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Number 406

May | June 2023

SULPHUR

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New sulphur projects

Sulphur polymers

Sulphuric acid catalyst design

Processing bio-feeds



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Cover: An aerial view of a modern biofuel plant.
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New elemental sulphur from refinery and sour gas projects



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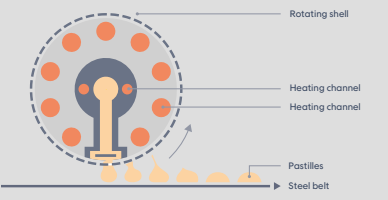
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END TO END SULPHUR PROCESSING AND HANDLING SOLUTIONS

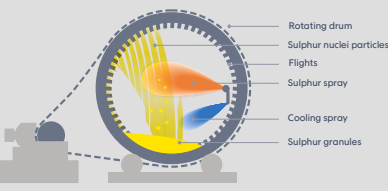
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 - ✔ Process simulation to suit all conditions.
 - ✔ Simple operation, precise control.

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Relying on AI



A reader wrote to me recently asking if I had considered the impact of general artificially intelligent systems like ChatGPT on the publishing industry. As a matter of fact I had, but only, somewhat narrowly and selfishly, on how it might impact my own job in the future. But the dramatic shift in AI capabilities that we have seen in the past couple of years is certainly food for thought, and I've seen no end of articles predicting the death of the creative industries.

One of the key benefits of using ChatGPT is its ability to analyse large amounts of data and generate insights that might not be immediately apparent to human writers. With its access to a vast array of information sources, ChatGPT can quickly identify trends and patterns in the sulphur industry and draw connections between seemingly unrelated factors. This can help writers develop more nuanced and well-informed opinions about the industry, leading to more insightful and persuasive editorials.

Well, as some of you may have guessed, I didn't actually write that previous paragraph. As a test, I asked ChatGPT to write an editorial about the impact of ChatGPT on writing *Sulphur* editorials. And it was okay as far as it went, if a little bland and generic. Even so, it is clear that AI performance is – at least in some areas – getting closer and closer to human performance. We have been used to machines replacing humans in physical work; that has been the legacy of the industrial revolution, and a process that we have lived with for over 200 years. But machines replacing cognitive work has been a much more recent development, beginning with simple mathematics and pocket calculators, but now starting to extend even to creative and artistic tasks. The process is far from perfect; anyone who has seen AI generated art cannot help but notice that the AI doesn't seem to understand how many fingers human beings usually have, or what text means on a signboard or the like within an image.

But the real pitfalls in the process are not the obvious, glaring errors, but the hidden ones that are not immediately noticed, because not everything is

what it seems. The problem with ChatGPT is that it does not produce accurate output; rather, it produces what it thinks the person giving it the prompt wants to read. So what it writes does not need to be true, only believable enough to fool the person reading it. And where the machine is unable to scrape reliable data from the internet, it simply makes up something plausible sounding. I also asked it to write an article about sulphur storage, and what came out might be superficially convincing to a high school student, but to someone who knows the industry it was simply wrong. For example, while it correctly pointed out fire risks and – albeit a bit obliquely – about sulphur's potential conversion to acid in the presence of water, it did also end up telling me with a straight face that the best way to store sulphur as a liquid is to dissolve it in a suitable solvent. It would be best not to rely on that kind of AI for safety critical systems just yet!

In all fairness, even ChatGPT recognises some of its own current limitations. In its editorial piece, it wrote: "Of course, there are potential drawbacks to using ChatGPT as well. One concern is that the language model may not be fully capable of understanding the nuances of the sulphur industry and may therefore produce opinions that are not fully informed." That's not a problem confined exclusively to AIs, of course, but it was nevertheless something of a relief. At any rate, it appears I may still have a job for a few more years at least – even if it's only until the programs become better at what they do. ■

Richard Hands, Editor

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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 continued to soften between March and April, and this trend is expected to continue in the short term, with the potential for some slight uplift in the month of July before resuming the softer trend. The fourth quarter could also see a slight increase based on expected demand emerging in key import markets, and the trade balance currently reflecting a deficit for the quarter. Spot market interest was sluggish through the month of April, adding continued downward pressure on pricing as new business was concluded for May shipment arrivals at further lows. Looking to the key driver of sulphur market prices, processed phosphates, there is likely to be a ceiling on potential price recovery over the next year. Sulphur demand is forecast to rise in the fertilizer sector as phosphoric acid production rises relative to the slowdown in 2022. On the one hand, this will support sulphur trade over the course of the coming months, but the continued expected downward trend in processed phosphates pricing through until at least the first quarter of 2024 will likely keep sulphur prices subdued.

Average monthly Middle East prices decreased by around \$33/t between March and April, down to \$95/t f.o.b.,

over \$380/t lower on prices a year earlier. Qatar's state-controlled Muntajat set its May Qatar sulphur price at \$86/t f.o.b. Ras Laffan/Mesaieed, down by \$24/t from the April QSP of \$110/t f.o.b. The May QSP level implies delivered pricing to China of \$112-117/t c.fr at freight rates at the end of April. Kuwait's KPC set its April Kuwait sulphur price (KSP) at \$109/t f.o.b. Kuwait, reflecting a decrease of \$26/t on the March price. Meanwhile Abu Dhabi's state owned ADNOC set its April official sulphur price (OSP) for liftings to India at \$115/t f.o.b. Ruwais, down by \$19/t from the March price.

In supply news, Kuwait's KPC has restarted one of two crude distillation units (CDU) at its 615,000 bbl/d Al-Zour refinery on 21 April after resolving technical issues that led to its closure. The status of the refinery's No.2 CDU, which also went offline in early April because of technical issues. One March shipment of sulphur has been lifted so far from the new refinery with further sulphur liftings delayed. But Argus expects to see export availability continuing to rise in the region to make up the shortfall from the refinery. The increase in sulphur remains a key influence on short term pricing from the region. Sulphur export availability is forecast to rise by over 1 million t/a in 2023 on a year earlier, driven by an increase in

production. Saudi Arabia and Kuwait lead growth with the continued ramp up of new capacity in the refining sector.

The north Africa spot c.fr price was assessed by Argus at \$95-115/t c.fr. at the end of April. This compared to the contract range for supply for delivery during the second quarter at \$105-130/t c.fr. This was down on the first quarter levels of \$156-265/t c.fr. and the decrease reflects the softer tone in the market. This sluggish sentiment is expected to prevail through the rest of the second quarter, based on a weak global sulphur market and downward pressure from processed phosphates prices.

On the demand front in north Africa, one potential supportive factor is the expected increase in consumption in the phosphoric acid sector. Moroccan demand is expected to grow on 2022 levels but the growth expectation is at risk as OCP was operating at below capacity rates in April following a period of slow demand for processed phosphates exports. Short term spot demand from the sulphur buyer was not expected to emerge. The uplift in demand is possible from the third quarter which would support trade and provide a floor to the downturn in pricing.

Sulphur demand in China is expected to rise in 2023 on year ago levels. A key driver is the industrial sector, following only a limited increase last year. While there is still much focus on the developments of export quotas on processed phosphates in 2023, we expect sulphur consumption for phosphoric acid production will only see a minor increase. Some processed phos-

phates producers plan to cut production in May because of weakening domestic demand and the erosion of end product prices in the export market. Some smaller sized producers have already been operating at lower levels since March. Run rates were estimated at around 50-60% in southern China and around 60-65% in the river area in April. The reduction in output will slow sulphur consumption and adds to the more bearish sentiment for short term pricing in the market.

SULPHURIC ACID

Average global sulphuric acid prices have softened since the start of the year but showed signs of stabilizing or ticking up in April. The uptick is expected to continue in the short term but will be gradual. Concerns and risks remain around the continued downward trend in processed phosphates market prices, and with sulphur price softening, this has added to the potential for a ceiling on the sulphuric acid price recovery.

Latin American markets have been sluggish since the start of the year, with limited spot interest emerging in key market Chile as arrivals have been moving under contracts. End user tanks were reported to be at full capacity in April, supporting the view for limited spot volumes to encourage prices to rise. A closure was planned at the port of Mejillones in late April to 10 May, which will add to congestion, but end users were under-

stood to be planning around the shutdown with a healthy line up through April. The Chilean acid market is expected to remain long in the short term but it remains to be seen how increased potential demand at copper mines could impact the balance. Price ideas for third quarter shipments have dropped down to \$90-105/t c.fr owing to the weaker demand view. Over in Brazil terminal operations were suspended at Paranagua port in April while some repairs were underway. Prices in the country were assessed by Argus at \$75-85/t c.fr on 27 April.

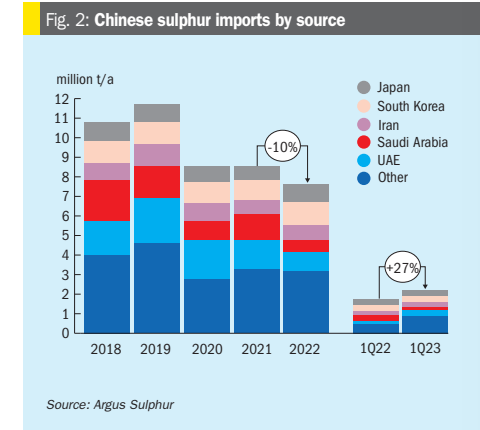
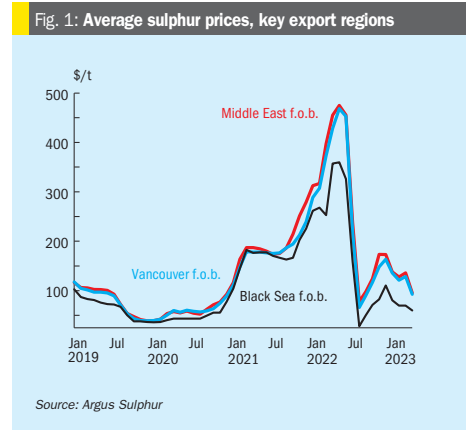
Base metal prices on the London Metal Exchange (LME) rose at the end of April as China's Politburo – the foremost economic decision-making body of the country's ruling Communist Party – reiterated its focus on economic growth, pledging possible fiscal and monetary policy support for the world's top metals consumer through the second quarter. But price gains were capped by a more bearish outlook for Western demand, where sticky inflation has potentially left the door ajar for longer-lasting policy intervention by the US Federal Reserve and the European Central Bank (ECB).

While China's economy continues to recover this year – its economy grew at a faster than expected pace in the first quarter – demand headwinds remain for the country and analysts have argued that growth has mostly been uneven so far this year. Recovery in the real estate sector has been choppy with end-sales remain-

ing low, with a persistent debt squeeze and a slowing world economy impacting a complete recovery from Covid-19 and supply shocks of last year. The Politburo has renewed its focus on improving consumption and private investment, creating optimism in base metals markets as a result. An upward trend in metals prices will support operating rates at mines and sulphuric acid consumption.

Major Chinese smelters Jiangxi Copper, Tongling Nonferrous, Yunnan Copper and Zijin Mining have planned maintenance on part of their production lines during April-June, which will result in reduced copper concentrate demand and sulphuric acid production in the second quarter. China's sulphuric acid output and export availability is a key consideration for the market balance and pricing outlook in the short term following record export levels in 2022. New capacity is expected to come online in the short term, adding to the expectation for strong exports this year.

Meanwhile in Morocco key sulphuric acid importer OCP has been largely on the sidelines so far this year on the back of low operating rates at its processed phosphates operations. Acid imports were close to 63,500t in January-February 2023, well below the 319,000t imported a year earlier. China remains the largest supplier so far this year, followed by South Korea. North Africa acid prices were assessed at \$45-105/t c.fr with further softening expected in the short term.



Price Indications

Table 1: Recent sulphur prices, major markets

Cash equivalent	December	January	February	March	April
Sulphur, bulk (\$/t)					
Adnoc monthly contract	180	160	134	134	115
China c.fr spot	195	170	158	150	132
Liquid sulphur (\$/t)					
Tampa f.o.b. contract	90	125	125	125	103
NW Europe c.fr	123	123	132	130	130
Sulphuric acid (\$/t)					
US Gulf spot	150	135	95	80	70

Source: various

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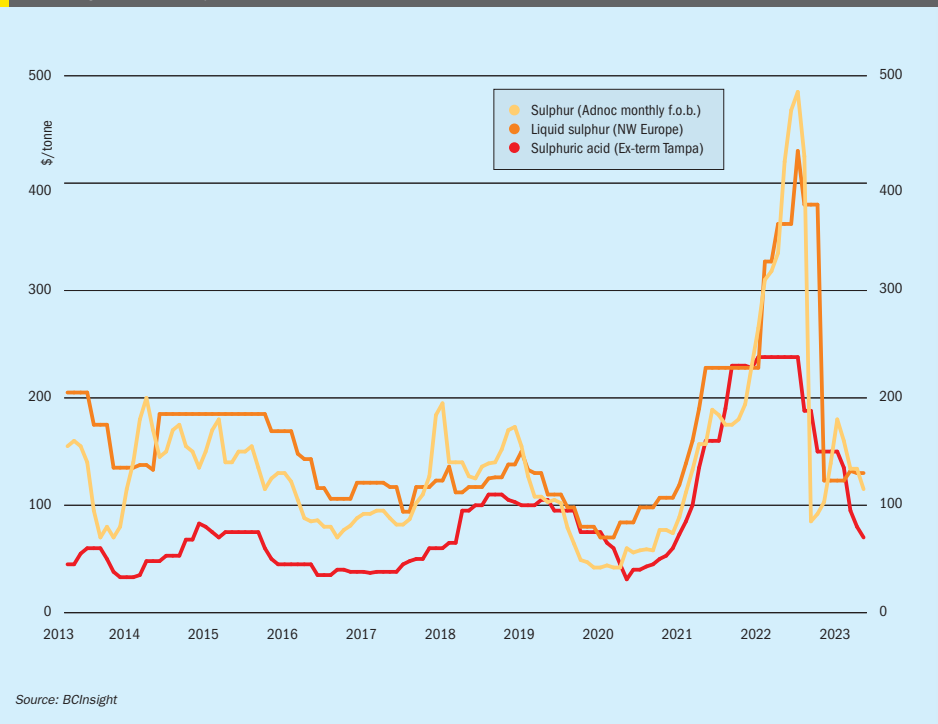
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Market Outlook

Historical price trends \$/tonne



Source: BCInsight

SULPHUR

- New sulphur burning capacity in India is expected to come online in the coming months at fertilizer producer operations. This will lead to an increase in sulphur import demand but also impact sulphuric acid imports to the country.
- The ramp up of new refining capacity in China continues to push up the view for sulphur production in the short term and limit expected sulphur imports for the year. The rate and pace of start up will impact spot market activity.
- Indonesian sulphur demand at HPAL nickel operations continue to drive trade to the country and support pricing. This is likely to be a bright spot in the short term for consumption but is not expected to be enough to support the market during a period of weakness in processed phosphates.
- The start of construction at Lithium Americas' Thacker Pass lithium mine in

Nevada in the US is a key point of interest for the market but sulphur demand is not expected until the 2026-27 period. The electric vehicle and battery materials markets remain key drivers for new demand growth for sulphur in the medium term.

