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SULPHUR

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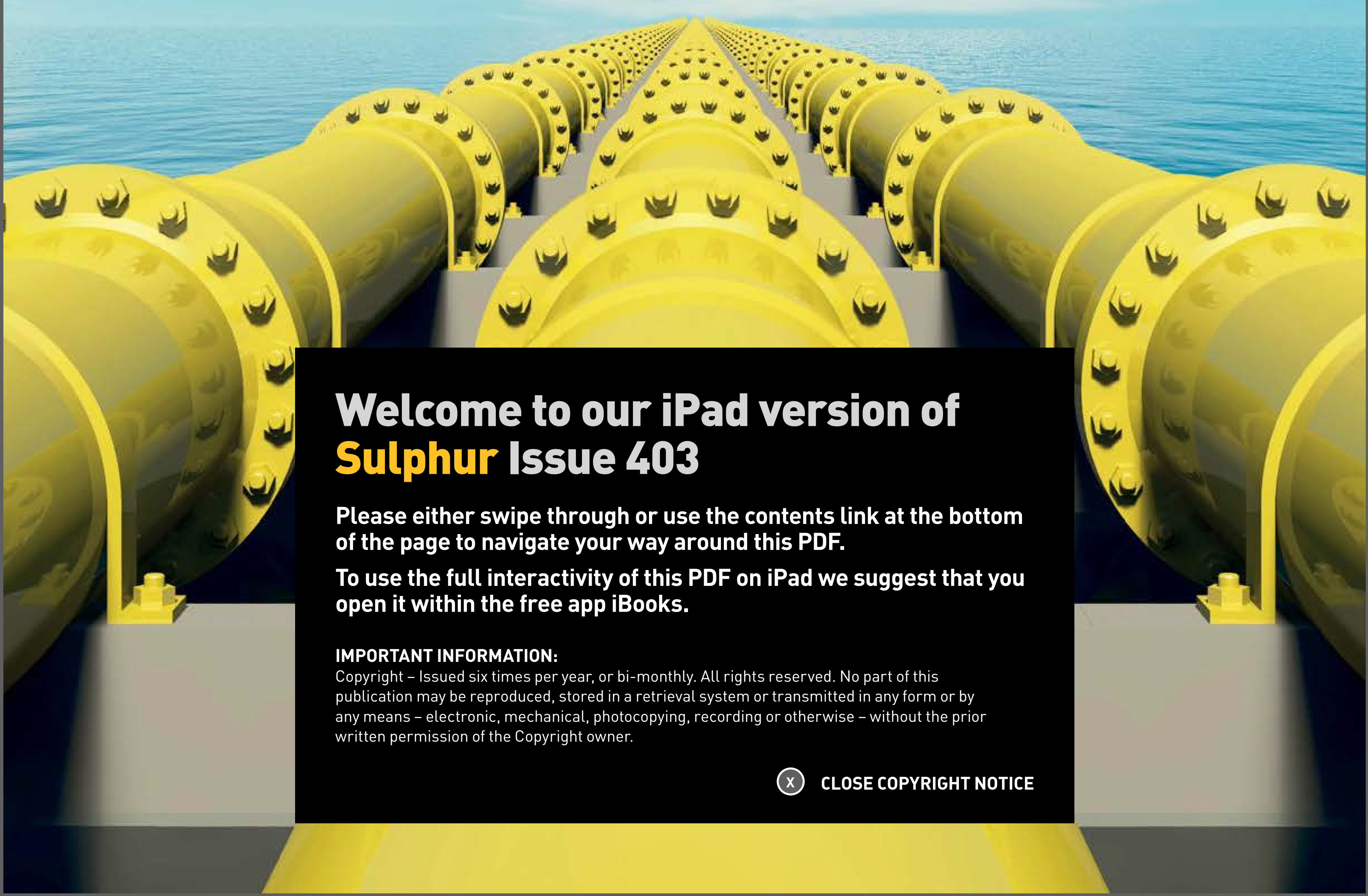
Acid demand for rare earths

The road to sustainability

Acid mist elimination

Amine plant commissioning



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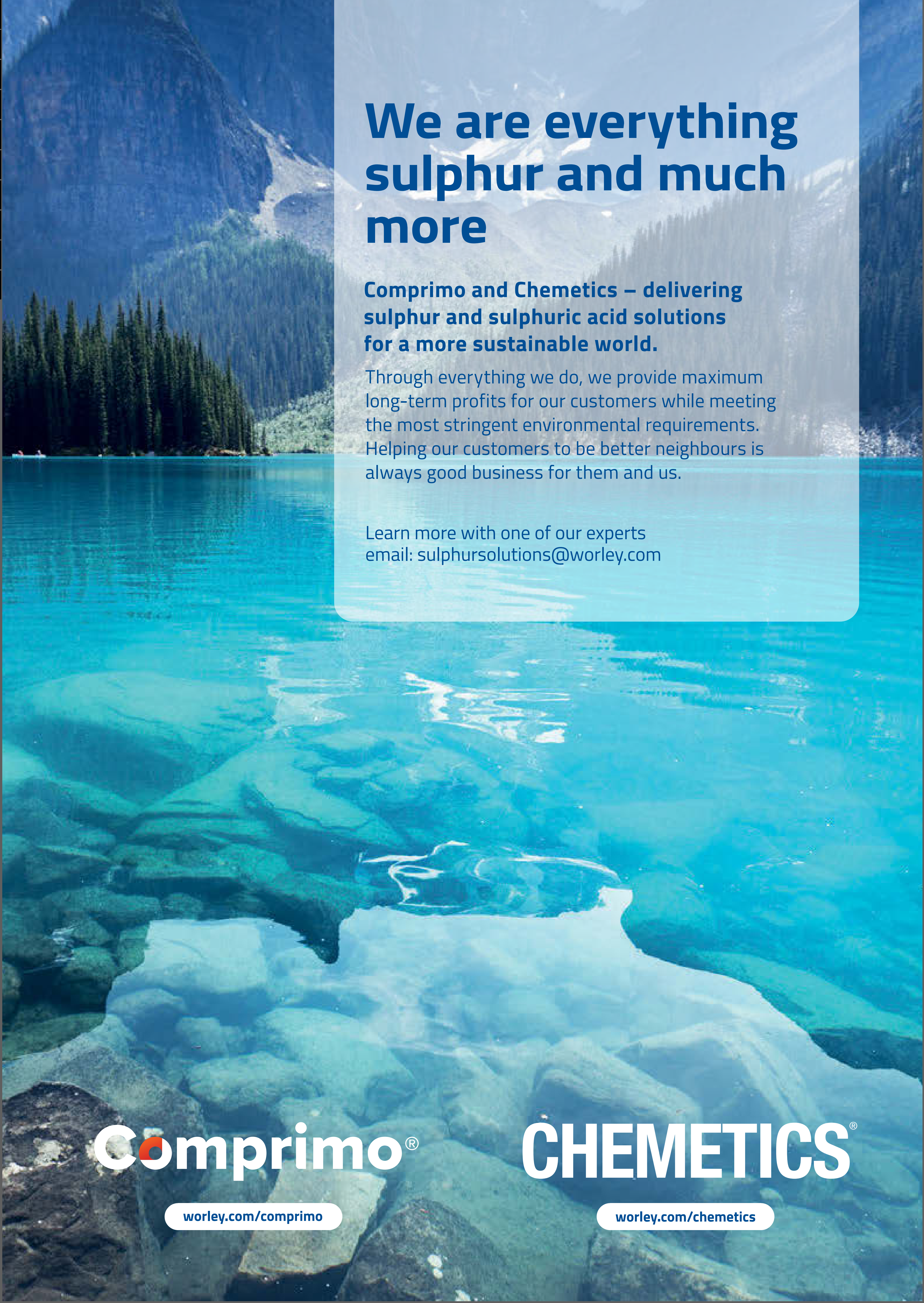

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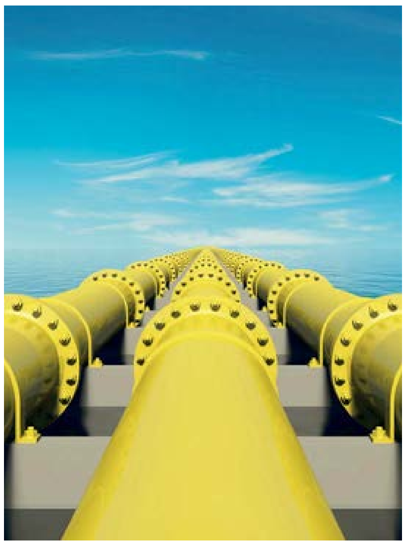

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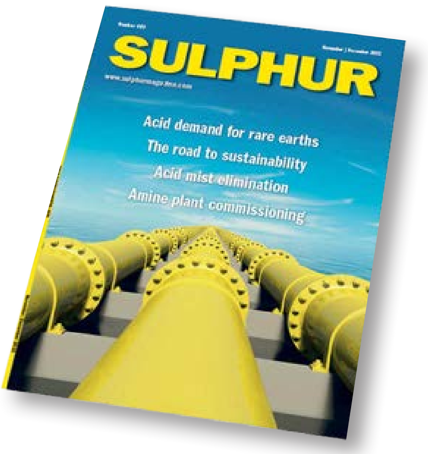
BCInsight

Editorial

Back on the rollercoaster



Sulphur markets suffered a correction in July-August that was more of a collapse; from $500/t to less than $100/t. Though it seems to have been something of an over-correction, and prices have moved back up since then, it is one of the most extreme price swings that sulphur has ever seen, comparable to the peak and precipitous fall in 2008. Indeed, at a time when commodity prices of all kinds have seen extremely high levels of volatility, sulphur has been more volatile still than just about all of them.

Many factors seem to have conspired to cause this. On the run-up, the war in Ukraine has obviously made export of sulphur from Russia much more difficult, though prices were climbing long before the war due to tight supply more generally. And on the fall, the decline seems to have been driven particularly by the phosphate industry, with prices falling rapidly in that sector a few weeks in advance of sulphur as demand failed to materialise. CRU estimates that world phosphate demand will see a fall of 9% in 2022 compared to 2021. Difficult planting weather has been a contributing factor, but high phosphate prices another – a knock-on effect of the gas crisis in Europe which has driven ammonia, one of the key inputs into MAP and DAP, to record price levels.

> **"For sulphur it probably means more volatility.**

But underlying all of this is the slowdown in the Chinese economy. China has dominated every commodity market for the past two decades as its rapid industrialisation saw record growth. The covid pandemic and a heavy-handed response to it has certainly played its part, but, moreover, China is also now facing the kind of demographic cliff that Japan encountered in the 1980s and 90s. Coupled with over-building of capacity in just about every sector, and an often unheralded pivot towards cleaning up the environmental mess that the country's industrialisation has caused, this has led to industries being forced to close, rapidly rising debt and a collapse in the real estate sector symbolised by the default and near collapse of property giant Evergrande; almost a Lehman moment for China. Climate change is also playing its part, with heatwave and drought shutting down hydroelectric power. Demographics and market saturation mean that China's economy has been slowing for a decade, from the peak growth rates of 14% in the late 2000s to around 6% pre-covid. The covid years, with the 2020 freeze caused by lockdown and the resulting rebound in 2021 averaged 5.2% between them. But this year the forecast is somewhere less than 3%, and that spells trouble for all of us.

This year's energy price crunch, a by-product of the Ukraine conflict, is already leading to recession in Europe, and though it is much better insulated by domestic production and consumer spending, there is a chance of it doing so in the US. A slowdown in China, the world's factory, will only make things tougher. And for commodity markets it means some leaner years ahead before growth can take off again elsewhere. Lower industrial growth means less demand for copper and nickel, which have been major drivers of sulphuric acid production and consumption. Lower demand for oil and gas means less sulphur being recovered, and possibly explains OPEC+'s decision to tighten oil markets in October. For sulphur it probably means more volatility, as the timing of expansions and contractions in various producing and consuming markets are unlikely to be simultaneous. At CRU's recent Sulphur and Sulphuric Acid Conference in The Hague, John Bryant of The Sulphur Institute advised sulphur buyers to get their supply chains in order, as there are undoubtedly choppy waters ahead, and it's advice that might be well taken by all sectors of the commodity industries.

Richard Hands, Editor

Price Trends

MARKET INSIGHT

Meena Chauhan, Head of Sulphur and Sulphuric Acid Research, Argus Media, assesses price trends and the market outlook for sulphur.

SULPHUR

Global sulphur prices have been on the rise following a collapse during the back end of the third quarter. There appears to be further room for prices to firm through November, underpinned by expectations of a slight deficit during the month. Liquidity in the processed phosphates market has been reducing, with prices expected to ease further in some regions going into the new year.

Contract negotiations for fourth quarter delivery to north African buyers were reported ranging $103-130/t c.fr. This includes supply from the Middle East and Central Asia. Reduced volumes of crushed supply are expected to flow from Central Asia through the remainder of the fourth quarter following an explosion on a bridge that links Russia to Crimea on 8 October. OCP Morocco increased sulphur purchases once it secured the full volume in an Ethiopian tender to buy NPS. Tenders to South Asia were also secured. OCP has earmarked 4 million tonnes of fertilizers for Africa in 2023, double the volume in 2021. We currently expect sulphur demand to rise by over 2 million t/a in 2023 on this year, leading Morocco to become the top global sulphur importer.

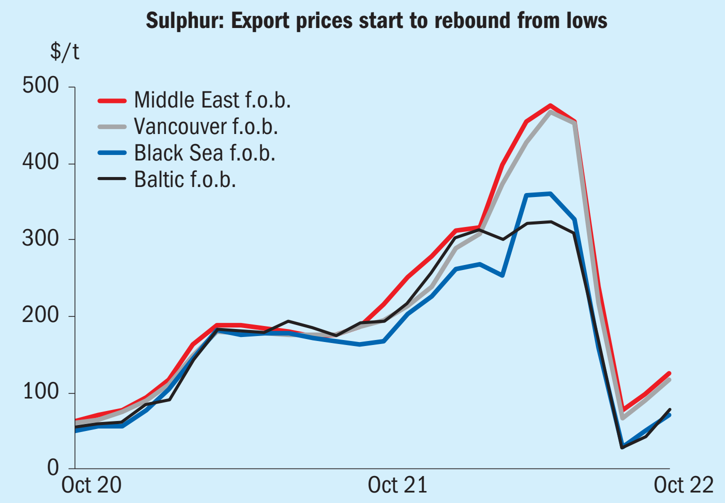
Strikes in sub-Saharan Africa meanwhile have been disrupting product moving from Zambia to the DRC. The National Union for the Protection of Truckers in the DRC blocked freight trucks from crossing the border into Haut-Katanga and Lualaba over 5-10 October. Drivers in these provinces were protesting against violent crime at roadblocks, against the $50-150/truck tolls imposed by local communities, and against the presence of unregistered foreign workers. Sulphur inventories at ports in Africa have been a topic in the market, with estimates of high inventories at high prices alongside the logistical challenges.

Average Middle East prices have increased by $46/t between August and the beginning of November 2022 at $124/t f.o.b., but are around $188/t lower than prices at the start of the year. Kuwait's KPC set its October sulphur lifting price at $105/t f.o.b., up by $10/t from the September price. ADNOC set its October official sulphur price (OSP) for liftings to India at $103/t f.o.b. Ruwais, up by $11/t from the September price. Meanwhile Muntajat set its October Qatar sulphur price at $104/t f.o.b. Ras Laffan/Mesaieed, and announced its November price at $149/t f.o.b., up by $45/t on the October price. This marks a continued uptick with a $72/t increase since the month of August. This is indicative of the market direction, with momentum for this to continue in the short term. The November QSP implies Chinese delivered prices at $178-183/t c.fr based on freight rates at the end of October of around $29-31/t to south China and $33-34/t to Chinese river ports.

The China c.fr all forms range was assessed by Argus at $60-175/t c.fr at the end of October, with the low end reflecting molten product and the high end granular sulphur. Average prices have increased by around $31/t since August, in line with market demand and fob values trajectory. China imports were broadly stable in January-September 2022 compared with a year earlier at around 6 million tonnes. Shipments from South Korea continue to dominate this year at just under 900,000 t in the period while the UAE was the second largest supplier at close to 700,000 t. Projects expected to impact the short-term view for new sulphur capacity in China include PetroChina's Jieyang refinery and Shenghong Petrochemical's Lianyungang refinery. The rise of domestic sulphur production continues to impact the forward view for import demand. A decrease in imports is expected in 2023 as further domestic capacity is brought online.

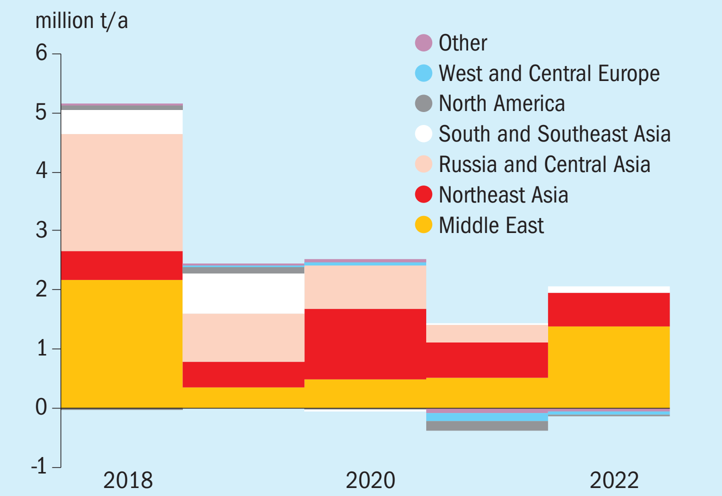
Over in the US, fourth quarter Tampa molten sulphur contracts settled at a drop of $262/long tons to $90/lt delivered. This was the lowest price since the fourth quarter of 2020. The increase in production alongside reduced demand from the processed phosphates sector because of demand destruction and technical issues were factors in the drop. US production in January – August 2022 totalled 5.3 million tonnes, 450,000 t/a higher than the same period a year earlier, according to USGS data. The upward trend has been driven by a recovery and improvement in fuel

Fig. 1: **Sulphur export prices, October 2020 to October 2022**



Source: Argus Sulphur

Fig. 2: **Global sulphur capacity changes by region**



Source: Argus Sulphur Analytics

demand following global pandemic related reductions in 2020-21. Sulphur recovery was also healthy through the rest of the third quarter. Our current expectation is for 2022 production to total 8.2 million t/a, similar to levels last seen in 2019, although we do not expect oil-based production to return to pre-2019 levels in the outlook.

SULPHURIC ACID

Global sulphuric acid prices have continued to deteriorate in recent months, although signs of stability started to emerge in October. Major contract negotiations remain under way at a time when liquidity has been limited, leading to some stability in key prices in the first half of October. Demand remains a concern for the short-term view but with the recent rebound in sulphur prices, acid prices are expected to remain stable to firm. The downstream processed phosphates sector has been the main concern on the demand front. Demand destruction in recent months will impact projected consumption levels for the remainder of the year. In Japan and South Korea, the upturn in sulphur prices led to smelters awaiting firmer acid f.o.b. prices at the end of October before concluding deals, with incoming bids understood to be unworkable.

Average northwest European acid prices have dropped by over $110/t between August and the end of October down to $40/t f.o.b., around $190/t below prices at the start of the year. The energy crisis in Europe continues to affect operating rates at smelters. Nyrstar's Budel zinc smelter in the Netherlands remains offline operations were halted in mid-August because of high energy costs. Nyrstar is likely to maintain this course of action into the winter with the increasing uncertainty around energy prices. In August Nyrstar said its Auby site in northern France would continue "at the curtailed production levels announced last year". Shutdowns at Umicore in Belgium and at Zijin Bor in Serbia are contributing to further tightness in smelter acid during the fourth quarter. Meanwhile Glencore was expected to put its zinc smelter at its Nordenham plant in northern Germany under maintenance beginning 1 November, because of high energy costs. Some major European producers finalized fourth quarter smelter acid contracts leading the range to be assessed at €146-176/t c.fr. This reflects rollovers and a drop of €10-15/t in some cases.

A fire at Mejillones port in Chile has caused concerns over port logistics including the unloading and storage of sulphuric acid. The full impact is uncertain with another terminal still operational. The import demand outlook for Chile is unclear with mixed views on when operations will be back to normal. Some industry sources expect a reopening at the end of November, while others consider this timeline to be optimistic and expect a year end resolution. The acid deficit for 2022 is expected to reach 3.2 million t/a, dropping slightly next year based on the supply and demand balance. Contract discussions for 2023 are continuing with freight still a core factor affecting the short term forward view for acid. Freight from South Korea/Japan to Chile was estimated at $150-160/t at the start of November.

Codelco has lowered its copper production guidance for the year after output and profits fell sharply in the first nine months of 2022. Codelco produced 1.06 million tonnes of copper in January-September, down by 10.4% on the year, according to the company's most recent filing. Falling production was driven by lower grades and recovery rates in Ministro Hales, and lower ore grades and a drop in recovery rates at copper concentrator plants in Chuquicamata and El Teniente. Problems at Chuquicamata smelter also impacted output. Codelco will carry out major maintenance at the smelter in November.

Chinese sulphuric acid exports are still expected to reach record levels in 2022 with trade data showing a 74% increase in the January-September period on a year earlier at 3.1 million tonnes. Chile, Morocco and India were the top three markets so far this year, absorbing 2.2 million tonnes of Chinese exports combined. A slower fourth quarter is expected but total exports are forecast at close to 4 million t/a. In the year ahead, we would expect exports to rise, but domestic demand will play a role in availability. Uncertainty remains around export restrictions on processed phosphates for 2023, a return to more regular trade would increase sulphur and sulphuric acid consumption in the country, potentially absorbing some of the surplus in the market. ■

Price Indications

Table 1: **Recent sulphur prices, major markets**

Cash equivalent	June	July	August	September	October
Sulphur, bulk ($/t)					
Adnoc monthly contract	485	425	85	92	103
China c.fr spot	450	150	120	150	165
Liquid sulphur ($/t)					
Tampa f.o.b. contract	481	352	352	352	90
NW Europe c.fr	430	380	380	380	123
Sulphuric acid ($/t)					
US Gulf spot	238	188	188	150	150

Source: various

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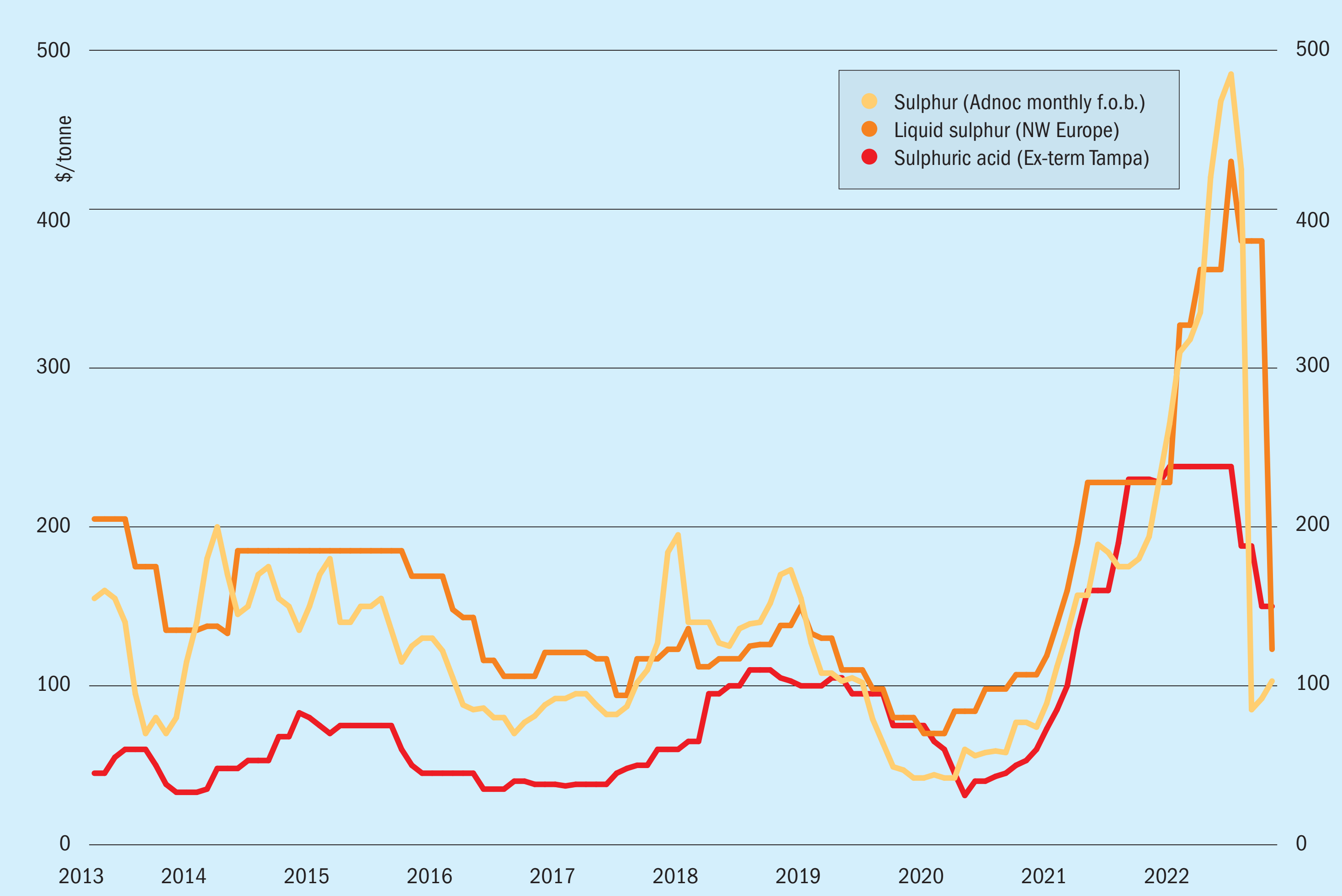
Market Outlook

Historical price trends $/tonne



Source: BCInsight

SULPHUR

- New supply-side capacity additions in 2023 will increase export availability from the Middle East. Projects have already been ramping up in Qatar, Saudi Arabia and Kuwait.
- Phosphates-based sulphur demand is expected to see some recovery in 2023 following demand destruction this year. This should mean increased sulphur import demand in key markets.
- The ongoing Ukraine crisis is a significant uncertainty for the outlook, particularly because of Russian sulphur trade being hampered by economic and financial sanctions. Two tier pricing is expected to remain in place for product moving from the region.
- Strength in the nickel market as demand for battery materials continues to rise will impact sulphur trade flows. Indonesia nickel-based demand will see further increases with supply needed for the fourth quarter. The year ahead also looks robust for trade to the country as HPAL projects continue to ramp up.
- **Outlook:** Global sulphur prices will continue to rise with the potential to stabilise towards the end of the year, another rebound is likely at the start of 2023 but much will hinge on Chinese buying activity in January. The year ahead should see less dramatic increases and decreases in prices based on the current view for supply/demand. The second half of 2023 is expected to be a deficit market, likely supporting another price uptick.

SULPHURIC ACID

- Energy costs will continue to impact operating rates at both suppliers and end users in Europe. Tighter availability of smelter acid has been a feature of the market this year and is likely to persist into the new year.
- Downstream operations in Europe with associated sulphur burners are at risk because of a looming threat of recession and slowing demand in some sectors. Reductions in operating rates will impact acid consumption. In some cases, burners are operating at higher levels for energy generation.
- Availability of acid from China is expected to drop on 2022 levels next year but is forecast to remain over 3 million t/a. Projects adding new acid capacity in the short term in China include Nanguo Copper and Daye Non-Ferrous Copper.
- **Outlook:** Developments in the freight market will be key to price direction for sulphuric acid in the short term. Expectations are for prices to rebound in the short term but a ceiling is likely from the more bearish view for processed phosphates. Uncertainty prevails around Chilean import demand for the remainder of the year but a decrease in demand in 2023 points to lower average prices compared with the levels achieved this year.

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Sulphur Industry News

WORLD

OPEC+ agrees output cuts

At the organisation's first face to face meeting since covid, in Vienna in early October, OPEC+ ministers agreed to cut global oil supplies by 2 million bbl/d in November. OPEC+ is a group of 24 oil-producing nations, made up of the 14 members of the Organisation of Petroleum Exporting Countries (OPEC), and 10 other non-OPEC members, including Russia. In a statement, the group said the decision to cut production was made "in light of the uncertainty that surrounds the global economic and oil market outlooks."

The move comes in spite of pressure by the US and European governments to keep production at current levels, with threats of the imposition of a cap on Russian oil prices from December. Oil prices had been falling since their high point in June, and Brent crude had reached $85/bbl after peaking at $120/bbl due to rising interest rates and fears of global recession, as well as releases from the US Strategic Petroleum Reserve of around 680,000 bbl/d. Prices jumped back to $97/bbl after the announcement and have stayed at that level since, though the impact of the cut is likely to be muted, as many OPEC members had been having trouble maintaining even existing quota production, and the net supply cut is expected to be closer to 800,000 bbl/d to 1.1 million bbl/d.

UNITED STATES

New sulphur fertilizer plant

Jōb Industrial Services, an engineering, procurement and construction company serving the oil and gas, power, materials and chemical industries, has broken ground on a new green field fertilizer facility for Tessenderlo Kerley in Defiance, Ohio. The new plant will occupy 50 acres and is set to become operational in 2024. It will serve the eastern Great Lakes region through its distribution partners and will include terminals for rail cars and tanker trucks. It includes a liquid fertilizer plant to produce sulphur-based crop nutrition products.

