels and the customer estimates that their payback time for the entire CATACEL_{SM} SSR charge is two years based only on fuel savings alone. This does not count savings to be realized over the years to come by eliminating catalyst and tube changes.

Case studies

The development path for CATACEL_{SM} SSR catalyst has demonstrated the product benefits in two small can reformers, with the operators of these plants having achieved improved performance compared

to conventional pellet catalysts. However, the majority of the syngas industry uses box reformers, either top fired or side fired. A series of case studies is given here and is based on plant performance modelling. These demonstrate the many scenarios in which CATACEL_{SM} SSR technology can improve steam reformer operations for typical top fired and side fired reformers.

Hydrogen plant uprate

In the first case study we will consider a small hydrogen plant that was initially designed to operate on naphtha feedstock. The feedstock was changed to natural gas when this became available at the plant site. One outcome of the feedstock change was a reduction in the combustion air flow requirement, resulting in reformer fans with spare capacity. The heat exchange duty in much of the plant was also reduced because a lower steam ratio is required with the natural gas feed.

The reformer is now operating close to the tube wall temperature limit and the spare fan capacity cannot be utilized. In an attempt to moderate the peak tube wall temperature at the top of the tubes, a high excess air is being used as the fans have spare capacity.

The operator now requires an additional 15% hydrogen production. Whilst the rest of the plant is capable of operating at this higher capacity, the tube wall temperatures are the limiting factor. A retube could remove this operating limit, but this would be an expensive and premature change as the tubes are relatively new.

Another option to release the available capacity in the rest of the plant is to change from a pelleted catalyst to CATACEL_{SM} SSR

Table 1: Impact of CATACEL_{SM} SSR catalyst on a hydrogen plant reformer

| Case | Base | 1 | 2 |
|---------------------------------|------------|---------------------------|---------------------------|
| Catalyst | QUADRALOBE | CATACEL _{SM} SSR | CATACEL _{SM} SSR |
| Description | Base | Same throughput | Additional throughput |
| Relative feed flow, % | 100.0 | 100.0 | 115.0 |
| Relative fuel flow, % | 100.0 | 99.5 | 112.5 |
| Relative combustion air flow, % | 100.0 | 99.4 | 105.0 |
| Excess air, % | 15.0 | 15.0 | 7.5 |
| Exit temperature, °C | 860 | 860 | 861 |
| Methane slip, mol-% dry | 2.80 | 2.75 | 2.80 |
| Max tube wall temperature, °C | 890 | 885 | 891 |
| Approach to equilibrium, °C | 2.8 | 1.8 | 2.1 |
| Pressure drop, bar | 1.29 | 1.01 | 1.28 |
| Flue gas exit temperature, °C | 997 | 991 | 1,012 |
| Relative hydrogen make, % | 100.0 | 100.2 | 115.0 |

catalyst in the steam reformer. The higher heat transfer and higher activity of the CATACEL_{SM} SSR catalyst can reduce the tube wall temperature significantly, allowing higher throughput and firing. Additionally, the chosen CATACEL_{SM} SSR catalyst allows a higher throughput for the same reformer pressure drop. Table 1 below shows the reforming parameters for the hydrogen plant based on the market leading KATALCO_{SM} QUADRALOBE and CATACEL_{SM} SSR catalysts.

The base case defines the maximum operating point of the plant based on the current limit of tube wall temperature and pressure drop.

Case 1 shows the impact of installing the CATACEL_{SM} SSR catalyst in the reformer at the current throughput. There is a significant improvement in both the pressure drop and the maximum tube wall temperature. The reduction in the maximum tube wall temperature is modest in this case because the peak temperature occurs in the lower portion of the tube where the heat flux is lower. There is a small reduction in fuel flow rate and a small increase in production due to the lower approach to equilibrium.

Case 2 shows what increased throughput can be achieved within the existing constraints of tube wall temperature and pressure drop. A 15% increase in throughput is possible with the maximum tube wall temperature increasing by just 1°C and the pressure drop remaining consistent with the base case. The fuel required rises by 12.5% and the combustion air rises by 5%. This

reduces the excess air making the furnace more efficient, with the result that the flue gas temperature increases by just 15°C.

In order to confirm the overall achievability of this proposal, the plant performance has been checked throughout by the engineering contractor. The main plant items are within their proven operating range, with the exception of a small number of control valves. Installing CATACEL_{SM} SSR catalyst in this plant can provide a simpler and more cost-effective way of achieving the increased throughput required. The customer in this case has purchased CATACEL_{SM} SSR catalyst for installation in 2015 to support the plant uprate.

Ammonia plant production increase

In the following case study the ammonia plant is operating at its maximum capacity and is again limited by the tube wall temperature in the primary reformer. The secondary reformer is operated with the maximum process air flow available from the compressor. During the warmest days of the year, the primary reformer also becomes limited by the combustion air flow. However, during most of the year extra fuel could be used if the tube temperatures could be reduced.

Installing CATACEL_{SM} SSR with its significantly higher heat transfer will reduce the tube wall temperatures. Additionally, increased activity will reduce the approach to equilibrium at the exit of the tubes, reducing both the exit temperature and the methane slip for the same primary reformer

Table 2: Impact of CATACEL_™ SSR catalyst on an ammonia plant reformer

| Case | Base | 1 | 2 |
|-------------------------------------|------------|--------------------------|--------------------------|
| Catalyst | QUADRALOBE | CATACEL _™ SSR | CATACEL _™ SSR |
| Description | Base | Same firing | Extra firing |
| Relative feed flow, % | 100.0 | 100.0 | 100.0 |
| Relative fuel flow, % | 100.0 | 100.0 | 102.0 |
| Relative process air flow, % | 100.0 | 100.0 | 100.0 |
| Primary exit temperature, °C | 766 | 765 | 769 |
| Primary methane slip, mol-% dry | 14.96 | 14.54 | 14.10 |
| Primary max tube temperature, °C | 892 | 871 | 875 |
| Primary approach to equilibrium, °C | 10 | 6.3 | 6.2 |
| Primary flue gas temperature, °C | 903 | 892 | 899 |
| Secondary exit temperature, °C | 890 | 894 | 900 |
| Secondary methane slip, mol-% dry | 1.29 | 1.21 | 1.10 |
| Relative ammonia make, % | 100.0 | 101.0 | 102.6 |

Table 3: Impact of CATACEL_™ SSR catalyst on a methanol plant reformer

| Case | Base | 1 | 2 |
|-------------------------------|------------------------------|---|--|
| Catalyst | QUADRALOBE | CATACEL _™ SSR | CATACEL _™ SSR |
| Description | Base Firing biased to top | Same throughput Firing biased to top | Additional throughput Firing biased to bottom |
| Relative feed flow, % | 100.0 | 100.0 | 104.5 |
| Relative fuel flow, % | 100.0 | 100.0 | 100.0 |
| Exit temperature, °C | 880 | 880 | 875 |
| Methane slip, mol-% dry | 2.29 | 2.06 | 2.28 |
| Max tube wall temperature, °C | 947 | 938 | 944 |
| Approach to equilibrium, °C | 14 | 7 | 9 |
| Flue gas temperature, °C | 1012 | 1003 | 962 |
| Pressure drop, bar | 3.14 | 2.91 | 3.07 |
| Relative methanol make, % | 100.0 | 100.5 | 104.4 |

representing the average additional firing that can be achieved over the year when cooler temperatures are taken into consideration. The natural gas feed rate to the tubes remains the same and there is a slight increase in tube exit temperature, a further reduction in methane slip and an overall increase in ammonia production of 2.6%. The maximum tube wall temperature still remains lower than for the base case. This means that the CATACEL_™ SSR will have a longer catalyst life before the maximum tube wall temperature reaches the limit, making further economic savings. Likewise, the flue gas temperature remains lower than the base case; hence there is

no need to check whether the convection section needs modification due to higher flue gas temperatures.