- **Outlook:** Global sulphur prices are forecast to drop further before reaching a point of stability and potential rebound. Sluggish demand from a weakening processed phosphates market and ample supply remain the main bearish factors in the short term. The potential for an uplift in the market will come later in the year as demand improves and the global balance turns to a trade deficit.

SULPHURIC ACID

- The NW European acid market has moved to balance in the short term despite the absence of key importer OCP in Morocco. Smelter based producers are sold out until July and the spring

maintenance schedule through the second quarter will tighten spot availability.

- Indonesian sulphuric acid imports have increased to record levels so far in 2023. First quarter imports totalled 214,000 tonnes, up over 300% on a year earlier. China was the leading supplier. Demand has been boosted by nickel HPAL operations and remains a bright spot for short term trade and pricing.
- The US acid market remains balanced despite a busy turnaround schedule in the second quarter. Spot demand is expected to emerge later in the quarter, testing the pricing outlook when a major smelter goes into turnaround.
- **Outlook:** The short term outlook is for stable pricing but the downturn in sulphur and processed phosphates prices alongside slower import demand in India and Morocco may weigh on the recovery. Potential demand uplift could support pricing in the second half of the year.

Sulphur Industry News

QATAR

Bedeschi to supply sulphur handling equipment



Bedeschi has been awarded a contract by Tecnicas Reunidas and Wison Engineering for the engineering and supply of new sulphur-handling equipment. Tecnicas Reunidas and Wison Engineering are working in a 70-30 joint venture partnership on the North Field Expansion Project (NFXP) Sulphur Project, which forms part of the overall Qatar North Field Expansion Project. Last year were awarded a \$600 million contract to process and export sulphur from the projected expansion of the liquefied natural gas (LNG) facilities in Ras Laffan Industrial City. The new sulphur plant will have the capacity to process an average of 5,000 t/d of molten sulphur.

As part of their contract, Bedeschi will supply six conveyor belts with a total length of 1,400 meters with a capacity of 550 t/h, including galleries and transfer towers; four conveyor belts with a total length of 480 meters with a capacity of 2,000 t/h, including galleries and transfer towers; one conveyor belt with a total length of 120 meters with a capacity of 3,700 t/h, with gallery and transfer tower; two trippers with a capacity of 550 t/h; a double arm portal reclaimers with a capacity of 2,000 t/h; a travelling slewing shiploader with a capacity of 2,000 t/h; and a radial shiploader with a capacity of 3,700 tonnes per hour.

KUWAIT

Axens to license technology for gas-treatment plants

Axens says that it is supplying the process design packages for the gas treatment of two gas plants in North Kuwait. The engineering, procurement and construction contract is being managed respectively by SPETCO and Jerah. Axens is licensing two HySWEET units for acid gas removal, as well as two Smartsulf units for the sulphur recovery and two triethylene glycol (TEG) units for gas drying. The units for both gas plants are now under process design phase and the plants will be commissioned in early 2024. Each HySWEET unit will treat 163.4 million scf/d of gas to remove the acid gases including H₂S, CO₂, COS and mercaptans to meet sales gas specifications.

HySWEET is a hybrid process for simultaneous removal of mercaptans and acid gases from natural gas, developed by TotalEnergies and commercialised by Axens. It is based on the selection of the

most suitable non-proprietary physical solvent for blending a variety of commercial amines (DEA, MDEA, formulated MDEA) and maximises mercaptans removal along with the absorption of the acidic species while minimising hydrocarbon co-absorption which can potentially be harmful for the downstream sulphur recovery unit.

KAZAKHSTAN

NCOC sued for excess sulphur storage

The Kazakhstan Ministry of Ecology and Natural Resources says that it has filed a lawsuit against the North Caspian Operating Company (NCOC) consortium, the operator of the Kashagan oil field, for breaching safety guidelines for storing sulphur. The country's Oil and Gas Strategic Partnership Development Council (Petrocouncil) further reports that the Ministry is suing for a total of \$5.1 billion for what it describes as "environmental pollution". At issue is the volume of sulphur being stored at the Bolashak oil and gas treatment plant, which receives and processes associated gas from the giant off-

shore Kashagan field. There are six sulphur pads with a reported total permitted capacity of 730,000 tonnes, but according to a government environmental audit seen by Petrocouncil, total storage allegedly reached 1.7 million tonnes in November 2022. The Ministry also alleges that the sulphur was not covered with a membrane as per local regulations to prevent sulphur dust being carried away from the site. Other allegations include a lack of dust suppression, dumping waste water without treatment and failure to recycle water, and lack of automated emissions monitoring. NCOC said in response that it had no information about the government lawsuit and that the company carries out its sulphur management activities responsibly and in accordance with the laws of Kazakhstan, as well as in accordance with applicable standards and best practice.

This is not the first time that the Kazakh authorities have cracked down on operating companies in the country over alleged environmental breaches. In 2012 Kazakhstan obtained a 10% stake in the Karachaganak Petroleum Operating Company project as a result of the settlement of a dispute running back several years, and again including alleged violations of sulphur storage regulations and H₂S emissions monitoring, and there are suggestions in local media that the government is "flexing its muscles" to try and put pressure on operators to extract more money or a better deal over upcoming projects. The government is also looking to increase transport costs for oil by up to three times their current value by May 1st.

NCOC normally produces around 1.4 million t/a of sulphur and exports 1.0-1.2 million t/a of this overseas.

UNITED STATES

Battery can use non-chemical grade sulphur

Houston-based Zeta Energy says that it has developed a safe, low-cost, high performance, and sustainable battery for the electric vehicle and energy storage markets, which can use 'unrefined' sulphur in its proprietary lithium sulphur battery technology with no loss of performance. This means Zeta can produce batteries with locally available sulphur just about anywhere in the world rather than having to use highly pure chemical-grade sulphur.

Sulphur is considered an ideal battery material because of its potential for extremely high energy density, low weight and low cost, but historically a problem

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Fugro's multi-purpose survey vessel the *Fugro Proteus*.

known as the "polysulfide shuttle effect" has resulted in low cyclability of sulphur-based batteries. Zeta uses a proprietary sulphurised carbon material which prevents this effect, resulting in sulphur-based cathodes with better stability and performance.

Chief Science Officer Rodrigo Salvatierra commented, "We are absolutely thrilled with these results. Most companies working with sulphur use highly purified chemical grade sulphur, which has higher cost and requires more energy and processing time. We have now shown that our processes work with unrefined sulphur, such as that derived from oil refining or used in the fertilizer industry, with no additional refining steps. This gives us a big advantage in our ability to meet the actual low cost of sulphur, and increase the sustainability, of making batteries."

LIBYA

Bids invited for gas processing complex

Libya's state-owned National Oil Corporation (NOC) has invited prequalification bids from contractors to build a major new gas production complex and export pipeline at its Atshan project in the onshore Murzuq basin. In 2019, NOC gave the go-ahead for its wholly-owned subsidiary the Zallaf Oil & Gas Exploration and Production Company to begin work on a plan to process large volumes of associated gas from the Murzuq basin, close to the border with Algeria. The pipeline specifications call for a 24" line which can transport up to 200 million scf/d of treated dry gas from the Atshan field to the Obari power plant. The power plant is currently fuelled by oil and switching to gas will allow Libya to export an additional 15,000 bbl/d of oil. The Atshan gas processing plant will have a capacity of 280 million scf/d of gas. Libyan gas is typically around 0.6-1.0% hydrogen sulphide.

UNITED ARAB EMIRATES

Contract for offshore services

Fugro says that it has been awarded a contract for site characterisation services in support of "one of the largest long-term field development programmes in the United Arab Emirates". Although Fugro did not name the project, ADNOC's largest offshore development is the Upper Zakum field; the fourth largest oil field in the world. Production currently runs at 750,000 bbl/d, but ADNOC plans to lift that to 1.0 million bbl/d next year and has further expansion plans out to 2030.

Fugro says that from April 2023, it will perform a series of offshore surveys including geophysical, geotechnical and remotely operated vehicle (ROV) inspections supported by advanced engineering and geoconsulting studies to help inform the Front End Engineering Design (FEED). The project consists of approximately 600 km pipeline route assessment with 800 crossings, 49 jacket surveys and island offshore surveys.

Tim Lyle, Group Director Middle East and India at Fugro said: "We are delighted to be supporting a project of such calibre. This significant award will allow Fugro to support our client's vision and sustainability targets whilst strengthening our commitment to in-country value (ICV) by working closely with our local supply chain."

SAUDI ARABIA

Aramco to begin refinery construction

Aramco and joint venture partners NORINCO Group and Panjin Xincheng Industrial Group say that they will start construction of a major integrated refinery and petrochemical complex in northeast China in the second quarter of 2023.

Huajin Aramco Petrochemical Company (HAPCO), a joint venture between Aramco (30%), NORINCO Group (51%) and Panjin Xincheng Industrial Group (19%), is developing the complex. It will combine a 300,000 bbl/d refinery and a petrochemical plant with a production capacity of 1.65 million t/a of ethylene and 2 million t/a of paraxylene. Construction is due to start in the second quarter of 2023 after the project secured the required administrative approvals. It is expected to be fully operational by 2026. Aramco will supply up to 210,000 bpd of crude oil feedstock to the complex, which is being built in the city of Panjin, in China's Liaoning province.

Mohammed Y. Al Qahtani, Aramco Executive Vice President of Downstream, said: "This important project will support China's growing demand across fuel and chemical products. It also represents a major milestone in our ongoing downstream expansion strategy in China and the wider region, which is an increasingly significant driver of global petrochemical demand."

Zou Wenchao, NORINCO Group Deputy General Manager, said: "This large-scale refinery and petrochemical complex is a key project of NORINCO Group to implement and realize the joint development of the high-quality Belt and Road initiative, promote industrial restructuring, and enhance the oil and petrochemical sector to become stronger, better and larger. It will play an important role in deepening economic and trade cooperation between China and Saudi Arabia, and achieving common development and prosperity."

Jia Fei, Panjin Xincheng Chairman of the Board, said: "The project is of great significance for Panjin to promote increasing chemicals and specialty products, strengthening integration of the refining and chemical industry. It is a symbolic project for Panjin as it seeks to accelerate the development of an important national petrochemical and fine chemical industry base."

Aramco has also made other recent investments in China. It has agreed to acquire a 10% stake in the private Rongsheng Petrochemical Co Ltd for about \$3.6 billion. The deal includes the supply of 480,000 bbl/d of crude oil to the Rongsheng-controlled Zhejiang Petrochemical Corp (ZPC) for 20 years. Aramco has also signed a memorandum of understanding with the southern Chinese province of Guangdong to explore cooperation in sectors including energy, finance, research and innovations. ■

Sulphuric Acid News

AUSTRALIA

Worley Chemetics to supply sulphuric acid technology

Worley has been awarded a contract to supply Chemetics' *CORE-SO2*™ technology for a sulphuric acid plant and associated oxygen unit at the Arafura Rare Earths project, sited 135 km north of Alice Springs in Australia's Northern Territory. A greenfield mine will extract and process neodymium and praseodymium to create ultra-strong permanent magnets for a range of applications, such as household electronics and high-performance motors for electric vehicles.

Worley says that the sulphuric acid plant will achieve significant sustainability improvements over similar capacity plants, thanks to its ability to idle while keeping the catalyst warm for extended periods of time, and high turnaround capability. It will be able to operate with 95% reduced sulphur dioxide (SO₂) emissions, when compared to traditional double contact double absorption (DCDA) plants. The high-pressure steam production within the *CORE-SO2*™

process will further reduce greenhouse gas emissions by enabling the generation of CO₂-free electrical power. This will eliminate the need for a diesel or natural gas start-up burner. *CORE-SO2*™ is also 60% smaller than traditional sulphuric acid plants, leading to significant construction advantages; fewer pieces of equipment, and increased scope for modularisation. This minimises construction and assembly work for the remote mine site, leading to safer and more cost-effective project delivery.

"Arafura Rare Earths is very pleased to be working with Chemetics Inc as a global leader that is able to provide the Nolans Project with highly efficient, robustly engineered and low-emission sulphuric acid technology. This sulphuric acid plant represents a key component in achieving our sustainability goals," said Stewart Watkins, General Manager Projects at Arafura. ■

INDIA

Larsen & Toubro to build phosphate plant

Vedanta Group has contracted Larsen & Toubro to engineer and build a 500,000 t/a fertilizer plant for Vedanta subsidiary Hindustan Zinc Ltd at Chanderiya, Rajasthan. The order includes setting up a 180,000 t/a phosphoric Acid Plant and a 510,000 t/a ammonium phosphate plant within the battery limits of the existing fertilizer complex.

Vedanta to carry out maintenance work at Sterlite

India's Supreme Court has allowed Vedanta Ltd. to carry out maintenance work at its closed Sterlite Copper Plant located in Tamil Nadu's Tuticorin. The order came after the company filed applications to ensure proper upkeep of the copper smelter, which was shut in 2018. The Supreme Court took evidence from a report by the High Powered Expert Committee and the recommendations of the Tamil Nadu State Government. In 2018, the Tamil Nadu Pollution Control Board (TNPCB) ordered the closure of the controversial Sterlite Plant after protests by locals and environmental activists who alleged that the facility was causing severe pollution.

DEMOCRATIC REPUBLIC OF CONGO

Production at Kamoak-Kakula up after debottlenecking

Ivanhoe Mines says that production at its Kamoak-Kakula copper complex in the DRC produced 93,603 tonnes of copper concentrate in 1Q of 2023, including a record breaking 34,915 tonnes in March. The Phase 1 and 2 concentrators are now operating at an increased processing rate of 9.2 million t/a, following completion of a \$50 million debottlenecking programme. The programme was completed on-budget and ahead of schedule in late February, increasing production capacity up to 450,000 t/a of copper concentrate.

Ivanhoe Mines' founder and executive co-chairman Robert Friedland commented: "The operating performance at Kamoak-Kakula continues to impress as the team focuses on optimising the concentrator plant following the successful completion of the Phase 1 and Phase 2 debottlenecking program, once again ahead of schedule and on budget, during the first quarter. We're particularly excited about the improving trends in copper

recovery, which saw the concentrator plants operating at recoveries as high as 90% in March... driving record production numbers into the end of the month. With the Phase 3 expansion well on track for 2024, Kamoak-Kakula represents a truly rare, high-margin growth story across the copper industry... As the rainy season in the Democratic Republic of Congo ends our geological team will also be ramping up exploration activities on Ivanhoe's 90-100%-owned Western Foreland Exploration Project next door, where we



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expect to drill around 75,000 metres this year. We're looking forward to the many successes to come with our partners and shareholders in 2023 and beyond."