Brian Fox, project manager, Tessenderlo Kerley, said "We are pleased to have selected Jōb as our EPC firm for this important project in Defiance, Ohio. We know they will be a great partner in the safe execution of our vision, building a state-of-the-art facility in an area with such a great and supportive community."

Martin Midstream sells Stockton sulphur terminal

Martin Midstream Partners has sold its Stockton sulphur terminal to Gulf Terminals LLC. The net proceeds of approximately $5.25 million will be used to reduce outstanding borrowings under the Partnership's revolving credit facility. Bob Bondurant, president and chief executive officer of Martin Midstream L.P., the general partner of MMLP, said:

"Over the last several years, the partnership has sought opportunities to strengthen our balance sheet and reduce outstanding debt to lower our leverage. As a result, we have successfully completed multiple non-core asset sales allowing us to focus on our refinery services business segments. While the sulphur business remains a strategic piece of our operations, the Stockton terminal was considered a non-core asset as it is geographically removed from our focus on the US Gulf Coast area where our primary sulphur assets are located."

Martin Midstream recently reported 3Q results which included a net loss of $28.0 million, including a $21.8 million inventory valuation write down, for the three months ended September 30, 2022, bringing the total for the first nine months of the year to a net loss of $10.0 million. Bondurant said that in the Partnership's Sulphur segment, both the fertilizer and sulphur groups faced pricing instability resulting in lower fertilizer sales volumes, as well as "unplanned maintenance expenses related to the marine assets deployed in support of the business." Sulphur Services made an operating loss of $6.7 million for 3Q 2022, including a $3.3 million inventory valuation write down.

EUROPEAN UNION

New sanctions to include sulphur recovery technology

In October the European Council adopted the EU's eighth package of sanctions against Russia following their announcement by the European Commission late September. The sanctions regime has been expanded to include bans on the import and export of many chemical products; including a large number of basic petrochemicals and inorganic chemicals, intermediates, plastics, fertilizers, and specialties. Fertilizer imports included in the new package include phosphates, potash, and NPK fertilizers, as well as nitrates. Hydrochloric acid, nitric acid, phosphoric acid, and sulphuric acid are also on the list, as well as methanol. The package also lays the basis for the required legal framework for the EU to implement an oil price cap envisaged by the G7 nations. The measures, also adopted by the UK, further include "refinery fuel gas treatment and sulphur recovery technology (including amine scrubbing units, sulphur recovery units, tail gas treatment units)".

INDIA

Nuberg to build SRU for IOC

The Indian Oil Corporation (IOC) has awarded domestic project management company Nuberg EPC the lump sum turnkey EPC contract to build an $80 million, 400 t/d sulphur recovery unit as part of the expansion of IOC's Vadodara refinery in Gujarat. The contract also includes construction of a control room and electricity sub-station for the refinery sulphur block. It form's part of the Petrochemical and Lube Integration Project at the Vadodara facility. Nuberg is also building a 1.5 t/d ultra-pure (fuel cell grade) hydrogen purification, compression, storage and dispensing facility at Vadodara.

Nuberg EPC says that it is using French technology for the project to 'future proof' IOC's environmental sustainability and augment its sulphur production capability. The plant is expected to be completed in 28 months from the award of the contract. A. K. Tyagi, Nuberg Engineering commented; "we are thankful to Indian Oil Corporation Limited for entrusting another turnkey project to our engineering capabilities and EPC services and solutions."

Collaboration on clean energy partnerships

A series of memoranda of understanding (MoUs) have been signed by Indian and US oil and gas companies including ExxonMobil to strengthen clean energy partnerships between the two countries, at a meeting in Houston convened by advocacy group the US-India Strategic Partnership Forum

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(USISPF), in partnership with the Consulate General of India. Aavantika Gas Ltd, a joint venture between the Gas Authority of India Ltd (GAIL) and Hindustan Petroleum Company Ltd (HPCL) entered into an MoU with Baker Hughes for emissions measurement and abatement solutions support. Another was signed between Engineers India Ltd (EIL) and UOP; UOP will assess EIL's tail gas treating technology for adoption in UOP's sulphur recovery projects on a global platform. An MoU was also signed between Indraprastha Gas Ltd and Baker Hughes to jointly evaluate opportunities in emissions monitoring and detection, hydrogen technologies and sustainability.

IRAN

New sulphur recovery capacity

The Isfahan oil refinery has completed the installation of a new diesel hydrotreater at a cost of $600 million to produce low sulphur diesel with a sulphur content of less than 10 ppm according to the Iranian Oil Ministry. The unit will boost sulphur output at the refinery by 300 t/d. The National Iranian Gas Company has further said that a new acid gas condensation tower has been completed at the Shahid Hasheminejad Gas Processing Company in Khorasan Razavi province. The new facility will help remove sulphur from acid gases in the gas plant that used to be burned off in flares, and will boost sulphur output by 11,000 t/a. It is also reported that the processing plant at the South Pars Gas Complex (belonging to phases 2 and 3) increased its sweet gas and sulphur output in the first half of the current Iranian year (March-September) compared with the same period of last year. Sulphur output was 59,000 tonnes for the six month period, 4% up on last year. According to the company, the unit has also produced 10 million cubic meters of gas condensate.

MALAYSIA

Technip to design Lang Lebah gas plant

Technip Energies has been awarded the front-end engineering design (FEED) contract for the Lang Lebah Onshore Gas Plant 2 (OGP2) project in Bintulu, Sarawak by PTT Exploration and Production (PTTEP). The contract covers the design of the onshore gas plant including the flow assurance of CO_2 capture, compression and transportation via pipeline up to the offshore wellhead platform, where it will be re-injected into the well. Gas coming from the Lang Lebah offshore field will be treated before being sent to the Malaysia LNG complex. Lang Lebah OGP2 is one of the key projects in the Sarawak Integrated Sour Gas Evacuation System (SISGES) development, and is expected to be the catalyst for further development of untapped sour gas resources off the coast of Sarawak.

"We are very pleased to have been selected by PTTEP for this landmark gas development in Sarawak. Bringing Technip Energies expertise in designing large scale gas plants with CO_2 capture and transportation, we are committed to making this project another successful milestone in our long-standing relationship with PTTEP and our history in Malaysia," said Loic Chapuis, SVP Gas & Low-Carbon Energies at Technip Energies.

Lang Lebah is an offshore sour gas field estimated to be up to 2 tcf in size. While most of the acid gas is carbon dioxide, hydrogen sulphide content is reported to be 0.5-1.0%.

MOROCCO

New sulphur handling project

OCP has awarded Bedeschi an EPC contract for the supply of three new automated storage facilities: two for fertilizer and one for sulphur, with a capacity of 300,000 tonnes of material. The new equipment will be installed at the Phosboucra complex, 30 km from the city of Laayoune, in the Western Sahara region. It forms part of OCP's 'Southern Axis' development of the complex.

Bedeschi says that its scope of supply consists of material handling equipment for the storage of imported sulphur in import and the storage of fertilizer for export. In particular, the company will supply, among other things, 3 trippers, 3 reclaimers and 6 conveyor belts with a capacity of up to 2,000 t/h. The equipment will be similar to the those already already supplied to OCP for the Jorf Lasfar plant in Morocco.

Bedeschi's handling facilities at Jorf Lasfar, Morocco.

GERMANY

Hydrogen process wins industry award

Clariant and its engineering and technology partner Technip Energies were presented with two industry awards for their *EARTH* technology. ICIS selected the technology as the "Best Process Innovation" in the ICIS Innovation Awards 2022. *EARTH* also won the "Best Refining Technology" category of the Hydrocarbon Processing Awards 2022 – a program that honours the downstream energy segment's leading innovations. Based on recuperative steam methane reforming, *EARTH* is a drop-in solution that enables a capacity increase in the production of hydrogen while contributing to energy savings and an improved CO_2 footprint.

In parallel, Clariant and Technip Energies reached another milestone by successfully installing *EARTH* technology at a large-scale hydrogen plant in one of Europe's biggest refineries. The loading of *EARTH* internals and catalyst in the existing reformer tubes was achieved within the scheduled turnaround period, resulting in a successful start-up this year. The revamp is expected to increase the plant's production capacity by up to 20%.

Created and patented by Technip Energies, *EARTH* combines a concentric tubular assembly in the steam methane reformer with a tailor-made structured catalyst, jointly developed with Clariant which improves the efficiency of hydrogen production. Compared to the performance of Clariant's traditional catalysts in a standard reformer, *EARTH* is proven to increase hydrogen yield by up to 20%, while decreasing CO_2 emissions by up to 10%, and reducing make-up fuel consumption by up to 50% per unit of hydrogen produced.

Sulphuric Acid News

UNITED STATES

CSB criticises refinery use of hydrofluoric acid

In its final report on the June 2019 explosion and fire at Philadelphia Energy Solutions in southwest Philadelphia, the US Chemical Safety Board has said that US refineries need to strengthen their safeguards surrounding the use of hydrofluoric acid, and has also recommended that the US Environmental Protection Agency take steps to improve its oversight of the chemical, which is used as an alkylation agent.

The incident occurred when a corroded pipe elbow ruptured, releasing process fluid into the refinery's hydrofluoric acid (HF) alkylation unit. During the incident, over two and a half tons of toxic HF were released, a 17 ton vessel fragment was launched off-site and landed on the other side of the Schuylkill River, and an estimated property damage loss of $750 million resulted.

CSB Interim Executive Authority Steve Owens said, "This is one of the largest refinery disasters worldwide in decades in terms of cost. the local community in Philadelphia fortunately was not seriously harmed, but given the refinery's location, it could have been much worse. This incident should be a wake-up call to industry to prevent a similar event from occurring in the future."

Of the 155 refineries currently in operation in the US, 46 operate HF alkylation units. The CSB is that HF is "one of the eight most hazardous chemicals regulated by EPA's Risk Management Program (RMP)" and says that the more widely used sulphuric acid route an "inherently safer design". Although sulphuric acid is highly corrosive and can cause skin burns upon contact, it remains a liquid upon release and does not present the same risk to surrounding communities as HF, which vapourises upon release and has the potential to travel offsite. The CSB recommends the EPA require refineries to conduct analysis of alternatives as part of the RMP. ■

Joint venture to make electronic-grade sulphuric acid

Martin Midstream Partners has entered into a joint venture agreement with Samsung C&T America, Inc. and Dongjin USA, Inc. to form DSM Semichem LLC. The joint venture will produce and distribute electronic-grade sulphuric acid using Martin's existing assets in Plainview, Texas and installing additional facilities "as required". The acid will meet strict quality standards required by the semiconductor industry. In addition to owning a 10% non-controlling interest in DSM, Martin will be the exclusive provider of feedstock to the sulphuric acid facility and, through its affiliate Martin Transport, Inc., will also provide land transportation services to end-users of the acid.

Bob Bondurant, President and Chief Executive Officer of Martin Midstream GP LLC, the general partner of MMLP stated, "We are excited to partner with Samsung C&T America, Inc. and Dongjin USA, Inc. in this unique opportunity to capitalise on the diverse and complimentary skillsets, operating expertise, and vast market knowledge of the three parties. The new facilities will incorporate technology currently being utilized to produce ELSA in Taiwan, which exceeds the quality of sulphuric acid being produced in the United States today".

Freeport in talks to buy Arizona copper smelter

Freeport-McMoRan is reportedly in talks with Grupo Mexico SAB to buy the latter's Hayden smelter, owned by its subsidiary Asarco. Freeport operates seven copper mines in the US including five in Arizona and is increasing operating rates in the country. An additional smelter would enable more refined production for the company at a time when domestic demand for the wiring metal is expected to grow and as the US looks to boost critical mineral supply chains.

BRAZIL

New acid plant for pulp mill

Brazil's largest paper manufacturer Klabin has successfully started up a new sulphuric acid plant supplied by Andritz at the company's Ortigueira plant in the southeastern state of Parana. The has the capacity to produce 150 t/d of commercial-grade sulphuric acid per day via sulphur burning combined with sulphur-rich off-gases. It serves the pulp lines at Klabin's Puma pump mill and makes the site completely self-sufficient in sulphuric acid by recycling sulphur from the waste streams, removing the need to transport hazardous cargoes to the site. Klabin says that the plant helps it control the sodium and sulphur balance and the sulphidity of the mill. As a result, less sulphate will now be discharged, improving the efficiency of input use at the Ortigueira plant. As the sulphuric acid plant meets stringent air emission limits, the process significantly improves the overall environmental footprint of the Ortigueira mill. The Andritz scope of supply included technologies on on EPCC basis for handling elemental sulphur, combustion of sulphur and concentrated non-condensable gases to form sulphur dioxide, and conversion of sulphur dioxide into concentrated sulphuric acid, as well as a flue gas treatment system.

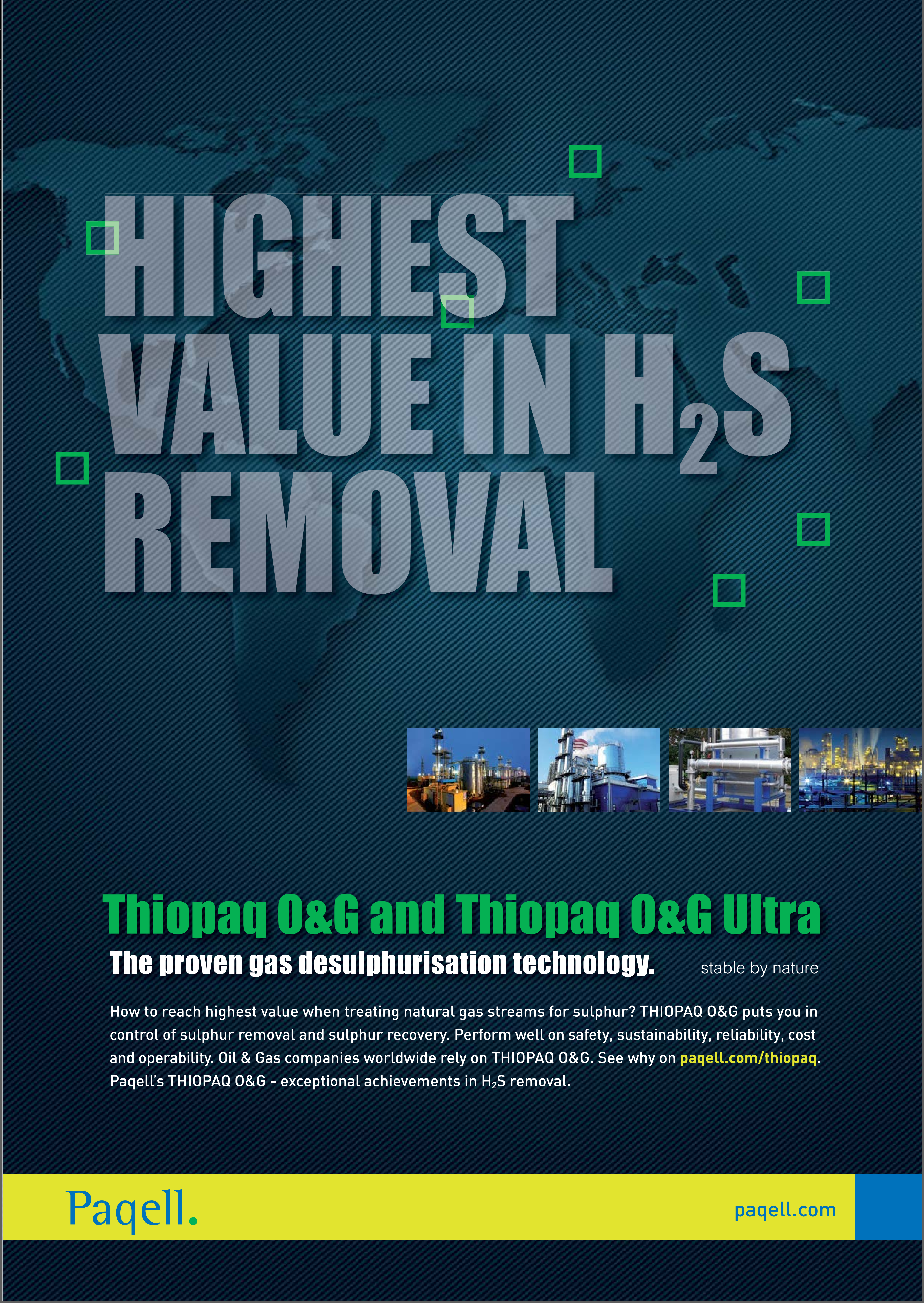
Klabin's Director of Projects and Engineering, Joao Antonio Braga, said: "operation of the sulphuric acid plant at the Puma Unit, Ortigueira, represents a significant advance in the circularity of the installation. The new plant allows the unit to be self-sufficient in sulphuric acid, with the additional option of selling any excess production to the market. This innovative technology, a first in this industry worldwide, supports our efforts to optimise productivity and is an important milestone in our ambition to achieve our sustainability goals."

DEMOCRATIC REPUBLIC OF CONGO

Outotec to supply direct blister furnace to Kamoa-Kakula

Kamoa Copper SA has selected Metso Outotec to supply a high-capacity direct blister furnace to the company's copper mining complex expansion project in the Democratic Republic of Congo. The value of the contract is believed to be between €30-40 million ($30-40 million). Metso Outotec's scope of delivery consists of key equipment and automation for the direct blister furnace designed for the production of blister copper in a single flash furnace without the need for separate converting stages. The 500,000 t/a copper throughput furnace will have the largest licensed flash smelting capacity in the world, according to Metso Outotec. The scope also includes intelligent safety and monitoring automation systems for the furnace.

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



Jyrki Makkonen, Vice President, Smelting at Metso Outotec, said: "Non-ferrous metals play a key role in the green transition, and a major increase in global copper production is required to support this transition. We are pleased to support Kamoa Copper in their ambitious expansion project, in which high capacity and reliable, sustainable processes play a vital role. Our collaboration has been excellent throughout the initial stages of the process, including the initial study work, basic engineering as well as pilot testing."

Upon commencement of Phase 3 production, Kamoa-Kakula will have a processing capacity in excess of 14 million t/a, with increased copper production capacity of approximately 600,000 t/a. Commissioning is expected at the end of 2024.

INDIA

Fertilizer subsidies double

The Indian federal government has doubled the budget continency for fertilizer subsidy for the post-monsoon (rabi) season. Combined subsidy across all nutrients was estimated at 519 billion rupees ($6.3 billion), more than double the previous estimate. The full year estimate is likely to be 36% higher than for the 2021-22 financial year. The government blamed high prices on international markets due to the Ukraine-Russia conflict and logistics issues relating to the covid pandemic. The subsidy will bring the cost of a bag of diammonium phosphate from 2,650 rupees ($32) to 1,350 rupees ($16.50). Most of the subsidy goes to urea, but the cost of phosphates, potassium and sulphur are also underwritten by the government. The government said that the move "will enable smooth availability of all P and K fertilizers to the farmers during rabi 2022-23 at affordable prices and support the agriculture sector. The volatility in the international prices of fertilizers and raw materials has been primarily absorbed by the Union government."

SWITZERLAND

Arkema to divest phosphorus business

Arkema says that it plans to sell its subsidiary Febex, which specialises in phosphorus-based chemistry, to Belgian group Prayon. Febex is a global supplier of phosphorus derivatives, including high purity phosphoric acid and sodium hypophosphite and derivatives, used primarily in electronics and the pharmaceuticals industry. Febex reported sales of around €30 million in 2021, employs 59 people, and operates a single site in Switzerland. The companies said that, by joining Prayon, Febex will benefit from the Belgian group's growth ambitions in this area. This deal, which is expected to be finalised in 1Q 2023, is subject to consultation with employee representative bodies in France and approval by the relevant Swiss authorities.

CHILE

Codelco's El Teniente copper mine, Chile.

Cochilco output falls

Chilean copper commission Cochilco's latest report shows that Chile's production of copper in the first six months of 2022 was down by 160,000 tonnes, 6.1% lower than for the same period of 2021. The agency said that the prices of mining inputs, including sulphuric acid for SX/EW leaching facilities, were to blame. The price of sulphuric acid was up 187% compared to 2021, the price of diesel fuel up 91%, concentrate freight and insurance 45% and electricity 9%. These costs also impacted other inputs into mining, such as tires, explosives, grinding balls and bars, chemical reagents, oils, lubricants, and spare parts, among others.

However, there are indications that this trend may have reversed during 3Q 2022. Antofagasta recently reported that copper output was 40% up in 3Q compared to 2Q 2022 after improved water availability helped output almost double at its Los Pelambres mine, though the company says that overall copper production for the current financial year will be 640-660,000 t/a, which is at the low end of its target range. Production to 3Q 2022 was 450,000 tonnes, down 17% on the same period for 2021. It projects that for the subsequent year, when construction work at the Los Pelambres desalination plant is set to be finished, output will rise to 670-710,000 t/a. Antofagasta shares have fallen by around a quarter over the past 12 months as pre-tax profits dropped by 62% to $680 million, and the company announced a cut in dividends after record earnings in 2021. Higher inflation and interest rates are causing a fall in commodity prices and an economic slowdown across many major economies, including China, where the company ships much of its iron ore. Production at the company's Centinela mine was 14% down on 2021, but output at Antocoya was around the same as last year.

CHINA

China tightening restrictions on imported copper concentrate

The China Nonferrous Metals Industry Association is consulting with domestic smelters on tightening standards on the presence of heavy metals within imported concentrates, including lead, arsenic, cadmium and mercury. The proposal would lower the maximum allowable arsenic content in copper concentrate to 0.4% from 0.5%; the level allowed in lead concentrate from 0.7% to 0.6%; and that for zinc concentrate lowered to 0.4%, compared with the current 0.6%. According to an estimate by the International Copper Study Group (ICSG), less than half of the world's copper concentrate has an arsenic content equivalent to or lower than 0.5%. The date for imposition of the new standards is believed to be late 2023 or early 2024. Last year, China imported 23.4 million t/a of copper concentrate, 3.6 million t/a of zinc concentrate and 1.2 million t/a of lead concentrate.

WORLD

Copper smelting activity down

Earth-i, which maintains satellite surveillance of up to 90% of copper smelter facilities worldwide, says that global copper smelting activity declined in October due to fears of a recession, weak demand and maintenance shutdowns. Smelting activity fell in all regions except North America, according to the company. The production index for China, the world's largest refined copper producer, fell for a fifth straight month in October, as tightness in scrap supply appears to be weighing on smelter utilisation rates. There is also reportedly weakness in China's nickel pig iron output. Thirteen of China's 31 NPI plants were inactive at the end of October as stainless steel demand remained weak. Meanwhile in Europe, nearly two thirds of capacity was

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

inactive due to a combination of a recession and prohibitively high electricity costs.

Elsewhere, Glencore said that its copper production was down 14% in the nine months to September 2022 at 770,500 tonnes, compared to the same period for 2021. The company said that this decrease was due to previously reported land access, geotechnical and processing constraints at Katanga, the basis change arising from the sale of Ernest Henry in January 2022, Collahuasi lower ore mined due to mine sequencing and lower copper units produced within Glencore's zinc business.

GERMANY

Smelter hit by cyber attack

Aurubis, Europe's biggest copper smelter, says that it was targeted as part of a wider cyber attack on the metals and mining industry on the night of October 28th which forced it to shut down its IT systems and disconnect them from the internet. Aurubis said in a press statement that the attack was "apparently part of a larger attack on the metals and mining industry," though it did not name other companies affected. Aurubis said it was able to largely maintain production even though it was forced to shut down numerous systems at its sites and disconnect them from the internet as a precaution. It added that the extent of the impact is being assessed, and that it is working with investigating authorities in Germany.

Phosphorus recycling from sewage

There is increasing focus on recovery of phosphate nutrients from sewage waste, both to avoid eutrophication in water courses and assist with the 'circular economy'. Now researchers from the Leibniz Institute of Freshwater Ecology and Inland Fisheries (IGB) claim to have made a breakthrough in phosphate recovery at municipal wastewater treatment plants. Phosphorus can be more easily recovered if it is present bound in salts such vivianite; an iron-phosphorus compound from which phosphorus can be relatively easily recycled. IGB investigated which factors promote the formation of vivianite and thus increase the amount of recoverable phosphorus, analysing the properties and compositions of sludge samples from 16 wastewater treatment plants, as well as the plants' process parameters, to determine the factors influencing vivianite formation.

High iron content proved to be the most important factor in favouring vivianite formation. High sulphur content, in turn, decreased vivianite formation. "There are sulphur-containing and sulphur-free precipitants. We were able to show by comparison that the use of sulphur-containing precipitants can increase the sulphur content in the sludge and thus counteract vivianite formation. The choice of precipitant can therefore have a significant influence on phosphorus recycling," said IGB doctoral student Lena Heinrich, lead author of the study.

Adjusting the conditions can make a difference: In the 16 wastewater treatment plants, the proportion of phosphorus bound in vivianite varied from around 10% to as much as 50%. This range shows the great potential to increase the yield of vivianite.

"For us as aquatic ecologists, the findings are very important because iron-containing precipitants can also be considered for restoration of lakes that are eutrophic, or polluted with nutrients. The efficiency of an iron salt addition is much greater if it results in the formation of stable vivianite in the sediment, which is then, perhaps one day, also available for the recovery of phosphorus," said Hupfer.

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

People

Topsoe has made a number of changes to its board. **Kim Saaby Hedegaard** has been appointed as the company's new Executive Vice President, Power-to-X. Hedegaard has served as interim Head of Power-to-X since May 2022. Before that, he held the position as Chief Operations Officer (COO). He joined Topsoe in 1999 and has since held various leadership positions within engineering, technology, and sales. Since 2017, he was responsible for Catalyst Production and Technology globally. He holds a MSc in chemical engineering from the Technical University of Denmark. He is replaced as COO by **Andreas Bruun Jørgensen**.

The company has also appointed **Morten Holm Christiansen** as interim CFO as his predecessor Philip Eickhoff is returning to the healthcare industry. Christiansen previously held the position of CIO and will maintain those responsibilities in parallel with his position as interim CFO. He has had a long career in Maersk and the Novo Nordisk Group as CFO.

Topsoe CEO, Roeland Baan, commented: "We are on a fast track to build a strong commercial position based on our decarbonization solutions, and I have no doubt that Morten with his extensive leadership experience and financial background is the right person to support the organization in delivering on our strategy, while we look for a more permanent solution. Philip [Eickhoff] has done a great job in building a strong foundation and team to help drive our transformation, and I want to thank him for his contribution and dedicated efforts for Topsoe the past two years. I truly wish him all the best in his future endeavours."

Chief Communications & Brand Officer **Kristine Ahrensbach** is also leaving Topsoe. Ahrensbach joined Topsoe in 2014 and was responsible for Marketing the first six years. In her place, **Kasper Westphal Pedersen** is joining Topsoe as Vice President of Communications & Brand and will report to Chief Human Resource Officer, Peter Kirkegaard. Pedersen has a track record of working with the sustainability agenda as a Communications executive. For the past seven years, he has worked as Director of Communications & Branding at Rambøll. Prior to that he spent almost ten years as communications agency executive with responsibility for clients within environment, energy and sustainable development, and he has previously worked as Press Secretary to the Danish Minister of Environment.

First Phosphate Corp. has announced the appointment of **Bernard Lapointe** to the advisory board of the company. Lapointe founded Arianne Phosphate Inc. in 1997 and served as its president until 2013. He holds a PhD in mineral resources from the Université du Québec à Chicoutimi. Before Arianne Phosphate, Bernard was director of the Fonds Minier du Saguenay-Lac-St-Jean, Quebec. He currently sits on the Board of Directors of several public companies in the resource and fertilizer sectors.

"Bernard Lapointe's decades spent developing the Arianne Phosphate project gives him immeasurable experience that will be made available to First Phosphate in establishing our best practices for internal operations and for environment stewardship," said John Passalacqua, CEO of First Phosphate. "I look forward to working closely with Bernard as we roll out First Phosphate's six-phase integration strategy within the North American and global LFP battery industry."

"I am excited about First Phosphate's development plan and its commitment to producing battery-grade phosphate through clean and environmentally responsible processing methods, for a consistent and ethical supply right here in Quebec," said Mr. Lapointe. "I look forward to bringing my experience in the phosphate industry to First Phosphate and to supporting the development of best practices for the business from the experience that I gained during my years with Arianne Phosphate."

Calendar 2023

FEBRUARY

1-3

SulGas Conference 2023,
MUMBAI, India
Contact: Conference Communications Office, Three Ten Initiative Technologies LLP
Tel: +91 73308 75310
Email: admin@sulgasconference.com

20-23

Laurance Reid Annual Gas Conditioning Conference, NORMAN, Oklahoma, USA
Contact: Lily Martinez, Program Director
Tel: +1 405 325 4414
Email: lmartinez@ou.edu

27 – MARCH 1

CRU Phosphates 2023 Conference,
ISTANBUL, Turkey
Contact: CRU Events, Chancery House,
53-64 Chancery Lane,
London WC2A 1QS, UK
Tel: +44 (0)20 7903 2444
Email: conferences@crugroup.com

MARCH

13-16

The 8th Sulphur and Sulphuric Acid Conference 2023,
CAPE TOWN, South Africa
Contact: Gugu Charlie, Conference Organiser
Southern African Institute of Mining and Metallurgy
Tel: +27 73 801 8353
Email: gugu@saimm.co.za

APRIL

2-5

2023 Australasia Sulphuric Acid Workshop,
BRISBANE, Australia
Contact: Cathy Hayward, Sulfuric Acid Today
Tel: +1 (985) 807 3868
Email: kathy@h2so4today.com

MAY

DATE T.B.A.