Methanol plant throughput increase

Consider now a methanol plant with a side fired reformer in which is operating to a firing limit set by the combustion air fan (due to increased throughput after debottlenecking modifications). It is also operating at the maximum allowable pigtail temperature and the tube wall temperature limits. To keep the tube wall temperature within the allowable range, the firing on the bottom rows of burners is trimmed back as the peak tube wall temperature is close

to the bottom of the tubes. This means that extra firing is forced towards the upper rows of the reformer where there is less residence time for the flue gas to transfer heat; hence the reformer is less fuel efficient and runs with a higher than expected flue gas exit temperature.

In this case, the change to CATACEL_™ SSR catalyst will allow the operator to increase plant throughput without additional firing or combustion air flow. The CATACEL_™ SSR catalyst will have a three-fold effect.

The lower pressure drop will allow an increased throughput for the same pressure drop.



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The higher heat transfer coefficient will reduce the tube wall temperature. This will allow an increase in firing on the bottom rows of burners which is more efficient than using the upper rows of burners. Therefore, the throughput can be increased for the same firing limit.

The increased activity will allow operation at a reduced exit temperature for the same methane slip, again reducing the tube wall temperature at the bottom of the furnace.

The outcome of these changes will be an increased natural gas feed rate and the potential for an increased methanol production rate for the same combustion air flow rate on the reformer. There will be less heat recovered in the convection section, but on this plant there is spare capacity in the auxiliary boiler to generate the shortfall in steam. Debottlenecking modifications will be required in the rest of the plant, but there will be no need for modifications to the reformer to allow the production rate to be increased. Table 3 below shows the reforming parameters for the methanol plant based on the market leading KATALCO_{JM} QUADRALOBE and CATACEL_{JM} SSR catalysts.

The base case shows the key parameters for the reformer operation at the base case conditions of 100% feed and 100% firing with the fuel biased towards the upper rows of burners.

Case 1 shows the same reformer operation with the same feed and firing with the CATACEL_{JM} SSR catalyst installed. The approach to equilibrium is reduced significantly and the methane slip reduces for the same exit temperature, allowing a 0.5% increase in syngas production from the same feed rate. The maximum tube wall temperature reduces as does the pressure drop.

Case 2 shows the predictions for operation with the CATACEL_{JM} SSR catalyst if the firing on the bottom rows of burners is increased to the maximum rate and the firing is turned down on the upper burners to maintain the plant within the combustion air fan limit. This represents the most efficient operating point for the reformer in terms of radiant box performance.

This will allow a 4.5% increase in reformer throughput by bringing the methane slip back to the same value as the base case. In this case, the reformer exit temperature is reduced by 5°C at the same methane slip, which provides an extra 5°C reduction in tube wall temperature. Even

Table 4: Impact of CATACEL_{JM} SSR catalyst on a new terrace wall hydrogen plant reformer

| Catalyst | QUADRALOBE | CATACEL _{JM} SSR |
|------------------------------|------------|---------------------------|
| Number tubes | 352 | 322 |
| Number tube rows | 2 | 2 |
| Number tubes / row | 176 | 161 |
| Tube ID, mm | 108.0 | 111.4 |
| Tube OD, mm | 132.0 | 132.0 |
| Tube wall thickness, mm | 12.0 | 10.3 |
| Tube heated length, m | 13.72 | 14.00 |
| Furnace length, m | 36.03 | 32.95 |
| Furnace width, m | 2.00 | 2.00 |
| Heat load, MW | 134 | 134 |
| Catalyst pressure drop, bar | 3.31 | 3.31 |
| Minimum tube wall margin, °C | 34 | 34 |
| Relative cost, % | 100.0 | 90.2 |

Table 5: Impact of CATACEL_{JM} SSR catalyst on a new side fired ammonia plant reformer

| Catalyst | QUADRALOBE | CATACEL _{JM} SSR |
|------------------------------|------------|---------------------------|
| Number tubes | 264 | 248 |
| Number tube rows | 2 | 2 |
| Number tubes / row | 132 | 124 |
| Tube ID, mm | 125.6 | 129.7 |
| Tube OD, mm | 150.4 | 150.4 |
| Tube wall thickness, mm | 12.4 | 10.4 |
| Tube heated length, m | 13.00 | 13.10 |
| Furnace length, m | 35.88 | 34.00 |
| Furnace width, m | 1.84 | 1.84 |
| Heat load, MW | 129 | 129 |
| Catalyst pressure drop, bar | 2.06 | 2.06 |
| Minimum tube wall margin, °C | 27 | 27 |
| Relative cost, % | 100.0 | 91.6 |

with the extra firing, the maximum tube wall temperature is predicted to be lower than the base case.

New reformers designed for CATACEL_{JM} SSR catalyst

Over recent years there has been a trend towards reformer designs with larger diameter, longer tubes to take advantage of the improved catalysts and reformer tube materials available. Such designs result in a smaller number of tubes, which reduces the costs of headers and tube fittings such as pigtails, flanges and reducers as these are all based on the number of reformer tubes rather than the reformer duty.

The adoption of the CATACEL_{JM} SSR catalyst can have a significant impact on the design of new reformers due to its higher heat transfer, higher activity and lower pressure drop. The improved heat transfer and activity reduce the tube wall temperature allowing the use of thinner wall tubes, which in turn reduces the resistance to heat transfer and requires fewer tubes for the same heat transfer duty. The reduced pressure drop due to the CATACEL_{JM} SSR catalyst plus the reduced tube wall thickness allows the use of a smaller number of longer tubes for the same overall pressure drop.

Several reformer designs have been

Table 6: Impact of CATACEL_{JM} SSR catalyst on a new top fired methanol plant reformer

| Catalyst | QUADRALOBE | CATACEL _{JM} SSR |
|------------------------------|------------|---------------------------|
| Number tubes | 728 | 636 |
| Number tube rows | 14 | 12 |
| Number tubes / row | 52 | 53 |
| Tube ID, mm | 115.0 | 115.6 |
| Tube OD, mm | 134.4 | 134.4 |
| Tube wall thickness, mm | 9.70 | 9.40 |
| Tube heated length, m | 13.18 | 14.2 |
| Furnace length, m | 14.96 | 15.22 |
| Furnace width, m | 32.52 | 27.94 |
| Heat load, MW | 263 | 263 |
| Catalyst pressure drop, bar | 2.83 | 2.78 |
| Minimum tube wall margin, °C | 79 | 79 |
| Relative cost, % | 100.0 | 92.0 |


investigated, with a redesign based on CATACEL_{JM} SSR catalyst compared to the original design. Cost comparisons have been made between the two reformer designs to show the savings that can be made. The reformer designs have been made on identical pro-

cess duties, i.e. the same feed, the same reformed gas heat load, the same fuel and combustion air flow, resulting in the same flue gas exit temperature, the same process pressure drop and finally the same design margin between the maximum tube


wall temperature and the 100,000 hour life temperature.