Surface earthworks for Phase 3 concentrator plant and associated infrastructure well advanced, with first flotation cells delivered in March. The Phase 3 expansion will consist of two new underground mines known as Kamoia 1 and Kamoia 2, located approximately 10 km north of the existing Kakula underground mine and the Phase 1 and Phase 2 concentrators. A new, 5 million-t/a concentrator is under construction adjacent to the new Kamoia mines, which are also under development. Foundations have also been laid for the direct-to-blister furnace building, as part of the 500,000 t/a flash copper smelter. Ivanhoe says that construction of the smelter is 36% complete and proceeding on schedule. All smelter off-gas streams, including the acid plant tail gas, will be treated through the desulphurisation plant. The plant will produce 650-800,000 t/a of high-strength sulphuric acid, which will be sold domestically within the DRC copper belt.

GERMANY

Lead smelter reopens after sale

Metals company Nyrstar, owned by commodities group Trafigura, has reopened the Stolberg lead smelter in Germany. Stolberg, previously owned by Ecobat, was closed in 2021 after flooding in the west and south of the country and remained shut during its sale to Trafigura. The Stolberg plant largely supplies European battery producers with lead. It has the capacity to produce 155,000 t/a of lead, as well as more than 100 different types of lead alloys, and also can produce up to 130,000 t/a of sulphuric acid.

SWEDEN

Boliden scrap smelting returns to pre-covid levels

Boliden says that the Rönnskär smelter in northern Sweden recycled 83,000 t/a of electronic scrap in 2022, up 14% from 73,000 t/a the year before, and a return to pre-pandemic levels. Rönnskär is one of the most advanced copper smelters in the world, with most of its e-scrap feedstock coming from Europe. In addition to e-scrap, Boliden also processes lead-acid batteries and residuals from various industries. Overall, Boliden recycled about 321,500 t/a of recovered materials in 2022, down from 330,400



PHOTO: BOLIDEN

The Ronnskar smelter, Sweden.

metric t/a in 2021. The recycled input rate in 2022 was 12%, the same as the year before. The facility recycled 160,000 t/a of secondary materials, down 5% from the year before. Of that total in 2022, scrap electronics made up 52%. In 2022, mined copper concentrate made up 82% of input, with recovered materials making up the remaining 18%. E-scrap's portion of total inputs was 10%. According to the company's most recent annual sustainability report, in 2022 the facility produced 218,000 t/a of copper, 12 t/a of gold, 467 t/a of silver, 2 t/a of palladium concentrate, and 550,000 t/a of sulphuric acid (up 4% on 2021).

CHINA

MECS awarded spent acid regeneration plant contract

Sinopec Zhenhai Refining and Chemical Co., Ltd, China's largest integrated refining-chemical company, has awarded Elessent Clean Technologies subsidiaries MECS, Inc. and MECS Chemical Plants Equipment (Shanghai) Co., Ltd the contract for the license, design, engineering, and equipment provision for a spent sulphuric acid regeneration plant Sinopec's petrochemical complex in Ningbo, Zhenhai province. The spent acid regeneration plant will be built in conjunction with Sinopec's planned expansion of its sulphuric acid alkylation and acrylonitrile facilities at the Ningbo site.

The growing use of sulphuric acid alkylation by refineries and increased production of spent sulphuric acid from chemical plants necessitates additional processing of the spent acid. MECS says that its dry gas sulphuric acid regeneration (SAR) technology offers acid producers an effective solution that supports the production

of very high quality alkylate, while ensuring consistent on-stream time with limited maintenance requirements.

Eli Ben-Shoshan, CEO, Elessent, said, "We are honoured to play a role in a project that provides our customer, Sinopec Zhenhai, with a means to strengthen sustainability in the region. Our sulphuric acid regeneration technology allows Sinopec to keep sulfuric acid in circulation for as long as possible. This provides great value for our customer and allows them to incorporate another measure of sustainability into their refining operation."

FINLAND

Eurobattery increases stake in nickel cobalt project

Mining company Eurobattery Minerals AB has exercised its option to acquire 30% of the shares in FinnCobalt Oy, which is developing the Hautalampi nickel, cobalt and copper project. This is the company's second acquisition within the scope of its contracted right to acquire 100% of project out to May 2024. The current acquisition takes Eurobattery's share of FinnCobalt to 70%, making it the majority owner and bringing the right to nominate a chairman of the board and two ordinary board members and their deputies. The acquisition is expected to be completed during 2Q 2023.

The Hautalampi project is located near Outokumpu, near the famous Keretti mine where approximately 28.5 million tonnes of rock with a copper content of 3.8% were mined between 1912-1989. The project consists of one mining concession covering 227 hectares. On 20 March 2023, the company published a preliminary feasibility study for the Hautalampi project which put proven

and probable mineral reserves at 4.56 million tonnes of sulphide deposits, grading 0.30% nickel, 0.24% copper, and 0.08% cobalt. Ore processing will include crushing, grinding, metal flotation circuits to produce concentrate and a sulphur removal flotation circuit, followed by sulphuric acid leaching.

"We are very pleased to continue to deliver on our strategy to provide battery minerals from Europe to Europe, now as the majority owner of the Hautalampi mine project. With the pre-feasibility study just announced we know that the economic outlook for the battery mineral mine in Finland is strong," said Roberto Garcia Martínez, CEO of Eurobattery Minerals.

MOROCCO

OCP to 'solarise' phosphate production

The International Finance Corporation (IFC) says that it is providing a €100 million loan to OCP Group to support the construction of four solar photovoltaic plants to power the group's operations in Morocco. OCP intends to use solar power to reduce production costs and the carbon footprint of its operations in Morocco. The solar PV facilities will have a combined capacity of 202 MW, and will be built near the mining towns of Benguerir in the Rehamna region and Khouribga, 120 km southeast of the economic capital Casablanca.

"Obtaining this loan is a testament to the partnership we are building with the IFC and the alignment of our institutions as we simultaneously tackle the global challenges of food security and climate change," explains Mostafa Terrab, OCP Group's chairman and CEO.

As part of this strategy, the group launched a new company in 2022 to guide its energy transition; OCP Green Energy, which will manage the solar array. OCP says that its renewable energy strategy is expected to avoid emissions of 285,000 t/a of carbon dioxide equivalent (CO₂).

CHILE

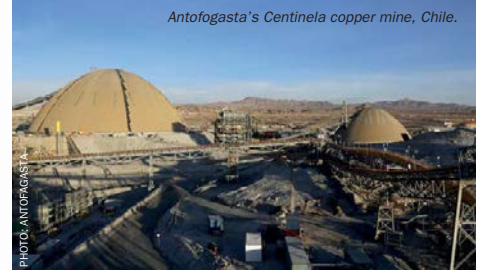


PHOTO: ANTOFAGASTA

Antofagasta's Centinela copper mine, Chile.

Antofagasta output up slightly after poor 4Q

Antofagasta plc says that 1Q 2023 copper production for 2023 was 145,900 tonnes, 5.1% higher than the same period in 2022, but 25% lower than the 195,700 tonnes produced in the fourth quarter of 2022. The 4Q 2022 decline was due to a temporary reduction in throughput at Los Pelambres due to lower water availability, and lower grades and scheduled maintenance at Centinela, according to Antofagasta. However, in a statement it said that it expected copper production to improve throughout the rest of 2023, with annual copper production guidance figures put at 670-710,000 t/a, and capital expenditure \$1.9 billion.

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People

PhosAgro's shareholders elected a new board of directors during the company's annual general meeting (AGM), held on 24 March. The new board includes: **Viktor Ivanov**, **Yuriy Krugovykh**, **Siroj Loikov**, **Natalia Pashkevich**, **Mikhail Rybnikov**, **Alexander Seleznev**, **Vladimir Trukhachev**, **Viktor Cherepov**, **Alexander Sharabaiko** and **Andrey Sharonov**. The AGM also approved the company's annual report for 2022, which reflected total production of 11.1 million t/a of agrochemical products (up nearly 5% year-on-year); and a one-third increase in investments to develop the company. PhosAgro CEO Mikhail Rybnikov said: "The consistent implementation of our long-term development programme enabled us to increase production last year, and we remained the leader in terms of the total supply of all types of fertilizers to the domestic market and expanded our support in the social sphere considerably. We intend to maintain this momentum of steady development. In 2023, we expect further growth in the production of agrochemical products, to 11.3 million tonnes. Our workforce laid the groundwork for this in January-February, as we increased production of phosphoric acid and sulphuric acid by 22% and 17% year-on-year, respectively, over this period."

"In 2023... the second start-up complex for the 10th horizon at the Kirovsky mine is expected to come online by the end of the year. In Cherepovets, in addition to projects to support capacities for the production of ammonia, phosphoric acid and sulphuric



Tareq Kawash

acid, a project to increase the processing of phosphate rock under development. In Balakovo, we are going to complete projects to increase the production of feed phosphates and sulphuric acid by the end of the year, and we are also starting the third stage in the development of the production facility by establishing a flexible arrangement for the production of MAP/DAP/NPS/NPK fertilizers. Our new million-tonne plant in Volkhov is expected to reach design capacity in 2023. Furthermore, the possibility of building new facilities for the production of ammonia and urea in Cherepovets and Volkhov is being analysed."

UK-based oilfield services provider Petrofac has confirmed the appointment of **Tareq Kawash** as Group Chief Executive Officer and Executive Director, replacing Sami Iskander from April 1, 2023. In a statement, the company said Iskander has stepped down from the board. Kawash was most recently working as McDermott's Senior Vice President of Global Onshore and Middle East Offshore

Business Lines, as well as a member of McDermott's Executive Committee.

"With 30 years' international EPC leadership experience and an impressive business development track record, Tareq is exceptionally well placed to build on the foundations laid by Sami," said Petrofac Non-Executive Chairman René Médori.

Itafos Inc. says that **Evgenij Iorich** has stepped down as member of the company's board of directors effective from April 6, 2023. Iorich had served as a director since July 11, 2017. "On behalf of the Company, and the Board of Directors, I would like to thank Mr. Iorich for his service and contributions," said Tony Cina, Chairman.

Colombia's majority state-owned energy company Ecopetrol has appointed **Ricardo Roa** as its new chief executive, assuming the role from April 30 at the latest. Roa's appointment follows the recent exit of former chief executive Felipe Bayon, who stood down from the role at the end of March. Ecopetrol announced in January that Bayon would be leaving the company, with his departure representing a shake-up for Colombia's biggest company and largest producer of oil. Roa, a mechanical engineer, has more than 30 years' experience, particularly in leading strategic transformations in the energy sector.

"My commitment is to lead with all the professional rigor, from this great company, a fair and sustainable energy transition for the benefit of the entire country," Roa said.

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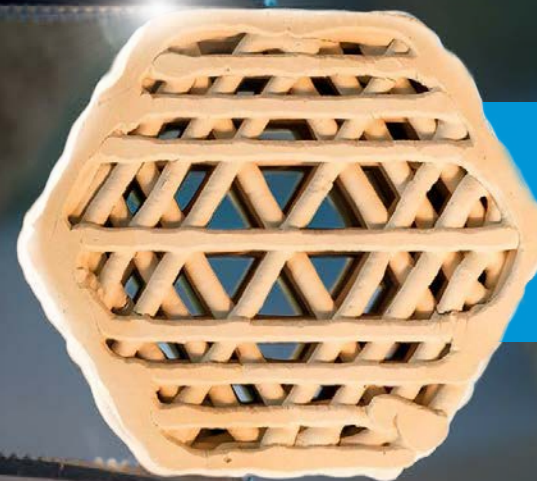
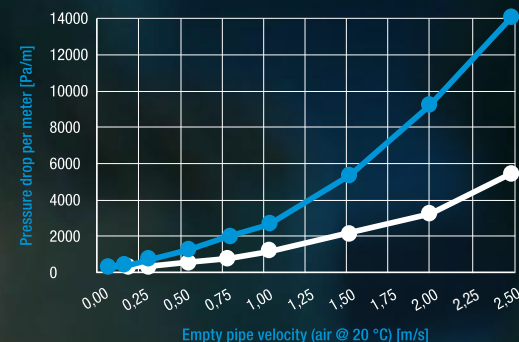
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Tel: +44 (0) 20 7903 2444
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Web: events.crugroup.com/middleeastssulphur/

23-25

Ninth International Acid Gas Injection Symposium, CALGARY, Canada
Contact: Alice Wu, Spheretech Connect
Email: alicewu@spheretechconnect.com
Web: www.spheretechconnect.com

JUNE

9-10

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

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ESA General Assembly, VIENNA, Austria
Contact: Francesca Ortolan, European Sulphuric Acid Association Sector Group Manager
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Email: for@cefic.be
Web: www.sulphuric-acid.eu

SEPTEMBER

11-15

30th Annual Brimstone Sulphur Symposium, VAIL, Colorado, USA
Contact: Mike Anderson, Brimstone
Tel: +1 909 597 3249
Email: mike.anderson@brimstone-sts.com

13-14

Oil Sands Conference & Trade Show, CALGARY, Alberta, Canada
Contact: Bruce Carew, EventWorx
Tel: +1 403 971 3227
Email: marketing@eventworx.ca

NOVEMBER

6-8

CRU Sulphur & Sulphuric Acid Conference 2023, NEW ORLEANS, Louisiana, USA
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New sulphur projects

Asia's new mega-refineries: the Hengli Petrochemicals refinery in Singapore.

Sulphur production continues to expand in the Middle East and China both from new refineries and major sour gas projects.

Elemental sulphur production continues to come almost exclusively from recovered sulphur from refineries and sour gas plants, with mined sulphur representing less than 1% of production. As recovered sulphur is involuntary production, its generation depends very much on the health of the refining and gas industries respectively. Nevertheless, in spite of some rocky years due to covid and the Ukraine war, production continues to expand in both sectors.

Refinery production

In general the trend for sulphur supply from refineries has been a steady increase for several decades, as regulations on the permitted sulphur content of fuels tighten to reduce emissions of sulphur dioxide, especially from vehicles, to reduce the impact on public health. The global push to reduce sulphur levels in vehicle fuels has, over the course of the past three decades, brought sulphur content of fuels from around 800 ppm in Europe and North America down to 10-15 ppm. The so-called Euro-V standard of 10 ppm has steadily become adopted worldwide, and by 2022 was in force in all of Europe and North America, Australasia and industrial East Asia, Russia, China, India and Chile. The Euro-IV 50 ppm standard was additionally adopted in most of southeast Asia and the Philippines, east and south Africa and parts of South America.