TSI Sulphur World Symposium 2023,
EDINBURGH, UK
Contact: Sarah Amirie, The Sulphur Institute
Tel: +1 202 296 2971
Email: SAmirie@sulphurinstitute.org

8-12

REFCOMM 2023, GALVESTON, Texas, USA
Contact: CRU Events
Tel: +44 (0)20 7903 2444
Email: conferences@crugroup.com

JUNE

DATE T.B.A.

45th Annual International Phosphate Fertilizer & Sulfuric Acid Technology Conference, CLEARWATER, Florida, USA
Contact: Michelle Navar,
AIChE Central Florida Section
Email: vicechair@aiche-cf.org
Web: www.aiche-cf.org

NOVEMBER

6-8

CRU Sulphur & Sulphuric Acid Conference 2023, NEW ORLEANS, Louisiana, USA
Contact: CRU Events
Tel: +44 (0)20 7903 2444
Email: conferences@crugroup.com

Transporting sulphur safely

PHOTO: ETIHAD RAIL

Sulphur is a relatively safe and inert solid. However, it has a number of unique physical and chemical properties which can give rise to hazards, particularly during transport and handling.

Left: Dry bulk sulphur being transported by rail, Abu Dhabi.

Sulphur falls under the UN RID dangerous goods code 4.1, classing it as a flammable substance. Sulphur burns readily and generates toxic sulphur dioxide when doing so. Normal fire prevention steps must thus be taken, such as forbidding naked flames around sulphur, and the restriction of cutting or welding equipment during normal operation. Electrical wiring and equipment must be properly protected and checked regularly.

Dust is the major hazard for handling dry sulphur. Solid sulphur is brittle and friable and can readily break down into smaller particles. Most organic dusts are combustible to a greater or lesser extent, but sulphur dust has a low ignition temperature of around 190°C or higher. It is also an excellent insulator, meaning that it can build up a static charge, and discharges can consequently cause ignition. In order to prevent sulphur dust explosions there are two basic strategies; to avoid suspensions of dust in the air, and to exclude sources of ignition.

Crushed bulk sulphur is the form most given to dust formation, so sulphur is usually formed into pastilles, granules etc, but these can also give rise to dust if poorly handled (see, e.g. 'Airborne sulphur particulate in formed sulphur handling', Sept/Oct 2015). Handling methods should therefore minimise dust formation by reducing the number of transfer points on conveyors to a minimum, using rubber belts conveyors or bucket elevators, properly earthed and minimising the use of front end loaders, which can crush sulphur under their wheels.

Good housekeeping is also a must. Operators need to develop and implement a hazardous dust inspection regime, with inspection of and cleaning of dust residues at regular intervals. Dust can also be suppressed by use of water sprays at transfer points and load-out stations. However, the effectiveness of water alone for dust control is limited by the hydrophobic nature of sulphur. This can be overcome by the use of special water-based chemical surfactants, provided that they are not used to excess.

Liquid sulphur

Sulphur is often transported as a liquid by rail and ship. By rail it is carried in insulated stainless steel tank cars which keep the sulphur at a temperature of 140°C. The Sulphur Institute has issued several sets of guidelines on sulphur rail cars, including a Molten Sulphur Rail Tank Car Guidance Document; Molten Sulphur Rail Tank Car Loading and Unloading Operations; and Guidelines on the Transportation Regulation of Molten Sulphur.

Liquid sulphur poses the greatest potential hazard during transfer. To avoid the possibility of an explosive concentration of sulphur vapour occurring, the temperature of liquid sulphur should not be allowed to exceed 154°C. The temperature however must also be maintained above 112°C to prevent the accumulation of solid sulphur crystals on internal tank surfaces exposed to air. Any sulphur deposits are corrosive to steel in the presence of moisture. As with solid sulphur, static charge build-up must be avoided.

Emissions

The other major hazard from both solid and liquid sulphur, is gaseous emissions, in particular, hydrogen sulphide. Direct from the Claus plant, sulphur typically contains around 300 ppmw H_2S which can be released during storage and/or transport, creating potentially hazardous conditions. Degassing the sulphur to reduce the H_2S content considerably reduces the potential hazards. In North America, sulphur degassing to <10 ppmw H_2S is regarded as best practice. All areas in which sulphur is stowed or used or which require the presence of personnel should be thoroughly ventilated.

Sea transport

The major issue for sea transport is corrosion. Dry bulk sulphur is not corrosive, but in the presence of water, sulphur can react with other elements. Sulphur is often loaded with a light water spray to keep down dust, or may otherwise be wet from rain when exposed in dockside storage. In a ship's hold, water in the sulphur cargo can settle to the bottom or into the bilges, added to by any seawater that is able to enter the hold due to improperly tightened hatches. There are two processes in particular which can be problematic. The first is acidic corrosion, where sulphur-oxidising bacteria (thiobacilli) directly oxidise the sulphur to sulphate, and generate sulphuric acid. The acid can then react with iron in the steel of the hold. The presence of chlorides – in the form of salts, such as sodium and potassium chlorides, such as are found in seawater – accelerates this reaction.

A more serious mechanism is electrochemical corrosion of iron by wet sulphur, which can auto-catalyse under anaerobic conditions to produce ferrous sulphide (FeS). This is a blackish-brown sludge or jelly which can display pyrophoric behaviour – when exposed to oxygen, such as during discharge of the hold, it can create sufficient exothermal heat to start a fire.

When carrying sulphur cargoes, it is therefore essential that the hold be properly prepared. All residues from previous cargoes, as well as loose paint, rust or scale, should be removed. As holds are often cleaned with seawater, chlorides should also be removed, preferably by washing with fresh water to a 'grain clear' standard – i.e. as clean as would be required for transporting grain. Holds must be inspected and approved and hatches must be watertight. A lime wash is also generally applied to act as a barrier and protect the steel by neutralising acid formation. ■

Sulphur and the aviation industry

PHOTO: SAN FRANCISCO AIRPORT

Fuelling using SAF at San Francisco: United Airlines has been an early adopter in the US.

A move towards so-called 'sustainable aviation fuels' (SAF) could see refineries having to recast their operations. What might this mean for sulphur production?

National governments are beginning to bear down increasingly heavily on reduction of carbon dioxide and carbon dioxide equivalent emissions in order to head off potentially disastrous climate change. In the transport sector, road vehicles are moving towards electric power trains, while shipping is looking at a number of low carbon fuels including green ammonia or methanol. The aviation industry, however, responsible for about 2.5% of all greenhouse gas emissions, has a tougher prospect for change ahead of it.

Two factors are shaping the way that the industry is approaching the coming energy transition. The first is the cost of commercial aircraft. Most commercial airliners cost in the region of $80-100 million. For this reason they are often kept in service almost continuously for long periods in order to recover and amortise this cost. This means that aircraft being purchased today may well still be in service in 2050 – the target date that many see as crucial for transition to a 'net zero' carbon economy. The other is that aircraft, unlike road vehicles, cannot be electrified – in order to store the same energy that an airliner can carry in its fuel tanks, it would need batteries that weight 30 or so times the weight of aviation fuel; impractical for an aircraft. While hydrogen from renewable sources has been suggested as a future aviation fuel, the fuel tanks would take up most of the fuselage as well as the wings even if the hydrogen were liquid, and will likely require new designs of plane. The assumption therefore is that aircraft will be using liquid hydrocarbon-based fuels not dissimilar to the ones they currently use for the foreseeable future. This leads to the concept of so-called sustainable aviation fuels (SAF).

Sustainable fuels

Sustainable aviation fuel has been defined by the International Civil Aviation Organization (ICAO) as a fuel that achieves net greenhouse gas emission reductions on a life-cycle basis; respects biodiversity conservation and ecosystems from where the feedstock is harvested; contributes to local social and economic development; and where the source of the biomass for this fuel does not compete with food and water requirements for humanity.

The main way that SAF is produced at the moment is via what are known as hydrotreated esters and fatty acids (HEFA). These use lower carbon sources of vegetable oils and fats, such as triglycerides and fatty acids from vegetable oils, (e.g. rapeseed, soybean and corn oil), tall oil, (a co-product from the pulp and paper industry), animal fats, and used cooking oil. The oils are then hydrotreated using hydrogen to remove oxygen and produce a form of diesel which has come to be known as 'biojet'.

Alcohols such as butanol and ethanol could be used as aviation fuels, and can be produced via fermentation or other biological processes. Other alternatives include gasification and Fischer-Tropsch (F-T) synthesis. Fischer-Tropsch is in effect a carbon polymerisation reaction, and means that a variety of feedstocks, from methane to various gasified solid feeds, can be used to generate the synthesis gas used in the reaction. It has been the basis of so-called gas to liquids (GTL) plants such as Oryx in Qatar. More recently there has been a focus on lower carbon solid feedstocks such as municipal solid waste (MSW), or biomass, e.g. from paper mills or other plant processing. Forms of pyrolysis or torrefaction have also been applied to biomass to generate liquid fuels, but these have not been widely commercialised. Most recently, there has been considerable interest in using hydrogen from electrolysis using renewable power as part of the syngas mix. The theory is that it would be used in conjunction with carbon dioxide captured from industrial processes or even the air to produce a diesel via F-T conversion that is effectively zero carbon. This does of course require access to cheap, renewable electricity, and direct air capture of CO_2 remains expensive and at early stages of development, with concentrated sources of waste gases a more likely source of feedstock gas.

Co-processing

Most of the above technologies are effectively stand alone, and do not need to be near or integrated into existing refineries. For refiners, however, co-processing of liquid intermediates in existing refineries is attracting interest. The most likely insertion points are the fluid catalytic cracker (FCC) and the diesel hydrotreater, with the latter the more suitable for SAF production. Currently only 5% blends of lipids and F-T liquids are allowed under ASTM D1655 (coprocessing), though across the whole refining industry this could still make for significant volumes overall.

Production at scale

If SAF is to play a major role in reduction of aviation industry emissions, large volumes will be required, estimated at more than 100 billion litres per year by the International Energy Agency. However, to date, commercialisation has been slow. The total volume of SAF being produced has increased substantially, from around 10 million litres/year in 2018 to around 150 million litres by 2021, but this represents only 0.1% or less of current aviation fuel, and forecasts for 2026 are only around 0.8% of aviation fuel. Most of these are likely to be using HEFA.

New 'biorefineries' are being built. Neste has been a pioneer, producing 100,000 t/a of MY Sustainable Aviation Fuel™ which reduces greenhouse gas emissions by up to 80% compared to fossil jet fuel. This will increase to 1.5 million t/a (around 1.88 billion litres) by the end of 2023. It is targeting large expansions in Rotterdam and Singapore which could take this to 4.5 million t/a over the next few years.

Eni is manufactures SAF at its Taranto refinery via co-feeding conventional plants with amounts of used cooking oil. It is also converting its Livorno refinery to distil bio-components produced at the Gela biorefinery via its proprietary Ecofining™ technology. Growth will continue from 2024 with the start of Eni Biojet production at Gela, where a project is already underway that will allow for an additional 150,000 t/a produced from renewable raw materials to be placed on the market, which will meet the Italian market's potential requirements by 2025.

TotalEnergies says it has begun production of SAF at its Gonfreville refinery in Normandy. It also has some capacity at La Mede refinery and Oudalle, and will produce SAF at its Grandpuits zero-crude refinery starting in 2024. All the biojet will be supplied to French airports and will be produced from waste and residue sourced from the circular economy.

Brasil BioFuels is using Topsoe's *HydroFlex*™ and *H2bridge*™ technologies for a new biorefinery being built in Manaus, Brazil, with a production capacity of 500,000 t/a. The plant is expected to start in 2025. *H2bridge* captures waste propane and carbon off-gas from the refining process, and converts it into hydrogen to be included in powering facility operations.

Chevron is teaming up with Gevo, Inc. to process inedible corn to produce SAF and corn oil and renewable blending components for gasoline to lower its carbon intensity. In addition to co-investing with Gevo in one or more projects, Chevron would have the right to offtake approximately 150 million gallons per year to market to customers. Chevron expects to create the capacity to produce 100,000 bbl/d of renewable fuels by 2030.

> **Co-processing of liquid intermediates in existing refineries is attracting interest.**

OMV says that its production of sustainable fuels and chemical feedstock will increase to 1.5 million t/a by 2030, with sustainable aviation fuels accounting for almost half the volume. OMV said it was also aiming to boost sales of SAF to more than 700,000 t/a by 2030.

However, although HEFA is the most widely used SAF pathway today, it is regarded the least scalable one in the long term because of the limitation on sufficient vegetable oil feedstock. A recent industry report suggested it might only be capable of providing 10% SAF by 2050 due to feedstock limitations, with alcohols and Fisher Tropsch pathways accounting for about 40% of the total and the remaining 50% from Power-to-Liquid, identified as being the most scalable in the future in terms of feedstock availability.

Impact on refineries

Although sulphur levels in ground vehicle fuels have been steadily declining over the past couple of decades, down to 10-15 ppm in much of the developed world, and the International Maritime Organisation (IMO) has taken steps to sulphur dioxide emissions from ships, especially in designated 'emission control zones' near heavily populated areas, the sulphur content of conventional aviation fuel still remains comparatively loosely regulated. Sulphur content of aviation fuels is capped at 3,000 ppm, though the average is currently around 600 ppm. Though there have been moves to lower this level, there is no regulation currently in the pipeline.

Production of sustainable aviation fuels bypasses this question by producing lower sulphur fuels as a matter of course, though SAF production will alter the sulphur balance according to the process. For biojet from hydrotreated vegetable oils, the sulphur content of the original seeds can be quite high – up to 1.0-1.5% for rapeseed or mustard seed. But most of this remains in the seed when the oil is extracted. Rapeseed oil, for example, only has a sulphur content of around 10-15 ppm, and this level is even lower for other vegetable oils. Gasification also varies widely according to the feed. The sulphur content of municipal solid waste is around 0.1%, all of which must be removed prior to the Fischer-Tropsch step, while for power to liquids, there is of course essentially zero sulphur in a process using pure hydrogen and carbon dioxide.

Co-production of HEFA can probably be accomplished using existing refinery sulphur recovery sections, but grassroots plants will be dealing with much lower levels of sulphur and may need appropriate dedicated solutions such as scavengers or bioprocessing. Either way sulphur output will be appreciably lower if there is a large scale switch to biojet, as seems to be the case.

PHOTO: LYNAS RARE EARTHS

Lynas Rare Earth's site at Mt Weld, Australia.

Sulphuric acid in rare earths processing

Global demand for rare earth metals is increasing, particularly for electric vehicle batteries and renewable energy devices, potentially leading to increased use of sulphuric acid in their extraction.

The 'rare earth' elements are generally considered to be the 14 lanthanide metals (see Figure 1), as well as yttrium, element 39, which sits directly above lanthanum in the periodic table. Scandium, which sits above yttrium, is also sometimes considered a rare earth element. They were first discovered in rocks found at an old quarry at Ytterby near Stockholm in Sweden in 1787 by chemist Carl Arrhenius, which is why the otherwise unremarkable village gave its name to four of the initially seven new elements found there – yttrium, erbium, terbium and ytterbium. In spite of their name, they are not necessarily particularly rare in terms of abundance in nature; there is actually more cerium, for example, in the earth's crust than there is copper. However, they are not found as often in large deposits like transition metals such as cobalt and copper, which makes them harder to extract economically. The most common are yttrium, lanthanum, cerium and neodymium.

Their properties are varied, as shown in Table 1. Cerium, lanthanum and neodymium are important in alloy making, and in the production of fuel cells and nickel-metal hydride batteries. Ce, Ga and Nd are important in electronics and are used in the production of LCD and plasma screens, fiberoptics, lasers, and medical devices. Cerium and lanthanum are also important as catalysts, especially for fluid catalytic cracking (FCC). Neodymium is important in magnet production and it and similar metals are used in the electric motors of hybrid and electric vehicles, generators in wind turbines, hard disc drives, portable electronics, microphones and speakers. Overall, rare earth demand is expected to rise by about 10% year on year over the next decade, more than doubling from its present value by 2030.

Production

Rare earth metals occur in various minerals, but the most prominent are bastnasite, a fluorocarbonate ore with iron found Inner Mongolia; monazite and xenotime, both of which are phosphates, found in Mountain Pass, California, and Kerala, India; ion-adsorption clays formed by the weathering of rare earth rich volcanic rock; and minerals such as euxenite and gadolinite. However, over 95% of rare earths occur in the three ores bastnasite, monazite, and xenotime.

Processing of rare earth ores can be done by various means[3], usually proceeding via beneficiation, decomposition of the mineral concentrate to extract the rare earth elements, and then impurity removal and separation of individual rare earths to produce purified saleable products. Bastnasite can be treated using a variety of decomposition methods. Mountain Pass uses a hydrochloric acid leach because it delivers a purer product, but the most widely used technique is sulphuric acid 'baking', which is used at Bayan Obo in China's Mongolia region – the largest rare earth deposit in the world – and at Mt. Weld in Australia. Sulphuric acid baking in Mongolia was estimated to be responsible for more than 60% of China's total rare earth production in 2015. The process converts rare earth salts to

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Fig. 1: **Periodic table of elements**

Period \ Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Source: Reference 1

Table 1: **Rare earth elements and their properties**

Element	Symbol	Percentage of rare earth	Primary uses
Lanthanum	La	32.7	Catalyst (esp for FCC), batteries, Lenses and glassmaking
Cerium	Ce	29.9	Glass additives, catalyst
Praseodymium	Pr	6.8	Magnets
Neodymium	Nd	18.5	Magnets
Samarium	Sm	0.4	Batteries
Europium	Eu	0.3	Phosphors
Gadolinium	Gd	1.0	Magnets
Dysprosium	Dy	1.0	Magnets
Holmium	Ho	0.1	Glass additives,
Erbium	Er	0.1	Glass additives, phosphors, metallurgy
Terbium	Tm	0.1	Fuel cells, phosphors, magnetic sensors
Ytterbium	Yb	0.1	Glass additive, gamma ray source,
Lutetium	Lu	0.1	Phosphors, electronics
Yttrium	Y	9.0	Phosphors, ceramics

Source: Long[2]

sulphates by reaction with concentrated sulphuric acid at elevated temperature (200-300°C) in a ratio of approximately 1-2.5:1 acid:ore. The sulphates are then dissolved in a water leaching step before separation.

Monazite ore has in the past usually recovered using sulphuric acid, but the caustic route using sodium hydroxide has become preferred. The residue is then dissolved into hot acidic solution, either nitric or sulphuric acid, with subsequent solvent extraction using amines on the solution. Xenotime, effectively the yttrium version of monazite, is also almost always processed using a sulphuric acid bake.

Other extraction techniques

Phosphogypsum, a by-product of phosphate fertilizer production, mainly contains gypsum ($CaSO_4$) as well as impurities from the phosphate rock such as silicon, barium, iron, aluminium, titanium and uranium, but it also can contain small amounts (0.03-0.1% w/w) of rare earth elements. It has been estimated that the deposition of phosphogypsum stacks in Florida alone could incorporate up to 30,000 t/a of rare earth metals. Because of the low concentrations of rare earths, processing could be difficult and expensive. Nevertheless, methods have been proposed, including physical methods such as hydrodynamic sedimentation, flotation and high gradient magnetic separation, and use of various organic chemicals. But the most economically viable appears to be acid leaching. Though HCl and nitric acid have been shown in laboratory tests to be slightly more efficient at leaching rare earths, sulphuric acid would be preferred commercially because it is cheaper. Rainbow Rare Earths has a gypsum leaching project under development at Phalaborwa in South Africa, with first production anticipated in 2025.

It is also possible to recover rare earths from magnets or other devices containing them, though this can be costly to gather sufficient materials and large scale recycling is still in its infancy.

Supply

Until the 1950s rare earths were mainly extracted from alluvial deposits in Brazil and India, but the Mountain Pass mine in California, which began production in 1952, quickly came to be the dominant source throughout the 1960s-1980s. But beginning in the 1980s, China began mining rare earths on a large scale, and by the 1990s it had become the largest global producer. By 2000 China produced more than 90% of the world's rare earth supply, and by 2010 that had become 97%. However, in 2010 China began to introduce export quotas in order (according to the government) to conserve resources and protect the environment. In 2012 three of the eight mines in China, representing 40% of supply, were closed down. This led to a spike in rare earth prices which galvanised the development of new mines elsewhere, in the US and Australia. As Table 2 shows, Chinese share of rare earth production now runs at 60% of world supply, though China also owns the rare earth mines in Myanmar and has invested in other production in southeast Asia. China's production is concentrated in the provinces of Fujian, Guangdong, Hunan, Jiangxi, Shandong, Sichuan, Yunnan, Guangxi and Mongolia. The largest mining operation is Baotou Rare Earth's Bayan Obo mine, which produces iron ore as well as bastnaesite and monazite as the main rare-earth minerals.

In Australia, Lynas Rare Earths Ltd began production at its Mount Weld carbonatite complex in Western Australia in 2011, and production has now reached 22,000 t/a, with a processing site in Malaysia. India has two small scale state producers, Indian Rare Earths Ltd. and Kerala Minerals and Metals Ltd. (KMML). The US reopened the Mountain Pass mine in California in 2012, operated by MolyCorp, but a glut of rare earths on the market led to production being idled there again in 2015. The mine was bought by MP Materials and production restarted again in 2017.

In addition to these, there have been a flurry of new project proposals, encouraged by the desire of countries such as the US and Europe to gain a degree of strategic autonomy in rare earths production, and be less dependent on Chinese supply. The Biden administration in the US has pushed domestic development of rare earths capacity. As a result there are new projects proposed in Australia, including Nolans Bore in the Northern Territory, Australian Strategic Materials at Dubbo in New South Wales, both of which are at the advanced feasibility study stage. Iluka Resources is developing a project in Western Australia at Eneabba, with a projected on-stream date of 2025. New project proposals in the US include Bokan Mountain, Alaska; La Paz, Arizona; Diamond Creek and Lemhi Pass in Idaho; Pea Ridge, Missouri; Elk Creek, Nebraska; Thor, Nevada; Round Top, Texas; Energy Fuels in Utah and Bear Lodge, Wyoming. There are also projects in Canada including Ashram, Buckton, Clay-Howells, Elliot Ridge and several others. Other project proposals include Greenland, Tanzania, South Africa, Madagascar, Kenya and Sweden.

Table 2: **Rare earth production and reserves, tonnes**

Country	Mined production		Reserves
	2020	2021	
China	140,000	168,000	44,000,000
United States	39,000	43,000	1,800,000
Myanmar	31,000	26,000	Not known
Australia	21,000	22,000	94,000,000
Thailand	3,600	8,000	Not known
India	2,900	2,900	6,900,000
Madagascar	2,800	3,200	Not known
Russia	2,700	2,700	21,000,000
Vietnam	700	400	22,000,000
Brazil	600	500	21,000,000
Burundi	300	100	Not known
Canada	0	0	830,000
Greenland	0	0	1,500,000
South Africa	0	0	790,000
Tanzania	0	0	890,000
Other countries	100	300	280,000
World total (rounded)	**240,000**	**280,000**	**120,000,000**

Source: USGS

Acid consumption

Not all of these projects will come to fruition, and not all will use acid leaching, but given the small quantity of rare earth per tonne of ore, a great deal of rock must be processed in order to extract the 170,000 t/a of rare earths that are currently used, requiring perhaps 5-10 times the final amount of metal as acid. Downstream processing of rare earth concentrates is still by and large located in China and southeast Asia at present. Mountain Pass actually exports concentrate to China for processing.

Supply of acid can be crucial to the success of these projects. For example, Lynas Rare Earths is under pressure to close down its Malaysian processing site because of concerns about low level radioactive thorium residues from the leaching process, and is instead building a processing site in Kalgoorlie, Australia to handle ore from Mt Weld, which is due to become operational by 2025. The company is said to have reached a deal with BHP for supply of sulphuric acid from its nickel smelter at Kalgoorlie to run the plant. Overall, while rare earths processing remains a niche use for sulphuric acid, this rapidly expanding industry could be consuming another million t/a by 2030.

References

1. Wikimedia Creative Commons, user Sandbh.
2. Long, Keith R. "Rare-earth mining." AccessScience, McGraw Hill, 2013.
3. J. Demol, E. Ho, K. Soldenhoff, et al., The sulphuric acid bake and leach route for processing of rare earth ores and concentrates: a review, Hydrometallurgy.
4. US Geological Survey Professional Paper 1802-O, Rare Earth Elements

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Sulphur + Sulphuric Acid 2022

Evening lights at Binnenhof palace, The Hague, Netherlands.

PHOTO: ADAM ZOLTAN / SHUTTERSTOCK.COM

A report on CRU's annual Sulphur + Sulphuric Acid conference, which returned to being face to face meeting at the end of October 2022.

It was with some sense of relief, I think, that delegates gathered in the Hague in the Netherlands at the end of October for the CRU Sulphur and Sulphuric Acid conference, as it was the first time in three years that the conference had been held as a face to face even, following the covid pandemic. Though numbers were down slightly on pre-pandemic times, the combination of the conference with the REFCOM refining meeting drew 470 visitors.

The format was slightly changed from previous runs, with the first morning devoted to a series of technical showcases. These were short, 15 minute presentations on specific products or services by the likes of Kimre, MECS-Elessent, Blasch, Begg Cousland and Steuler, and appeared to be popular with the delegates.

Market papers

On Monday afternoon the conference proper began. CRU's Peter Harrison started as is traditional with the sulphur market paper. He reflected how sulphur prices had slumped in Q3 2022 from 14-year highs of $500/t to 14-year lows of $80/t. Demand had rebounded and supply was tight in the first half of 2021. Moving into the second half of the year, exports were weak, with overrunning turnarounds in the Middle East and issues at Astrakhan in Russia. Of course, for the first half of 2022 the war in Ukraine had dominated markets, leading to prices climbing sharply as consumers became concerned where to source sulphur. The recent collapse in prices by up to 90% has been driven by demand destruction and reduced demand in China caused by quotas for phosphate exports. However, after an overcorrection, prices have bounced back towards $150/t. The outlook for the full year is a small contraction in supply and a larger one in demand due to lower fertilizer applications, but new refinery capacity and sour gas plants will keep supply growing, while a rebound in fertilizers and new metals demand will dive growth in demand out to 2027.

Regionally, Europe is likely to swing to being a net importer by 2026 as domestic supply falters with the closure of the Grossenknetten gas plant and some refinery closures, and by 20227 the continent could be importing 200,000 t/a of sulphur. In North America, there has been a short term supply jump to 7.9 million t/a in the US due to extra sulphur from refineries, but output will fall from next year. Canada will see a return to oil sands supply growth, but Alberta sour gas production continues to see an overall steady decline. Consumption will see an uptick over the forecast period due to new metallurgical use, and overall net US imports may rise to more than 2 million t/a by 2027. CIS supply continues to find its way to the international market, with Turkmenistan expected to see supply growth. In the Middle East, there is more sulphur from Kuwait's refineries, the Shah 2 project in Abu Dhabi, and incremental supply from Iran and Qatar. Indian imports may grow over the next five years in spite of some new refinery sulphur due to new sulphur burning acid plants at phosphate producers. In China refining is also boosting domestic supply, with import requirements dropping by 2.3 million t/a out to 2027. Finally, in southeast Asia, Indonesian nickel production is driving demand growth, as new HPAL plants appear to have started up more efficiently than previous plants elsewhere in the world.

Trade continues to shift, though, with the war showing up how exposed some markets are to disruption – the share of Senegal's imports coming from the CIS is more than 70%, and for Brazil the figure is close to 50%, with Europe at 34%. Over the next five years, Morocco will see more import demand growth to feed phosphate production, with most supply growth coming from the Middle East. As far as the price outlook goes, the market is in notional oversupply, and will be into 2023, but thereafter demand growth will overtake supply growth, leading to a small overall deficit by 2025. Continuing lower prices are forecast to Q4 2023, rising after that.

Erisa Pasco of CRU followed with the sulphuric acid market presentation. Acid prices have followed sulphur prices this year, but have been less volatile. The first half of 2021 was a period of tighter supply from smelter acid, and prices reached $250/t, but this year Asian prices have weakened and in 3Q 2022 prices have fallen as Chinese acid volumes entered the market and demand weakened, dragging f.o.b. prices to $50/t as a fall in DAP, sulphur and nitrogen prices have all weakened price support for sulphuric acid. Local demand has been lower in China, pushing more acid onto international markets. Chinese exports were 2.9 million tonnes for January to August 2022, compared to 2.8 million tonnes for the whole of 2021; an 88% rise for the first eight months of the year. However, Chinese demand is expected to recover from 2023, and exports will gradually fall, dropping to an estimated 1.5 million t/a by 2026. Chile will see import demand fall as copper projects fail to replace demand losses from closures. Chilean demand will drop from 8.1 million t/a in 2021 to below 7.0 million t/a in 2027. Meanwhile Indian sulphuric acid capacity growth will continue. Coromandel, Iffco and PPL are all building or considering new sulphur burning plants, and the new Hindustan Zinc smelter will start up next year. The Adani smelter project could also add another 3 million t/a of capacity from 2025. Even so, demand growth is expected to outpace new supply and import requirements will rise slightly. Morocco is also adding sulphur burning capacity, and its imports of acid are expected to fall. Europe has seen a supply drop this year from scheduled smelter maintenance but should see a return to normal next year. The outlook for the rest of 2022 is stable prices in the $50-120/t range for f.o.b. and delivered acid respectively, with the Jiangsu burner break-even cost expected to drive floor prices of $70-80/t in 2023.