Tables 4, 5 and 6 give the results for several different reformer configurations and duties where the design based on the market leading KATALCO_{JM} QUADRALOBE has been modified for CATACEL_{JM} SSR catalyst. The key dimensions of the furnace are given along with the key targets of the same process gas heat load, pressure drop and tube wall temperature margin. All cases have the same feed and the same fuel and combustion air. The final row in each table gives an estimate of the relative cost of the radiant box for both pelletized catalyst and CATACEL_{JM} SSR catalyst. The cost does not include the convection section, fans, stacks and air preheater as these components will be the same for both reformer designs.

The data show a capital cost saving of the order of 8-10% for each of the designs listed. Additional studies over a wider range of reformer duties have shown that this is repeatable for most reformers with the smallest savings of no less than 5% and some redesigns showing a cost saving of 15%. ■




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Piperazine activated solvents for CO₂ removal

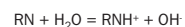
As part of a review of a solvent change-out from amine promoted hot potassium carbonate to piperazine activated MDEA, **R S Alvis, N A Hatcher** and **R H Weiland** of Optimized Gas Treating, Inc. present the results of a quantitative study of the piperazine promotion of MDEA, specifically the effects of piperazine to MDEA ratio, total amine strength, and the treating temperature on the performance of a typical ammonia syngas CO₂ removal system. The potential of piperazine-activated Alkazid DIK as a solvent for CO₂ removal applications is also discussed.

In the early days of ammonia production, monoethanolamine (MEA) was commonly used for CO₂ removal from the synthesis gas using the Girbotol process. Somewhat later, hot potassium carbonate (the Benfield, or Hot Pot process) was used, often in a split flow configuration described as a two-stage Benfield LoHeat process for energy conservation. In the last 20 years, a very substantial fraction of these plants have been retrofitted using the aMDEA[®] process which was first patented by BASF in 1982 and is still used in the majority of the world's ammonia plants.

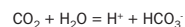
N-Methyldiethanolamine (MDEA) is a tertiary amine whose amino group is incapable of reacting with CO₂. However, it is alkaline and so is an excellent sink for protons produced by CO₂ hydrolysis. Because of its very low regeneration energy, removing CO₂ using MDEA alone would be preferred; however, the reaction in solution is extremely slow and the absorption process is controlled entirely by resistance to mass transfer in the solvent phase. Although MDEA can be activated by a number of amines, piperazine is the most commonly used promoter in applications involving CO₂ removal from syngas, as well as from natural gas in LNG production. Piperazine is highly reactive with CO₂ which greatly enhances CO₂ absorption rates. Yet because only relatively small concentrations of piperazine are needed, solvent regeneration energy requirements are not much higher than for MDEA alone.

Using tertiary amines for CO₂ removal

Before looking at specific chemical solvents, it is beneficial to describe the function of an amine that is completely non-reactive towards CO₂, in the CO₂ absorption process, and to give a quantitative picture of how effective piperazine really is. Like all amines, tertiary amines dissociate in water and produce hydroxyl ion:



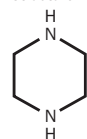
The hydroxyl ion is what gives amines their alkalinity. However, CO₂ does not react with a tertiary amino group because this group lacks the mobile hydrogen necessary to exchange for the CO₂ and form carbamate. Instead, the CO₂ merely absorbs into water and hydrolyses:



The liberated proton is neutralised by the amine's alkalinity as represented by the hydroxyl group. Thus, unless one can directly catalyse the hydrolysis reaction itself (as can be done using carbonic anhydrase, for example), CO₂ absorption rates are not enhanced at all by reaction and will be no faster than they would be into essentially pure water. The function of the tertiary amine then, is not to enhance absorption rates through chemical reaction, but rather to increase dramatically the *capacity* of the solvent. The trouble with straight MDEA, however, is that the CO₂ absorption rate is almost always too slow for it to be used alone, except for bulk CO₂ removal at high

pressure. It simply cannot be used effectively for the deep CO₂ removal required for syngas and LNG production. The CO₂ reaction must be promoted, and piperazine is an excellent promoter.

Piperazine is a cyclic diamine with the structure:



It reacts with CO₂ about ten times faster than MEA. Its second order rate constant at 25°C, for example, is about 59,000 L·mol⁻¹·s⁻¹ versus MEA at 6,000 L·mol⁻¹·s⁻¹. This makes piperazine the most

reactive promoter of CO₂ kinetics available commercially. In summary then, although MDEA alone can be used for bulk CO₂ removal at high pressure, its reaction rate with CO₂ is much too slow for it to be usefully applied to deeper CO₂ removal in columns of reasonable height. For that, an activator is required, and piperazine has evolved as the activator of choice. Today, most solvent vendors offer a form of piperazine-promoted MDEA under a variety of brand and code names.

Deep CO₂ removal using an MDEA-based solvent

Using an amine process simulator that is founded upon real, mass and heat transfer rates allows a virtual plant to be constructed on a computer. In the present work, the ProTreat[®] simulator was used. ProTreat is the world's only true mass transfer rate-based commercial simulator dedicated to gas treating. A virtual plant built using



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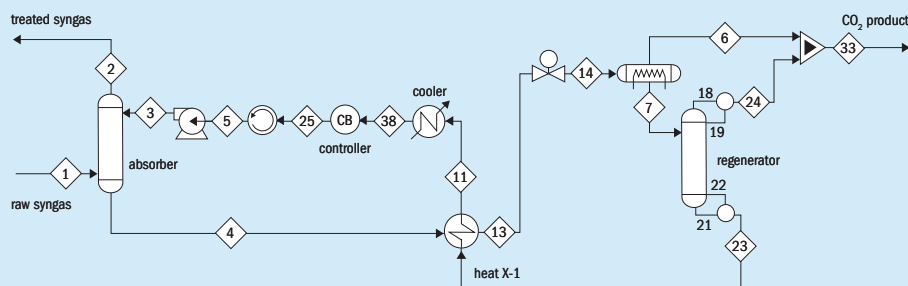
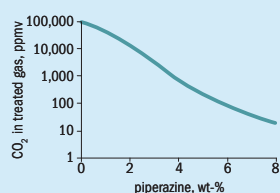
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Fig 1: Simplified syngas treating PFD

Fig 2: Effect of piperazine concn. in MDEA (total wt-% amine) on CO₂ level in treated syngas

ProTreat allows one to experiment with a wide variety of different process configurations and what-if scenarios. It is relatively easy to learn a great deal about a particular plant's performance characteristics and quantitatively understand how numerous plant operating parameters affect that performance. ProTreat has been used to answer such questions as, "What is the best solvent concentration and formulation to use?" and "How does the treating temperature affect performance?" Although no public-domain plant data exist, or are available to us on the use of DiMGly as a solvent for syngas purification, a rather limited amount of fundamental data on vapour liquid equilibrium and physical properties is sufficient to determine a great deal about how this chemical will perform in a syngas treating situation.