As more markets move to lower sulphur standards, so refineries in those countries must extract that sulphur during fuels production. But moreover, refineries in major

exporting countries must also meet these standards if they wish to service those markets. This means that large, export-oriented refineries in e.g. the Middle East or Nigeria must meet Euro-V standards even if local regulations are looser. All of this is driving increasing sulphur production from refineries. In Saudi Arabia, the Ras Tanurah and Riyadh refineries are being revamped to meet Euro-V standards.

At the same time, there has been a significant change in maritime fuels, previously often using refinery bottoms with high sulphur content. The IMO regulations on SO₂ emissions have led to widespread adoption of fuels with less than 0.5% sulphur content for ships, although use of exhaust gas scrubbers to allow continued use of cheaper, high sulphur fuel oil (HSFO) has spread, especially among larger ships. So-called Emissions Control Areas (ECAs), where the sulphur limit is 0.1%, are also spreading with the Mediterranean Sea to switch to being an ECA by 2025.

However, concerns over the use of fossil fuels are also affecting demand and use for refined fuels. Use of electric vehicles is spreading rapidly, with the proportion of new vehicles that use an electric power train rising rapidly from 8% in 2021 to 13% in 2022 and likely to reach 17% this year. Ageing global populations (who drive less), the saturation of vehicle ownership in formerly industrialising economies, and the increasing use of ride sharing apps and other shared mobility services are all converging to counter the increased number of vehicles on the roads. The International Energy Agency's most recent (March 2023)

forecast puts global oil demand at 101.9 million bbl/d this year, with growth concentrated in non-OECD countries, buoyed by a resurgent China, and declines by 390,000 bbl/d in OEC countries. It also sees demand likely fairly flat across the rest of this decade, peaking before 2030. This view has been challenged by some, including OPEC, who of course have a stake in oil demand continuing to rise, to 108 million bbl/d by 2030, but even so, demand increases over the next few years look to be modest.

It also means that liquid fuel demand is continuing to slowly shift from west to east. The covid pandemic has helped accelerate this trend, leading to 1.1 million bbl/d of refinery closures in the US and 0.8 million bbl/d in Europe. Some European refiners have also suffered from the interruption in crude supply from Russia. Elsewhere, Japan has shed 0.3 million bbl/d of refinery capacity since 2017 due to its declining, ageing population and the switch to electric vehicles. In the US, LyondellBasell has announced the closure of its Houston refinery this year, although there are expansions elsewhere at Beaumont, Port Arthur and Galveston.

Biorefineries

An additional major trend at the moment is a switch in the US and Europe towards biorefinery conversions. In the US, Valero converted its refinery in Louisiana last year, and Marathon and Phillips 66 are both converting refineries in California this year and next. In Europe Neste has converted Por-

vo in Finland and Total its Grandpuits and La Mede refineries in France. Shell is also building a large scale biorefinery at Pernis in the Netherlands, and Eni has discussed converting its 500,000 bbl/d Livorno refinery. Production includes hydrotreated vegetable oil (HVO). All of these will reduce sulphur output. While some vegetable oils such as rapeseed oil have up to 0.9% sulphur, most vegetable oils have a much lower sulphur content, often as low as 20 ppm.

Asia

Conversely, new refining capacity continues to come onstream in Asia. China is the largest destination for new capacity. The country has moved rapidly to a Euro-IV standard in 2008, for the Beijing Olympics, to Euro-V in 2013-18, and Euro-VI from 2021-23. Refinery capacity has grown rapidly and last year actually overtook the US, with 18.4 million bbl/d of capacity by end 2022, though utilisation rates and hence overall output remain lower. Table 1 shows the current slate of new refinery construction in China, with up to 3 million t/a of new sulphur output. In a bid to meet 2030 emissions targets, the Chinese government has announced a cap to refinery capacity of 20 million bbl/d by 2025, and it is trying to target small, less efficient refineries to close. China has a large sector of small independent so-called 'teapot' refineries with capacities of less than 40,000 bbl/d. However, these refiners have survived previous rounds of closure. As a result, no new projects smaller than 200,000 bbl/d are being approved, and larger refinery approvals are often contingent on shutdowns of smaller refineries.

Outside of China, Malaysia saw restart of the Pengerang RAPID refinery last year after 2 year closure due to fire. Capacity there is 300,000 bbl/d and 0.6 million t/a sulphur, but the refinery is not running at full capacity at the moment. India has a major programme of refinery expansions out to 2026, including expansions at the Nagapattinam, Jamnagar, Visakh, Numaligarh, Kumali, and Barauni refineries. In all some 830,000 bbl/d is being built over the next couple of years, responsible for approximately an extra 0.8 million t/a sulphur. In addition, there is the West Coast Refinery Project (WCRP) in Maharashtra state west of Mumbai. This 60 million t/a (1.2 million bbl/d) project has been on the cards for several years, with domestic producers IOC, BPCL and HPCL partnered by

ADNOC and Aramco. However, the project is currently in abeyance due to local environmental opposition.

Middle East

The other major centre for new refining capacity is the Middle East. Historically the region focused on the export of oil, with relatively simple local refineries and very lax standards on sulphur content of fuels. However, as noted earlier this is changing as end use markets evolve and refining capacity and complexity is increasing. Several large new projects are now either operational or nearing completion, including Al Zour in Kuwait (1.3 million t/a sulphur capacity), Duqm in Oman (0.3 million t/a), Jazan in Saudi Arabia (0.3 million t/a), Karbala in Iraq and the Abadan expansion in Iran. Saudi Arabia is also revamping Ras Tanura and Riyadh to Euro-V standards.

Sour gas

The other main source of sulphur is from processing of sour gas. Use of natural gas has been on a rising trend for many years, rising 35% during the previous decade from 3.23 trillion cubic metres in 2011 to 4.04 tcm in 2021, according to BP figures. Last year saw an overall slight decline in world natural gas consumption, particularly in Europe, where price pressures due to the invasion of Ukraine and gradual suspension of Russian gas supplies led to a 19% fall in EU gas consumption. Elsewhere, however, gas is still in demand for power production, as it is seen as cleaner than coal in terms of carbon emissions and gas-fired power stations are cheaper and easier to set up. The rapid growth of a global LNG market has made access to natural gas cargoes available to anyone who can build a receiving terminal, and a

much more liquid gas market has eased it away from being tied to oil indexed pricing. Nevertheless, as more renewable and nuclear power is installed, so the 'dash for gas' that characterised the previous three decades is slowing.

Globally around 40% of all gas resources are classed as sour, though in the Middle East this figure is as high as 60%. Sour gas processing was pioneered in Europe and Canada, though most of these fields are now closed or in decline. The major centres for sour gas production are now Sichuan province in China, the Caspian Sea and surrounding area in Central Asia, and the Middle East. The imperatives for sour production include avoiding wasteful flaring, which is both carbon intensive and burns potential revenue; there is also a push to avoid burning coal in China for environmental reasons or oil in Saudi Arabia to free up more oil for export. Sulphur extracted from sour gas can also be used for fertilizer production, metals extraction etc, though this can be a problem in Central Asia where there are no ready markets for all of the sulphur produced, meaning that expansions projects increasingly rely upon acid gas reinjection into the well. Sour gas production also faces other challenges such as corrosion of steel, additional cost burdens etc.

Major new sour gas projects that will produce additional sulphur volumes are centred on the Middle East. Abu Dhabi in particular has pioneered sour gas extraction to supply the UAE's own burgeoning gas demand at the same time that it exports LNG. The massive Shah project is undergoing an expansion. Gas at Shah is highly sour; around 23% H₂S. Production has already been lifted from an initial 1.0 bcf/d in 2016 to 1.28 bcf/d, and is set to rise to 1.45 bcf/d. Sulphur capacity, currently at 4.2 million t/a, will rise concomitantly. Further down the timeline is the offshore Hail/Ghasha field

Table 1: Major new Chinese refineries

Refinery	Capacity, kbd	Onstream	Sulphur, million t/a
Jieyang	400 kbd	2022	0.8
Lianyungang	320 kbd	End 2022	0.6
Zhenhai	300 kbd	2021/2024	0.4
Yulong	400 kbd	2024	0.6
Tangshang	300 kbd	2025	0.3
Panjin (Aramco)	300 kbd	2026	0.3
Total			3.0 million t/a

Source: BCInsight

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Table 2: New sour gas sulphur production

Project	Location	Sulphur capacity	On-stream date
Middle East			
Shah Expansion	Abu Dhabi	+1.6 million t/a	2024+
Hail/Ghasha	Abu Dhabi	3.5 million t/a	2025+
North Field	Qatar	+1.0 million t/a	2025-27
Tanajib	Saudi Arabia	1.0 million t/a	2025
Jafurah	Saudi Arabia	0.4 million t/a	2025+
China			
Chuangdongbei	China	+0.4 million t/a	2023
Total		+7.9 million t/a at capacity	

Source: BCInsight

expansion in Abu Dhabi. Here ADNOC is targeting production of 1.5 bcf/d gas with 15% H₂S content, partnered by Eni (25%), Wintershall (10%), OMV (5%) and Lukoil (5%). EPC contracts are expected this year and ADNOC says that first gas may flow as early as 2025, though production will take a couple of years to ramp up. Final sulphur output could be up to 3.5 million t/a.

In neighbouring Qatar, after a decade or more without major project activity, Qatar-Energies is gearing up for the massive North Field Expansion Project. The North Field, the world's largest gas field, has lower H₂S content; around 0.5-1.0%, but the volumes of gas are much larger. The field already feeds Qatar's 77 million t/a of LNG exports, as well as domestic GTL production and the Dolphin export pipeline. Qatar is now aiming to lift LNG exports to 110 million t/a. QatarEnergy has a 75% stake in the new projects, with Total, Eni, Shell, ExxonMobil, and ConocoPhillips as partners. First gas is again scheduled for 2025, ramping up over the next two years. Total additional sulphur could be around 1.0 million t/a.

Finally, Saudi Arabia is building the massive Jafurah gas plant to process gas mainly from onshore shale gas fields in the east of the country, where there are approximately 200 tcf of reserves in place. The fields are also liquid rich, with condensate and natural gas liquids (NGLs). By 2030 production is expected to be 2 billion scf/d of natural gas, 420 million scf/d of ethane and 630,000 bbl/d of NGLs, with first production once again targeted for 2025. The H₂S content of the shale gas is relatively low, but the volumes of gas to be handled are high, and so the site is budgeting for a sulphur output of approximately 230,000 t/a.

Saudi Arabia is also developing the Tanajib gas plant as part of the Marjan oil field expansion programme. Output is to rise from 500,000 bbl/d to 800,000 bbl/d, with the Tanajib plant processing associated offshore gas. It will have a capacity to process 2.5 billion scf/d, and completion is expected in 2025. Sulphur production capacity is around 1.0 million t/a.

Outside of the Middle East, the main expansion will be at the Chuandongbei gas plant in China's Sichuan province. The operating company is a joint venture between the China National Petroleum Company (CNPC) with 51%, and Chevron with the minority 49% stake. Total reserves put at 6.3 tcf and the gas H₂S content averages 7-11%. Chuandongbei is a three phase project, taking gas from the Luojiazhai and Gunziping, Tieshanpo and Dukhoue-Quilibei fields. The first phase (260 million scf/d) reached capacity in April 2016, and the second phase begins this year 2023. Sulphur output is about 400,000 t/a in each phase.

Overall, new sulphur from sour gas processing could reach nearly 8 million t/a over the next few years (see Table 2).

Sulphur forming

Finally, on the subject of new sulphur projects, it is worth mentioning sulphur forming projects. While most sulphur is transported as a dry bulk solid, North America and Europe both for historical reasons have a large liquid sulphur transport sector. Transporting sulphur as a liquid has both pros and cons. On the pro side, it is both produced and consumed as a liquid, and keeping it a liquid in between avoids having to use energy-intensive sulphur remelters. ■

However, it requires specialist tankers to keep the sulphur molten at over 120°C. It also means that only specialised receiving terminals can handle it, and this in turn restricts the pool of potential customers. In order to diversify supply options, there is a continuing trend towards installing sulphur forming capacity to transport it more easily as a solid. The TCO consortium which operates the Tengiz field in Kazakhstan installed 1,300 t/d of granulation capacity at Atyrau in 2021. In Europe, Solvadis brought the Dival pastille granulation plant onstream in Belgium in 2022, and this year in Alberta Keyera will start up its new South Cheecham, Alberta wet prilled sulphur facility. This will have the capacity to handle up to 4,000 t/d of sulphur, and joins the Heartland Sulphur forming facility further south in Edmonton which has 2,000 t/d of capacity. Reduced demand from Mosaic in Florida and the installation of the New Wales sulphur melter is changing the pattern of North American sulphur use and transport, and forcing Canadian producers to look at solid sulphur exports south via rail or west to the port of Vancouver.

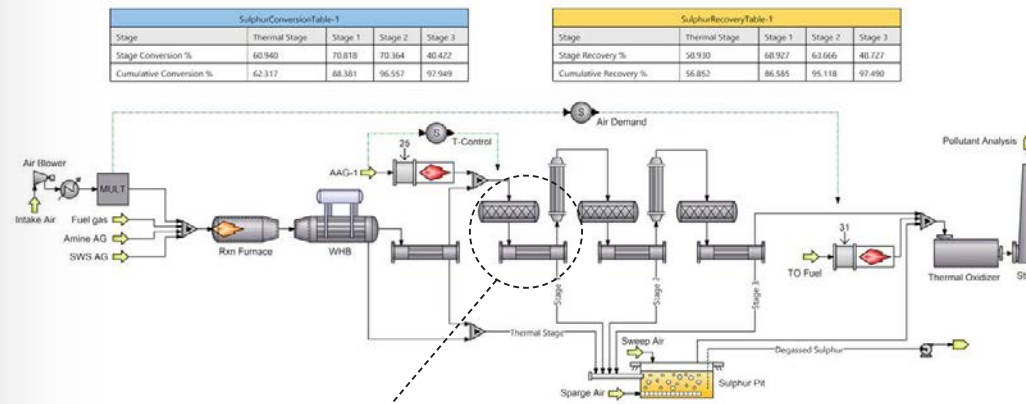
Supply/demand balance

At the moment, new supply from refining and sour gas, taken together, adds about 13 million t/a of new sulphur production capacity out to 2027-8, provided that there are no further project delays, most of it in the Middle East and China, though delays in commissioning and ramp-ups in production may mean that actual volumes of sulphur produced are smaller. The market is, and continues to be in surplus, at least on paper, but the balance is a fine one, and delays to projects either on the supply or demand side could alter this in any given year.