The trio of market papers was completed by CRU's Glen Kurokawa, who presented the phosphate outlook. DAP prices have risen recently faster than crop prices leading to less affordability for farmers. Phosphate demand is consequently expected to decline in 2022, with MAP/DAP demand down 9% year on year, comparable to the fall seen in 2008. Consumption will return as prices ease from their current high levels, however. Chinese phosphate exports, which represent around one third of the traded market for MAP and DAP, have been subdued due to restrictions and quotas to keep prices lower domestically. These will rise in 2023 but increases may be impeded by lingering export restrictions, rising production costs and competition from other countries. Morocco, which represents 15% of global phosphoric acid production, is seeing production and exports increase as OCP continues to expand phosphate production. However, in 2021-22 it raised prices, leading to lower exports despite its low costs. This may not be a sustainable strategy in the long term. US production has declined, and in spite of a recovery in 2023 will probably continue to see some declines in production, while Russian phosphate exports are expected to grow in spite of sanctions, as its main export destinations, India and Brazil, are not affected. European production is stable but dipped in 2022 due to high prices and disruption at Lifosa in Lithuania. India remains the biggest importer, though high prices have led to more domestic production and lower imports in 2021. Import subsidies have been raised this year and imports are expected to increase, but out to 2026 there will be increased domestic phosphoric acid production due to government policies to favour domestic production. India remains at the high end of the cost curve. Further declines in phosphate prices are expected next year as crop prices fall and there may be lingering demand destruction, with increased exports from China and Morocco.

"Indian sulphuric acid capacity growth will continue."

The final paper in the commercial session was provided by John Bryant of The Sulphur Institute (TSI). He argued that sulphur as a business driven by supply chains, is at a crossroads. Pricing has been more volatile over the past 15 years since the financial crisis than at any time in the history of the industry, and it is facing factors such as covid, shutdowns, an economic slowdown, labour shortfalls, the green energy transition, the Ukraine conflict and its knock-on effects, inflation, higher fuel and freight costs etc. The potential impacts of these are longer supply chains, higher costs and longer delivery times; unplanned delays, cost inflation, offtake and delivery problems, and more besides. However, what is not changing is that sulphur production continues to be involuntary, but remains of high value to many sectors, with a distinction between solid and liquid transport, the molten assets tending to be dedicated and highly utilised. Exacerbated volatility adds market costs to ownership, while supply chain interruptions will increase and threaten operating rates. Industry responses to this could take the form of new attitudes about owning the full supply chain, additions to storage capacity, new transforming assets for forming and melting, new transport assets, and sharpening and improving commercial terms for greater price transparency.

Sulphur technology

With demand for hydrogen projected to reach 290 million t/a by 2050, the sulphur technology strand of the conference began with two papers on recovery of hydrogen and carbon dioxide from Claus plants. Marcus Weber of Fluor showed that Fluor's oxygen enriched *COPE* process could produce a gas stream richer in H_2 and CO_2 at a lower capital cost and footprint than standard post-combustion carbon capture, if oxygen levels were greater than 95%. Moderate levels of steam injection can boost hydrogen output. Gerritt Bloemendal of Worley Comprimo offered a similar scheme with >95% oxygen enrichment and again with hydrogen and CO_2 recovery post tail gas treatment and pre-incinerator. A cold flash for CO_2 recovery was recommended, but a chemical solvent option could be optimised.

Matt Coady of Delta Controls presented a new camera system, *ProSpection*, for SRU monitoring – there is a fuller article elsewhere in this issue. Moving further downstream, Diego Scilla of Siirtec Nigi showcased his company's *DegaSN* degassing system, capable of reducing dissolved H_2S in sulphur down to less than 10 ppm. Liquid sulphur is fed to a sprayer before being mixed with low pressure steam and a slipstream of stripping air, the latter is bubbled through mass transfer elements to achieve intimate contact between the liquid and gas phases.

Refineries must deal with a variety of feeds these days, and Marco van Son of Comprimo looked at the impact of biological feeds on sulphur recovery. In a co-processing situation, existing amine and SRUs can process the revised sour products, but the sour water stripper may need debottlenecking and there is the potential for increased emissions. However, in a new grassroots biorefinery sulphur throughput may be only 1% of conventional diesel production and other sulphur recovery options may be appropriate.

David Savage of Matrix described options for above ground liquid sulphur storage as an alternative to sulphur pits, including pitfalls to be avoided in terms of tank heating and insulation and fire safety and suppression systems.

Mason Lee of Aecometric introduced at the theory and practice of reaction furnace design, and ASRL's Chris Lavery looed at reaction kinetics for COS and CS_2 conversion on Claus catalysts; enefficieny conversion of which can lead to loss of sulphur recovery efficiency. Alumina and titania catalysts tended to show lower end of run conversion in experimental tests.

Wednesday morning saw a Middle East Sulphur Conference (MESCon) round table discussion hosted by Angie Slavens on the subject of corrosion considerations for sulphur plant operators. At the end of the second day, Worley Comprimo also ran a workshop covering sulphur recovery techniques with a recovery above 96.5% highlighting differences in capex, opex and CO_2 footprint, as well as showcasing *Insight*, a digital tool for plant data analysis.

Emissions monitoring and control

On the final day, David Inward of SICK AG began with a look at emission reporting from SRUs; the limits for SO_2 and – increasingly – other releases such as NOx and CO/CO_2, and the techniques used to measure them. A field trial at a European refinery in 2020 proved the suitability of a hot, wet extractive infra-red analysis system to measure tail gas emissions.

Jeff Weinfield of Optimized Gas Treating also looked at SO_2 emissions, this time a slip from a TGTU caused by hydrogenation reactor poisoning. The plant in question was reporting cloudy quench water and thiosulphates in the amine section, but could not detect SO_2 in the feed gas – possibly indicating an intermittent problem. Jeff used a modified *SulphurPro* model which indicated that a small slip of excess Claus air led to a 100ppm+ SO_2 slip exceeding the quench ammonia buffer capacity and passing on into the amine system.

Finally, Neils Seijsner of Fluor ran through a variety of processes for removing SO_2 and SO_3 from flue gas, highlighting their respective strengths and weaknesses.

SRU case studies

A number of case studies detailed operator experiences with sulphur plants. ADNOC Sour Gas presented two papers, the first dealing with optimisation of catalyst loading in a sulphur recovery unit and a tail gas treatment unit respectively. The SRU loading was able to minimise titania loading to 30% without compromising performance, while the TGTU eliminator reactor internals and used a low density catalyst to reduce pressure drop and minimise catalyst volume. ADNOC also presented a report on refractory and shell damage to the incinerator downstream of the TGTU due to condensation in the absorber overhead line.

Adel Najar of Saudi Aramco's Ras Tanura refinery detailed issues with sulphur fume emissions from a sulphur pit. Investigation found a steam ejector valve was giving a wrong open/closed indication leading to sulphur pit steam coils leaking inside the pit.

Sulphuric acid technology

The acid technology strand began with two presentations on digitalisation. Topsoe reviewed their ClearView digital services suite, highlighting its 'real world' use and effects at a Topsoe wet sulphuric acid (WSA) plant at Anglo-American Platinum in South Africa, while Susanna Voges of Voovio Technologies extolled the virtues of operator training using 'digital twin' technology.

Two catalyst papers followed, beginning with BASF, who highlighted their new X3D catalyst shape, produced using 3D printing to generate more complex geometries, for a 66% lower pressure drop at the same activity level and slightly higher conversion level. A case study installed in a third catalyst bed at a sulphonation plant showed a 75% decrease in pressure drop across the catalyst bed and conversion increase form 97.3% to 99%. Topsoe presented their VK-38 acid catalyst, with modified support and optimised melt formulation to give increased steam generation and acid production.

Clark Solutions introduced their *SafeHR* and *SafeHX* acid cooling systems, which avoid any potential for acid-water contact by using an inert fluid circuit as an intermediary. *SafeHX* is a recent improvement on the original system, with no intermediate pump and fewer valves for easier maintenance.

Simon Puels of SensoTech looked at the monitoring of acid and oleum concentrations in real time using *LiquiSonic* ultrasonic sensors, to an accuracy of 0.03-0.05%, maintenance free, and CG Thermal and Wilk Graphite presented Extracid, an acid concentration/dewatering system based on a heat exchanger which can recover up to 70% of input energy.

Greener production

Sulphuric acid production is already a zero carbon source of power, but opportunities exist at all phases of a plant's development to improve its environmental performance, said Rene Dijkstra of Chemetics, including plant location, choice of technology, plant design and plant operation and maintenance. Colin Shore of Elessent added to this with a look at heat recovery and energy optimisation in an acid plant, and potentially upgrading heat to low pressure steam and LP steam to HP steam.

Operating experience

Several papers covered acid plant operating experience. Frans Kodeda of Metso Outotec presented a case study of the engineering and delivery of an Edmeston SX absorption circuit for BASF, wjhile Randal Sarrazin of NORAM described the replacement of a converter at Simplot's Rock Springs acid plant in Wyoming – a significant undertaking! And in a joint paper, UBE and Sulphurnet explained a case study involving the extension ofoperational lifetime of a converter which had been experiencing problems with dust.

On the subject of practical modifications to plants, Hector Gonzales of Industrias Basicas de Caldas in Colombia described how new waste water legislation had forced a rethink of how their acid plant dealt with sulphonation. They had built a return for exhaust gas from sulphonation to the acid plant, converting more than 80% of the SO_2 to SO_3 and managed to generate additional acid and reduce water consumption. Meanwhile, Georgi Deganov of KCM in Bulgaria explained how a new batch process lead smelter at the site, generating variable quantities of SO_2, had been integrated into the existing acid plant flowsheet.

Hydrogen safety

The issue of hydrogen formation in acid plants is a topic that is assuming ever-greater prominence in the industry. Rick Davis, Hannes Storch of Metso Outotec, Jurgens Hanekom of Elessent and Rene Dijkstra of Chemetics presented findings from the International Hydrogen Safety Working Group. It is important to quickly acknowledge when acid concentrations are out of range, keep blowers running and examine the potential for venting at high points in the plant where hydrogen can collect. Stagnant space should be minimised, especially at side gas outlets. Alloy towers seem to show greater potential for corrosion and hydrogen formation. Early detection is vital with conductivity and pH analysers on water returns. The good news is that there have been fewer incidents since 2019 and more open and transparent reporting. German plant operators have published a set of guidelines, although at present they are only available in German – an English version is planned.

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Road to sustainability

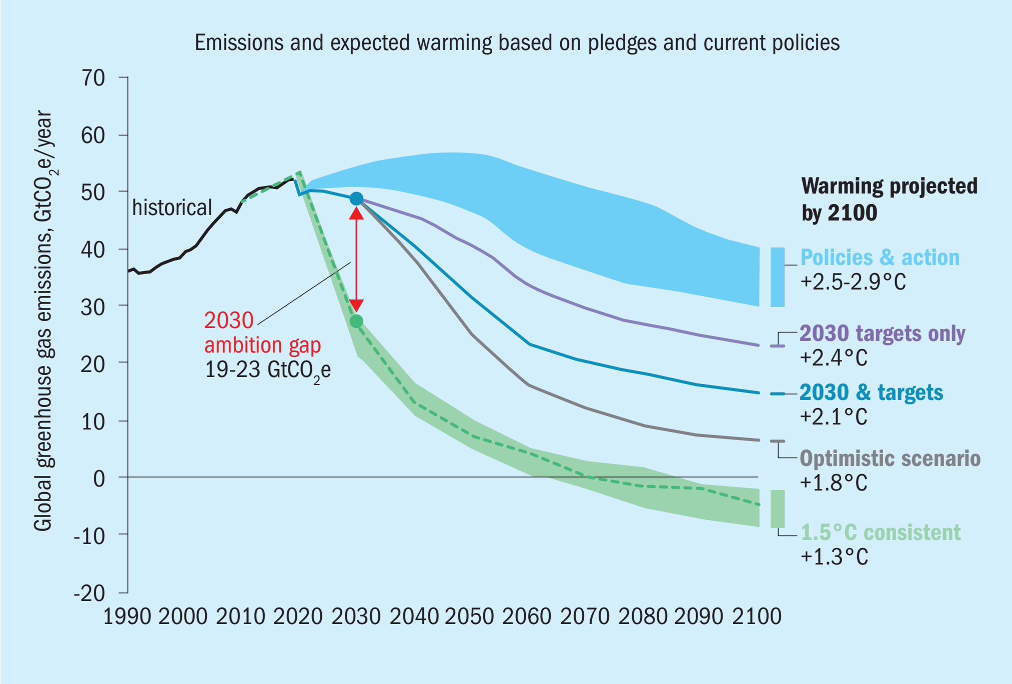
The energy transition has already commenced and while sulphuric acid production is already virtually carbon free, there will likely still be impacts on the sulphuric acid industry resulting from this energy transformation. **Hannes Storch**, **Shailesh Chandrol**, **Collin Bartlett** and **Jens Kleiber** of Metso Outotec present their view on a roadmap to sustainability, preparing for energy transition in the sulphuric acid industry through permanent product development, digitalisation and new technologies.

The reality of climate change and the consequences of it are becoming visible; the average temperature of the globe is rising; ever more unprecedented weather events can be observed. In Fig. 1 the effect of greenhouse gas (GHG) emissions on global warming is illustrated for different scenarios[1]. Even early action to the GHG issue will result in an optimistic view to a warming limit of 1.5°C and delayed actions predict dramatic increases in temperature.

At the moment the focus of greenhouse gas reduction certainly lies in building up a renewable infrastructure and pushing forward the decarbonisation of energy intensive industries, such as cement, steel and aluminium. It has to be acknowledged however that all commodities will be impacted by this energy transition and need to develop their own commercial and technical roadmap for the coming decades if the warming limit of 1.5°C is to be achieved.

The focus of this article is a holistic review of the sulphuric acid industry from a technology provider's view and also highlights areas where Metso Outotec considers further development is required.

Fig. 1: Climate Action Tracker's 2100 warming projections[1]



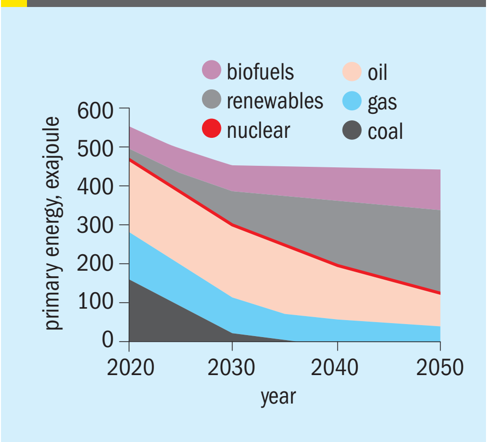
Energy transition

The key element to fight the climate change is an energy transition from hydrocarbon dominated to renewable energy sources. On this subject there are numerous studies and scenarios available which all include the same elements, however the timeline to achieve a "Net-Zero scenario" differs significantly.

One example, detailed in a recent report[2] entitled "The Net-Zero Transition", McKinsey & Company is detailed here. This article offered the scenario of primary energy production by 2050 based on Network for Greening the Financial System (NFGS) – refer to Fig. 2.

Fig. 2 shows a significant reduction firstly in the use of coal, followed by oil and gas in a relatively short period of time.

Fig. 2: McKinsey's NGFS Net Zero 2050 energy transformation scenario[2]



In different regions and commodity industries it can already be observed that the process has already commenced.

Implications of energy transition on the sulphuric acid industry

Although sulphuric acid production is already virtually carbon free, the energy transition may well have potential impacts on the industry:

- long-term global sulphur supply/demand and availability dynamics from a reduced use of hydrocarbons;
- short- and mid-term requirement for more sustainable solutions to further increase operational KPI's, i.e., kWh/t acid, m³ cooling water/t acid, etc.;
- regional/local requirements to shift to an alternative sulphur source, i.e. pyrite, natural sulphur, phospho-gypsum to bridge upcoming supply/demand shortfall.

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Fig. 3: **Sulphuric acid outlook to 2040**[3]

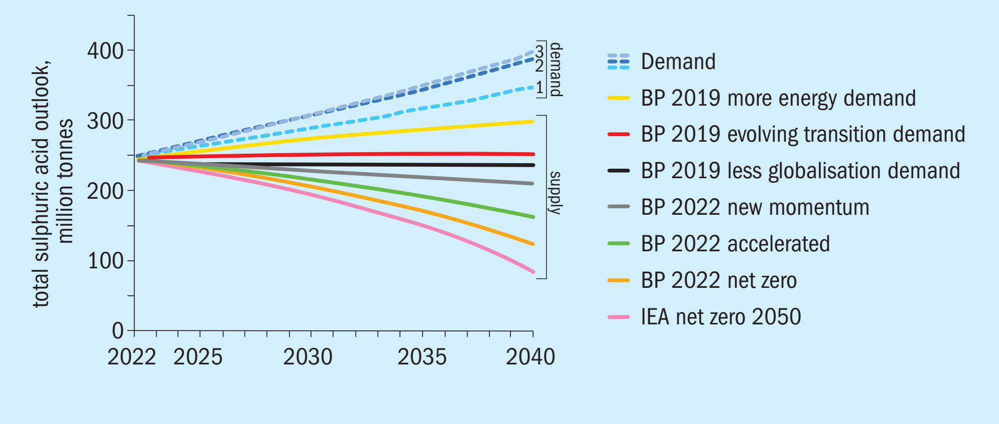
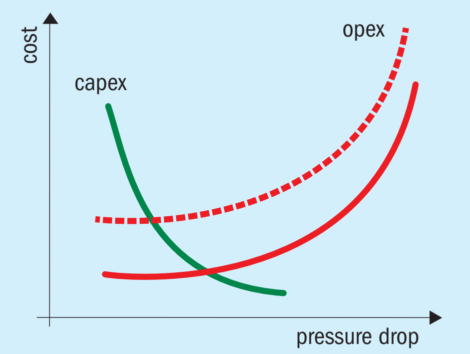


Fig. 4: **Capex/opex versus pressure drop**



Source: Metso Outotec

A recent report[3] by Maslin et al. (2022) summarises the supply/demand gap for different scenarios on intensity of the energy transition. It indicates that "Sulphuric acid demand is set to soar just as sources are likely to shrink" and this is encapsulated in Fig. 3.

Road to sustainability in the sulphuric acid industry

Metso Outotec's view, as a technology provider to the acid industry, is that energy transition and its transformational facets requires a roadmap today and this "road to sustainability" should consist of three areas to address and provide technologies and solutions to the industry at large:

- permanent product development;
- digitalisation;
- new technologies.

Permanent product development

Permanent product development is an ongoing process that focuses on improvement of safety, reliability and efficiency KPIs of acid plant technology and its products. Numerous products have been developed to address those key areas. However, the transition phase of energy transition requires further focus/re-thinking of specific operational key performance indicators (KPIs). Redefined KPIs in order to minimise specific energy consumption will support the use of equipment/technical solutions that are today not always considered as standard in the sulphuric acid industry, for example:

- Use of energy efficient equipment
  - filter, packing
  - VSD for blower, process pumps, etc.
  - more conservatively designed process equipment
- Significantly more attention to maintenance
  - Preventive maintenance supported by digitalisation
  - Managing pressure drop increases during operation
  - More catalyst screening, etc.
- Stronger focus on opex-based cost benefit analysis (CBA) over the plant's lifecycle rather than front end capex optimisation.

Fig. 4 shows one example relating to cost development over pressure drop. Historically, optimisation of plant pressure drop took place considering stable low level energy pricing; due to increased energy prices and carbon taxation this will potentially change in future. In case-by-case analysis it should be evaluated if higher initial capex for lower energy consuming plants offsets the anticipated opex over the lifecycle of the plant.

Digitalisation – the next leap in efficiency

One key element to support the optimised operation of acid plants will be digitalisation. There are numerous applications supporting all phases of the plant life cycle. A few prominent examples of applications that have already been established in the wider sulphuric acid industry are:

- connectivity, data storage and transfer (big data);
- optimising the process with data analytics;
- remote expert support;
- digital twins;
- predictive/interactive maintenance;
- future use of digi-connected tools, i.e. 3D spares printing, etc.

Metso Outotec has significant experience in the development and application of operating process optimisers and has a palette of references associated with a wide variety of industries. Such solutions are expected to have a place in the acid operators' toolkit in future – refer to Fig. 5.

Today, many of these digital solutions can be considered as stand-alone, however in the future they will need to become an integral part of an integrated digital solution, encompassing the concept of the 'mine-to-ship' philosophy.

New technologies

Besides the elements of permanent process development and digitalisation, a review of different traditional and future feedstock is required. Table 1 shows some of Metso Outotec's historical and current technology portfolio. Table 2 shows some of Metso Outotec's ideas on future technologies to respond to the disruptive scenarios of energy transition.

For traditional feedstock materials, the overall maturity level can be considered as high, and the focus of developments remains more on permanent improvement in respect to energy efficiency, emission and impurity control. In the case of pyrite as feed material, developments to significantly increase throughput via new designs in combination with the use of oxygen have to be considered as relevant.

Potential alternative feedstocks, namely phosphogypsum, would require significant efforts in their development. Fig. 6 shows a simplified block diagram of one potential process to use phosphogypsum. In this process hydrogen and renewable energies (such as solar) are used to decompose the phosphogypsum and the SO_2 gases are cleaned from impurities

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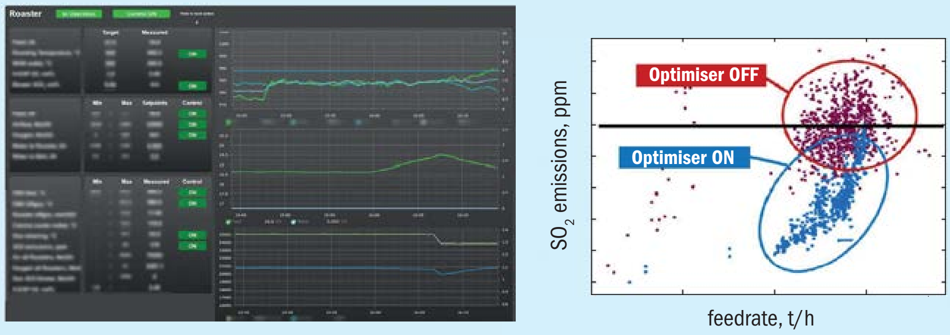
Fig. 5: **Industrial reference for a process optimiser**



Challenges

- Increase capacity within emissions limits
- Increase plant availability

Solution & benefits

- **Capacity:** increased >5%
- **SO_2 emissions:** reduced >25% over plant limit
- **Water consumption:** reduced by ~50%

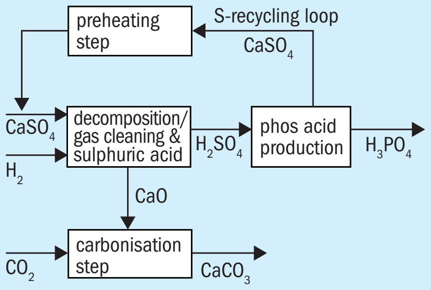
Optimiser tool includes complete train and is based on process first principles. Integration of optimiser in next generation digital ecoysystems possible!

Source: Metso Outotec

Other new concepts, such as the use of pure oxygen for the combustion of sulphur or processing metallurgical ores are already in use in industry and might see more relevance in the future and particularly once oxygen as a by-product from hydrogen production becomes more economic.

It is fully acknowledged that for all potential new process routes the maturity level has to be considered low and collaborative development initiatives between producer and technology provider will be required.

Fig. 6: **Sulphuric acid from gypsum/ phosphogypsum**



Source: Metso Outotec

and processed in a sulphuric acid plant. The solid product of the process (CaO) is used in a separate process step for the production of $CaCO_3$, which can be used in different industries. The key characteristics of the process are:

- use of hydrogen and renewable energy sources;
- development of a (local) circular sulphur economy by reusing phosphogypsum;
- carbon dioxide fixation;
- stabilisation of impurities;
- adaptation of existing technologies/ process steps.

References

1. Climate Action Tracker climateactiontracker.org
2. Mckinsey & Company, "The net-zero energy transition – what would it would cost, what would it bring?" (Jan 2022).
3. Maslin M., Van Heerde L., and Day S.: "Sulfur: A potential resource crisis that could stifle green technology and threaten food security as the world decarbonises", The Geographical Journal (Aug 2022).
4. Schiemann R., Haus S., Runkel M., and Hammerschmidt J.: "Experience with digital process optimization of zinc roasting plants." In PbZn 2020: 9th International Symposium on Lead and Zinc Processing, pp. 377-388. Springer, Cham, 2020.
5. Steffen H., Linhoff K., Runkel M., and Hammerschmidt J.: "Outotec Pretium Roaster Optimizer – Recent developments and machine learning in fluidized bed plant operation". Paper presented at EMC (2021).

Table 1: **Metso Outotec's historical/current sulphuric acid technology portfolio**

	Metallurgical off-gas feed (Cu, Zn, Ni...)	**Pyrite feed**	**Sulphur feed**
Maturity level	High	High (mainstay in the 1950s)	High
Trends	• Impact by circular economy • Degradation of ore grades • "Green commodities"	• Technology used in roasting of i.e. Zn, Au, treatment of residues etc. • Projects linked to precoius and battery metals content • Use of oxygen; plant size	• Energy recovery options • Emission control (NOx/S fumes) • Plant size • Use of "Frasch" sulphur?

Source: Metso Outotec

Table 2: **Metso Outotec's ideas on future technologies to respond to the disruptive scenarios of energy transition**

	Gypsum/phosphogypsum	**Sulphur + pure oxygen**	**Alternative flowsheets**
Maturity level	Low	Idea screening initiated	n/a
Aspects	• Pollutants in phosphogypsum • Circular sulphur economy • Use of hydrogen/solar energy • Carbon fixation	• Potential use of oxygen by-product and sulphur (with/without pressure) • Capex and opex significantly lower (30-50%) compared to conventional • Parts of process are already proven	• Consideration of old and new flowsheets • Disruptive technology replacing acid consumption • Economic viability of the flowsheet will play a role

Source: Metso Outotec

Maximising energy efficiency in acid plants

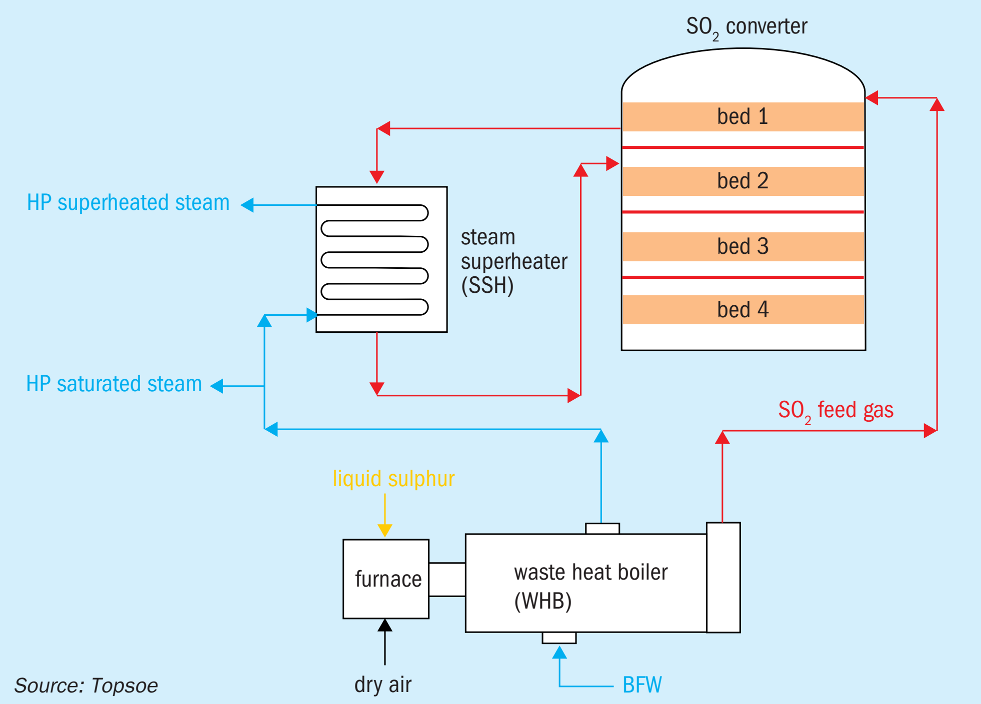
With energy prices skyrocketing, sulphuric acid plant operators face a heightened challenge to improve plant efficiency. **Martin Alvarez** from Topsoe discusses how the company's new high-activity catalyst, VK38+, can help acid plants maximise energy efficiency to secure important economic benefits while simultaneously reducing their carbon footprint.