The ProTreat process flow diagram for the amine section of a typical ammonia syngas plant has a single absorber and identical-twin regenerators in parallel. There is also a rather complex scheme for returning part of the condensate from the regenerator overhead condensers to

a short wash section in the absorber for recovering amine vapours. The flowsheet is quite a bit more complex than needed to illustrate the main points of this article so it has been greatly simplified to the process flow diagram shown in Fig. 1. The simplified flow sheet has a single regenerator and we have eliminated any consideration of an amine recovery section atop the absorber. The plant was designed to treat 208 000 NCMH raw gas at 26.4 bara and 37°C containing 60.2 mol-% H₂, 20.9 mol-% N₂, and 17.9 mol-% CO₂ with the balance being trace amounts of argon, methane, carbon monoxide, and water vapour. For this study, the absorber was packed with 15.25 m (50 ft) of #50 IMTP tower packing. The regenerator was also packed, and contains 10.4 m (34 ft) of #3 Cascade Mini-rings. Although this absorber had a little deeper packed bed than found in many syngas CO₂ plants, the conclusions of the paper are in no way affected.

MDEA-piperazine composition

The most commonly used total-amine strength for generic MDEA and MDEA-based blends is 50 wt-% although, as we shall see, this is sometimes not the best concentration to use. Figure 2 shows how the relative concentrations of piperazine and MDEA in a 50 wt-% total-amine blend affect the CO₂ left in the treated gas. It is apparent from the figure that about 4 wt-% piperazine is needed to achieve < 1 000 ppmv CO₂ and that 5 or 6 wt-% piperazine allows one to achieve in the vicinity of 100 ppmv CO₂. The treating performance is very sensitive to the concentration the piperazine additive and this is why it is so important to monitor solution strength for piperazine content. Unfortu-

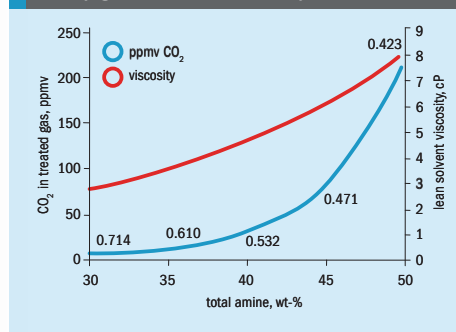
nately, piperazine is somewhat volatile so its concentration tends to fall with time more rapidly than does MDEA. Plant performance depends critically on maintaining the right concentrations of the solvent ingredients.

Solvent total amine strength

Having established that this plant will operate quite comfortably with 5 wt-% piperazine and 45 wt-% MDEA, the effect of total amine strength on the CO₂ content of the treated gas was investigated. Figure 3 summarises the findings. The numbers next to points on the ppmv CO₂ curve are the corresponding CO₂ mole loadings (per mole total amine) of the rich solvent from the absorber.

It might be surprising that the higher the amine strength the worse the treating. Using 50 wt-% total amine (Base Case), the simulated treated gas has 208 ppmv CO₂ and a very satisfactory rich solution loading of 0.423 moles CO₂ per mole of total amine. However, 45 wt-% amine allows a 75 ppmv CO₂ gas to be produced and 40 wt-% amine reduces the CO₂ to about 30 ppmv. With 30 wt-% amine the residual CO₂ is even lower. However, on the negative side, the rich solution loading increases to unacceptably high levels from a carbon-steel metallurgy corrosion standpoint. Of course, stainless cladding in the right places, and the use of stainless exchanger bundles, would overcome this objection.

The reason for improved treating with lower solvent strengths is the lower solvent viscosity that accompanies reduced amine concentration. CO₂ absorption is a process whose rate is controlled by mass transfer resistance in the liquid, or solvent,

Fig 3: Effect of total amine strength on CO₂ level in treated syngas and on solvent viscosity

phase, and the more viscous that phase is, the greater the resistance. As Fig. 3 shows, dropping amine concentration from 50 wt-% to 30 wt-% reduces solvent viscosity by a factor of nearly three. This allows CO₂ to be absorbed faster and allows the 15+ metres of packing to extract enough extra CO₂ to reduce the treated gas concentration from 208 ppmv to just a little over 7 ppmv. Solvent viscosity is an important factor in absorber performance, and any successful effort to lower it will pay dividends. Another way to lower viscosity is to use a hotter solvent.

Solvent temperature

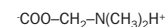
As Fig. 4 shows, setting the solvent temperature at 50°C, say, rather than 26°C lowers the viscosity by a factor of nearly three as well, and treating improves dramatically over the base case. The simulated results shown in the figure are for a 45 wt-% plus 5 wt-% piperazine solution. Treated gas CO₂ content drops rapidly with temperature but eventually it levels out, then experiences a precipitous rise. In this case, a temperature of just over 50°C presents an operational cliff. As temperature rises, of course, the vapour pressure of CO₂ over the solvent goes up as well, and near 50°C the point is reached where reduced solubility prevents absorption of enough CO₂ even to come close to meeting a <1 000 ppmv CO₂ specification. The ppm CO₂ level suddenly rises because the solvent's capacity has been reduced to a level insufficient to absorb enough CO₂. The excess CO₂ in the inlet simply passes right through the column and CO₂ breakthrough is experienced. Operationally, it would be very dangerous to operate too

close to this temperature because it would become impossible to maintain control of outlet CO₂ levels.

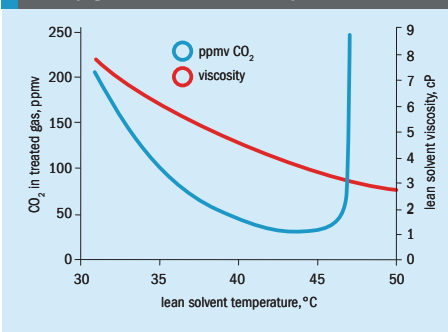
Amino acid salt based solvent – potassium dimethylglycinate

Potassium dimethylglycinate (KDiMGly) is the potassium salt of dimethyl glycine, and was known under the BASF trade name Alkazin D.K. This is a tertiary amino acid salt that since 1935 had been used quite successfully and extensively, mainly in Europe, for selectively removing H₂S from such problematic streams as refinery and coke oven gases. These gases tend to be heavily contaminated with various components known to be hard on conventional amines. With the advent of MDEA, its use diminished, and eventually it stopped being offered commercially. However, KDiMGly has certain properties such as zero vapour pressure and possibly oxidation resistance that are making it more attractive in post-combustion CO₂ capture, and which may make it a useful alternative to MDEA for ammonia syngas.

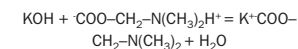
As the name implies, amino acids contain an amino group at one end of the molecule and a carboxylic acid group at the other. In aqueous solution, dimethyl glycine exists as a so-called zwitterion:



Because the amino group is protonated, it is completely nonreactive towards CO₂ and it is pH neutral which, from the standpoint of life on earth, is probably a good thing. But as a solvent for CO₂ it is virtually useless, having neither reactivity nor absorption capacity. However, when the acid group is titrated (neutralised) with KOH the

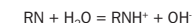
Fig 4: Effect of solvent temperature on CO₂ level in treated syngas and on solvent viscosity

amino group deprotonates and produces what is now an alkaline, tertiary amine.