On a regional basis, the Middle East continues to be the largest exporting region, as new refineries and sour gas projects push additional output much higher than projected demand increases from Saudi Arabia's phosphate processing. But the largest change may be in China. China has long been the largest national importer of sulphur, but new refineries and sour gas projects may add up to 4 million t/a of sulphur production over the next few years at the same time that rationalisation continues in the phosphate industry. There is also the question of additional acid production from new smelter capacity which may displace sulphur demand among phosphate producers. ■



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The Come-by-Chance refinery, Newfoundland, now undergoing conversion to biofuel production.

Sustainable refineries

PHOTO: SHHEWITT/CREATIVE COMMONS

Liquid fuels will be with us for decades to come, but refiners will be pushed to decarbonise their activities, via greater use of biofuels, and green/blue hydrogen use.

The refining industry, already battered by covid and the associated reduction in demand for refined products that saw 1.1 million bbl/d of refinery closures in the US and 0.8 million bbl/d in Europe, faces an uncertain future. Consumer demand for refined products is likely to peak during this decade, while an increasing use by governments of carbon pricing and other disincentives to production add costs to already squeezed margins. Production of electric vehicles is growing rapidly. Indeed, it is projected that EVs will form the majority of new vehicles sold globally by 2028. Demand for transportation fuels will thereafter decline by the equivalent of one major refinery per year worldwide. Concawe, the European refiners association, estimates that road fuel demand will decline by 31% between 2021 and 2035, from 343 million t/a to 232 million t/a. The pressure on capacity is likely to be strongest in North America and Europe, where operations are more expensive and EV take-up is fastest.

Low carbon operations

According to US EPA figures, the average refinery produces 1.2 million t/a of CO₂ equivalent, with 95% of that coming from fuel combustion and catalytic cracking/reforming. Refinery operations are likely to face increasing costs as carbon taxes and carbon pricing is imposed, particularly in Europe, where carbon prices are already approaching \$100/t CO₂e. Reducing car-

bon emissions is likely to become a major factor in refinery operations to avoid these costs. Various strategies are available to the operator.

The least costly means of reducing carbon footprint, and the most effective, is to improve a refinery's energy efficiency, via optimisation of operations and reduction of the gas, steam, and power needed to operate them. This can involve heat recovery systems, lower emission furnaces, thermal energy storage, and using digital tools to optimise operation.

Refineries can also offset their emissions switching to renewable energy sources, both to power their own operations and to sell back into the power grid. Other lower carbon fuel sources can also be used, including biomass, synthetic gas produced from biomass, biogas produced from other organic sources such as municipal waste and sewage sludge, and biomethane, which is produced by upgrading biogas.

Where operations are intensive in use of hydrogen, refineries can lower emissions by shifting from the production of hydrogen via steam methane reforming to green hydrogen made from entirely renewable sources of power. The cost of production has historically been high compared to gas-based production, but the cost of electrolyzers and green electricity are both falling, and there are already over 800 green hydrogen projects announced worldwide, with a total capacity of approximately 29 million t/a, with financial incentives offered by governments, such as the US Inflation

Reduction Act. IRA tax credits for renewable electricity and clean hydrogen can reduce the cost of green hydrogen production by almost half, falling to nearly \$3/kg hydrogen for a project starting in 2023.

Finally, for large scale reduction of carbon emissions, there is the option of carbon capture, utilisation, and storage (CCUS). This can include production of so-called 'blue' hydrogen, using conventional steam reforming but capturing and using or storing the carbon produced, regarded as the more cost-effective option for large scale generators compared to green production, at least at present. CCUS does however require access to depleted oil and gas reservoirs, saline aquifers, basalt formations, or coal deposits that cannot be mined, or investment in downstream use of CO₂, such as chemical synthesis (including green methanol production), algae synthesis, etc.

Switching operations

Another option is to move away from refining altogether. Increasing integration with petrochemical production has been seen as an attractive way forward for some refiners. Many refineries already benefit from physical integration with a petrochemical plant and are co-located and operated as a single site. This integration leads to reduced costs of handling and moving exchanged streams; better overall optimisation of refining and chemical plant throughput; and scale-driven efficiencies in the cost of maintenance and operations support.

Biofuels

An option that has gained considerable traction in recent years is to switch the refinery operation to the production of biofuels. In Europe, there had already been significant production of biofuels as FAME (fatty acid methyl ester) biodiesel, using vegetable oils or used cooking oil combined with methanol. However, only a fraction of this has come from conventional refineries. The FAME biodiesel market has blending restrictions, and also overbuilt capacity in Europe. New production is mainly coming from hydrotreated vegetable oil (HVO), using a mix of both virgin vegetable oils and from waste and residues, as well as lignocellulosic and waste based feedstocks. This is proving an attractive option for European refiners. Around 75% of investment in European refineries is going towards biofuels production. Total has converted two conventional refineries at Grandpuits and La Mède in France which had been scheduled for closure into 'biorefineries' that able to produce bio-jet fuel, biodiesel, and bioplastics. Shell is looking at a huge 800,000 bbl/d facility in the Netherlands,

and Eni is reportedly considering converting its 500,000 bbl/d Livorno refinery in Italy.

Renewable diesel and sustainable aviation fuel (SAF) plants are also proliferating in North America. Eight refineries have announced conversions to produce renewable fuels, with a combined capacity of 240,000 bbl/d, more than double US current biofuel output. In 2022, domestic renewable diesel and other biofuel plant capacity was just under 1.8 billion gallons per year, or 114,000 bbl/d, according to the Energy Information Administration (EIA). Government policy is driving change here, including tax credits and environmental regulations ranging from California's low-carbon fuel standard to the federal Inflation Reduction Act (IRA).

Refinery conversions include Marathon Petroleum and Phillips 66, who are both in the process of converting refineries near San Francisco to produce renewable diesel, the former in partnership with Neste. HF Sinclair is adding a renewable diesel unit to its Navajo refinery in New Mexico, and there are also conversions in the US Gulf Coast. Valero Energy is engaged in a massive expansion of its Diamond Green Diesel facilities in Louisiana, a joint venture

with Darling Ingredients. Fellow independent PBF Energy is adding renewable diesel capacity to its Chalmette, Louisiana refinery as well. In Alabama, Vertex Energy, a firm that specialises in processing used oils into products, is tweaking its Mobile refinery to produce renewable diesel. In Canada, Newfoundland's Come-by-Chance facility is aiming to begin producing renewable diesel and SAF in the second half of this year.

Sulphur production

The impact of these changes will of course be a reduction in sulphur output. Although biofuel feeds contain some sulphur, it is often at very low levels, usually less than 150 ppm. At the moment the level of conversion has not had an appreciable effect on output; US refinery sulphur output actually increased in 2022 from 6.9 million t/a to 7.5 million t/a due to a combination of higher run rates and use of higher sulphur crudes. But towards the end of the decade these increasing conversions and closures will start to impact sulphur production, first in North America and Europe, but likely worldwide over the subsequent years. ■

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Developments in sulphur polymers

PHOTO: RAWPREL

Incorporating sulphur into polymers is known to improve their properties. New research is looking into the varied world of sulphur co-polymers, unlocking new materials for batteries, structural applications and clean technology.

“Sulphur copolymers have also been found to have a high refractive index. Refractive index determines... the light-guiding nature of optical fibres.”

Above: Optical fibres: a potential use for sulphur copolymers.

Sulphur's versatility as an atom is well known; almost as versatile as carbon. Its ability to form chains and rings are responsible for many of its unique properties as a material. Throughout the long history of sulphur's use, various attempts have been made to harness these properties to enhance the properties of other materials. Perhaps the most widely known is that of so-called vulcanisation of rubber, developed in the 1830s by Henry Goodyear to solve a problem he was having with his rubber tyres – that during hot road conditions the rubber would become sticky and collect debris. He discovered that by heating rubber with sulphur at 140-160°C, the rubber became strengthened and less subject to tackiness at high road temperatures. What had happened was that the sulphur had formed bridging strands of sulphur atoms between the long polymer chains of the rubber, creating a more stable composite material.

For a long time vulcanisation was the main way of incorporating sulphur (not usually in its pure state, but as a disulphide) into materials. However, during the 1960s and 70s, the generation of large volumes of elemental sulphur from sour gas and refinery processing meant the ready availability of elemental sulphur on a large scale and at relatively low cost, and so there were attempts to find uses for all of this excess sulphur. This broadly coalesced into two thrusts; using sulphur as a binder in concrete, and using sulphur as a binder

in asphalt. In concrete, sulphur is used at roughly a 20% concentration to replace the cement binder. It produces a faster curing, harder and more wear resistant material with good resistance to acidic conditions. It also avoids some of the CO₂ emissions involved in conventional concrete production. Sulphur concrete is licensed by Shell as Thiocrete, and has been used, e.g. for railway sleepers on French and Belgian railways. However, it is generally more expensive than ordinary concrete, and this has limited its use to some niche applications.

In asphalt, sulphur is able to mix more intimately with the various carbon compounds that make up the bituminous base. Sulphur is mixed at around one third to two thirds bitumen in sulphur-extended asphalt (SEA). As with vulcanisation, it is able to cross-link and harden the asphalt, and forms a more durable road material. Shell also produces a pellet additive using sulphur and wax to make SEA, which they market as Thiopave. During the 2000s, Qatar became interested in SEA as a use for large quantities of sulphur being recovered from gas processing, and conducted a programme of research, leading to SEA being used on some roads in the Kingdom. However, concerns about recyclability of the sulphur asphalt (asphalt is often remelted and relaid for road repairs) and the potential for the evolution of hydrogen sulphide during the process, as well as the additional expense of the sulphur, again constrained wider adoption of SEA.

Inverse vulcanisation

More recently, research on sulphur-based materials has begun to focus on the phenomenon of so-called 'inverse vulcanisation'. Here, rather than sulphur acting as a bridge between carbon polymer chains, sulphur itself can act as a monomer, developing long chains stabilised by carbon bridges instead. Elemental sulphur exists mainly as an eight-atom ring, but this melts at about 159°C to form thyl radical chains with bi-radical ends forming linear sulphur polymers (polysulphanes). Polysulphanes are unstable and readily depolymerise back to octet rings. But in its molten state it can directly copolymerise with hydrocarbon co-monomers.

In the early 2010s, again due to concerns about the large volumes of sulphur that would be produced from ADNOC's sour gas extraction, Abu Dhabi's Petroleum Institute investigated the addition of up to 15% sulphur to low- and high-density polyethylene, as well as polypropylene and engineering plastics such as polyamide. In high density polyethylene (HDPE), the researchers found that the plastic's elongation at break was increased by up to 50% with the addition of 15% by weight sulphur. This in effect can improve the plastic's toughness.

Further research has been conducted by other institutes on vinyl copolymers with sulphur, again showing that they have improved tensile strength and breaking strain, toughness and hardness. The cross-linked polymers were also found to be resistant to common solvents but could be chemically dissolved and recycled in dimethylformamide, dimethylacetamide, or n-methyl-2-pyrrolidone (NMP), which could allow intentional removal and recovery. Additionally, despite their cross-linked structure and improved mechanical properties, the polymers were found to still maintain highly recoverable thermal recycling and showed excellent shape memory behaviour even with complex shaped designs, which would not be possible to achieve with poor mechanical properties.

Refractive index

Sulphur copolymers have also been found to have a high refractive index. Refractive index determines the focusing power of lenses, the dispersive power of prisms, the reflectivity of lens coatings, and the light-guiding nature of optical fibres. High refractive index materials are particularly sought for applica-

tions requiring high transmission of light, but these are often brittle inorganic materials such as glass, while more flexible materials like plastics often have a low refractive index. A team of researchers at Khalifa University in the UAE has made stable sulphur polymers by reacting elemental sulphur with 1,3-di-isopropenylbenzene cross-linker inside a polystyrene matrix, where it diffuses into the matrix, ensuring even dispersion of the sulphur. The refractive index of the final polymer can be tuned as needed by varying the amount of cross-linkers. These polymers can be molded into objects or films without altering transparency. And, since they are highly soluble in most organic solvents, they can be made into ultra-thin films that are clear and stable.

Low thermal conductivity

The same team at Khalifa University have also been working on porous sulphur foams with very low thermal conductivity. Water-soluble template-embedded cross-linked polysulphides were prepared and hot-pressed to the required shape and size. Pores were then generated by dissolving the template in water. The porosity of the foam was altered by varying the particle size of template materials. The sulphur foam with a smaller pore size and high porosity showed a significant decrease in thermal conductivity, much lower than that of pristine sulphur and close to high performance insulating materials. The method also allows flexibility to modify the foam structure and properties during preparation and processing.

Environmental sorbents

Sulphur has long been known to form strong bonds with heavy metals such as mercury. Research has therefore also been ongoing on developing sorbents for toxic heavy metals such as mercury using sulphur polymers. As with the thermal foam, above, sodium chloride can be used at up to 70% during the formation process and then dissolved to leave a porous structure which has a higher surface area for binding to mercury.

Lithium sulphur batteries

Finally, sulphur copolymers are finding application in lithium sulphur battery materials. Rechargeable lithium sulphur batteries are a very promising line of battery research with much higher capacities than conventional lithium ion batteries, have drawn significant attention as next-gener-

ation energy storage systems, but have suffered from comparatively low numbers of recharge cycles due to the migration of sulphur from cathode to anode. Sulphur copolymers are a promising alternative cathode material to elemental sulphur as they can mitigate this problem. Recent research shown that polysulphides can be tuned in terms of sulphide chain lengths and the resulting reaction pathways during electrochemical cycling. The improved cyclability of these cathodes comes from carbon cross-links acting as anchors that fix the polysulphides to the polymeric network during cycling, preventing their diffusion into the electrolyte.

Early days

This is clearly a very promising field of study, but one of the more surprising things about current research into sulphur copolymers is how little studied they are, especially structurally. In part this is due to them often having low solubility in organic solvents that allow them to be processed in IR spectrophotometers etc. In terms of new uses for sulphur there are clearly many different avenues potentially open, with battery cathodes one of the largest scale potential uses, although the impact on the overall sulphur market for such high performance and relatively niche uses is likely to be limited. Perhaps this is just as well; one of the things that tends to be repeated in the preambles to papers on the subject is the notion that sulphur is widely available and cheap. As anyone who buys or sells sulphur knows; this is not necessarily always the case, and as fossil fuels are phased out, sulphur may become more expensive and sought after.

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TSI World Sulphur Symposium 2023

The Sulphur Institute (TSI) held its World Sulphur Symposium in Edinburgh from April 25th to 27th.

This was the first return to a face to face meeting for TSI since 2019's conference in Prague, after three years of disruption due to the covid pandemic. The venue was the old Caledonian Hotel in Edinburgh, now the Waldorf-Astoria, looking out onto Princes Street and the castle, and the conference came complete with pipers and whisky tasting.