With geopolitical tensions leading to a sustained increase in electricity prices, improving the energy efficiency of acid plants has become a priority for many sulphuric-acid operators. However, this isn't a straightforward task since it can require expensive revamps, or the installation of new, advanced heat recovery systems. A cheaper option is to upgrade the catalyst loading using the new potassium-promoted VK38+ catalyst, which was introduced in 2020, to tip the scales in operators' favour as new operational necessities arise.

Case 1: Increasing steam generation

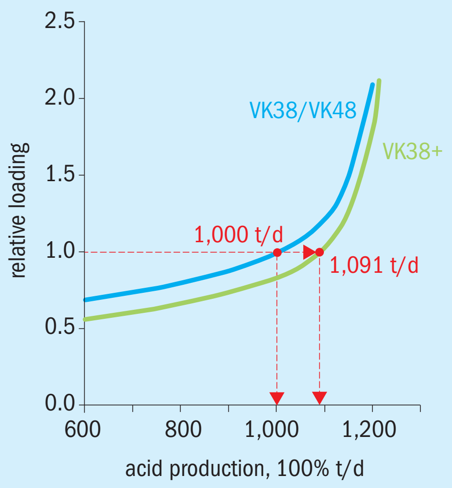
A typical sulphur-burning unit has a steam system designed to recover the heat generated across the various process units; a major portion of the recovered heat originates from the combustion of the molten sulphur into SO_2 gas. This SO_2 feed gas exits the furnace and is cooled in a waste heat boiler (WHB) to the optimum inlet temperature required for entry into the first bed of the SO_2 converter. Once the gas enters the converter, the oxidation of SO_2 to SO_3 occurs in the different catalyst beds. The conversion process is exothermic, so recovery of as much reaction heat as possible in the interbed coolers, will prove economically attractive. As shown in Fig. 1, the gas exiting bed 1 is typically cooled in a steam superheater, which uses this energy to superheat a portion of the saturated steam produced by the WHB. Since the recovered steam can be used a) to generate electricity in a steam turbine, b) as a heating medium in other parts of the unit, or c) exported to other customers, increasing steam production is often of key importance.

Fig. 1: **Typical steam circuit in a sulphur-burning plant**



Source: Topsoe

Fig. 2: **Acid production for different loading sizes for VK38 and VK38+**

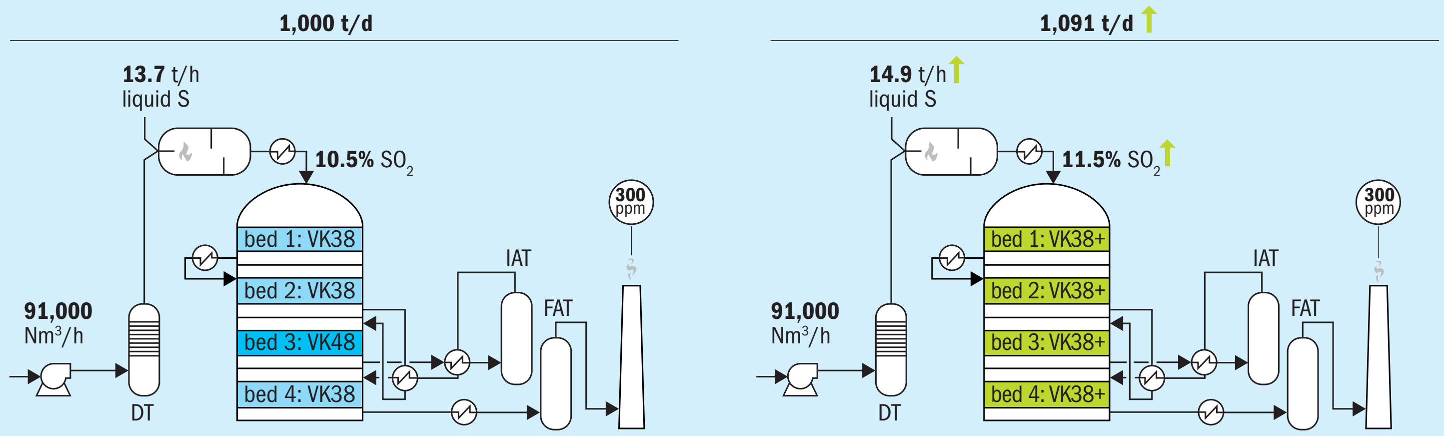


Source: Topsoe

How can VK38+ help to increase steam and acid production?

One of the ways to increase the steam generated in a sulphur-burning plant is by increasing the amount of sulphur that is burnt in the furnace, while maintaining the air flow rate constant. This would be very attractive for most acid producers because it would enable, at the same time, an increase in the production capacity of the unit without increasing the gas volume handled by the plant. However, keeping the air-flow unchanged while burning more sulphur will increase the SO_2 concentration at the inlet of the SO_2 converter. And if the catalyst solution isn't upgraded, then a stronger gas will inevitably generate higher SO_2 emissions. There are two alternatives for utilising stronger feed gas without experiencing

Fig. 3: **Effect of increasing the gas strength using the same volume of VK38+ catalyst**



Source: Topsoe

such an emission increase. The first is to increase catalyst volume, but free converter space is usually very limited or unavailable altogether. The second alternative is the use of a more active catalyst.

Fig. 2 displays the catalyst volume needed for a sulphur-burning unit to reach a certain level of emissions at different acid production rates. Both curves have been made considering a constant airflow of 91,000 Nm^3/h, and the different production capacities have been achieved by increasing the strength of the feed gas. The VK38+ curve remains consistently at the right of the VK38/VK48 curve, showing that a VK38+ solution can, in general, accept stronger gases and higher capacities from the same catalyst volume.

Fig. 3 explains how this concept can be applied to a 1,000 t/d plant operating initially with 10.5% SO_2 gas. By switching the catalyst from VK38/VK48 to the same volume of VK38+, the catalytic converter would be able to admit the same feed gas flow at a higher SO_2 concentration, keeping the emission level unchanged. The increase in the gas strength from 10.5% to 11.5% will lead to a production increase from the original 1,000 t/d to 1,091 t/d. Using a sulphuric acid price of €117/t, these 91 extra daily tonnes of acid will bring an annual benefit of around €3.50 million.

As this increase in the gas strength is achieved by burning more sulphur in the furnace, the sulphur combustion heat increases by around 3.10 MW. Provided that the steam system has thermal capacity available to recover this additional heat, these 3.10 MW are equivalent to an extra HP steam production of approximately +110 t/d. The extra steam production is achieved without increasing the pressure drop of the unit and therefore improving the energy efficiency of the plant.

Using the natural-gas cost of the steam generation, 110 tons of extra steam, delivered daily, would represent around €3.79 million/year, according to the current gas prices at the Dutch TTF (€130/MWh). On the other hand, assuming a liquid sulphur price of €350/t, the additional 1.2 t/h of liquid sulphur that needs to be added to the furnace in order to increase the SO_2 strength to 11.5% would have an extra cost of €3.45 million/year.

Overall, after deducting the liquid sulphur costs, the economic benefit of the VK38+ solution would be around €3.84 million/year. This is summarised in Table 1.

The extra amount of steam generated will result in a carbon emission reduction of approximately 4,500 t/year of CO_2.

Table 1: **Benefits of using VK38+ in a 1,000 t/d sulphur-burning unit**

Outputs	
Extra heat, MW (compared to VK38/VK48 case)	+3.10
Extra steam produced, t/d (compared to VK38/VK48 case)	+110
Extra acid produced, t/d (compared to VK38/VK48 case)	+91
Inputs	
Additional liquid sulphur burnt, t/h (compared to VK38/VK48 case)	+1.2
Benefits/cost	
Extra steam earnings, million €/year	+3.79
Extra acid production earnings, million €/year	+3.50
Extra sulphur costs, million €/year	-3.45
Total earnings, million €/year	**+3.84**

Source: Topsoe

Case 2: Reducing the blower's energy consumption

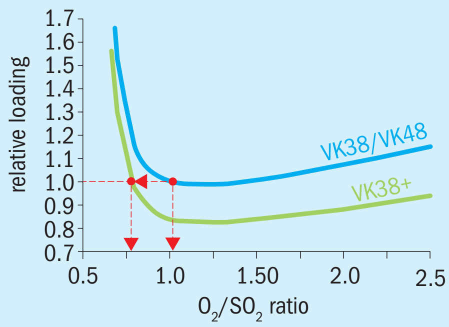
The power consumption of the blower is another process point to focus on when optimising the energy efficiency of a sulphuric acid plant. There are two ways to reduce the blower's energy consumption: reducing the feed-gas flow rate or reducing the pressure drop.

How can VK38+ help reduce the gas flowrate without losing production?

Reducing gas flow won't be a very attractive option, since solely doing so will reduce acid production to the same degree. However, if reduced feed-gas flow is compensated by increased feed-gas strength, acid production can be maintained, even with the plant operating at a lower flow rate.

As discussed in the previous section, in order to avoid an increase in the emission level, an increase in the gas strength needs to be accompanied by an increase in catalyst activity. Fig. 4 displays the catalyst volume needed for a 1,000 t/d sulphur-burning unit that reaches a fixed emission level at

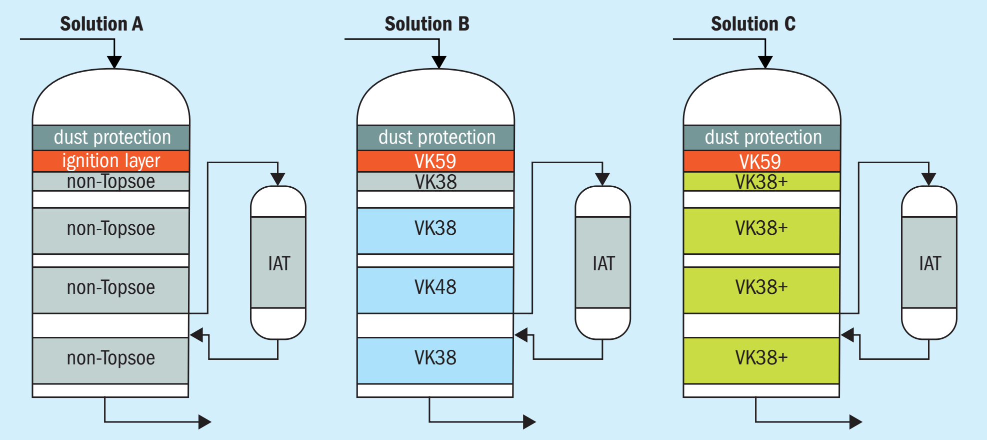
Fig. 4: **Difference in VK38/VK38+ loading volumes at various O_2:SO_2 ratios for a 1,000 t/d unit**



	VK38/VK48	VK38+
O_2/SO_2 ratio	1.00	0.78 ↓
SO_2% feed gas	10.5	11.8 ↑
Flow, Nm³/h	91,000	81,000 ↓
Production, t/d	1,000	1,000
Emissions, ppm	300	300

Source: Topsoe

Fig. 5: **Three different loading sizes for a 2,900 t/d project at a certain emission level**



Source: Topsoe

Table 2: **Energy consumption levels for three different proposed solutions**

	Solution A	Solution B	Solution C
Catalyst type	Non-Topsoe	VK38/VK48	VK38+
Capacity, t/d	2,900	2,900	2,900
Relative loading	**1.16**	**1.00**	**0.85**
Catalyst pressure drop, mm WC	451	390	335
Energy consumption, GWh/year	3.42	2.96	2.54
Blower energy cost, €/year	846,000	731,000	628,000

Source: Topsoe

various feed gas O_2:SO_2 ratios. Similar to the previous case, the VK38+ curve remains consistently below the VK38/VK48 curve, showing that a VK38+ solution can accept lower O_2:SO_2 ratios, i.e., stronger gases, for a given catalyst volume.

For example, a 3+1 double absorption sulphur-burning plant that originally processes 1,000 t/d with 91,000 Nm³/h of 10.5% SO_2 gas requires a certain volume of VK38/VK48 to meet an emission level of 300 ppm. If this plant switches from use of VK38/VK48 to the same volume of high activity VK38+ catalyst, then it will be able to operate with an SO_2 strength of 11.8% and a lower gas flow of 81,000 Nm³/h, without experiencing a change in production or emission level.

This flow rate reduction from 91,000 Nm³/h to 81,000 Nm³/h will cause a reduction of 18% in the total converter pressure drop. This will translate to a reduction in the blower's power consumption of around 215,000 kWh/year, which corresponds to €53,000/year, using current European electricity prices (€0.247/kWh). Additionally, these 215,000 kWh/year will correspond to a CO_2 reduction of 150 t/year.

How can VK38+ help reduce the pressure drop?

For some units, the use of a higher SO_2 strength might not be possible due to certain equipment design limitations. In such cases, pressure drop can still be reduced by using a smaller volume of a higher activity catalyst to meet the required target. This is illustrated by the following example.

Fig. 5 compares three possible solutions proposed for a project of a new copper smelter unit, operating at 2,900 t/d, across two-year campaigns. Solution A utilises a non-Topsoe catalyst loading, Solution B utilises a VK38/VK48 catalyst design, and Solution C utilises a VK38+ catalyst solution. Each case assumes the same feed gas flow rate and composition, the same converter diameter, and the same SO_2 emission level.

Estimated pressure drop and energy consumption for each scenario is shown in Table 2.

As shown in Table 2, the VK38+ solution could provide energy savings of up to 0.88 GWh per year. Across a two-year campaign, the same energy savings could be as high as €436,000 compared to Solution A and as high as €206,000 compared to Solution B.

These power consumption savings will also have a positive impact on carbon footprint: the VK38+ solution can reduce CO_2 emissions by 1,200 t more per campaign, than the non-Topsoe solution, or around 600 t more than the VK38/VK48 solution.

Finally, it should be noted that reducing catalyst volume reduces screening work, which will most likely translate to shorter shutdown durations and more days spent producing acid. Reduced catalyst volume will also decrease associated catalyst disposal costs. These savings aren't considered in the numbers shown in Table 2.

Conclusions

Switching from a standard design (VK38/VK48) to a VK38+ setup provides the possibility of operating with stronger gases. This, in turn, gives operators the flexibility needed to reduce flow while maintaining production levels, which saves blower energy, or maintain flow in exchange for considerable acid and steam production increases. In cases where an increase in the strength is not possible, energy efficiency can be improved by reducing the catalyst volume and taking advantage of the higher activity of VK38+.

Whether the goal is to maximise acid and steam production or to reduce the blower's power consumption, optimising the energy efficiency of the plant with VK38+, will not only rapidly compensate for the additional costs of a higher activity catalyst, but will also deliver important long-term financial and environmental benefits. ■

Acid mist removal

NORAM has recently introduced a patented acid entrainment mitigation device (EMD) to deal with acid mist carryover from sulphuric acid towers.

In sulphuric acid plants acid mist carryover can occur due to a number of factors:

- fine mist carryover from the gas cleaning section into the dry tower;
- excessive acid entrainment from acid tower distributors and/or packing;
- failure of demisters in the dry, interpass and final towers;
- excessive cooling of the gas downstream of acid towers causing increased condensation.

The effects of acid mist carryover can cause the following issues:

- corrosion and damage of equipment such as blowers, gas-to-gas heat exchangers, converters and ducting;
- fouling and increased pressure drop in gas-to-gas heat exchangers;
- catalyst fouling, increased pressure drop and unwanted plant shutdowns to perform catalyst screening (lost production);
- reduced equipment life.

NORAM's patented acid entrainment mitigation device (EMD).

EMD features and performance

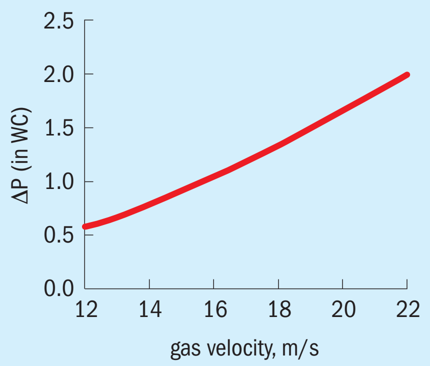
NORAM's EMD is designed to achieve significant acid entrainment removal while maintaining low gas pressure drop. The equipment pressure drop is between 1- and 2-inches WC. The droplet capture efficiency increases for larger particles. The best performance is found for particles above ten microns in diameter.

The EMD features a bundle of swirl tubes that are designed to remove acid droplets from the process gas using a cyclonic principle. The captured sulphuric acid flows along the ducting internal walls and is drained to an existing tank or a drainpot with level indication to act as an early-warning system to alert operators if acid entrainment collection has increased, and therefore identify issues of upstream towers.

The EMD is made of acid resistant alloys and does not require replacement of internals (equipment only to be inspected at plant turnarounds). It does not require a new civil foundation. It will fit in the available space. It can be installed in-line and inside of a process gas duct and does not create an obstruction for process gas.

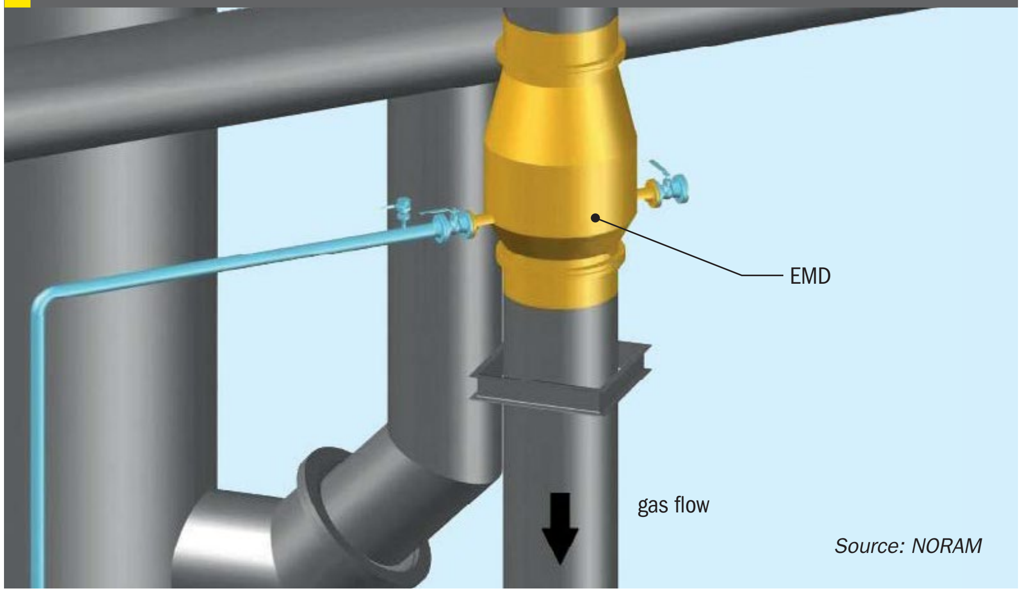
Tube bundle.

Fig. 1: **EMD gas pressure drop**



Source: NORAM

Fig. 2: **EMD in-line installation**

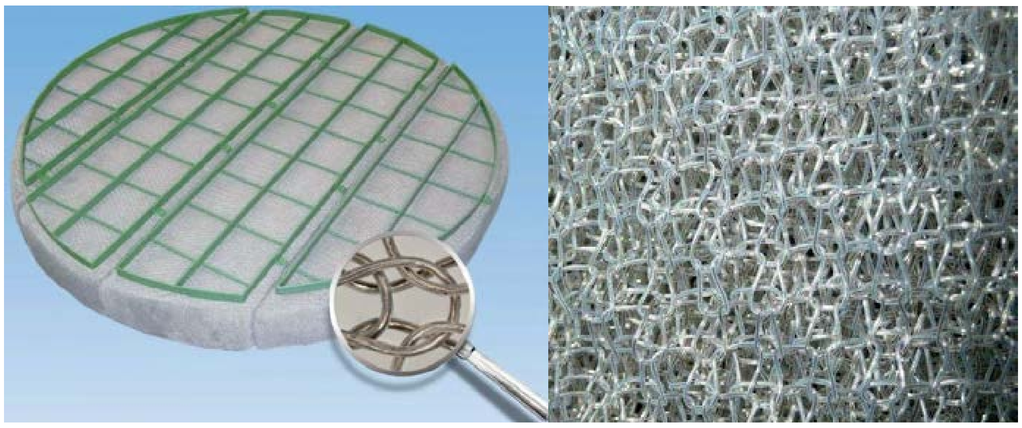


Source: NORAM

Mist elimination challenges in corrosive applications

Daniel R. Egger of Sulzer Chemtech Ltd discusses mist elimination challenges in strong sulphuric acid applications and presents the unique Sulzer KnitMesh XCOAT™ mist eliminator as an ideal solution for corrosive services such as in sulphuric acid drying towers.

Droplet removal plays a very crucial role in preventing damage to downstream equipment. This issue becomes more alarming in highly acidic applications such as in sulphuric acid drying towers. Poorly designed, corroded or fouled drying tower mist eliminators are common sources of excessive entrainment. In drying towers, the operating life of mist eliminators is affected by two primary factors: corrosion and fouling. A new high corrosion and temperature resistant fluoroplastic filament used in the Sulzer KnitMesh XCOAT mist eliminator provides an innovative approach to these problems.



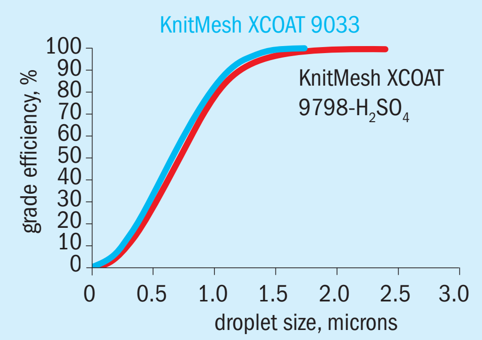
PHOTOS: SULZER

Fig. 1: Sulzer KnitMesh XCOAT™ mist eliminator.

Challenges in strong sulphuric acid applications

Proper selection of equipment for mist elimination in sulphuric acid drying and absorption towers is still a challenge from the performance and material points of view. Operating evidence shows that the gas-liquid interface represents one of the highest risks of corrosion and since mist eliminators operate in this region, they are one of the most challenging corrosion environments in the plant. In sulphuric acid drying towers, knitted wire mesh pads are the principal type of equipment used. One of the common sources of excessive entrainment in drying towers is corroded and fouled mist eliminators which causes acid condensation during shutdowns and thus degradation of the catalyst. Several factors have therefore to be considered in the selection of the mist eliminator type and the material of construction where the longevity depends on the operating conditions, acid concentration and material used.

Fig. 2: **Grade-efficiency curve of Sulzer KnitMesh XCOAT 9033 and 9798**



Source: Sulzer

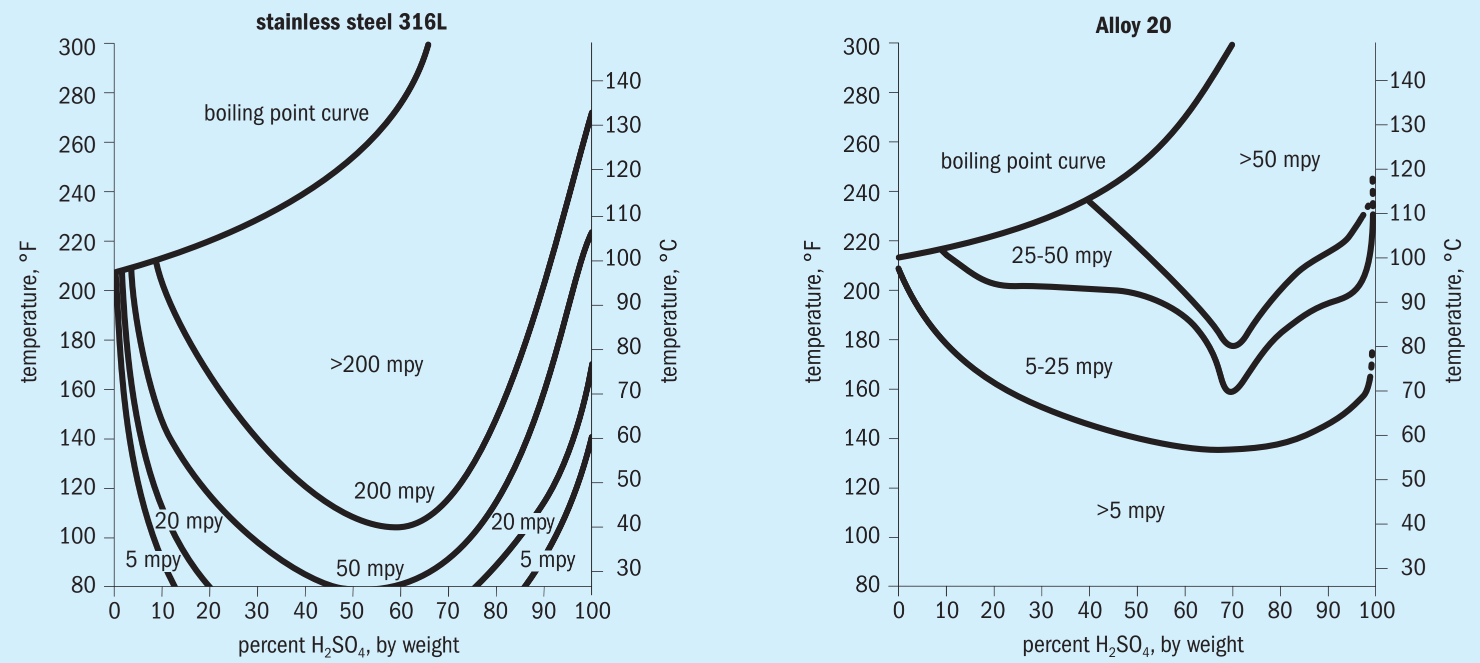
Acid mist eliminators

Knitted wire mesh mist eliminators are used as a low cost, highly versatile and efficient method of removing liquid entrainment from gas streams. They are produced as a bed of knitted mesh which presents a tortuous path and large surface area to the droplets entrained in the gas stream. Separation is achieved by impingement and capture by the filaments of the mesh where droplets coalesce and drain. High performance mesh mist eliminators provide excellent separation efficiency down to droplet sizes as small as 2 microns and with a pressure drop typically less than 7 mbar. Fig. 2 provides the grade efficiency for Sulzer KnitMesh XCOAT 9033 and 9798. 100% of the entrainment larger than 2 microns and a significant percentage of droplets below 1 micron diameter are removed.

Impact of corrosion on lifetime

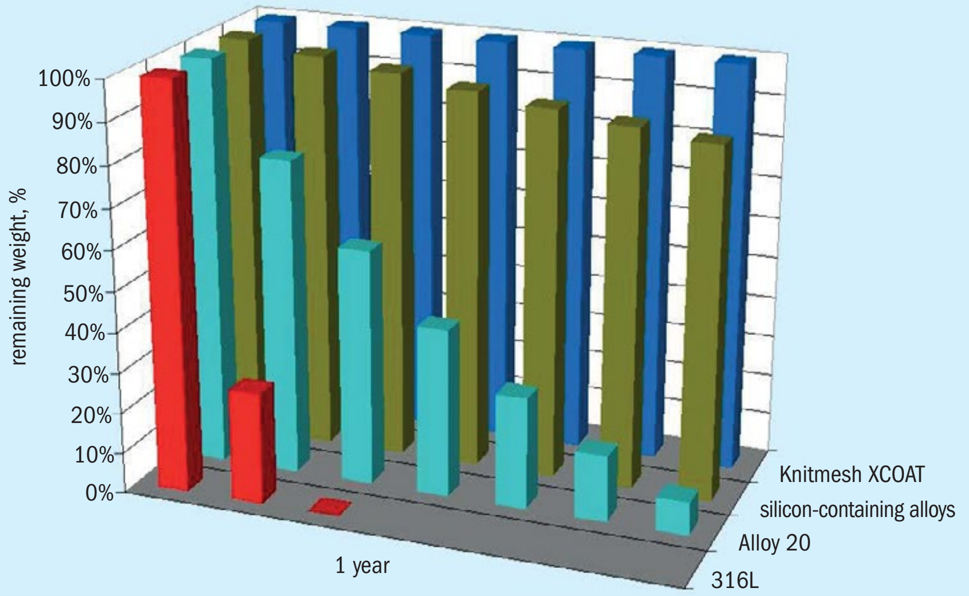
Most common drying tower mist eliminators comprise stainless steel wires which have a standard diameter of 0.28 mm. Even with low corrosion rates, it will not take long for the wires to corrode through.

Fig. 3: **Corrosion rates of stainless steel 316L and Alloy 20 in sulphuric acid**



Source: Sulzer

Fig. 4: **Corrosion rate of Sulzer KnitMesh XCOAT™ compared to other materials**



Source: Sulzer

Assuming a corrosion rate of 0.1 mm/year (4 mpy) the wire will be destroyed in two years or less.

Nickel-based alloys such as Alloy 20 can typically be used to reduce the rate of corrosion and to improve the service life of the mist eliminators (Fig. 3). However, there are cases where even Alloy 20 is not sufficient because the temperature and/or sulphuric acid concentration is in a range where increased corrosion occurs. Drying tower mist eliminators face dangers from such swings in the acid concentration and temperature. Both of these factors can result in a significant decrease of service life.

Silicon-containing stainless steels provide an improved corrosion resistance towards sulphuric acid. But, depending on the alloy type, operating temperature and acid concentration, the corrosion rate can rapidly achieve a critical level for mist eliminator wires where only 0.05 mm of corrosion allowance exists. In addition, the presence of fluorides should be avoided since it will attack the silicon in the alloy.