An important property is that KDiMGly and all other amino acid salts exist in water as fully-dissociated salts, making them completely non-volatile. Furthermore, amino acids are already partially oxidised which may give them better resistance to further oxidation.

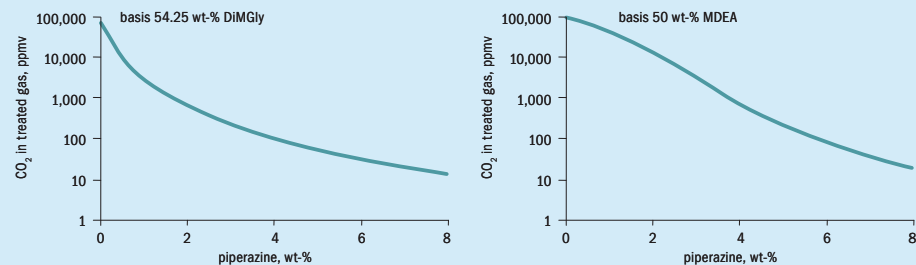
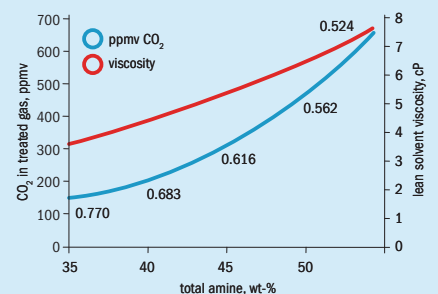
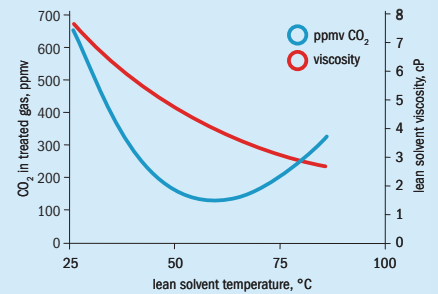
In the case of KDiMGly, the two additional methyl groups are attached to nitrogen at the amino end of the molecule, depriving the amino group of the proton necessary for reaction with CO₂. The amino group is tertiary; however, is it nonetheless highly alkaline in the same way as MDEA and, in solution, dissociates according to:



Just as for MDEA, tertiary amines do not react with CO₂ (no carbamate or other reaction products with the amine are formed) so the CO₂ absorption rate will be nearly identical with what it would be in water, i.e., extremely slow. But the alkalinity gives the solvent high CO₂ holding capacity, if only the CO₂ could get into solution in the first place. This is done by promoting the solvent with very fast-reacting piperazine.

Model studies of the KDiMGly-piperazine solvent

Because chemicals are bought and sold by weight, we are used to thinking about solvent strength in terms of the weight percent of the active ingredients. However, chemistry works on the basis of moles. To do as nearly a one-to-one comparison with piperazine-promoted MDEA as possible it

Fig 5: Effect of piperazine concentration on CO₂ level in treated syngasFig 6: Effect of total amine strength on CO₂ level in treated syngas and on viscosity of KDIMGlyFig 7: Effect of solvent temperature on CO₂ level in treated syngas and on viscosity of KDIMGly

is necessary to use equal molar concentrations of the main constituent, and it turns out that 54.25 wt-% KDIMGly is equivalent to 50 wt-% MDEA. Therefore, this was the base concentration used in the amino acid study.

KDIMGly-piperazine composition

Figure 5 shows that even without the piperazine additive, KDIMGly removes more CO₂ (6.96 mol-% CO₂ in the treated gas) than the MDEA molar equivalent (9.068 mol-% CO₂). This suggests higher driving force for absorption (low vapour pressure of CO₂) when KDIMGly is used in a plant operating under otherwise identical conditions of solvent rate, reboiler duty, equipment details, and so on. Considerably less piperazine (2 wt-% versus 4 wt-%) is needed to achieve 1 000 ppmv treated gas, and the response to piperazine addition is higher. Lower piperazine concentrations mean reduced potential vapourisation losses and, of course, the completely nonvolatile nature of KDIMGly eliminates this inventory loss mechanism.

Effect of total amine strength

Lower total amine concentration is simulated to have an effect similar to MDEA, although the viscosity reduction is not as great (a factor of two versus a factor of three for MDEA) and therefore the impact of lower total amine concentration is not as great. Figure 6 shows the simulation results. The numbers beside each simulation data point are the rich solution CO₂ loading values, which are higher than corresponding rich loadings for MDEA. KDIMGly is harder to strip than MDEA because for the same loading value the CO₂ vapour pressure is lower. In other words, because of its higher pH (e.g., 12.05 for 54.25 wt-% KDIMGly versus 11.72 for 50 wt-% MDEA, both at 26.5°C) KDIMGly has higher affinity for CO₂ than MDEA does. The lean solution loading for piperazine activated MDEA is typically 0.003 but for KDIMGly under similar conditions it is 0.13; the question is whether a difference of 0.13 loading units makes a KDIMGly solution more corro-

sive than MDEA under the same conditions. Because it is bicarbonate that is responsible for corrosion, the answer is probably yes, and some stainless metallurgy in vulnerable sections of process equipment and piping would be prudent. However, there is another significant benefit to be gained from using piperazine-promoted KDIMGly.

Effect of treating temperature using KDIMGly

As shown in Fig. 7, higher solvent temperatures (lower viscosity solvent) lead to significant improvements to the residual CO₂ concentration in the treated gas. Unlike the MDEA-based solvent, there is no precipitous loss of performance when the temperature reaches high values. Instead, there is a broad minimum in the treating performance curve. This results from the competing effects of increasing absorption rates (from diminished solvent viscosity), versus increasing equilibrium CO₂ vapour pressure (reduced driving force for absorption) with higher temperatures.

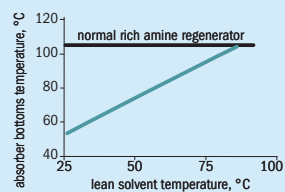
Solvent temperatures anywhere between 35 and 85°C permit very satisfactory treating; however, the ability to use a high temperature solvent offers potential advantages.

Advantages to treating with hot solvent

Figure 8 shows how lean amine temperature affects the temperature of the rich solvent leaving the absorber. Here one can see that in the present case, for a lean amine temperature of 85°C, the rich amine will be at nearly 105°C. This means that the rich solvent requires no preheating to ensure it enters the stripper at a reasonable temperature. The cross exchanger can be completely eliminated from the plant, and this would be possible even with a lean solvent temperature of 60°C where the best CO₂ removal is achieved. The ability to run hot has a certain parallel with the Hot-Pot process but does not need a semi-lean process flow sheet configuration. Instead, the process flow sheet is even simpler than for conventional amine treating.

Piperazine-promoted KDIMGly appears to be a viable option for CO₂ removal from ammonia syngas. It's a question of whether the cost of better metallurgy

Fig 8: Effect of lean solvent temperature on rich amine temperature



(which may already exist in a piperazine promoted MDEA plant) exceeds the benefits of lower amine losses, smaller heat exchangers, and the elimination of the usually quite large cross exchanger.

Summary

This article shows that with piperazine activated MDEA:

- One must be careful to monitor solution composition and control the piperazine

level because performance is quite sensitive to this parameter.