Introducing the conference, TSI president and CEO John Bryant began with presenting the answers to an illuminating questionnaire posed to TSI members, asking them, among other things, what their biggest supply headache was (rail services, sulphur supply, trade flow shifts and associated uncertainties); what impact the Ukraine war and sanctions had had upon them (price volatility, supply security concerns, inflationary pressure on energy prices, and general uncertainty); and what issues and opportunities they were most concerned about (lithium and competition for sulphur, rail transport, supply chain optimisation, the US Inflation Reduction Act, crude slates and price volatility). Asked to rank the most impactful issues on business over the next 12 months, most led with inflation, government policies and decarbonisation, with covid, interestingly, placed last.

Global economic outlook

The conference proper began with a global economic outlook presented by Andrei Potlogea, assistant professor of economics at the University of Edinburgh, once home to Adam Smith himself. Last year had seen the global economy emerge from the pandemic. Demand had outstripped supply, leading to inflation, policy tightening and labour shortages. The Ukraine war had compounded this with disruptions to supply chains, and a spike in food and commodity prices, ameliorated slightly by government price support to households. But economies had proved more resilient than expected, and the energy and



Edinburgh Castle.

commodity price spikes are abating, and shipping rates have fallen back to pre-pandemic levels. China's economy has also been expanding post-covid. Some weaknesses remain. Inflation is proving persistent, and bank collapses have highlighted financial system fragility. There is high indebtedness, and geopolitical tensions remain high. Global GDP forecasts are for a 2.8% rise this year and 3.0% next, well below trend, and especially sluggish in developed economies. There has been 'deglobalisation' and a decline in foreign direct investment since the 2007 financial crisis, and China faces a real estate bubble. Nevertheless, there are reasons for optimism. Labour shortages may drive productivity growth, there is a stock of savings from the pandemic, and some expansionary industrial policies such as the US IRA. There are also signs that a period of technological stagnation may be ending with new developments in vaccines, self-driving cars and artificial intelligence.

Energy futures

Paul McConnell of S&P Global outlined a range of scenarios for the energy transition out to 2050. In the short term, he said, EU gas demand has fallen in response to the Ukraine crisis and European supply has shifted decisively from Russia to LNG. Despite progress on the energy transition, China continues to produce record amounts of coal. On the other hand, renewables demand has consistently exceeded expectations, and oil demand has fallen more than expected. But questions remained: can developing Asia, especially India, swing the balance on decarbonisation? And can institutions, governments and companies deliver on the commitments they have made? Paul foresaw electrification of end use demand and an expanding role for renewables across all outlooks, but mainly post-2030. Thereafter, liquids demand depends on electric vehicle penetration and gas demand depends on renewable power penetration.

Dry bulk freight

Ghigo Ravano of shipbrokers IFCHOR described the dry bulk freight market, via which most sulphur is traded. Freight rates peaked in mid-2021 and have been in decline since then. Lots of ships were built in the period 2005-2015 leading to overcapacity, since when there has been a major correction and very few ships built in the period 2015-2020. Net fleet growth is very small at present (approximately zero in the Handy-size class). The order book: fleet ratio is at a 10-year low. Many fleet owners are putting off decisions on new ships until it becomes clearer what the future fuel situation will be, with low carbon ammonia and methanol, LNG, biodiesel and even nuclear all under consideration. This may lead to a supply bottleneck in a few years. Demand for minor bulks (including sulphur) has been growing well, with exports up 2% year on year.

Sulphur as a nutrient

Wednesday ended with a paper by Dr Ismail Cakmak from Sabanci University in Turkey, leading into an afternoon seminar on sulphur nutrition. Ismail pointed to some factors readers of sulphur may be all too familiar with: rates of atmospheric sulphur deposition in e.g. the US have fallen from 6.6 kg/ha in 1989 to just 1.6 kg/ha in 2017 as power plant flue gas scrubbing and lower sulphur content of fuels reduce SO₂ emissions. This is leading to increasing requirements for sulphur application to fields and sulphur deficiency in some areas. He ran down the biochemistry of sulphur deficiency. Plants' biological response to e.g. drought/water stress depends on sulphate-containing compounds. Low plant sulphur levels lead to greater water loss from leaves. Likewise plant disease response relies on sulphur-containing compounds as natural bacteriocides or fungicides, and healthy levels of sulphur lead to greater disease tolerance. Plants with low sulphur are also more susceptible to iron and zinc deficiency in soils, something that affects up to one third of all cultivated soils, especially in Africa and India. Sulphur-containing chelates allow insoluble Fe/Zn to become soluble and carried into plants. Sulphur also correlates with nitrogen uptake, with sulphur containing amino acids responsible for conversion via protein synthesis. This also leads to less nitrate leaching and lower nitrate concentrations in plants which can have deleterious human health effects. Finally, sulphur-defi-

cient plants also have large concentrations of asparagine ammonia acid, which converts to acrylamide when heated (e.g. fried or cooked potatoes), a compound not regarded as a probable carcinogen. There are some issues. Plants high in sulphur have a lower molybdenum and selenium uptake, possibly indicating the need for microdosing in sulphur-containing fertilizers.

Dr Malcolm Hawkesford from Rothamsted Research in the UK expanded on the synergy between nitrogen and sulphur. Sulphur can lead to a reduction in nitrogen leaching of 60-70%, and a reduction in N₂O generation in the field by 40%. N₂O emissions spike when the nitrogen supply in the soil is in excess of plant demand.

Lithium ion batteries

Anna Fleming from Benchmark Minerals presented an outlook for batteries metals, particularly lithium. Demand for these obviously depends upon the uptake of electric vehicles. Anna estimated that the EV share of new vehicles produced in 2023 was 17% (up from 13% last year), but could be 100% by 2040 assuming no raw material supply constraints. Lithium ion batteries' production has increased 8% year on year since 2017 while price has decreased by 14% year on year as new technologies and economies of scale are developed. Batteries remain the largest cost driver for EVs, and raw materials are the largest cost (ca 70%) for batteries. Demand for lithium is projected to increase 12% year on year. Lithium ore supply currently comes mainly from China and Australia, but there are new projects in Europe, North America, Africa and Brazil as well as these locations. Current mine developments look set to meet projected demand out to 2028, but thereafter many more new projects need to be developed if demand is not to outstrip supply. As the supply chain scrambles to keep pace, the threat of price volatility escalates. There are also potential issues with shortages of equipment, infrastructure and skilled labour and potential impacts on project economics.

Phosphate outlook

The phosphate market presentation was given by the always entertaining Andy Jung of Mosaic. Agricultural commodity prices were still elevated compared to 2021, he said, even after coming down from price spikes caused by the Ukraine invasion. Agricultural demand looks flat this year compared to

last, but stock: use ratios are at their lowest for 20 years, supporting a rebound in phosphate demand. Weather could also be a wild card. After three years of La Nina, this year looks to be an El Nino year, with potential drought in Asia, especially India and northern Brazil, but drought relief in southern Brazil and North America. Other factors influencing grain markets include increasing use of biorefineries and sustainable aviation fuel. Phosphate prices are now in line with their level in 2021, with affordability improved. Overall demand for 2023 was likely to be a return to around a 2021 level after last year's falls due to high prices and supply constraints. Mosaic is also seeing a growth in demand for sulphur enhanced products. China remains the key swing supply factor. China's MAP and DAP production continues to decline due to environmental pressures and a switch to industrial production (e.g. lithium iron phosphate batteries). Chinese phosphate exports have fallen from around 10.5 million t/a to 6 million t/a in 2022. There may be a rebound this year but only to 7.5 million t/a.

Sulphur and sulphuric acid

Finally Freda Gordon and Fiona Boyd of Acuity gave the sulphur and sulphuric acid market presentation. Sulphur prices peaked in 2022 due to supply disruption from Ukraine leading to demand destruction. This in turn led to a drop in prices by 76% from June to September last year. After an overcorrection prices picked up in 4Q 2022, but have seen a steady decline in 1Q 2023. Trade flows have reshuffled due to the sanctions on Russia, with Russian and Kazakhstan sulphur exports via Ust-Luga challenged as fewer shippers are willing to handle cargoes. Kazakh product is now being shipped via ports like Taman and Batumi on the Black Sea, the latter in Georgia, to places such as Egypt, Brazil, South Africa and eastwards to Asia. Longer term, supply looks to be down in the western hemisphere due to refinery closures and up in the Middle East and Asia, again in no small part due to refinery capacity growth. Sulphur supply will rise from 67.4 million t/a in 2022 to 69 million t/a this year, and demand from 65 million t/a to 67 million t/a, Freda said. On the demand side, there are phosphate expansions in Morocco and Egypt, and new metals demand from Indonesia and the African copper belt, offset in part by new smelter capacity. China in particular is seeing a sulphur supply surge due to refineries and sour gas sulphur. ■

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A new era in catalyst geometric shape selection

BASF is challenging traditional catalyst shapes and performance relationships by introducing a radically new shaping concept resulting in materials with step change properties and performance. This innovative concept using 3D-printing technology is applicable to a wide range of reactions in the chemical industry and BASF is using sulphuric acid catalysts as the pilot to pioneer new ground.

Jochen Willersinn, Marco Kennema, Dirk Hensel, BASF SE

BASF has produced sulphuric acid for various industrial applications since 1866 and has been producing catalyst for the sulphuric acid process since the early 20th century. A first patent for a vanadium pentoxide catalyst was granted to BASF in 1913. Today, BASF operates six sulphuric acid and 13 sulphonation plants with inline SO₂ oxidation units worldwide, all using BASF's in-house catalyst technology, with world class plants operating at emission levels below 50 ppm SO₂. The last 15 years have brought new challenges such as tighter emission regulations and cost pressure to the sulphuric acid market. This has led to BASF being on the forefront of cutting-edge research into one of the oldest catalysts of the portfolio.

In alignment with the new strategy of BASF, sulphuric acid producers and their needs are even more in focus, driving improvements in catalyst technology. BASF works directly with customers to make sure customers achieve the best performance under the specific design and operation conditions of their reactors. This is enabled through BASF's state-of-the-art testing facility and analytics combined with more than 150 years of research and experience.

New extruded shapes

The production of sulphuric acid catalysts is generally conducted by extrusion of a precursor paste to yield shaped catalyst

bodies. The extrusion process not only defines the shape of the catalyst bodies, but also impacts other crucial properties such as pore structure and mechanical stability of the catalyst. These properties are also related to the fluid properties of the precursor paste in the extrusion device. The extrusion process has to cope with pastes of varying composition for different catalyst types. Fluid properties of precursor paste and control of the entire extrusion process are strongly determined by the specific design of extrusion dies. In particular, the detailed design of the internals of the dies has a significant impact on quality and capacity of extrusion. This becomes an immediate challenge when entirely new shapes for a catalyst family are to be extruded and new dies have to be found.

Continuous progress through a commitment in extrusion technology has been key for successfully turning a lab idea into an established and reliable commercial product. With the help of BASF's Technology Verbund, with in-house competence on computational fluid dynamics (CFD) and metal powder 3D-printing technology, it was possible to develop and optimise dies for extrusion devices in a short time period. This is evidenced by an international patent family filed by BASF on extrusion dies for catalyst production¹.

In 2016, BASF reaped the benefits from years of catalyst development launching the Quattro geometry with O4-115 Quattro being

the first sulphuric acid catalyst^{2,3} leading to 5-8% increased plant capacity in the first commercial application. Many additional customers have chosen the Quattro geometry since, all benefiting from performance improvements. With the completion of the Quattro family in recent years, sulphuric acid production has been raised to a new performance level. The question arising from this accomplishment was of course, whether the limit of catalyst shaping had been reached or whether there was any possibility to further improve sulphuric acid catalyst shape geometries to surpass the performance benefits of the Quattro range.

A step change in performance with 3D-printing technology

Due to the significant limitation of geometric flexibility, it is necessary to move away from standard line extrusion processes in order to achieve higher performance via larger pore sizes, higher surface areas, and lower pressure drops. Each and every variation in the geometry requires a new extrusion mould, a process that significantly increases equipment and labour expenses for its implementation. Moreover, standard extrusion methods are not capable of being extended to more complex geometries due to their limitation to formulate continuous channel designs. Therefore, new ways of producing catalysts needed to be found to overcome the limitations to reach these goals. A new

way of producing elaborate geometries with dedicated purposes is already established for plastic material parts, metal powders and even construction materials through the use of 3D-printing technologies. 3D-printing has the outstanding benefit that the shape and geometry of the desired part can be precisely designed based on the final material requirements and virtually any design is possible. Novel geometries can be designed and optimised in silico with the help of computer-aided design programs, and subsequently printed allowing fast iteration cycles to optimise shape geometries. As the need

for mould production and optimisation is entirely bypassed, 3D-printing offers unique benefits for catalyst design and production⁴.

In addition to the benefits of 3D-printing already mentioned, the printing process itself is similar to the extrusion process. In analogy to extrusion, the 3D-printed material consists of active material which is mixed with additives such as binders and rheology modifiers. The paste is also extruded by pressure and heated to generate the final structure, but on a smaller scale. This has the significant benefit that the chemistry of the catalyst material as

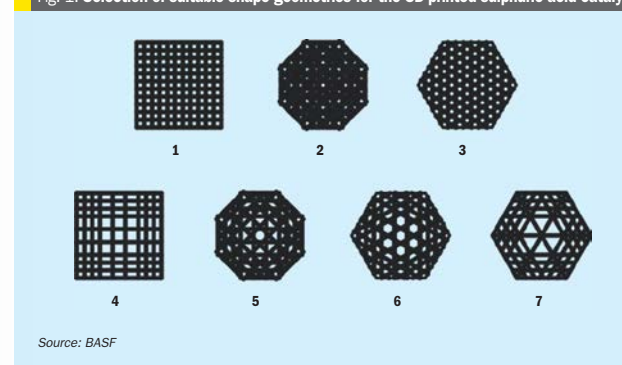
well as the post processing can be kept similar to the standard extrusion process.

With the introduction of its X3D™ technology, BASF has launched a new range of 3D-printed catalysts that are custom designed to significantly improve performance in their dedicated application processes. This article focuses on O4-115 X3D™, a sulphuric acid catalyst produced by 3D-printing and already implemented in three commercial sulphuric acid plants⁵.