Non-metallic materials such as fluoroplastics like PTFE, PFA, ETFE or FEP are also known to be very resistant to corrosion. However, they lack mechanical strength and are prone to shrinkage at higher temperatures causing gaps between the mist eliminator sections and gas bypassing. Amongst these materials, PTFE and PFA show the best results in resistivity and durability at high temperatures and are totally resistant to sulphuric acid.

Extension of service life with the Sulzer KnitMesh XCOAT mist eliminator

To address these concerns, Sulzer has introduced a new mist elimination solution for corrosive media. The concerns related to corrosion, shrinkage, collapsing is sustainably solved by the Sulzer KnitMesh XCOAT mist eliminator which combines the excellent chemical and temperature resistance of fluoroplastics with the mechanical strength of a stainless steel wire. The Sulzer XCOAT material consists of a 100% pure best-class fluoroplastic monofilament which contains a stainless steel wire core. This leads to extremely high resistance to deformation, corrosion and temperature, and makes it particularly ideal for corrosive environments such as in sulphuric

Table 1: **Pros and cons of wire mesh eliminators made of different materials**

	Separation efficiency	Corrosion resistance	Capacity	Temperature resistance	Opex***
Stainless steel	✓	✗✗	✓	✓	✗
Alloys	✓	✓✗**	✓	✓	✓✗**
Fluoroplastics	✗*	✓	✗	✗	✗✗
Sulzer Knitmesh XCOAT™	✓	✓✓	✓	✓	✓

** Due to shrinking of material causing by-passing*

*** Concerned due to temperature concentration and/or acid concentration swings*

**** Raising Opex due to more frequent requirement to shutdown the plant to replace the mist eliminator*

Source: Sulzer

acid applications. Characterised by these features, the Sulzer KnitMesh XCOAT is the world's first, unique wire mesh mist eliminator being a fluoroplastic 'monofilament' and integrating all the valued advantages of metal wire mesh pads.

Field and lab tests have been conducted to demonstrate the corrosion resistance of the Sulzer KnitMesh XCOAT. Fig. 4 compares the corrosion of Sulzer XCOAT and various stainless steel and alloy wires in the presence of 93-98% sulphuric acid, at 60-80°C, over the period of one year.

Table 1 summarises the pros and cons of wire mesh mist eliminators made of different materials.

Case story

One of the world-leading sulphuric acid plant and clean technology providers contacted Sulzer for the replacement of a fluoroplastic build wire mesh mist eliminator in a SO_2-sulphuric acid wet gas scrubber in a zinc factory. The existing wire mesh pad was completely constructed of fluoroplastic with no metal or alloy as virtually no metal contamination (max. 25 ppb) is tolerated in the product stream. While the scrubber is operated at a relatively high operating temperature of around 120°C the existing fluoroplastic mesh pad showed very severe shrinkage (see Fig. 5), requiring replacement of the pad every six to ten months.

Fig. 5: Shrunken fluoroplastic wire mesh mist eliminator which was exposed to a temperature of ~120°C.

Once the mesh pad was replaced with the Sulzer KnitMesh XCOAT, shrinkage of the mist eliminator was no longer a problem. To meet the low metal contamination requirement in the product stream the metal grids of the KnitMesh XCOAT pad were also coated with a best-class fluoroplastic overlay for this service. Based on client's information the KnitMesh XCOAT has been in service for many years without any requirement for replacement, and the payback for this turnaround was achieved in less than a year. Truly a big success story.

Conclusion

Benefits of longer turnaround cycles, payback and opex calculations as well as the maintenance culture have an impact on the selection process by plant management. The information provided in this article serves to explain the benefits of the Sulzer KnitMesh XCOAT mist eliminator as regards service life, efficiency, and capacity.

A novel thermal stage process camera for sulphur plants

Enhancing the reliability of sulphur plant starts in the thermal stage. **Matt Coady** and **Martin McCallister** of Delta Controls report on a recently developed and launched insertable process camera that monitors the vessel interior of online Claus thermal reactors, providing valuable process data which will allow plants to make better informed operation decisions.

Over the past decade, the refining industry has seen a shift from achieving environmental targets to emphasising reliability. Unreliable sulphur plants now have financial implications by posing the risk of reducing refinery throughput. In addition, long term plant reliability is a priority as runtimes are being extended between planned shutdowns. How can the reliability of sulphur plant operations increase to maintain throughput and avoid outages? A logical place to start is with the Claus thermal reactor in the sulphur recovery unit (SRU) as the thermal stage is most prone to fail due to intense operating conditions. Thus, reliability improvements made here are beneficial to the entire SRU performance.

However, improving reliability is a complex and challenging task. The trend of increasing instrumentation installed on the thermal reactor to achieve more process awareness is common. Instrumentation – including analysers, flame scanners, and temperature indicating devices such as pyrometers and thermocouples – is often connected to the SIS system and is key to understanding the process status. While these instruments provide critical process data, there still remains many unknowns when it comes to the health of the thermal reactor. Current instrumentation cannot effectively detect damage to the burner, refractory or tubesheet protection system. Often an operator's only method for visual inspection is through sight ports, which have a number of common issues. Sight ports fundamentally suffer from a narrow field of view due to the constriction of the bore along the sight path. Additionally, sulphur often occludes on the glass or in the bore which limits the view as seen in Fig. 1.

Fig. 1: Traditional sight ports are ubiquitous but suffer from blockage, glass occlusion and a limited view.

In the effort to increase reliability, the challenge becomes how to predict and identify a root cause before symptoms appear or are detected by current instruments. The ability to internally view the inside of a vessel will allow users to make pre-emptive operational decisions based on the condition of the burner, tubesheet, and refractory. High resolution images and video feed of these reactor components provide the data needed to make informed decisions, avoid major equipment failures, and reduce vessel downtime. Delta Controls Corporation is excited to announce the launch of ProSpection™, a process camera designed for continuous online inspection of the SRU thermal reactor.

ProSpection™ process inspection camera

The primary design considerations for the process inspection camera include achieving the best view of the vessel's interior, the camera's usability and reliability, and most importantly the camera assembly's safety.

A wide-angle lens placed at the refractory hot face with an insertable probe assembly provides the most useful view of the critical components of the vessel interior (Fig. 2). A number of significant challenges for this design were taken into consideration by the Delta Controls design team. For example, the camera and lens have a melting point near 65°C, which requires the use of a consistent cooling system to survive the internal operating temperature of the Claus reactor. Another challenge was developing a stainless steel probe assembly that could be sufficiently cooled while accurately maintaining a surface temperature above the sulphur dew point corrosion but also below high temperature sulphidation.

To overcome these material, corrosion, and temperature limitations, the camera design incorporates a patent pending thermal regulation system that uses water or air circulated through a series of channels to accurately regulate the probe's temperature between the sulphur dewpoint corrosion and high temperature sulphidation limits, as well as maintain the camera circuitry within its temperature limits. Furthermore, the thermal regulation system maintains the lens temperature above sulphur's freezing point to prevent lens occlusion.

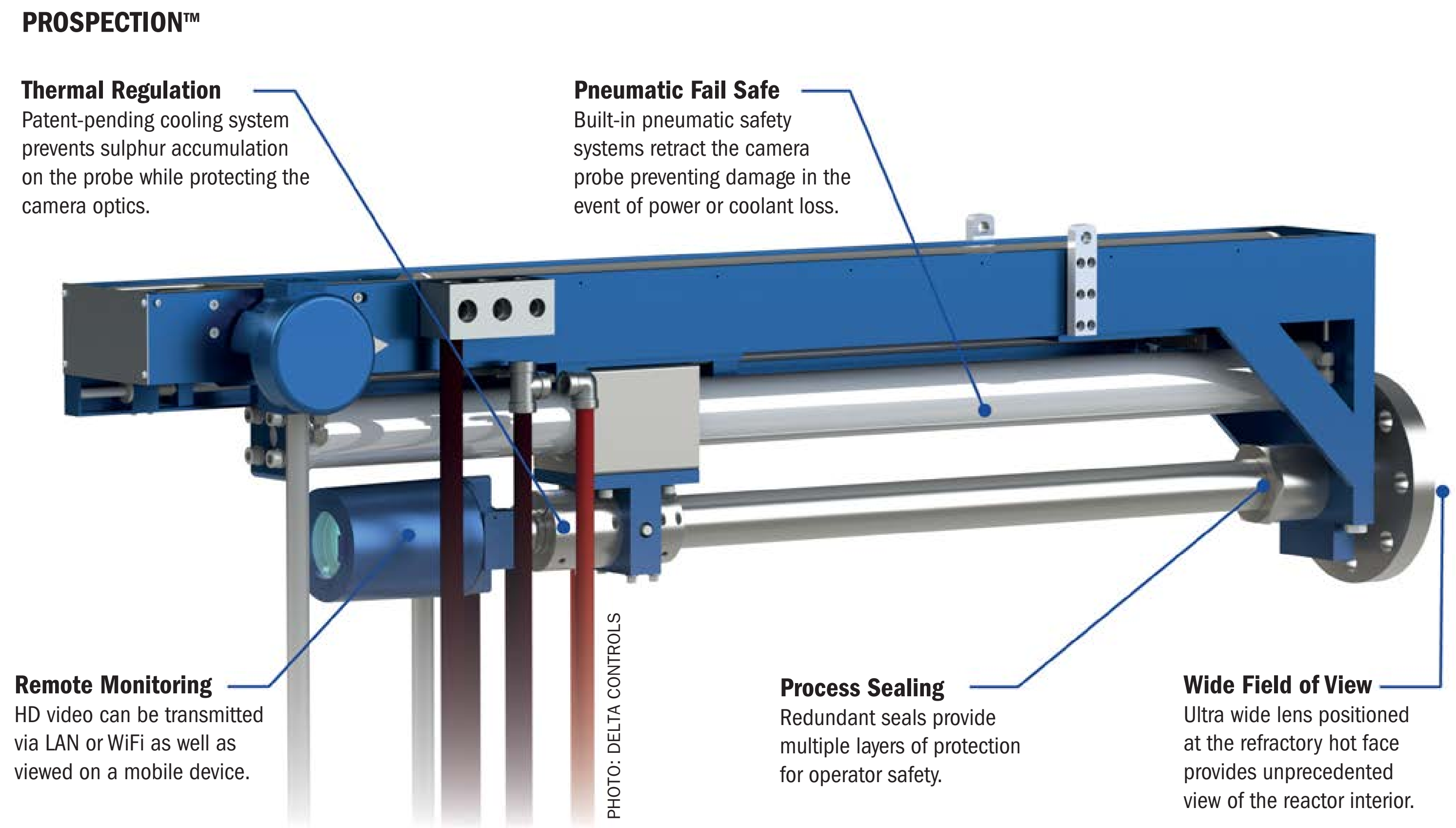


Fig. 2: ProSpection™ process camera incorporates numerous reliability measures to make it suitable and reliable for sulphur recovery service.

The camera probe assembly is designed to be inserted through an isolation valve while a vessel is online and is either left installed indefinitely for long term monitoring or used for a temporary inspection. A flanged seal assembly mounts to a three-inch or larger nozzle flange and incorporates multiple redundant seals to allow for the camera to insert and retract without process leakage. As an added safety feature, a nitrogen supply applies a positive back pressure to the seals that is higher than the process pressure. Thus, in the event that a seal is compromised, nitrogen would flow through the damaged seal and into the reactor. An inline flow meter would indicate flow and therefore that a seal had been compromised. This system serves to prevent any process gas leakage as well as an indication of seal integrity.

To automate the insertion and retraction of the camera probe assembly, the ProSpection™ inspection camera utilises a pneumatically driven extraction system that actuates the camera into and out of the vessel through the flanged seal assembly. This system allows for failsafe features to optimise the camera for long-term operation. The camera can automatically order its own retraction from the process for any number of fault conditions such as loss of coolant, rising camera temperature, loss of power, or loss of instrument air. As an additional fail-safe feature, the system also contains an onboard air tank with enough air capacity to safely remove the camera in the event of an air supply loss.

To support the camera and the extraction assembly on a nozzle flange, the Delta Controls engineering team designed a suspension system that offloads any force from the nozzle (Fig. 3). The suspension system supports the weight of the camera system and allows for the entire assembly to freely move as a vessel thermally expands. This support design allows for travel in multiple directions as the vessel expands radially and longitudinally during start-up. Additionally, the system provides uniform support as the assembly's centre of gravity changes when the camera moves from the inserted or retracted state. There is a supplemental spring and damper assembly that stabilises the camera when the vessel experiences vibration.

The camera's optical design is optimised for the incandescent environment found inside a sulphur recovery unit. A series of optical filters protect the camera lens from infrared energy and filter specific light wavelengths. Video and images are sent to the control room in the visual spectrum and can be set to provide continuous live video or capture still images from specified intervals. The ProSpection™ process inspection camera is designed to function well with units using conventional firing as well as the brighter interior of a unit using oxygen enrichment.

Use cases: monitoring critical components

The ProSpection™ process inspection camera allows new views into online reactors that provide more information and thus can better guide decision-making. Common critical areas of interest include the burner, refractory lining and tubesheet protection system. Catching early failures in any one of these areas can be a huge benefit to the unit operator.

Starting with the burner, continuous monitoring with a camera can provide significant data improvements over other instrumentation such as flame scanners. Burners are oftentimes the root cause of many larger failures seen in sulphur plants. A failing or poor performing burner can not only cause poor chemistry but also damage to the refractory, waste heat boiler, checker wall and tubesheet. The camera's view allows operators to detect a burner tip that has become distorted or out of alignment. A loss of tip concentricity can lead to flame impingement on the refractory, poor mixing, and further damage to the burner assembly. The end result is extremely poor reactor performance that likely would not be detected using

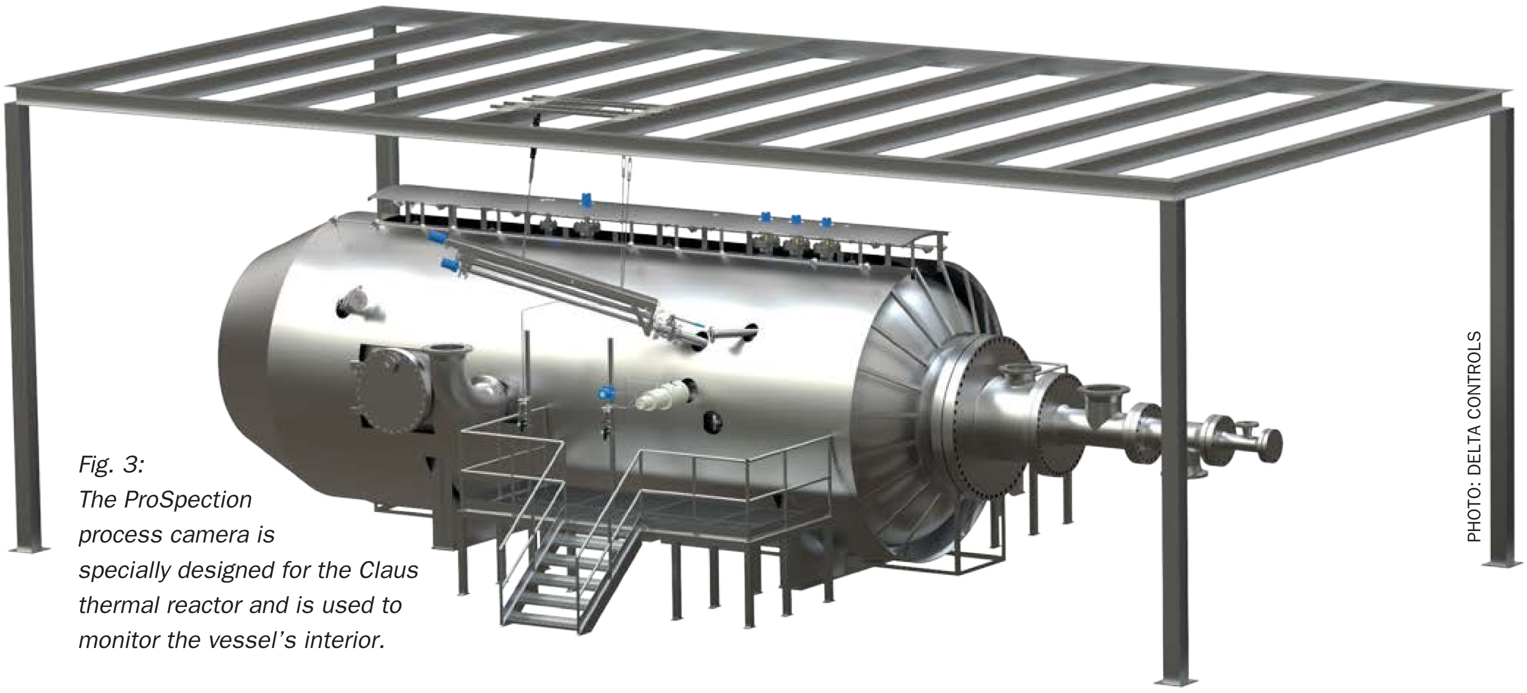


Fig. 3: The ProSpection process camera is specially designed for the Claus thermal reactor and is used to monitor the vessel's interior.

traditional methods. Burner tips can also suffer from other failure mechanisms, such as back burning and the tip metal being consumed by the flame front. These changes in the burner structure would be visible by comparing images taken during routine inspections using the camera. If the burner is found to be compromised, operators could choose to take actions such as reducing flow rates to the burner or shifting throughput to another unit. All of this can be done before further damage is made to the refractory, tubesheet, waste heat boiler, and vessel.

Identifying refractory damage early can prevent major failures such as burn throughs, corrosion problems, and further refractory collapse. The camera's wide-angle view at the refractory hot face could identify sagging or shifting within the vessel. It could also identify early stages of refractory damage such as vitrification of the refractory brick from direct burner impingement, which could lead to cracking. Since refractory often suffers a point failure and temperature measurement is a bulk measurement, the camera identifies problems that traditional temperature instrumentation might not detect. Comparing images taken at regular intervals over a period of time allows operators to detect subtle shifts in any of the refractory components. The refractory images are also valuable before and after a start-up or shutdown event when thermal cycling can stress the refractory. Furthermore, the camera can be used to verify the completion of a refractory dry out, with a camera inspection replacing the need of a physical re-entry for a refractory inspection. Additionally, the camera may prevent the need for a shutdown if there is a suspected problem. Users can identify problems with the refractory before it devolves into larger issues such as a burn through, shell corrosion, or complete refractory failure. This information can lead to operational decisions, such as reducing the vessel load, planning for refractory replacement, or contacting vendors for root cause assistance.

A final focus for camera inspection is the transition to the waste heat boiler: the tubesheet protection system, including ceramic ferrules. Regular inspection can provide insights into reactor performance and avoid major failures related to the waste heat boiler operation. Any process disturbance which affects the reliability of the ferrules would be visible upon inspection. During oxygen enrichment, fuel gas firing or any other thermal event, it is possible to vitrify and or damage the microstructure of the ceramic ferrules. The process camera could be used for in-situ inspection of the ferrules with the potential to identify differences in surface texture, development of crack formation as well as any shift in the position of the ferrule lining (Fig. 4). It would also be able to identify a leaking boiler tube as the water would stain the surrounding area. Identifying these types of problems in service will help identify any issues in the early stages and potentially prevent extensive damage of the boiler equipment. The digital images of the in-situ tubesheet condition can be a useful tool during any root cause analysis that is performed following a major shutdown.

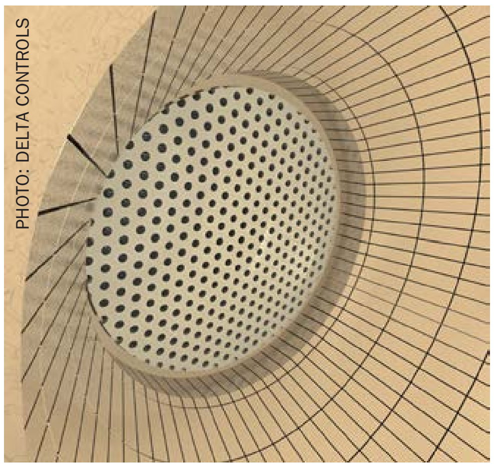


Fig. 4: The ProSpection™ process camera provides online images of the burner, refractory lining and tubesheet protection system, as shown here.

Conclusion

Utilising the ProSpection™ camera allows operators to make more informed operational decisions early on and potentially avoid unnecessary shutdowns and equipment failures. Avoiding unnecessary downtime using photo or video inspections leads to large cost savings. Pre-turnaround discovery can now be done prior to shutdown, allowing users to shorten scheduled or unscheduled turnarounds with fewer surprises in the thermal reactor. Delta Controls Corporation firmly believes the ProSpection™ will be of significant value to the sulphur recovery industry by providing more data about an online SRU reactor than available before. Now operators can shorten downtime, avoid major equipment failures, and make more informed decisions with the ProSpection™ process inspection camera.

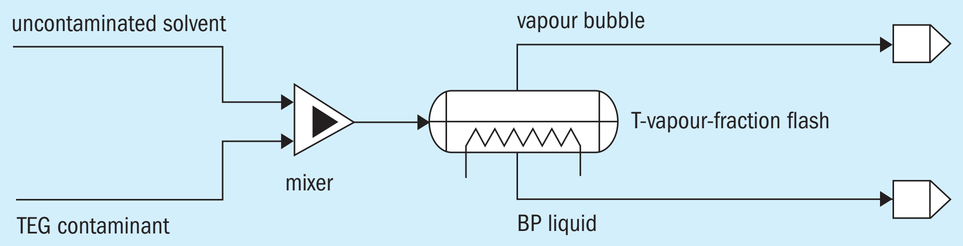
Effect of amine contamination by TEG

The capabilities of OGT's ProTreat® simulator were recently enhanced by the addition of gas treating with hybrid solvents. The functionality was developed generically to make it as broadly applicable as possible. In this article, **Ralph H. Weiland** of Optimized Gas Treating investigates the effect of TEG as a contaminant on the performance of DEA, MDEA, and piperazine-promoted MDEA in a gas treating application.

Hybrid solvents are a class of extractive agents in which, typically, some of the water and amine content of a conventional amine-based solvent is replaced by a physical, non-aqueous, non-reactive component. The earliest commercial example is the solvent Sulfinol-D™ as developed and licensed by Shell Catalysts & Technologies over the last 60 years. There, some of the water and some of the amine (diisopropanolamine, DIPA) are replaced by the purely physical solvent, sulfolane. Later, Sulfinol-M™, and Sulfinol-X® were developed for other gas treatment applications. But, by no means is the inert component in an amine-containing chimeric solvent limited to sulfolane. In principle, any inert solvent could be a candidate. In what follows, triethylene glycol (TEG) replaces sulfolane in the solvent, with a view to quantifying the effect of TEG as a contaminant on the performance of DEA, MDEA, and piperazine-promoted MDEA (referred to as pMDEA here) in a gas treating application.

Glycols are used for gas dehydration, so glycol-contaminated solvents are fairly rare in the refining industry because drying gases is not a usual concern there. However, finished natural gas usually enters a pipeline system where there are strict restrictions on the permitted moisture content of the entering gas. Dehydration is done following amine-based acid gas removal, so carryover is not usually responsible for contamination by glycols, but there are numerous other routes, including misaligned piping, deliveries of the wrong material placed into the wrong tanks, and tank trucks not cleaned out after the previous delivery. The purpose of this article is to shine light onto the question as to how serious the effects of contamination really are on the performance of an amine unit.

Fig. 1: **Creating contaminated solvent for temperature-VF flash calculation**



Source: Optimized Gas Treating

The approach uses the OGT | ProTreat® process simulator. ProTreat's capabilities were recently enhanced by the addition of gas treating with hybrid solvents. The functionality was developed generically to make it as broadly applicable as possible. It is not limited to sulfolane but includes any non-reactive solvent component in the software's database, e.g., dimethyl ether of various polyethylene glycols, sulfolane, MEG, DEG, and TEG.

Important parameters

There is a long list of parameters important to absorber and regenerator performance in gas processing, but only a handful stand out as potentially more sensitive to significant concentrations of contaminant. These include acid-gas vapour-liquid equilibrium (VLE), solvent capacity, and circulation rate. All are interrelated. VLE is obviously important because it:

- controls the driving force for absorption rate of the acid gases;
- sets the maximum achievable treating level in a column and for a component whose removal is directly related to solvent lean loading (moles of removed component per mole of total amine), a normal and common situation referred to as a lean-end pinched column.

Other solvent properties do not determine the maximum achievable treating level, but they play a role in determining how quickly (or in how short a column) that level can be reached. Solvent capacity is directly related to the amine dilution resulting from the addition of an inert solvent component. Contamination by TEG will always lower solvent capacity simply because the amine strength is reduced, although this can be mitigated if the hybrid has increased capacity for acid gas because of more favourable VLE. Thus, before doing simulations of an actual column, examining how contamination by TEG affects VLE is in order. The assessment was done using the ProTreat simulator and treating the amine-water-TEG mixture as a hybrid solvent. This allows proper accounting to be done for interactions between various molecules at high concentrations.

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

Table 1: Effect of DEA strength on VLE with CO_2 or H_2S loaded to 0.1 mol/mol, with and without TEG

Diluted with TEG				Undiluted			
DEA (wt-%)	TEG (wt-%)	P_{CO_2} (Pa)	P_{H_2S} (Pa)	DEA (wt-%)	TEG (wt-%)	P_{CO_2} (Pa)	P_{H_2S} (Pa)
40	10	135	552	40	0	146	611
30	10	76	446	30	0	82	487
20	10	44	331	20	0	46	357

Source: Optimized Gas Treating

Table 2: Raw inlet gas

Component	Mol-%
CO_2	5.00
H_2S	5.00
C_1	0.25
H_2	60.2
CO	0.30
N_2	20.88
Ar	0.25
Water	saturated

Source: Optimized Gas Treating

Approach to VLE calculations

Simulations were designed to mimic contamination of an original TEG-free solvent. Fig. 1 shows how a specified mass flow rate of TEG is added to a given mass flow of uncontaminated (virgin) solution to produce a contaminated mixture. With temperature specified and the vapour fraction set to a very small number (say 10^{-6}) the liquid is forced to its bubble point without generating enough vapour to alter its composition.

Vapour-liquid equilibrium of CO_2 and H_2S

OGT | ProTreat® already has a solid electrolyte thermodynamics framework for aqueous amine systems. Hybrid solvents just add another inert (nonreactive, physical) liquid component to the solvent. A rigorous thermodynamic model was implemented, originally focussing on sulfolane as the inert solvent component but extended to the glycols, to represent the VLE of mixed solvent systems that can simulate any arbitrary combinations of chemical and physical solvents. Chandran et al.[1] give examples for the amine-sulfolane system. The same approach for the amine-TEG-water system accurately represented acid-gas phase equilibrium over several orders of magnitude of partial pressure, spanning a wide range of temperatures, from absorber to regenerator conditions and corresponding to a number of different solvent formulations and a range of acid gas loadings.

As more and more TEG is added to the amine solvent, the amine becomes increasingly dilute, regardless of whether the diluent is TEG or water. Table 1 shows calculated acid gas partial pressures for a typical amine (DEA) at commercial strengths (20-40 wt-%) loaded to 0.1 mol/mol with either acid gas at 45°C, and with TEG contamination of 0 (no contamination) and 10 wt-%. In the interest of space, results are not shown for mixed gases, or other amines, blends, temperatures, or loadings. Suffice it to say all results are consistent with the trends in Table 1 – decreasing amine strength results in decreased acid gas partial pressure, in the case of CO_2 by a factor of three by diluting from 40 to 20 wt-% DEA. In other words, the act of dilution at a given acid gas loading causes a given amine formulation to exert lower acid gas partial pressure, allowing it to achieve a higher purity gas.

Closer inspection between the diluted and undiluted cases in Table 1 reveals that dilution even with just 10 wt-% TEG lowers the H_2S backpressure by nearly 10%. These observations suggest that based on phase equilibrium alone, we should expect that amine solvents contaminated with significant TEG concentrations might perform somewhat better than the virgin solvent in terms of the lowest achievable acid gas content in the treated gas. Granted though, the differences are not huge. It may be noteworthy that dilution of the 40 wt-% virgin DEA solvent with water (to 30% and 20%) is directionally similar to dilution with TEG from 0% TEG to 10 wt-% TEG.

Effect of TEG contamination on CO_2 and H_2S VLE in DEA, MDEA, pMDEA

A wealth of information can be garnered from simulation based on reliable chemistry and physics of the processes occurring, much more than can be presented in a short technical article. Thus, the presentation is limited to representative cases only. All results for the VLE calculations presented here are at 45°C for 50 wt-% MDEA, 30 wt-% DEA, and (42 wt-% MDEA + 3 wt-% piperazine) as a piperazine-promoted MDEA (pMDEA) solvent.

Figures 2-4 show the simulated effect of contamination by up to 50 wt-% TEG on CO_2 and H_2S equilibrium partial pressures over MDEA, DEA, and pMDEA solvents. The decrease in acid gas backpressure can be up to a factor of nearly three and is similar for CO_2 and H_2S, although the H_2S backpressures generally decrease in the order DEA <pMDEA, MDEA at gas loadings

Table 3: Column details

	Absorber	Regenerator
Packing	IMTP 50	#3 Mini Rings
Depth	20 ft	34 ft
Diameter	12 ft	16 ft
Pressure	2.56 MPa(a)	65 kPa(g)

Source: Optimized Gas Treating

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

of 0.1-0.5 mol/mol. Of course, contamination at 50 wt-% TEG could be catastrophic because roughly a doubling of solvent circulation rate might be needed to give a similar level of treating.