- The maxim of always using 50 wt-% total amine solvent is false, and significant improvements to treating levels can be realised by operating at lower concentrations. The 50 wt-% rule should be examined in each and every case.
- When treating goals are not being met, using a colder amine may be a step in the wrong direction.
- Solution viscosity has a profound effect on CO₂ removal rates and whatever can be done to lower its value, consistent with other operating constraints, will be beneficial.

With KDIMGly there is potential to:

- Reduce heat exchanger surface areas.
- Eliminate the cross exchanger altogether.
- Lower potential amine vaporisation losses.
- Perhaps use a more robust amine as the base for the solvent.

References

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Improving the efficiency of CO₂ removal systems

L Tomasi of Giammarco-Vetrocoke reports on how the regeneration energy requirement of the GV low-energy CO₂ removal process, based on the hot potassium carbonate (HPC) solution, can be drastically reduced by integration with a stand-alone physical absorption system. A small sized physical unit added upstream of the existing CO₂ removal system allows the pre-absorption of 30 to 50% of the CO₂ from the process gas which is then fully recovered by flash without any regeneration energy requirement.

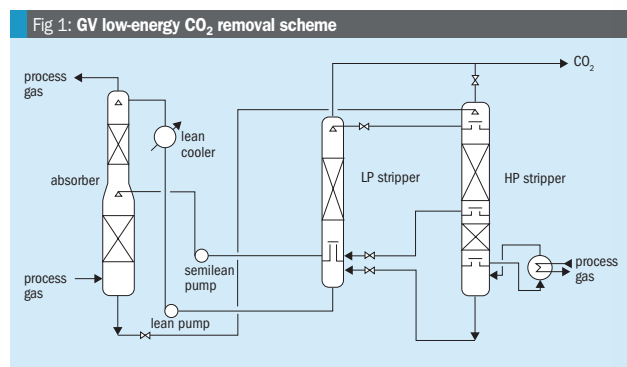
The global ammonia/urea industry is struggling in many regions with a shortage of available natural gas (NG). This worldwide scenario has led to huge instability of prices, making the economics of production quite uncertain. In order to be competitive with modern plants, it is important for older existing units to drastically reduce their energy consumption by decreasing the specific NG requirement per tonne of ammonia. The revamping of the CO₂ removal system, one of the major energy-consuming sections of the ammonia unit, is the most viable opportunity to achieve this goal.

GV low-energy CO₂ removal process

The GV low-energy process is a well-known technology applied in 65+ new and/or revamped units all over the world. The CO₂ is absorbed by a chemical reaction with potassium carbonate forming potassium bicarbonate.

The process is based on the use of two strippers operating at two different pressures, the HP (higher pressure) stripper and the LP (lower pressure) stripper. A typical flow diagram is shown in Fig. 1.

In the HP stripper the operating pressure is selected in order to achieve a solution boiling point in the bottom of 127-130°C. In this way, most of the steam generated by reboiling the solution, instead of leaving the top of the stripper with the desorbed CO₂, is condensed providing heat for the rich solution fed to the top of the HP stripper. The external heat required for the



whole solution regeneration is supplied to the HP stripper only, by the cooling down of the process gas which develops stripping steam from the solution through the process gas reboiler(s) connected to the HP stripper bottom.

The LP stripper operates autogenously with recovered steam, which flashes from the incoming lean and semi-lean solutions, when they are depressurised flowing from HP to LP stripper, providing the required amount for the regeneration of the rich solution fraction fed to the top of LP stripper.

The heat content of this flashed steam represents the net energy saving of the GV low-energy process over the conventional CO₂ removal technologies.

By optimising the process parameters, the fraction of rich solution feeding the LP stripper can be easily assessed at about

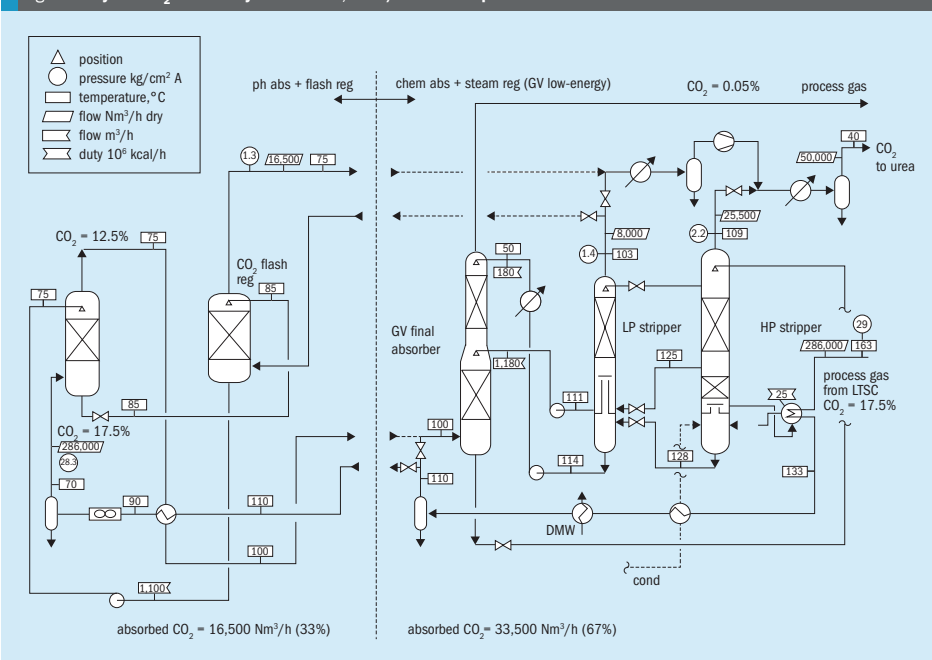
40% of the total circulating solution and consequently the external heat requirement for the solution regeneration in the HP stripper can be reduced to the same extent by at least 40%.

Features and the performance

The difference in the operating pressure between HP and LP (about 1 kg/cm²) allows a temperature drop of the solution entering LP by 18-20°C, ensuring efficient production of flashed steam at a higher rate than what is achieved with the ejectors multi-stage flashed steam, where the cooling is limited to 7-9°C.

The regeneration heat requirement for the GV low-energy process lies in the range 600-700 kcal/Nm³ CO₂, which is by far the lowest figure achievable by the HPC solutions processes.

Fig 2: GV hybrid CO₂ removal system for a 1,850 t/d ammonia plant



All the absorbed CO₂ is recovered at the battery limits at high pressure (up to 0.95 kg/cm² g) and at high purity (99.5-99.7% by utilising a flash tank on the rich solution line exit from the absorber).

The improved GV low-energy CO₂ removal process (GV hybrid scheme)

The revamping proposed by GV is an innovative CO₂ removal concept based on the integration of a physical CO₂ absorption and a chemical CO₂ absorption which is called GV Hybrid scheme. Fig. 2 shows a typical process flow diagrams for a 1,850 t/d ammonia unit.

The CO₂ physical absorption is implemented as a stand-alone unit upstream of the existing GV low-energy scheme to absorb a portion of CO₂ at higher partial pressure. Typically 30-35% of the CO₂ is easily absorbed from the process gas and is then stripped by flash without any need for stripping energy.

The existing GV low-energy system is kept as it is. All the existing equipment is

reutilised for the absorption/regeneration of the balance amount (65-70%) of CO₂ contained in the process gas.