X3D™ technology development

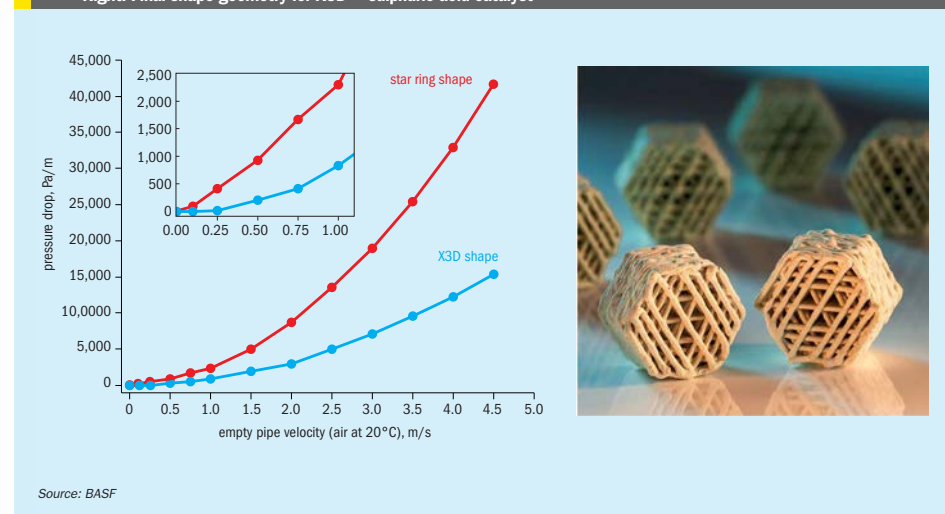
Based on the good experiences with CFD and computer tomography (CT) scans of catalyst beds during the development of the Quattro catalyst, the target was to further harness these technologies in order to improve the catalyst shape geometries. Despite good results in the early stage, it became clear that most of the key features, such as activity and surface area cannot be improved with standard extrusion techniques while maintaining the material strength. A new way of catalyst production was required which was able to decouple these intrinsic features of a catalyst from each other. 3D-Printing technology was identified as the most suitable tool to overcome these limitations, as mechanically stable structures can be produced in virtually every imaginable shape^{5,6}.

Fig. 1: Selection of suitable shape geometries for the 3D-printed sulphuric acid catalyst



Source: BASF

Fig. 2: Left: Simulated pressure drop vs. star ring shape catalyst obtained through CFD simulations based on a CT scan; Right: Final shape geometry for X3D™ sulphuric acid catalyst



Source: BASF

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Table 1: Property comparison between BASF's three catalyst shape geometries, star ring[®], Quattro and X3D™

Physical property	Star ring	Quattro	X3D
Packing density, kg/m ³	450	450	420
Rel. geometric surface area, %	100	130	150
Pressure drop Re=100, %	100	105 ±5	35 ±10

*Star Ring properties are regarded to be 100% for comparison.

Source: BASF

Table 2: Converter bed data from BASF internal reference

Converter bed	Volume, m ³	Catalyst loading, kg	Bed height, mm
1	1.0	450	550
2	1.0	450	550
3	1.2	510	650
4	1.6	720	850

Source: BASF

Following the decision to use 3D-printing, entirely new catalyst shapes were designed and assessed in silico using CFD and other simulation tools prior to any shape being physically produced. Based on these calculations^{7, 8, 9}, seven geometries were identified which can significantly surpass the geometric surface area of standard extrudates (Fig. 1).

The new shape geometries were 3D-printed in a test trial using the same catalyst paste that is used in the BASF production facilities and were subsequently evaluated in order to find the best design fit for the applications as a sulphuric acid catalyst. Catalyst shape geometry 7 (Fig. 2 right) was chosen to be the most suitable candidate for a commercial trial, as this shape geometry incorporates a high geometric surface area and mechanical stability. Moreover, shape geometry 7 displayed a significant benefit in contrast to the other shapes, a significantly lower theoretical pressure drop (Fig. 2 left).

As displayed in the graph in Fig. 2, the simulated pressure drop of the X3D™ catalyst obtained from the CT scans is 66% lower when compared to standard extruded star ring shape geometry. This is an outstanding achievement, as no extruded sulphuric acid catalyst could achieve such a low pressure drop.

When comparing the three catalyst shape geometries (Table 1), the benefits of BASF X3D™ catalyst is clearly visible. The transition from standard extrusion processes to 3D-printing afforded the design freedom for significantly higher

geometric surface. Moreover, the X3D™ catalyst design offers a way to decrease the packing density of the catalyst by 7% from 450 kg/m³ to 420 kg/m³ and significantly decrease the pressure drop by 66% compared to star ring geometry. In comparison to Quattro, the X3D™ shape geometry offers a 15% higher geometric surface area, which will also reflect in an increased activity of the catalyst providing even higher performance.

First commercial trial

Throughout the development of the X3D™ catalyst technology, it became clear that the new geometries had a significant impact on the pressure drop. This benefit of decreasing the pressure drop can help SO₂ converters with capacity limitations due to the pressure drop. When BASF was approached by the technical team of BASF Care Chemicals for the catalyst exchange of a sulphonation unit in 2018, after initial discussions it soon became apparent that the implementation of a custom designed O4-115 X3D™ catalyst would be an excellent fit to improve the situation of the plant. As sulphonation units operate at higher pressures, a decrease in the pressure drop results in a direct benefit for the plant due to a decreased blower power output and therefore immediate energy cost savings. The internal BASF sulphonation converter became the first commercial reference for O4-115 X3D™ using 3D-printed sulphuric acid catalyst in October 2019.

The facility of BASF's internal reference is a sulphur burning 4-bed single-absorption sulphonation plant with a sulphur burning rate between 330-480 kg/h with normal operation around 400-420 kg/h. The feed gas has an O₂/SO₂ ratio of 2.14. The catalyst O4-115 X3D™ was installed in the third bed. 510 kg of Cs-promoted catalyst were exchanged with 510 kg of O4-115 X3D™. The target of the trial was to test the impact of the X3D™ catalyst on the pressure drop in bed 3 and the overall converter, as well as the performance benefit with respect to the SO₂ scrubber which is used to remove any unreacted SO₂ before the emission of the off gas, while maintaining the same sulphur burning rate as before the changeout.

Catalyst installation

This plant was selected based on the relatively small size of the converter beds when compared to a standard sulphuric acid plant. The BASF internal reference plant has a converter diameter of 1,800 mm, and the beds are described in Table 2.

The catalyst was filled by the same method that is used when filling star ring catalyst into the converter, where the technician responsible for the filling can stand on top of the catalyst inside the converter without crushing the shape geometries. This further illustrates the strength of the O4-115 X3D™ monoliths (Fig. 3).

Performance overview

In contrast to typical sulphuric acid reactors which operate at relatively stable reaction conditions, SO₂ converters used for sulphonation plants need to adjust the production rates of SO₃ based on the demand for products from the sulphonation unit. As a result, measuring the pressure differences and the conversion of the catalyst under comparable conditions was a challenge. The data presented in the following section is therefore displayed as average values collected over a certain day and the fluctuations indicate a change in the production rate.

One of the results from the catalyst filling which is clear and undisputable is the decrease in pressure drop across bed 3. As predicted earlier in this report by the CT scan, the pressure drop of the catalyst is 75% lower than a standard catalyst (Table 3).

To date, the catalyst has been in operation for almost three years to the full satisfaction of the customer. As displayed in the graph in Fig. 4, there has been no significant increase of the pressure drop

Table 3: Total pressure difference*

ΔP	Before installation	After 4 months	After 28 months
Bed 3	31 mbar	5 mbar	4 mbar
Total	138 mbar	56 mbar	54 mbar

*Total pressure difference from inlet to outlet of each converter bed of the BASF internal reference at different points during the catalyst exchange at a sulphur burning rate of 440 kg/h. Major change was observed in bed 3.

Source: BASF

in bed 3 throughout this period and it is currently at 4 mbar.

The consumption of 50% NaOH solution in the gas scrubber was used in order to assess the conversion benefit of the X3D™ catalyst. As displayed in Fig. 5, a significant increase in overall conversion could be detected from the decrease of NaOH solution consumption from the point

when the new 3D-printed catalyst was implemented.

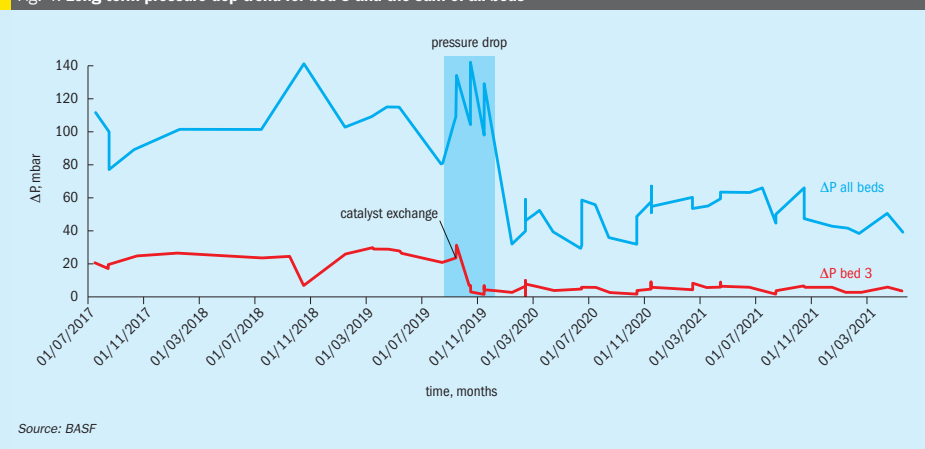
Using this measure, the SO₂ conversion prior to the changeout was approx. 97.7% which increased by up to 1.3% to almost 99% after the implementation of O4-115 X3D™. This is a significant increase in conversion for a single absorption unit and contributes significantly to the cost



PHOTOS: BASF

Fig. 3: Filling of the O4-115 X3D™ catalyst into bed 3 of the converter at the BASF reference plant.

Fig. 4: Long term pressure drop trend for bed 3 and the sum of all beds



Source: BASF

savings, as 20% to 45% less NaOH 50% solution is required to scrub the off-gas from remaining SO₂.

Economic benefits

The above-described outcome of the installation of O4-115 X3D™ in the third bed, namely a significant decrease in pressure drop and reduction in the NaOH consumption had a tremendous effect on the variable manufacturing costs. With the 3D-printed catalyst in place, significant cost savings have been made on a monthly basis over the last years (Table 4).

A total cost saving of 6% per month in energy costs and 20% per month for NaOH 50% solution demonstrates the potential of BASF's new X3D™ catalyst technology. To BASF's knowledge, this is the first sulphuric acid catalyst shape geometry

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Table 4: Relative savings after the installation of 04-115 X3D™ displaying a significant economic benefit

Measure	Savings/month, %
Decreased NaOH consumption due to higher conversion	Min. 20.0
Decreased electricity consumption due to lower pressure drop*	6.0

*As of 2019.

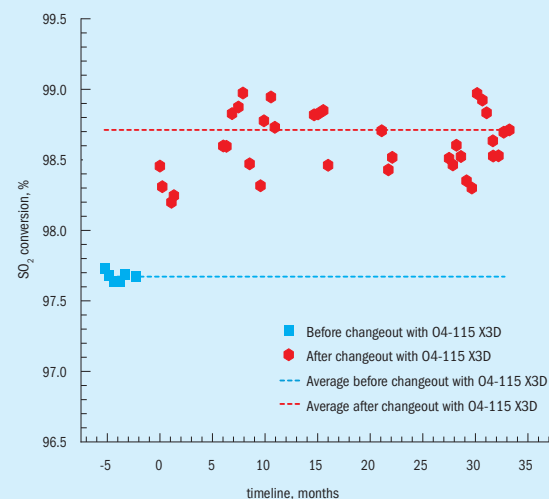
Source: BASF

Table 5: Solving common issues with X3D™

Common customer Issue	Can the X3D™ Help?	How?
High emission levels	Yes	Higher active surface area resulting in better SO ₂ conversion.
Pressure drop limitations	Yes	Custom designed 3D-printed shape geometry enables a significant pressure drop reduction through the catalyst bed.
Cost pressures on catalyst expense	Yes	Monthly savings of 6% of energy costs and a 20% lower NaOH consumption make X3D™ a viable option.

Source: BASF

Fig. 5: Converter conversion before and after changeout with 04-115 X3D™ determined through NaOH consumption



Source: BASF

obtained by an extrusion process which is able to achieve these benefits.

In summary the key benefits of the commercial reference at BASF are:

- 74% decrease in pressure drop in bed 3;
- 35% decrease in total pressure drop;
- 6% decrease in energy costs;
- 1.3% increase in SO₂ conversion;
- at least 20% decrease in consumption of NaOH 50% solution.

Conclusion and next steps

Table 5 shows how X3D™ can help with common customer issue.

Through continuous improvement, BASF has met its goal of producing a step change in catalyst activity and pressure drop decrease. The use of 3D-printing technology to produce a commodity catalyst, such as sulphuric acid catalyst, was not regarded as economically worthwhile before. However, with the introduction of the X3D™ catalyst technology, BASF has displayed the benefits in a commercial unit and the cost savings for the customer when the catalyst is employed. The outstanding results obtained from the first reference plant from 2019 onwards has already led to two further implementations of X3D™ catalysts in commercial converter units.

Furthermore, the X3D™ catalyst can be used to meet a variety of needs of a sulphuric acid producer. Due to the flexibility in catalyst design, the catalyst shape geometry can be custom tuned and manufactured to precisely meet the desired requirements. This will not only lead to better performing sulphuric acid units, but opens up the way for new converter designs in future, providing a higher efficiency and a decreased environmental impact.

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Impact and mitigation of processing bio-feeds in a refinery

The production of renewable fuels by retrofitting existing refineries and their infrastructure is witnessing exponential growth. The impact on the existing amine, sour water and sulphur recovery units is inevitable. Based on several case studies, **Marco van Son, Shashank Gujale and Tammy Chan** of Worley Comprimo discuss the various options available to holistically review the sulphur block to determine the impact and mitigation of processing bio-feed.

The production of bio- and renewable fuels is a fast-growing market. The increase in the use of these products is mostly driven by government incentives and mandates. Petroleum reserves are depleting and there is greater public awareness of climate change initiatives regarding global warming and limits on greenhouse gas (GHG) emissions. In the US, according to the US Department of Energy Renewable Fuel Standard (RFS), transportation fuel sold in the US must contain a minimum volume of renewable fuels. Oil refiners and gasoline and diesel importers are subject to the RFS. Significant fines are imposed for failing to meet RFS requirements.

Bio- and renewable fuels are made from recently living but dead plant materials and animal waste (biological material) and considered a renewable resource. On the contrary, fossil fuels are decayed plant and animal matter that died millions of years ago, hence non-renewable. Note that biodiesel and renewable diesel are biofuels, but they are not the same! They are produced in very different processes.

Biodiesel is made in the process of transesterification of oils and fats, which forms fatty acid methyl ester (FAME). FAME can lead to problems with corrosion when blending with other diesel pools as well as stability and decomposition issues. As a result, many car manufacturers have limited the amount of FAME that can be present in the diesel used in automobiles to

2 to 20% of diesel fuel by volume. Hence biodiesel is usually blended in with petroleum products designated as Bxx, where xx is the percent by volume of biodiesel in a gallon of fuel where the rest is No.1 or No. 2 diesel, kerosene, Jet A, JP8, heating oil or any other distillate fuel. Pure or neat biodiesel is B100.