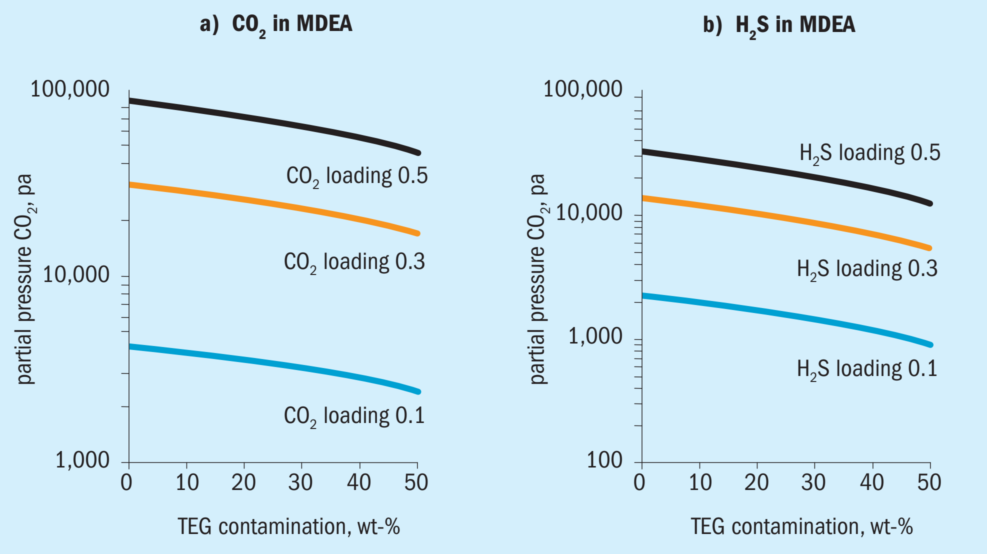
Mass transfer rate-based simulation

Simulating a separation process with ideal stages requires only accurate vapour-liquid equilibrium. The column internals are irrelevant, so the column could as well be empty as far as the effect of tower internals on the separation found from stage-wise calculations is concerned. Physical and transport properties are needed only for tower sizing calculations. The advantage is simplicity. The disadvantage is a calculated result that is extremely hard to translate into the reality of the separation in real equipment. There is inherent inability to translate theoretical stages into physical equipment.

When the simulation is mass transfer rate-based the physical, mass transfer, and hydraulic characteristics of the tower internals are merged with reaction kinetics and phase equilibrium thermodynamics and calculations are all done simultaneously. Mass transfer rates between the phases are calculated in a way that parallels how heat exchanger calculations have been done for at least a century. The methods are rigorous and reliable, they are based on sound scientific and engineering principles, and they provide simulated performance of extraordinary accuracy and reliability with absolutely no need to make any translation from theoretical stages to real internals[2].

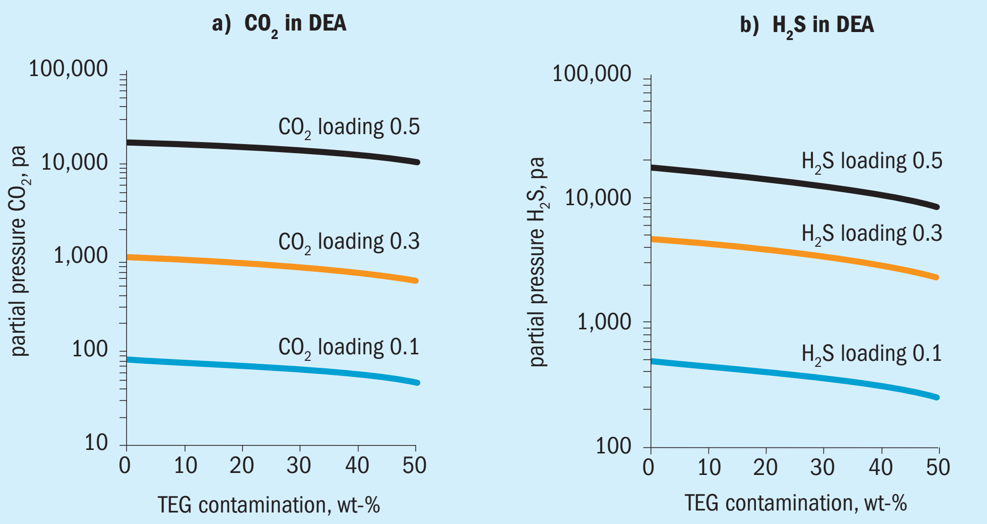
Mass and heat transfer behaviour of the tower internals are characteristics of the internals themselves, but they also depend on certain properties of the phases, and of the species being transported between them. Properties include density, heat capacity, phase viscosity, diffusion coefficients of species in the gas and liquid phases. Properties depend on the species present and their concentrations and usually require mixing rules to transition from pure components to mixtures. From a mass transfer standpoint, however, if a tightly designed system becomes contaminated with glycol, the loss in solvent capacity overrides all other considerations. Mass transfer rates and solvent properties become moot – solvent capacity limitations force the absorber to become rich-end pinched.

Fig. 2: **Effect of TEG contamination on VLE in 50 wt-% MDEA**



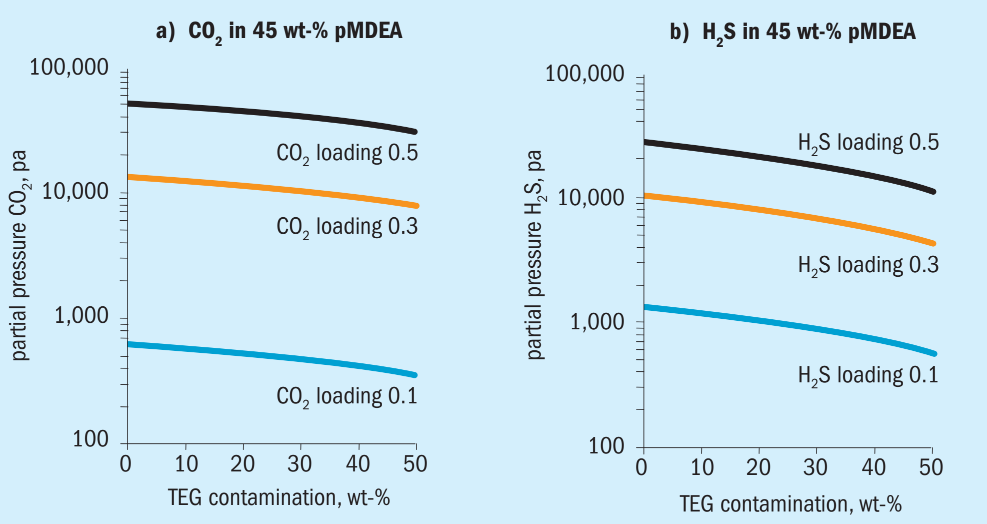
Source: Optimized Gas Treating

Fig. 3: **Effect of TEG contamination on VLE in 30 wt-% DEA**



Source: Optimized Gas Treating

Fig. 4: **Effect of TEG contamination on VLE in 45 wt-% pMDEA**



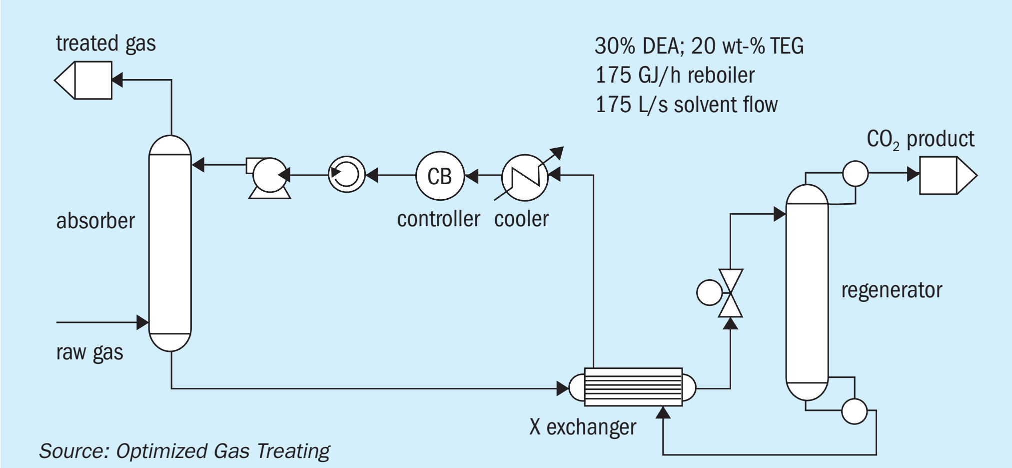
Source: Optimized Gas Treating

Effect of TEG contamination on treating

As a gas treating solvent, the amine content is reactive toward CO_2 and H_2S, but water is an essential ingredient because it allows the amine to react with the acid gases in the first place (aqueous and non-aqueous amine chemistries are quite different). Water allows the amine to dissociate and form ionic reaction products, thereby providing the solvent with high capacity to hold a substantial amount of acid gas. The inert part of the solvent (TEG) can also solubilise acid gases but not to nearly the extent as the amine because it is nonreactive.

For any solvent, the number and range of parameters that could be studied are prohibitive so, to keep the discussion manageable the same raw gas (Table 2) and identical column (absorber and regenerator) details (Table 3) were used for each of the three solvents explored. Solvent rates and reboiler duties are as noted (Fig. 5).

Fig. 5: **Simulation flowsheet**



Source: Optimized Gas Treating

MDEA

Models were run using the OGT | ProTreat® simulator on 50 w-t% MDEA virgin solvent using 0, 10, 20, 30, 40, and 50 wt-% TEG contamination at a total flowrate of 175 L/s. Regenerator reboiler duty was 175 GJ/h. Flowrate and reboiler duty were selected to reject as much CO_2 as possible while having the H_2S level in the treated gas close to 4 ppmv. Fig. 6a shows that for the conditions of this specific case, TEG contamination has minimal effect on both CO_2 slip and H_2S removal despite the total acid gas loading doubling. However, it may be noteworthy that substantial contamination by TEG actually slightly improves H_2S removal and, although not shown here, 50 wt-% contaminated MDEA shows a slightly higher temperature bulge (54.2°C vs. 50.3°C).

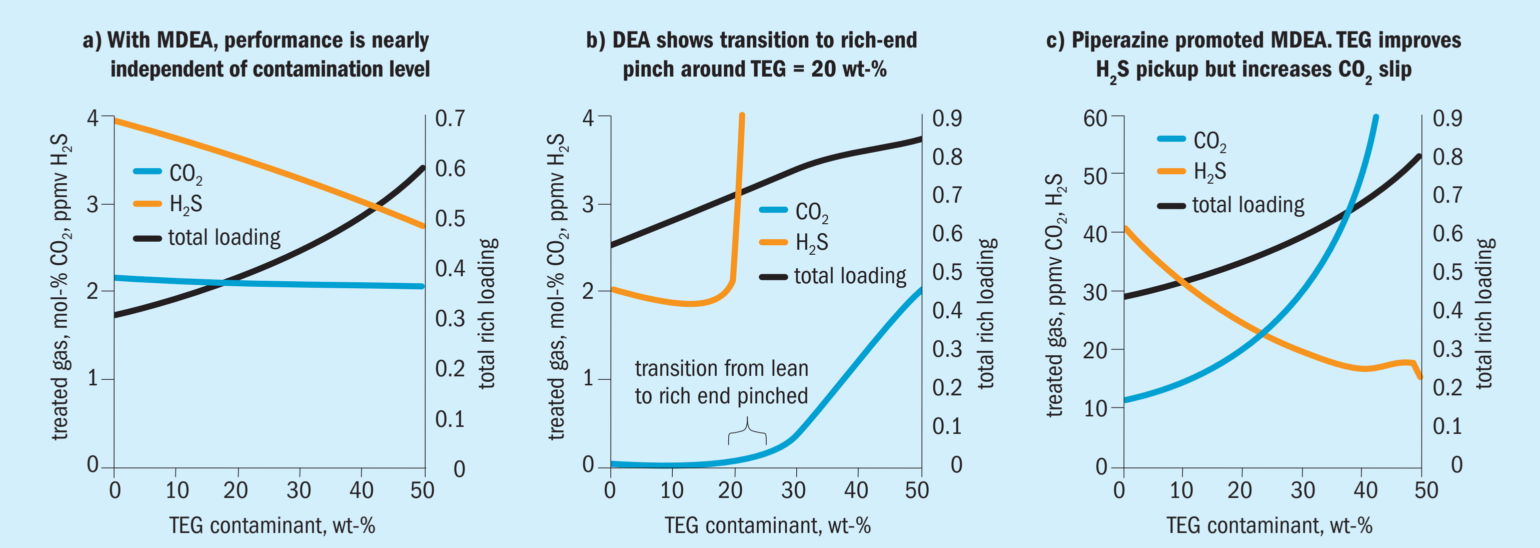
DEA

The TEG-free case was run under conditions that produced about 500 ppmv CO_2 (ammonia syngas quality) but lowered the H_2S content to about 2 ppmv. As the TEG level increases (Fig. 6b) a point is reached where the treating becomes determined not by solvent lean loading but by solvent capacity for absorbing acid gas. This kind of behaviour will occur for any amine because each has limited capacity. The initial improvement in H_2S removal results from improved VLE whereas with CO_2 the VLE improvement is insufficient to counterbalance the effect of TEG and CO_2 loading on viscosity.

pMDEA

With pMDEA, increased contamination for the case shown in Fig. 6c leads to enhanced H_2S removal and increased CO_2 slip. The H_2S content of the treated gas is completely determined by the vapour-liquid equilibrium because, at and below 47.5 wt-% TEG, the absorber is completely lean-end pinched with respect to H_2S absorption. This is illustrated in Fig. 7 which shows the actual and equilibrium H_2S partial pressure profiles for 47.5 wt-% merge at the top of the absorber (no driving force for absorption) but remain separated for 50 wt-% TEG. The 50 wt-% TEG case is mass transfer rate limited. Lower TEG levels are equilibrium limited so the effect of TEG on the VLE sets the level of treating for H_2S. It should be noted, however, that in a mixed gas system such as this one, CO_2 absorption has a direct effect on H_2S phase equilibrium.

Fig. 6: **Effect of TEG contamination on performance of MDEA, DEA, and pMDEA under specified circumstances**

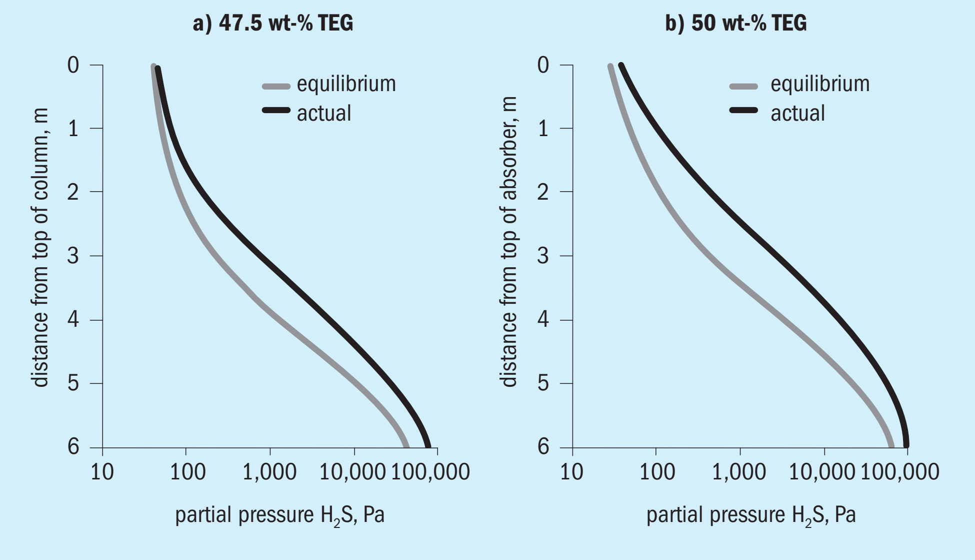


Source: Optimized Gas Treating

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

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

Fig. 7: **Partial pressure driving forces for absorption illustrating a lean-end pinch in Case 7(a)**



Source: Optimized Gas Treating

Summary

The effect of glycol contamination of amines on phase equilibrium and treating performance can be readily assessed by considering the contaminated amine as a hybrid solvent with glycol the inert component, and by using OGT I ProTreat's hybrid solvent simulation capability to do the analysis.

OGT I ProTreat® now offers a mass transfer rate-based simulation capability for hybrid solvents. The thermodynamic model uses a rigorous activity coefficient basis and develops the ternary and quaternary solvent description using mixing rules based on sound thermodynamics. Mass transfer rate calculations use the same proven and well-accepted rate model as is used in the ProTreat simulator generally. The result is highly reliable, predictive simulation of hybrid solvents. The non-reactive hybridising component in this case is TEG which is shown to increase somewhat the solubility of the acid gases in the hybrid. The effect offers a slight benefit to TEG contaminated amines compared with their virgin counterparts. ProTreat is now in a position to simulate sulfolane-based and TEG-contaminated hybrid solvents using a generalised framework that permits other hybrids to be simulated as well.

References

1. Chandran, P., Hatcher, N., Kaur, H., Weinfeld, J., Weiland, R.: "Gas Treating with Hybrid Solvents", Hydrocarbon Engineering (May 2022).
2. Weiland, R. H.; Dingman, J. C.: "Eliminating Guesswork", Hydrocarbon Engineering (Feb 2001).

Commissioning amine plants in extreme environments

Operating plants in extreme environments can present unique challenges. If these challenges are not anticipated and addressed in design and commissioning, the plant will not be able to start up nor meet its specification. This article examines the challenges faced in commissioning amine plants operating in three diverse environments (extreme heat, extreme cold, and offshore) and the technical and procedural solutions employed to resolve them. **Mike Sheilan**, **Ben Spooner**, **Kaiyr Tekebayev**, and **Philip le Grange**, Amine Experts.

The challenges and their technical solutions in the commissioning of seven amine units in very challenging environmental conditions are described in this article. The amine units operate in extreme conditions of ambient heat and cold and in locations with restricted access (i.e., offshore).

Environmental hazards for staff (hypothermia, dehydration, swaying platforms, etc.) make mechanical work both more dangerous and more difficult. Logistically, some of these locations can be hard to reach, rendering the replacement of chemicals or delivery of unanticipated piping/equipment difficult. As a result, corrections for design and commissioning errors can be very expensive and may delay plant start-up significantly.

It is the authors' hope that learnings from these stories will help our industry improve its commissioning practices in demanding environments.

Case 1: Extreme ambient hot and unusual inlet gas contaminants

An amine unit start-up can be a daunting experience at the best of times, but during the Middle East summer, when ambient temperatures can reach or exceed 50°C, the difficulty level increases dramatically. And when that start-up includes an owner who has never dealt with sour gas before, and then having to operate a plant designed and built by a firm that has never built one before, the pressure is even greater. It becomes hard to differentiate between the sweat caused by the heat and the sweat caused by the stress to force a new plant to operate to its design specification.

Fig. 1: Sour hydrocarbon-rich flare gas.

Fig. 2: Waxy solids removed from inlet slug catcher.

Amine Experts' involvement began after an initial failed start-up, resulting in a plant with plugged vessels, sour treated gas, and the flaring of large quantities of unprocessed sour gas (Fig. 1).

In the original start-up attempt, the plant was unable to process gas after just a few days of operation due to plugging in the contactor and flash drum. The treated gas did not achieve the required H_2S specification, so it did not meet contractual obligations for sale. The amine solvent was black and viscous and did not circulate well through the system.

Analysis of contaminants entering the amine unit revealed a mixture of solids (primarily iron sulphides) and heavy hydrocarbons, including asphaltenes and waxes (Fig. 2).

The heavier hydrocarbons which were the basis of the fouling material came from operating the lean amine much cooler than the hydrocarbon dewpoint in the gas such that the mixture moved into the two-phase region. Ideally, the feed gas temperature would be increased to stay above the hydrocarbon dewpoint, but this would require warmer amine as well, and then the contactor would not meet treated gas specification.

Improper inlet separation technology

The plant had been designed with a large vertical inlet gas separator and a filter-coalescer, with the intent that liquid and solids would be separated in the bulk vessel, and aerosol mists that happened to carry-over would be captured by the coalescer.

A review of the engineering drawings revealed that the inlet separator lacked a demister pad and the coalescer was installed incorrectly. Furthermore, the feed into the coalescer was connected to the outlet piping of the vessel (the upper chamber with the elements). Because of the insufficient residence time caused by the loss of volume occupied by the elements, the fluid level in the upper chamber rapidly exceeded the HHL (high-high level), flooding most of the chamber, and rendering the elements ineffective for coalescing as they were submerged. The separator/coalescer thus offered almost zero protection for the amine system.

Technology options for preventing fouling

The two options considered for correcting the feed gas conditioning problem were:

- A gas chiller followed by a second separator upstream of the original inlet separator and coalescer (design company)
- Retrofitting the current coalescer into a particle filter and installing a properly oriented coalescer downstream of the existing coalescer (Amine Experts)

The design and construction company suggested the chiller option, and even installed a unit 'free of charge' to the owner because they were confident that it was the solution. Amine Experts took issue with the chiller approach since it was felt that the tubes in the chiller would quickly plug with solids. Although the chiller was installed on a pad at the plant site, it was never connected and eventually dismantled. Instead, Amine Experts was contracted to design and construct the new coalescing device, which the client installed downstream of the existing coalescer. In turn, the existing coalescer was redesigned into a particle filter to protect the coalescing elements in the new vessel from solids. Ultimately,

Fig. 3: Fouled flash drum coalescer pads.

Fig. 4: Fouled activated carbon bed.

this combination proved to be the ideal fix, as the plant has run uninterrupted for over ten years, removing between 1-3 m^3/day of liquids from the feed gas, while not experiencing any fouling of the amine contactor.

Flash drum fouling

The original flash drum was too small for the design amine circulation rate. It provided a residence time of less than three minutes, much less than the recommended 25 minutes. Recognising the limitation, the designer tried to artificially improve the separation time by installing coalescer pads (which was simply structured packing) inside the vessel.

Rather than improving separation efficiency, the coalescing pads instead plugged off with heavy hydrocarbons and iron sulphide, which had entered with the feed gas due to the poor inlet separation, reducing the already short residence time to less than a minute. It is not good practice to install any device in a flash drum that is prone to fouling, as the inherently "dirty" nature of amine systems (especially on the rich side) will cause the device to plug rather than coalesce. The result in this plant is shown in Fig. 3. The owner decided to remove the offending coalescing pads and add a rich-side filter downstream of the flash drum to protect the lean/rich plate and frame exchangers. So far, that decision has proven to be a sound one as the lean/rich exchangers have remained clean.

Activated carbon bed fouling

As there was no lean amine pre-filter upstream of the carbon bed in either the original design or the as-built plant configuration, the flaw was obvious. This was an unfortunate decision, as carbon beds will act as impingement filters, and will easily plug with solids circulating in the lean solution, as shown in Fig. 4. The fouled pores then prevent the activated carbon from doing its job of removing foam-promoting contaminants in the amine. As such, foaming was a regular occurrence during the initial start-up. A pre-filter should have been installed.

System preparation

Due to the fouling experienced in the first start-up attempt, a thorough cleaning of the system was necessary before re-starting. Units with packed columns require an extremely clean circulating solvent or they will plug rapidly.

Amine Experts' strategy for cleaning included:

- In sequence:
  - Cold-water flush
  - Hot-water flush
  - Cool 3% amine flush
  - Hot 3% amine flush
- Selecting sample points for checking fluid condition and appearance.
- Setting up Millipore filters in certain locations on the lean and rich loops to ensure cleanliness.
- Instituting analytical protocols to check fluid quality and for enabling the decision to begin the next stage of cleaning.
- Setting up the flush fluid burn pit (this is not a standard feature on amine plants, so in most cases, provision for waste fluid disposal is necessary).

The initial cold-water flush was repeated twice to remove large solids from the system. The warm flush loosened more contaminants.

After the water flushes, a 3 wt-% amine solution was circulated since it has better detergent properties than water and prepares the system for the alkaline environment that will exist during operation. Soda ash can also be used instead of amine.

After several flushes the solution improved from a dark black to clear and

Fig. 5: First (left) and last (right) circulating amine-wash solution samples.

pale straw colour with no indication of any solids or secondary layers (Fig. 5), as hoped. With water being a rare commodity in a desert environment, the relatively clean final flush fluid was used as make-up water and the system then charged to the correct full 50 wt-% strength.

Once the system was clean, the inlet coalescers and filters were correctly installed, and the rich filtration system was in place, feed gas was introduced to the system on the expected date. As opposed to the initial start-up that failed after only a few days, the plant was operational for seven years before a turnaround was scheduled.

It is difficult to convey how uncomfortably hot it was for the entire project. Frequent breaks are essential despite the hectic schedule. Nerves are frayed. People suffer from lack of sleep and are easily frustrated. Persistent professionalism was required by all parties to get this plant successfully up and running.

Case 2: Extreme ambient heat

The ability of a lean amine solution to sweeten a feed gas stream is affected by the temperatures in the amine contactor. A warmer amine has less overall absorptive capacity than a cooler amine, so designs should always incorporate an environment-appropriate cooling system for the lean amine. For most plants around the world, forced-air coolers are the preferred equipment because apart from a few days per year, the ambient air is cool enough to achieve the necessary heat exchange on the hot lean amine. The requirement is that it must be 5-7°C warmer than the feed gas temperature. But in extreme heat environments, (45 to 55°C), aerial coolers will not be able to meet the process cooling requirements, so supplemental trim coolers, using water or propane, are specified in the designs.

An amine system in a hot Middle Eastern desert environment was started up with an aerial cooler followed by a propane chiller. It was working well to control the temperature in the absorber (which in the case of an MDEA-system optimised H_2S removal but also maximised CO_2 slip). A cooler amine absorbs less CO_2, which was critical to the performance of the sulphur recovery unit (SRU) which needed an acid gas feed with as little CO_2 and as much H_2S as possible.

A problem with the propane compressor was going to force a shutdown for repairs lasting several hours which would put the temperature of the lean amine at the mercy of the aerial coolers, a worrying proposition with an ambient temperature of 50°C. A decision was made by the operating company to chill the lean amine as much as possible while the propane compressor was still running to minimise the effect of its absence during the repair. The assumption was that by starting with a cold amine, the inevitable heating effect on the solvent could be delayed until all the inventory had made its way to the regenerator and then back to the absorber before there was an undesirable impact on the treated gas. Unfortunately, almost immediately, the absorber showed signs of foaming with an elevated differential pressure (dP). Before antifoam could be added to the unit, the absorber dP rose so dramatically that a large quantity of amine carried over from the absorber into the downstream dehydration system.

Amine Experts was asked to troubleshoot the foaming episode and it was clear that the foaming was caused by rapid condensation of a large volume of heavy-end hydrocarbons that raised the foaming tendency of the amine. The condensation was a direct result of the overzealous cooling of the lean amine to 15°C less than the feed gas temperature. A better option for preparing for the propane compressor shutdown may have been to complete the repairs at night when ambient temperatures were more amenable or recognising that the minimum target for the lean amine should never be colder than the hydrocarbon dewpoint. The plant should have also been better prepared to cut back the feed rate and dose the system with antifoam before the easily avoidable loss of a good portion of the system inventory.

Case 3: Extreme ambient heat

During a summer start-up of a large LNG facility, the hot ambient temperatures resulted in the lean amine feeding the absorber being warmer than expected. Although the treated gas CO_2 content increased it was still meeting specification. This was a concern to Operations and the problem was diagnosed as too much amine flow rate through the coolers, resulting in inefficient heat transfer. The circulation rate was subsequently decreased, reducing the lean amine temperature. Perplexingly, the CO_2 concentration in the treated gas continued to increase, eventually going off-specification.