Accordingly, the regeneration heat required is drastically reduced to 65-70% of the present specific energy consumption. The GV low-energy scheme is well referenced in India, with typical energy input of 600-700 kcal/Nm³ CO₂. Thanks to the GV hybrid scheme, the energy input can be lowered to 460-480 kcal/Nm³ CO₂, that is from 700 to 460-480 kcal/Nm³ CO₂. The proposed revamp also has good flexibility for further increase in plant capacity.

The revamping can be implemented in a very short time, typically during a planned plant annual turnaround, because the added physical absorption/flash regeneration unit can be erected during the operation of the existing CO₂ removal unit and hooked up within the normal annual turnaround time.

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

Benefits of the GV hybrid scheme

The benefits of the GV hybrid concept are the following:

- Installation of a small pre-absorber based on a physical absorption solvent, sized to absorb about 30% of the CO₂ from the process gas.
- The new added physical absorption/regeneration unit can be implemented as a stand-alone unit upstream of the GV CO₂ low-energy scheme.
- The existing equipment of the GV CO₂ low-energy scheme are totally reutilised with marginal or no modification at all.
- The tie-ins required for the hook up to the existing GV CO₂ low-energy scheme are very limited.
- The physical solvent is regenerated only by flash thanks to the high CO₂ partial pressure in/out the pre-absorber. However when required, the flash can be easily enhanced by feeding a CO₂ + H₂O stream taken from the GV steam regeneration section.
- The inventory/procurement of the new physical solvent minimal.

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NITROGEN+SYNGAS
ISSUE 337
SEPTEMBER-OCTOBER 2015

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Sourcing the right materials, in the right quantity, on time

Nitric acid plants face various challenges related to metallurgy and chemistry such as corrosion and therefore require special attention when it comes to which material grades are to be used. Special stainless steels with specific requirements have been developed to resist such environments but are sometimes difficult to locate and/or may result in long delivery times that could significantly impact the project or delay the repair. Material service provider for specialities and special products GEMACO discusses the importance of material selection.

Material selection for nitric acid environments depends on the acid concentration and operating temperature. Different grades can be used:

- **304 L** should contain no traces of Mo – destructive testing is used to check the chemical composition. This grade is difficult to find from stock and can only be produced in large quantities.
- **1.4306** has a higher nickel content than 1.4307 and therefore achieves better results in the Huey Test.
- **1.4306 S** is a typical 304L NAG (nitric acid grade) with very low carbon, silicon and molybdenum content. Excellent solution for concentrations between 50 and 70% if the temperature does not exceed 60°C, but quite impossible to find in small quantities.
- **304LN** with added nitrogen has better mechanical properties and can be used to reduce the wall thickness of reactors or absorbers, but should also be NAG.
- **WNR 1.4361** is a modified 304L with 18% Cr and 15% Ni, mostly used for highly concentrated nitric acid (98%) at high temperatures. The addition of 4% silicon creates a protective passive layer that reinforces the corrosion resistance. Different trademarks are: URANUS S1 from Industeel or ANTINIT A 610 from Böhler.

- **WNR 1.4335** is a heat resisting 310 with 25% Cr, 20% Ni, low carbon, low phosphorus & low silicon, to keep a more stable austenite microstructure and avoid intergranular corrosion. Probably the best solution in boiling nitric acid solutions (with less than 70% concentration). This grade is also called, for example, 2RE10 from Sandvik and URANUS 65 from Industeel.
- **WNR 1.4362** (SAF 2304 from Sandvik or URANUS 35 N from Industeel) is a duplex that also gives very good results, mainly when problems are caused by chlorides.

Other solutions like aluminum, titanium, niobium or zirconium exist but are more difficult to weld.

Each turnaround, revamp and debottlenecking project is different due to the metallurgy and chemistry involved. Even when the best material is bought, major problems can occur during fabrication and erection because forming, bending, welding, PWHT etc. can have a detrimental impact on the quality of the material if these operations are not performed correctly.

It has been experienced that a coarse grain size may have a negative effect on the corrosion resistance of the stainless steel. Preferably the grain size number according to ASTM E112 should be at least 5.

GEMACO proposes different options with specific capabilities and developed

solutions to deliver the the right material at the right time, for example:

- materials required urgently to repair or modify an installation;
- complete packages including different grades and different shapes;
- tailor made products, customised or machined pieces according to drawings;
- technical & logistic assistance;
- support from a services provider.

GEMACO covers a complete range of products including plates and sheets, pipes and tubes, bars, raw material for forgings etc. in many shapes and conditions, combining mill advantages with stock flexibility by using its own material to:

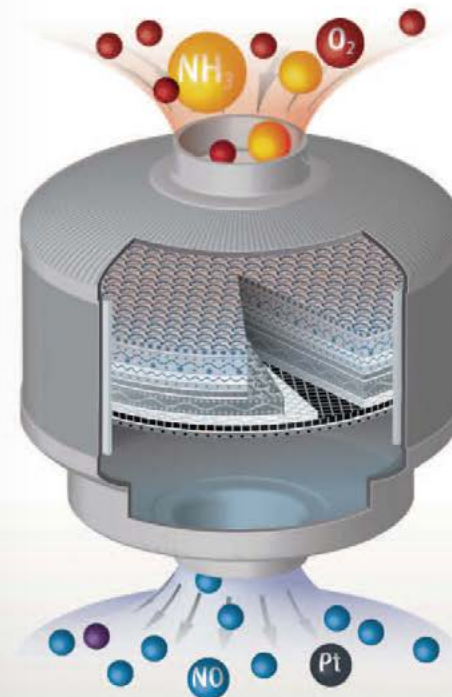
- anticipate fabrication of fittings during production of pipes and so reduce the delivery time;
- manufacture bendings with special radius, machined pieces, isometrics and spools, or special fittings realised according to customer specifications and drawings;
- provide items with smaller quantities or accept changes during erection or shutdown of the plants (no delay, no stock surplus);
- deliver spare parts after erection and during the cycle of life of the installation.

All of GEMACO's material is from European mills and approved suppliers. ■

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Extending the life of molecular sieve beds

In this article **V K Arora** of Kinetics Process Improvements, Inc. presents the key lessons learned to improve the life of molecular sieve beds in two large ammonia plants that were failing after less than half the expected life span of 60+ months, mainly due to excessive pressure drop build up. A holistic approach greatly helped in identifying the root causes. A similar approach can be applied in molecular sieve systems in most other industries to improve plant reliability.

Molecular sieve drying systems were added in two large ammonia plants as part of a revamp to provide the final synthesis gas purification by removing water of saturation, carbon dioxide and ammonia. Since the commissioning, the molecular sieve beds in both plants lasted significantly shorter run times compared to the typical expected life in excess of 60 months. The shorter life was due mainly to an excessive pressure drop build up over time.

The molecular sieve beds were configured in an up-flow mode with internal refractory lining and typical steps for absorption, regeneration and standby times. Each bed was loaded with type 10 x 20 molecular sieves.

The up-flow configuration is not the usual design for molecular sieve systems in ammonia plants and initially this was considered to be the main reason of the problem by the suppliers.

Following the premature replacement of four charges of molecular sieve beds, a detailed study was commissioned to review and analyse all possible causes of the short life span. A holistic approach of the complete system identified several other relevant and cost effective solutions besides a detailed review of the up-flow configuration.

Observations during inspection

The following key observations were made during the inspection of molecular sieve vessels before the change out of beds:

- caking of the bottom few feet of the beds;
- damage of the top and bottom insulation screens;

- pulverisation of the desiccant at the top of the beds.

Study methodology

Initially, the customer worked through the recommendations of the various molecular sieve suppliers but the problem persisted with two consecutive charges of molecular sieves. Suppliers mainly insisted on reversing the flow as the solution to the problem. At this point, the customer engaged KPI to provide an independent review and recommendations before implementing any of the changes.

KPI followed a holistic approach in reviewing the complete system design within and around the molecular sieve beds along with the inspection reports and the operating history to identify all the potential causes.

To support a thorough analysis of the system, KPI independently developed suitable models to verify the existing design of molecular sieve beds and the complete system with further review of alternative practical options.

The model provided the estimates of minimum fluidisation velocities, pressure drops, channelling, regeneration heating/cooling time and flow requirements using different sizes and types of molecular sieves with different volumes of mono/composite bed combinations and different regeneration gas compositions.

After verifying the existing design and related issues through the model, various alternative combinations were simulated to check if the problem could be mitigated without any changes to the current flow configuration.

During the study, KPI also gathered relevant inputs from molecular suppliers to further verify the results before putting together the recommendations.

Study findings

Based on the initial review and evaluation, the study findings indicated a combination of factors contributing to an excessive high pressure drop build up in the molecular sieve beds resulting in shorter life. The key contributing factors identified are listed below:

- incipient fluidisation during adsorption in the up flow mode
- upstream separator limitations resulting in liquid carry over
- under regeneration
- freezing/thawing of bed
- mal-distribution and bed channelling

Incipient fluidisation during adsorption in the up flow mode could potentially result in particle breakage and dusting of molecular sieves, particularly in the top portion of the bed which could contribute to pressure drop build up. KPI estimated as much as 83% of the minimum fluidisation velocity, which was a sufficient cause of concern as a contributor to the higher pressure drop.

Caking of the molecular sieve bed in the lower few feet was observed in most of the beds. Liquid carry over was suspected. The lower part of the bed being the wettest and the weakest will be prone to the most damage to sieves especially with potential liquid carry over and contaminants likely to cause agglomeration into clumps as

observed in the beds. Further, the smaller particle size of type 13X sieve does not provide the needed robustness and stability in the bottom of the bed for an up flow configuration.

A review of the upstream separator design indicated the following limitations in the upstream separator;

- undersized feed and vapour nozzles;
- inadequate demister pad.

The upstream separator is located upstream of the molecular sieve vessels.

The estimated high velocity through the feed nozzle at the operating loads with direct impingement on the existing baffle could also create a droplet shatter generating significant entrainment of much smaller droplets (< 10 microns) and uneven distribution leading to liquid carry over, which will have a detrimental effect on the sieves as these droplets will likely act as a hammer in the bottom sieves resulting in breakage, higher pressure drop and potential agglomeration due to over-saturation. The liquid carry over could also be a potential source of contamination of sieves further affecting its life.

The existing separation device and internals in the upstream separator were considered inadequate to efficiently capture the smaller droplets in the single digit micron size range.

Based on the bed configuration and operating loads and regeneration flow rate and temperature, the seven hours heating time was estimated to be grossly insufficient. KPI estimated about 14 hours heating time was needed for adequate regeneration, which was further verified through vendors.

From the operating data, it was noticed that the bed temperatures tend to fall below the freezing point of water to as low as 26°F (-3.3°C) after depressurisation. Even though sieves are suitable to handle such low temperature but the water freezing and subsequent thawing/revaporisation by quick heating in the molecular sieve pores may potentially result in breakage of the particles adding to the pressure drop problems.

The following additional concerns were listed for potential mal-distribution and channelling as contributors to pressure drop build up:

- absence of ceramic balls either on top or bottom of the bed – the absence of ceramic balls will result in an uneven flow distribution besides the potential plugging of the bottom screen which will

not only worsen the flow distribution but will also lead to screen damage due to the resulting higher differential pressure of channelling;

- liquid carry over coupled with particle attrition/breakage will further worsen the flow distribution leading to bed channelling and higher pressure drop.

Mitigation options

Mitigation options were considered for the molecular sieve beds, upstream separator and flow configuration.

Molecular sieve beds

- Increase the regeneration time.
- Slow down ramping of temperature to minimise thermal gradient and potential spalling of sieves with quick vaporisation.
- Replace the 13X pellets with 4A type beads to reduce the incipient fluidisation and to provide robustness and stability of operation
- To avoid bed temperature going below freezing and subsequent thawing, marginally increase the feed temperature by a few degrees, subject to syngas compressor limitations, if any, and slow down the depressurisation rate.
- Install ceramic balls with floating mesh and a hold down grid to reduce the effect of incipient fluidisation
- Consider using a composite bed to mitigate the shortcomings of the up flow design (for adsorption), e.g. use a composite bed-1/8" at the bottom (75% vol) and balance 1/16" at the top (25%) with the advantage of minimising the incipient fluidisation and lower pressure drop through the bed. However, a larger regeneration flow along with a larger regeneration heater with more steam consumption may not favour this option

Upstream separator

Modify the suction drum while retaining the vessel and its nozzles:

- install an even-flow feed distributor to mitigate the effect of undersized feed nozzles;
- replace the existing demister pad with a higher efficiency demister or a combination of vane and demister pad to capture smaller droplets.

A properly functioning upstream separator provides the least expensive insurance for sustained performance of the molecular sieve system.

Change flow configuration

To avoid the addition of a regen exchanger and additional steam and regen flow as noted with the composite bed option, reversing the flows (meaning adsorption and cooling down flow and heating up flow) remains another option. This option will also require changes to piping, instrument settings, control logic and its testing along with a Hazop which needs to be carefully reviewed and engineered. This may also require a longer down time.

Recommendations

As a result of the detailed study and practical considerations, the following recommendations were made and carried out in both ammonia plants:

- no changes in the up-flow configuration are warranted;
- modify the upstream separator internals with an even flow distributor and an efficient demister;
- provide heat tracing at the inlet of the molecular sieve beds;
- increase the regeneration heating time;
- marginally increase the feed inlet temperature to molecular sieve beds;
- replace the existing type 13X molecular sieve with type 4A molecular sieves;
- install ceramic balls in the top and bottom of the beds along with floating mesh screens and a hold down grid;
- reduce molecular sieve bed volume.

Implementation and performance

Following the review of the study, the plant decided to implement the recommendations along with a change of internals of the upstream separator in both ammonia plants.

KPI carried out the engineering and supplies of the recommended internals as custom designed. Engineering including custom design/fabrication were completed on an urgent basis within three months to meet the turnaround schedule of the plant. They were successfully installed and fitted without any issues.

Following the implementation of the recommended changes, all four molecular sieve beds have been performing well for nearly 40 months on the same charges. Based on the lower pressure drop trend since the operation of the modified system, the beds are expected to last for many more years before their replacement. ■

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GBP 425; USD 850; EUR 655

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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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BCInsight

Published by: BCInsight Ltd
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NITROGEN+SYNGAS
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