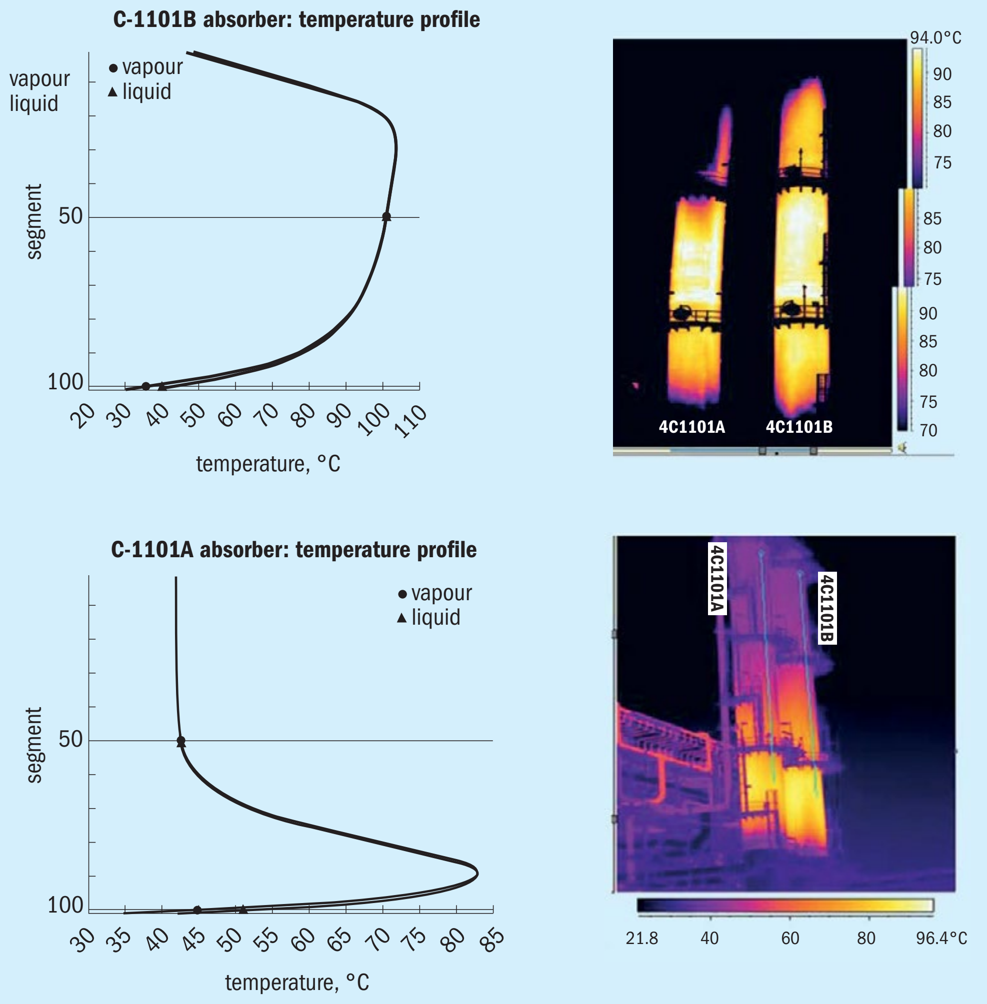
Amine Experts was contacted for troubleshooting support. A simulation of the system determined that the problem was an excessively high temperature bulge inside the absorber caused by the decrease of lean amine flow. Even though the new flowrate produced cooler amine, it was countered by the lack of "quenching" amine which allowed the exothermic temperature bulge to increase to an excessive degree. Unless there are thermal indicators on the tower, it is difficult to know what the temperature profile of an absorber looks like. Simulations showed much of the column exceeded 95°C (Fig. 6), which is so hot there is no absorption between amine and CO_2 and as a result the CO_2 content of the treated gas increased. The treated gas temperature also increased so dramatically that the downstream liquefaction plant had to cut back almost 40% on throughput because there was insufficient cooling capacity for this hot feed gas.

Amine Experts modelled the system and determined the optimum circulation rates, steam rates, and system temperatures to meet the required treated gas CO_2 specification and keep the treated gas cool enough to run at full capacity downstream in the liquefaction trains. The resultant absorber temperature profile (Fig. 6) lowered the bulge temperature to a manageable value and resulted in a much cooler treated gas. Optimisation of amine unit parameters not only improved the performance of the amine system, but also permitted full gas production through the liquefaction trains.

Case 4: Extreme ambient cold

A 27-year-old skid package that had spent several years mothballed in a boneyard was re-purposed and relocated

Fig. 6: **Absorber initial (top) and final (bottom) temperature profiles: Simulated (left) and IR camera photographs (right)**



Source: Amine Experts

Fig. 7: Valves plugged with silt and unit full of potential fouling and foaming material.

Fig. 8: Increasing clarity of continuously-circulating cold water as wash progressed.

Fig. 9: Creative solution for a missing section of the amine cooler and reflux condenser.

to sweeten fuel gas in a remote northern location, where temperatures can be as low as -40°C. Final plant construction and commissioning was scheduled for mid-winter as it was not possible to transport equipment by road during summer when the ice-roads turned to marsh.

System preparation

A site inspection of the vessels showed that when they had been mothballed they were filled with glycol to prevent them freezing. However, the glycol appeared to have been contaminated with fine silt. Silt is a potential fouling- and foam-promoting material. There were still appreciable amounts of this material in the unit and most of the drain connections were plugged (Fig. 7).

An aggressive program of unit cleaning was clearly needed. As a first step, the units were washed with high-pressure water lances while mechanical work was proceeding. With conventional techniques, the time needed to clean this system to an acceptable level would delay the start-up of the plant and other dependent units. A quicker cleaning program was developed in which the various rinse steps (see Case 1) were performed and the dirty cleaning solution was continually removed from several low points in the system and made up with fresh cleaning solution. While this generated considerably more waste, it proved time-effective (Fig. 8). In contrast to commissioning an amine plant in a desert environment, water was readily available.

Although the plant was located inside a heated building, the heating system depended on gas produced from the facility, which was not yet producing. Electric heating was used instead, with power supplied by portable generators, but they had difficulty keeping up with the demand and multiple power failures meant a constant battle against frozen lines as the washes began.

Methanol was added to the liquid-filled drain lines outside the plant enclosure to prevent them from freezing. Regardless, a section of reflux piping outside the building was not self-draining and froze despite insulation. Thawing it caused some delay because it could only be reached by crane.

Installation and equipment errors

A section of the aerial cooler that provides cooling for the lean amine and condenses the amine regenerator overhead gases did not arrive with the old plant package and its absence was not noted until commissioning began. This section, which recirculates warm air inside the exchanger, prevents overcooling the amine (which would have made it too viscous to pump) and freezing of cooler and condenser tubes. Waiting for fabrication and delivery of this missing piece would have delayed start-up by up to two weeks. This was deemed unacceptable, and some creative engineering resulted in a temporary solution that permitted start-up of the plant (Fig. 9).

The reflux pumps were wired incorrectly causing them to rotate in reverse and caused another short delay to the initial start-up. A much longer delay was caused by the lack of high-point purges on the hot-oil system (supplying the heating medium to the reboiler). Water contaminated the hot oil during its initial loading and boiling it out of the lines took considerable time because of insufficient vents in the hot oil circuit.

Post-weld heat treatment was done on all welds connecting the amine plant to its new service at Amine Experts' insistence. This prevents potential corrosive failures due to hydrogen-induced cracking (HIC) which has caused fatalities on amine plants in the past. It also reduces the hardness and the chances of brittle fractures.

Legacy issues

There can be a significant reduction in project capital expenditure (capex) if a suitable existing mothballed plant can be re-purposed as opposed to design and fabrication of a new plant. That said, there were several minor issues worth noting:

- Flash tank internal geometry was unclear; no drawings were available, and the borescope camera was unable to get a good view of the internals; a gamma scan was needed for clarity.
- Several redundant pipes were left over from the previous service. These should have been removed from drawings and not re-installed.
- Obtaining replacements for defective 1980s control instrumentation proved challenging.
- The heat-medium control scheme was not optimal and could have been re-worked to perform better. Being an old plant doesn't mean the control philosophy should be outdated.
- The process flow rates in the "new" system were less than the design of the original plant, resulting in pump impellers that were larger than necessary; appropriately sized impellers will make the plant easier to control and be more energy efficient.

After one false start because of some flange leaks (H_2S-detection equipment is critical in the start-up of a sour amine unit), the unit was successfully brought online before the project deadline and has been operating for years without any major process upsets.

Case 5: Mobile offshore facility

A floating production storage and offloading (FPSO) unit operating offshore in Asia was designed to treat up to 100 million std. ft³/d of gas to a specification of <16 ppmv H_2S and <3.5 mol-% CO_2. As is typical in offshore applications where space is at a premium, both the absorber and regenerator internals contained structured packing. Furthermore, getting equipment, tools, chemicals etc., are far more difficult on an FPSO unit compared to a land-based plant so when things don't work as planned, creative and outside-the-box thinking is often necessary to achieve success.

On commissioning, the FPSO unit tried for several days to meet the design H_2S specification. It was unsuccessful, with the H_2S concentration in the treated gas rapidly reaching as much as 300 ppmv. The longer the plant was in service, the greater the H_2S became, which coincided with a steady, gradual rise in the amine lean loading.

The parameters observed in the regenerator led operators to believe there was a flow distribution problem which allowed steam to channel through the structured packed interior and not contact (regenerate) the amine. The system was shut down, drained, and the regenerator inspected. Amine Experts was contracted to perform the inspection, then stay aboard to ensure successful start-up of the system.

A thorough mechanical inspection was conducted by Amine Experts and the hardware was generally in good condition and fit for purpose. Attention was therefore turned to the process itself.

Simulations out to sea

The initial start-up of this system relied heavily on operating parameters determined by simulations; however, simulations assume proper contact between vapour and liquid inside the absorber and regenerator. This of course is NOT the case if the liquid and vapour conditions are not right. It is important, then, that in the regenerator a certain minimum amount of steam always be generated such that contact with the amine can be guaranteed.

New, updated operating conditions were established for the regenerator, and to verify the conditions were correct, a temperature indicator on the pipe feeding lean amine to the reboiler was removed and replaced with a sample point (which had a cooling coil). This allowed the H_2S concentration in the amine feeding the reboiler to be measured. The H_2S content of the lean amine leaving the reboiler (which Operators sample on a regular basis) should be very similar. Measuring the H_2S in the amine feeding the reboiler is the best way of determining the effectiveness of the regenerator distributor and packing. Ideally, very little H_2S should be regenerated from the amine in the reboiler itself.

Amine Experts determined the minimum flows of liquid and vapour to ensure proper contact between steam and amine in the regenerator. A 20% safety margin was added to each value and the operators were instructed to hold these targets. The steam flow to the reboiler was set at a ratio of 120 kg of steam per m³ of amine circulation rate, which is more than the industry average of 100-110 kg/m³. Structured packing requires adequate vapour traffic to ensure proper contact and distribution of the liquid. Since none of the operators had experience using structured packing before arriving on the FPSO, this was a primary contributor to the failure of the original start-up – it was being operated like a traditional trayed regenerator.

Once operation had stabilised under the new operating targets, the treated gas was analysed repeatedly, with the H_2S concentration measured at as little as 0.2 ppmv and as much as 3.5 ppmv. The variance in H_2S was clearly related to the steam flow rate to the reboiler. When the H_2S was at its minimum, the steam-to-amine ratio was at the ideal target of 120 kg/m³ determined for this system. This ratio was the most important operating element to meeting the H_2S specification in this plant.

The sample point of amine feeding the reboiler proved useful in verifying that the operating parameters in the regenerator were set correctly. The reboiler inlet sample contained 700 ppmw H_2S while the outlet sample had 600 ppmw H_2S. The bulk of the regeneration of the amine was, therefore, correctly being done in the tower.

Staying on-line

While calculations and simulation outputs are useful in providing guidelines and targets for the operators to follow during start-up, the reality of bringing an amine plant on-line is that many operating parameters are initially very difficult to achieve. Although the H_2S remained on spec in the treated gas while Amine Experts-supervised the start-up, there were numerous obstacles:

- Maintaining a constant utility steam pressure proved to be a challenge; the target was for the steam to be 3-4 barg, which is at 145-151°C when saturated. Many times, the steam pressure dropped to as little as 2.5 barg, which is 139°C.
- The lean/rich exchanger worked better than predicted, delivering a regenerator overhead temperature of 115-120°C, as opposed to the expected 105°C. This increased the water content of the reflux system and triggered the reflux accumulator high-level alarm.
- The reflux temperature of 45°C could not be held constant, and the temperature was often 35°C or less. This, combined with the well-heated rich amine feeding the regenerator, overwhelmed the reflux system and there were frequent high-level alarms in the reflux accumulator. Reflux water had to be manually drained to the sump tank.
- The flash tank target pressure of 4 barg could not be maintained once gas rates were increased. At high rates, and with the pressure control valve wide open, the lowest pressure attained in the tank was 6.8 barg. On investigation, an incorrectly sized orifice plate was discovered which was holding pressure on the flash gas line. The orifice was replaced with one of the proper size (luckily there was one on board), and the flash pressure returned to design.
- The inlet gas temperature to the absorber was difficult to control. The target was 35°C, but most of the time it was 25°C. The concern was that this would overwhelm the inlet coalescing filter, but this did not happen, and there were no foaming problems. Fortunately, unlike the hot environment start-up, this gas was nowhere near its dewpoint.
- The suction strainers (Fig. 10) plugged frequently, and were eventually removed, because of a high solids content in the amine.

Fig. 10. Suction strainer plugged by particles from the amine solution.

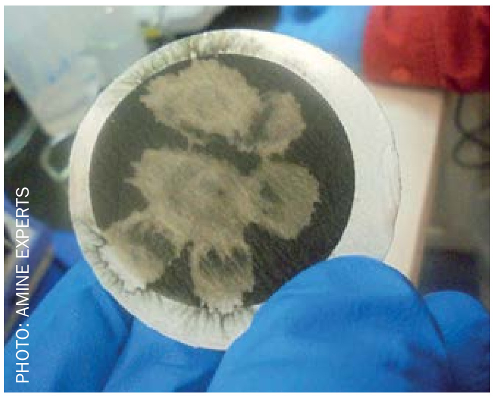


Fig. 11. Filtered solids after contact with acids.

The situation was exacerbated by the lack of operator training for the systems and equipment with which they were working. For example, single-use filter and coalescer cartridges were removed, rinsed, and re-used, resulting in amine that was heavily contaminated with solids and hydrocarbons. The solids were later identified as likely being iron, based on their reactiveness with acid (Fig. 11). This could have quickly led to fouling and foaming if a temporary remedy (circulating amine through the sump tank, which has a filter) had not been found.

Being offshore brings its own set of challenges:

- Inventories of disposable items can be low, and re-stocking filters was a long process. This encouraged operators to unwisely re-use their spent cartridges. And, if flanges are opened, the gaskets must be replaced with new ones. Make sure they are in stock before opening flanges or disconnecting equipment.
- Because the filters are hard to obtain the amine must be kept very clean. Minimise hydrocarbon contamination and corrosion at all costs.
- FPSO units are constantly moving, and this can cause amine to splash around inside vessels. This affects performance of the flash tanks, and eliminates the option of using trayed absorbers or regenerators.
- The hydraulics of structured-packed towers are quite different from those of trays. It's important to be aware of the differences and learn to not always rely on simulators to make accurate predictions.
- Safety is far more serious offshore due to the difficulties in evacuating an injured person. Only enter the plant when necessary, and always have all required PPE.
- Chemicals such as amine, antifoam, and laboratory titration solutions are difficult to acquire, so care must be taken to not waste them.
- Extreme weather and saltwater causes equipment to corrode quickly. Be prepared to expend a lot of energy opening equipment that has been sealed for several months.
- The surrounding oceanic environment is very ecologically sensitive, and the oil and gas industry are held to very high standards when it comes to pollution. No chemicals can be spilled into the water.

Case 6: Offshore gas

An offshore facility in the North Sea was designed with an exotic, expensive solvent to handle a feed gas that was predicted to contain close to 1 mol-% H_2S and 1,000 ppmv mercaptan. At start-up, the gas was found to contain less than 10 ppmv H_2S and no mercaptan, so the expensive amine system was only required to remove about 5 ppm of H_2S to meet the specification. This was an expensive mistake. With the correct feed gas composition, the amine solvent choice would likely have been different, or an alternate technology selected.

Like the hot environment case study in this paper, soon after the initial plant start up, the filters plugged with debris from an improperly cleaned system. In attempting to replace the filters, it was determined that the filters were only isolated by a single valve, rather than the mandated double block and bleed (double isolation) valves required for offshore systems. Because the filters could not be safely replaced, the amine system could not function properly, as there was no way to prevent the packed internals of the contactor and regenerator from plugging. Fortunately, the original design included a solid adsorbent bed for final H_2S and mercaptan removal if any passed through the contactor. The amine system was thus bypassed, with the feed gas flowing first through the adsorbent bed for H_2S removal, then to dehydration and on to sales. Without the adsorbent bed, the product gas would not have successfully met the pipeline requirements for H_2S content, although the adsorbent performance must be monitored constantly as it will need replacement before it is spent.

On review, Amine Experts identified:

- A failure to accurately analyse and predict feed composition led to large unnecessary expenditures on the plant design, construction, and solvent choice.
- Due to a failure to properly train staff on H_2S safety, the operators were unreasonably in fear of minute concentrations of H_2S.
- Improper hydraulic testing of the unit with salt water led to aggressive chloride corrosion in the amine unit.
- Improper construction of isolation valving for the filtration system prevented routine maintenance.

Case 7: Offshore gas

A sweetening platform offshore was designed to process a sour feed gas to less than 2 ppmv H_2S and 2% CO_2 in the treated gas. Shortly before the plant started up, however, the CO_2 specification in the treated gas was reduced, requiring the addition of an additive to the amine. The additive suggested by the amine vendor was piperazine.

Amine Experts was contracted to be on site for the start-up. Two major problems were encountered as gas was slowly introduced:

- The piperazine (which is extremely difficult to ship and handle as it crystalizes at 20°C) resulted in such a strong exothermic reaction with the CO_2 that the absorber was too hot to absorb H_2S, meaning the plant would not meet the specification. If the additive concentration was reduced, the H_2S would return to specification but there would be insufficient CO_2 removal. At Amine Experts insistence, the additive was replaced with a primary amine (DGA™, or vendor equivalent) which was strong enough to remove the CO_2 but without excessive temperatures in the absorber.
- Even with the correct additive in the amine, neither the H_2S or CO_2 specification could be met once gas flow rates exceeded approximately 60% of design capacity. Although the simulation closely matched plant conditions at lower gas flows, at higher rates the plant performance deviated sharply from the simulated predictions.

Amine Experts used a thermal imaging camera on the absorber bare shell to determine if the top section of structured packing was suffering from channelling. The measured temperature profile was inconsistent with the simulated prediction, and there were several cold spots where there should have been reaction between the gas and amine. The absorber was opened and inspected, and it was discovered that the amine distributor was resting at an angle of 30° off level. It had shifted during transportation of the platform from its fabrication in the Mediterranean to its final location in the North Atlantic. Because of this, the amine was not being distributed evenly across the top bed of packing. It did get re-distributed in the second bed, which was why the plant worked at reduced gas flow rates. The distributor was re-oriented, and the plant worked well thereafter.

Several design deficiencies in this platform were also detected while Amine Experts were on site:

- Poor design and incorrect elements in the inlet coalescer (resulted in significant hydrocarbon contamination of the amine).
- Poor hydraulics around reboiler, which was not situated at the correct level on the platform.
- Insufficient volume in the surge tank. It would run dry when trying to raise the flash drum level for skimming hydrocarbons. While space is limited on offshore platforms, designs must remain functional.
- Insufficient volume in base of regenerator (less than 30 seconds residence time) due to reboiler location.

New amine plant commissioning tips (many learned the hard way)

The seven cases studied here looked at various challenges that can be faced during commissioning of amine treating facilities. In this section an approach to commissioning amine plants is discussed that will minimise challenges and subsequently reduce delays in schedule and project costs (be it in extreme situations or not).

Although it is generally considered that commissioning occurs on-site during the final stages of the project, as seen from Amine Experts' experiences the preparation and planning should begin much earlier, in the engineering stage, to:

- develop a commissioning strategy and execution plan;
- define systems and sub-systems;
- develop commissioning procedures and checklists for cleaning, inspection, and testing;
- determine manpower, vendor, and specialist contractor requirements;
- determine the availability and required volumes of utilities and consumables;
- review operating manuals, vendor documents, and commissioning and start-up spares.

An early involvement of the commissioning team in the project allows commissioning to integrate with engineering and construction teams, participate in HAZOPs, model reviews, and other engineering conversations to provide feedback and commissioning requirements to the design team. It is easier to incorporate change requests at an early stage of the project. Modifications or changes needed during commissioning/start-up will have a negative impact on project cost and schedule.

When the commissioning team is mobilised, the on-site activities can be classified by discipline: piping, mechanical, instrumentation, electrical, and preservation.

Piping

Conformity checks: Piping circuits should be checked against P&ID drawings to verify correct installation of valves and instrumentation, to ensure that temporary piping components, isolation blinds, and valves used during pre-commissioning and commissioning are removed and permanent piping elements are installed.

Fig. 12. Debris found during flushing.

Cleaning: As discussed in Case 1, amine system circuits need to be flushed by circulating 3 wt-% aqueous soda-ash or amine solution. This type of cleaning is called "degreasing". But before degreasing, piping needs to be flushed with water to remove accumulated dirt and scale (Fig. 12). During this flushing step it is recommended to replace the permanent instruments with dummies or isolate them, and to bypass the columns to prevent dirt ingress into the columns, and to use commissioning strainers to protect pumps. Once dirt enters the columns, it is very difficult to remove and will plug off the column internals. Also, the commissioning pump capacity should be sufficient to generate the velocity in the piping to simulate operating conditions. Otherwise, there will not be enough force to move the dirt and scale from the bottom of the piping. If the permanent pumps will be used for flushing check with the pump vendor that the equipment is suitable for this purpose, and spare parts are available.

Flushing of the drain lines and cleaning of the drain sump is often underestimated and is sometimes left out. But these dirty drain lines will contaminate the system during operation if not cleaned at the beginning. Therefore, the drain lines need to be flushed (can be done by opening the drain lines for some time). After flushing the drain lines the drain sump needs to be cleaned before start-up.

Amine system utility circuits, such as nitrogen, instrument air, condensate, and steam flushing and blowing should also be cleaned. Typically, the line is considered clean when the flushing/blowing medium is free from visible contaminants.

In general, it is a good practice to follow so-called "clean spool policy" where the piping flanges are kept capped and spools are cleaned after each activity, beginning from fabrication.

Mechanical

Static equipment: In amine systems the static equipment can be put into four categories: columns (absorbers and regenerators), vessels (filters and drums), tanks and heat exchangers. For static equipment it is important to ensure:

- Column/vessel internals are installed as per the manufacturer drawings. For columns, a licensor or internals manufacturer presence might be required during final inspection.
- All foreign material is removed (desiccants, blanks and support(s) used during transportation, etc.)
- Filter cartridges are installed correctly and sealed tightly, so solvent doesn't bypass
- Activated carbon is loaded properly, avoiding carbon fines formation.

Rotating equipment: amine systems typically include pumps and fin-fan coolers. Once the installation checks are completed, dynamic runs for rotating equipment need to be completed to check their functionality and operability. Pumps need to run with commissioning strainers in place to protect the pump impeller.

Instrumentation

In any plant, the functionality of the ESD (emergency shut down) system is critical. Every C&E (cause-and-effect) case needs to be checked without exception; whenever possible, include the entire loop, starting from the sensing element all the way to the control room.

Alarm and trip set points need to be reviewed and adjusted whenever necessary. In some instances, the set points are too high or too low, which affects future operations and may lead to a spurious trip or add undue stress to the DCS operator. Needless to say, any change to the original design should follow the proper channels and needs to be completed through Management of Change (MoC).

In an extreme cold environment extra attention should be paid to the installation of steam and electrical tracing elements to instrument connections and PSV lines.

Control valve stroke and look-checks are to be done for every control valve. The fine tuning of the control loop should be completed at the later stages of commissioning.

Electrical

Electrical pre-commissioning and commissioning activities is a large topic and worthy of its own separate article. But one that directly related to the equipment is a motor solo run (also know as a "no-load" test). Like in any other system the motors of pumps and fin-fan coolers should undergo a motor solo run to confirm on site the functionality of the motor.

Overall system

Once discipline activities are complete, and prior to start-up, the entire system must be leak tested and made inert.

A purpose of the leak test is to test flanged joint connections for leakage, and not to test the piping integrity (which is done earlier in the construction phase by hydrotesting). Usually during a leak test the system or sub-system is pressured to a predetermined pressure (slightly less than the PSV setpoint) and all flanged joints, including the ones connected to instruments, are tested for signs of leakage by covering the joint with masking tape or using a soap solution. There are alternative methods but a discussion is beyond the scope of this article. Some absorbers in amine systems are designed to operate at high pressure meaning the leak test must also be carried out at high pressure, which requires a specific skill set. For such cases, it is worth considering engaging a specialised contractor.

Once the testing is complete, leaving the amine system in an inert state (usually by charging the equipment with nitrogen) is crucial not only because of the hydrocarbon feed but also to prevent amine degradation due to the presence of oxygen (especially when warming up the system).

Preservation

Depending on the size of the project, the duration between erection of the facility and its start-up can be between several months and several years. If the system is left unattended during this time it will result in significant challenges during start-up, which makes preservation a highly important subject.

In general, the amine system should be kept clean and without oxygen or moisture. A humid environment in the presence of oxygen will cause the metal to corrode. This is less aggressive than pitting or acid corrosion, but still forms a layer of rust which will contaminate the system once in service. A good practice is to keep the unit under slightly positive nitrogen pressure.

For rotating equipment, regular checks for oil level, shaft rotations, etc., need to be carried out as per vendor instructions.

If amine solvent is already in the system and the start-up is delayed, the solvent needs to be circulated periodically and sampled to obtain a detailed analysis to confirm the quality of amine.

If additives such as antifoam are already on site, and the start-up is delayed, the mixer needs to be started periodically to agitate the chemicals to maintain a uniform composition. Before starting up, it is recommended to check the effect of these chemicals on amine solvent foaming properties by performing a separate laboratory foam test.

Conclusions

Cold ambient conditions: In extremely cold environments, preventing freezing-related blockage of pipes during commissioning and operation is critical. The amine plant enclosure should be adequately heated. All lines outside the housing should be self-draining, with sufficient and readily accessible drain valves. There should be no liquid in the system when the unit is not operational (cold). It is crucial to be rigorous about insulation and electrical or steam tracing on all exposed lines.

Hot ambient conditions: Extremely warm environments can pose a challenge in terms of cooling the lean amine to the right temperature to meet the product specification. This is potentially aggravated by the relatively high hydrocarbon dewpoints of some of the streams being treated, giving the plants a narrow temperature window in which to operate. A good design includes appropriate feed gas conditioning, sufficient cooling capacity, and adequate Operations training about the importance of the gas dewpoint and its impact on operation.

Unique and remote locations: Because of limited plot space offshore, exchangers tend to be plate and frame and columns tend to have structured packing internals. These are both vulnerable to fouling, increasing the requirement for exceptionally good amine filtration and better operator training. The limited space offshore also sometimes led to vessels not containing enough amine inventory to allow for upsets which ultimately adversely affects the plant's reliability.

Logistical challenges caused by the facility location often made obtaining spares, replacement parts, and consumables very difficult and increased the cost of mistakes made during design and commissioning.

Design basis: In every story told in this article, the failure to correctly design the system contributed to the start-up dilemmas. By default, plant designs are based on assumptions and predictions with less than 100% accuracy. Competent and appropriately experienced designers will have the margins in place to account for expected inaccuracies and make the right decisions. Shortfalls in this area can translate into huge cost and schedule implications for a project. For instance, building the offshore amine plant discussed in Case 6 could probably have been avoided had the inlet gas composition in the design resembled the real feed gas.

Subsequently, it is vital that a design is checked with an appropriate simulator whose results have been verified in similar applications. Simulators are not created equal, and some are more appropriate for certain applications. Subsequent verification that a design follows best practices by independent specialists (who do not represent a specific technology) can be invaluable and minimise both capital and future operating costs.

Construction: During the plant construction, all carbon steel welds should be post-weld heat treated. Vessel nameplate stamps must be checked prior to transport to site. Vessel internals placement should then be verified on site for all equipment.

Pre-commissioning: While a diverse range of challenges may be encountered when commissioning an amine plant, a common flaw in all the systems described in the paper were deficiencies in the initial system cleaning and decontamination procedure. It is vital that these are done correctly, and that the system reaches an acceptable level of cleanliness prior to the introduction of the amine solvent. Time invested in cleaning can prevent months of failure to meet product specification, loss in system processing capacity, and associated operational chaos.

System-specific training: In many cases, operators had a generic understanding of the amine systems they were meant to manage. Training specific to the system they were given was often lacking. For instance, the structured packing used in offshore applications is not common to other amine systems and Operations need to be made aware of its unique requirements (Case 5). When the training is provided is as important as the quality of the training itself. Often, operating companies provide training to their personnel when they take ownership of the unit. By this time the unit is typically built, started-up and already in service. In our view, training (such as the ones provided by Amine Experts) needs to be provided at a specific time for different groups of attendees. For example, for project and engineering teams the training needs to be provided at the beginning of the detailed engineering. For the commissioning and operations teams, the training needs to be provided at the beginning of pre-commissioning activities. For operational teams preparing for turnaround, the training needs to be provided well before the turnaround commences. In this way the team can effectively apply freshly acquired knowledge during upcoming works and contribute to improving the reliability of the amine unit.

Health and Safety: Environmental safety risks while working in these unusual locations should always be considered and workers should educate themselves about the risks and their mitigation to prevent dehydration, hyperthermia or hypothermia sunburn, frostbite, limited workspaces, moving decks, and so on.

Summary: This article relates the stories of the start-up of seven facilities, each inspired by their harsh environment. The start-up engineer must use wit and guile to overcome the inevitable design flaws, differences between the expected design case and the actual operating conditions, simulation limitations, equipment malfunctions, missing spares, and process upsets. Experience and a good understanding of process fundamentals (process-specific training) is key to recognising anomalies and allows the engineer to make the correct decisions to bring the plant on-line quickly and safely. ■

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