Renewable diesel, also called green diesel, drop-in biofuel, or hydrogenated vegetable oil (HVO), is made by an altogether different pathway via hydrotreating, gasification, pyrolysis and other biochemical and thermodynamic technologies of biomass. It is functionally identical to petroleum fuels and fully compatible with existing products. The production of renewable diesel does not result in the formation of FAME, so it can be blended without restriction. Also, catalytic hydroprocessing is flexible in accommodating a wide variety of biomass such as: raw vegetable oils, waste cooking oils, animal fats, algal oils, products from solid biomass processing, and pyrolysis oils. Renewable diesel meets ASTM D975 specification for petroleum diesel. In addition, renewable diesel meets required CGSB, and EN standards for diesel fuels.

Because renewable diesel is made from "less raw" biomass, waste and residuals from actual crops, it has a low carbon intensity (CI). CI is a measure of lifecycle emissions from extraction or growth, refinement, distribution, storage and combustion, and is reported as grams of carbon dioxide (CO₂) equivalent per megajoule (MJ) of

energy. Renewable diesel made from the aforementioned byproduct feedstocks can be in the range of 22-25 g CO₂/MJ depending on the specific feedstock. By comparison, petroleum diesel has a CI about five times higher (CI=102). Renewable diesel produced from crops such as soybeans can have twice the CI (CI=53), as the CO₂ emitted from growing soybeans must be included in the CI calculation.

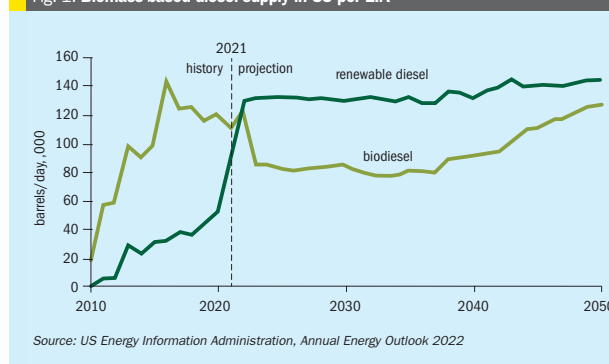
In recent years, the integration of renewable diesel facilities with the existing infrastructure of refineries has proven lucrative and numerous such renewable fuels projects are in various phases of operation, engineering or construction. The US Energy Information Administration (EIA) projects that renewable diesel supply will exceed that for biodiesel as shown in Fig. 1. Refineries can introduce hydrotreating of biofeed stocks through co-processing, complete conversion from fossil fuel feedstock, and/or grassroots installation.

Options for producing renewable fuels in refineries

Refineries seeking to produce renewable diesel can do so by co-processing, plant conversion, and/or grassroots installation.

In co-processing, a portion of the feedstock to an existing hydrotreater or FCC unit is converted to a renewable fuel feedstock. Typical values of 10-20% of the total feed are chosen to minimise the required modifications to the existing units. The

Fig. 1: Biomass-based diesel supply in US per EIA



co-processing of renewable fuel feedstock in an existing unit means that the unit still produces similar products containing H₂S and NH₃, however due to the higher oxygen content of the renewable fuel feed stock and lower content in nitrogen and sulphur, the concentrations of these components to be processed in the existing amine and sour water strippers can be substantially different: decreased sulphur tonnage, increase in CO₂ production but typically limited impact on the amount of ammonia. In addition, due to the presence of oxygen in renewable fuel feed stocks, which is not present in conventional hydrocarbon feedstocks, there will be potentially more sour water to handle. Alternatively, plants can also consider handling the "co-processing" of renewable fuel feedstock through the full conversion of a single unit in the refinery while maintaining conventional hydrocarbons in the rest of the units.

Another option could be to fully convert an existing refinery to process renewable fuel feedstocks or even install a full grassroots facility to produce renewable fuels. The terminology for these scenarios are conversion and grassroots facilities.

Due to the more pronounced impact on the sour components that need to be processed, grassroots/conversion projects require more complex studies of new technologies and their possible integration with the existing sulphur block compared to co-processing projects.

In general, the introduction of renewable fuel feedstock will have the following impact on existing sulphur complexes:

In the acid gas treatment (AGT), the amine system will experience an increase in the amount of CO and CO₂ to be

processed, forming corrosive salts, and changing the physical properties of the solvent, ultimately reducing the acid gas removal capability.

The long chain hydrocarbons in the renewable fuel feedstock can also increase the foaming tendency of the amine solvent. The acid gas feeds will also be leaner in H₂S with more CO₂, hence making low tonnage sulphur technologies such as Selectox, LO-CAT, and Thiopaq worth studying.

For the sour water stripper (SWS), the increase in sour water flow rate as well as an increase in CO₂ concentration, may result in an exceedance of the capacity of the existing stripper. The existing SWS may need to be debottlenecked, with additional stripping steam leading to a higher overall energy demand. Additional sour water processing capacity may need to be installed.

In the SRU, the acid gas feeds will have significantly higher CO₂ concentration and a higher ratio of sour water acid gas to amine acid gas.

The higher CO₂ in the feed to the sulphur recovery unit may not only make it a capacity bottleneck but also necessitate several modifications to maintain sufficiently high temperature in the thermal reactor to destroy contaminants such as ammonia. Integrating the existing SRU/TGTU for co-processing and conversion may be complicated to maintain existing emissions requirements.

The following case studies illustrate the impacts that producing renewable diesel through conversion has on the existing sulphur complex and show how different technologies can help address the additional and/or new process requirements.

Case study 1

A refinery conversion project based on processing 100% bio-feed resulted in new required total sulphur tonnage processing capacity of about 5% of the existing SRU/TGTU trains' nameplate capacity. The new amine acid gas flow rate was only 20% of the original design with only 15 vol-% H₂S compared to the original 75 vol-%. The project considered three options to process new lower and leaner amine and sour water acid gas rates, while meeting the emissions specifications:

- repurpose existing SRU/TGTU/incinerator trains
- technologies other than SRU/TGTU;
- install two new smaller SRU/TGTU/Incinerator trains.

In order to holistically evaluate these three options, each option was looked at with respect to the ability to meet the environmental requirements, installation and operational costs as well as ease of implementation.

Repurposing of existing SRU/TGTU/incinerator

The refinery had a total of five SRU/TGTUs, of which two were deemed possible candidates for the revised conditions after the conversion to renewable fuel feedstock. Each unit had a capacity of 141 t/d with the following original acid gas compositions:

- amine acid gas: 80% H₂S/9% CO₂;
- sour water acid gas: 25.5% H₂S/4% CO₂/40% NH₃.

After full conversion of the refinery to renewable fuel feedstock, the expected total sulphur capacity was 7-8 t/d, which represented a 20:1 turndown for the unit on a capacity basis.

In order to determine the feasibility of repurposing the existing SRU/TGTU to process the significantly lower sulphur tonnage, the major equipment items were evaluated to:

- identify if any existing equipment is limited to process the low sulphur feed;
- recommend process and equipment modifications to maintain overall sulphur recovery efficiency.

Based on a separate analysis to optimise the upstream amine system including future CO₂ capture, it was recommended to route the feed amine acid gas to the TGTU absorber which would act as the enrichment unit. The acid gas from the

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TGTU regenerator containing relatively higher concentration of H₂S would be recycled to the SRU front end where it would be fed to the main burner along with the sour water stripper acid gas.

Continuous natural gas co-firing was required to maintain a high enough temperature in the SRU thermal reactor to destruct the ammonia in the sour water stripper acid gas. The heat and material balance based on this continuous natural gas co-firing and iterative calculations using modified equipment (for example, plugged sulphur condenser tubes) was used for the equipment evaluations.

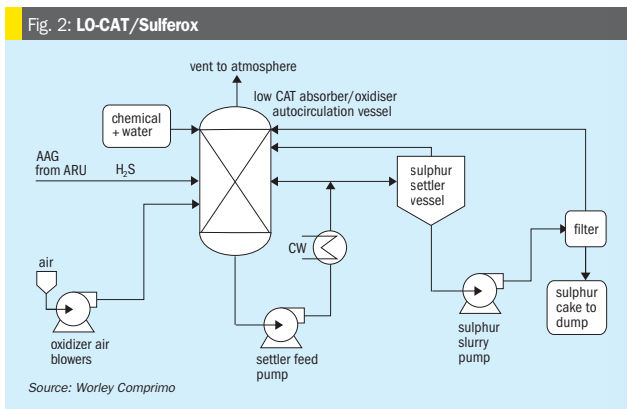
The key findings are described below.

- In general, it was feasible to repurpose the existing SRU/TGTU with minor modifications to process the future low-capacity feed because of the renewable diesel conversion while meeting the SO₂ emissions limit.
- The existing acid gas burner will need to be replaced as the required continuous natural co-firing rate is significantly higher than the original design.
- Natural gas co-firing is also expected to increase the quantity of COS and CS₂ that needs to be hydrolysed in the first catalytic reactor to minimise the loss of sulphur recovery efficiency. Therefore, the first catalytic bed is recommended to be made up to 25% alumina catalyst at the top and 75% titania catalyst at the bottom to enhance COS/CS₂ hydrolysis.
- Low gas throughput through the sulphur condensers can lead to sulphur fogging which has the potential to lower the sulphur recovery efficiency. Plugging of more than 70% of the tubes in the sulphur condensers is recommended.
- A metallurgy review recommended several upgrades to stainless steel material in piping or as lining to existing carbon steel vessels.

Non SRU/TGTU technology option evaluation

Processing the new bio-feed impacts the waste streams going to the SRU/TGTU as the hydrotreating unit will produce H₂S from the sulphiding agent and more sour water will be produced with small amounts of ammonia and CO₂. In order to find alternatives in case the existing SRU/TGTU could not adequately handle these changes, the following actions were taken:

- technical alternatives in lieu of SRU/TGTU were identified and evaluated;



- options for sour gas pre-treatment to remove NH₃ and process H₂S only were evaluated.

The following configurations were evaluated as part of the study.

LO-CAT/Sulferox

The LO-CAT™ process (Fig. 2) is a liquid redox technology that converts H₂S to elemental sulphur in an aqueous solution of iron with a proprietary blend of chemicals to enhance the catalytic performance of the iron. The Sulferox technology is similar. The H₂S is converted to elemental sulphur by the redox chemistry. The elemental sulphur is filtered from the solution as a 60-80 wt-% sulphur "cake", depending on the filtration method and amount of water wash.

Pros:

- gas stream leaving the unit typically contains <10 ppm H₂S (if this meets the local emission standards, the treated stream can be vented to atm.);
- inherently safe aqueous solution.

Cons:

- produces poor quality sulphur;
- expensive chemicals used in the process and get consumed as some tend to be lost with sulphur product;
- chemical degradation, plugging and foaming are concerns with this process.

The conclusion regarding the option for a redox type technology was that the sulphur produced is not saleable and is typically sent to landfill, which made the technology less desirable as an option.

Selectox

Selectox® (Fig. 3) is a catalytic sulphur removal technology using catalytic stages only and no Claus thermal section. It can handle amine acid gas with low or no NH₃ content and produces sulphur. The sour water acid gas containing H₂S and NH₃ is sent to a stoichiometry-controlled oxidation (SCO) unit for NH₃ destruction and complete redox combustion of H₂S. The flue gas is then cooled in the waste heat boiler (WHB) to recover energy by means of steam generation, which can be utilised for plant heating or other purpose. The flue gas from the WHB is then sent to a caustic scrubber unit to remove SO_x by using caustic. The treated gas is then released to the atmosphere via the stack.

Pros:

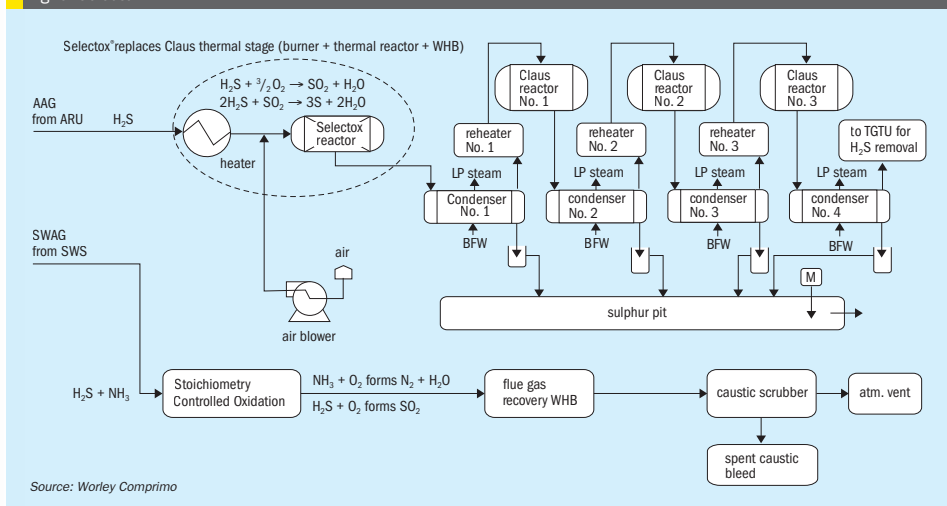
- complete removal of H₂S (>99.9% efficiency);
- no fired equipment and eliminates fuel gas co-firing, air and acid gas pre-heating (opex);
- produces premium grade saleable sulphur.

Cons:

- can handle only amine acid gas and not ammonia containing sour water acid gas;
- SWAG from SWS will need additional capex/opex for the SCO incinerator and caustic scrubber.

The conclusion for the option to use Selectox with separate combustion of the sour water acid gas was that this option was not cost effective as it involved the capex

Fig. 3: Selectox



for replacement of the Claus thermal stage and needs additional capex/opex for the SCO incinerator and caustic scrubber.

WSA (Wet Gas Sulphuric acid) technology

The Topsoe™ WSA technology (Fig. 4) is a wet gas catalytic process that turns sulphurous gases into commercial-grade sulphuric acid (typically 98% concentration). The H₂S in the feed is oxidised to SO₂ by combustion and NH₃ is destroyed in this process. Catalytic conversion of SO₂ to

SO₃ takes place in the catalyst beds. The thermal energy given off by this reaction is recovered between the catalyst beds. After the last conversion step, the gas is cooled, and the SO₃ reacts with water vapour to form gas-phase sulphuric acid. The process gas is cooled by a counter-current flow of air in the WSA condenser. Condensed commercial-grade sulphuric acid exits from the bottom of the condenser, where it is cooled and sent to storage and clean gas leaves from the top of this condenser to the stack.

Pros:

- produces commercial-grade 98% sulphuric acid and HP superheated steam for plant usage;
 - can process both amine and sour water acid gas in one technology.
- Cons:
- high capex;
 - very low production of sulphuric acid due to the low sulphur loads.

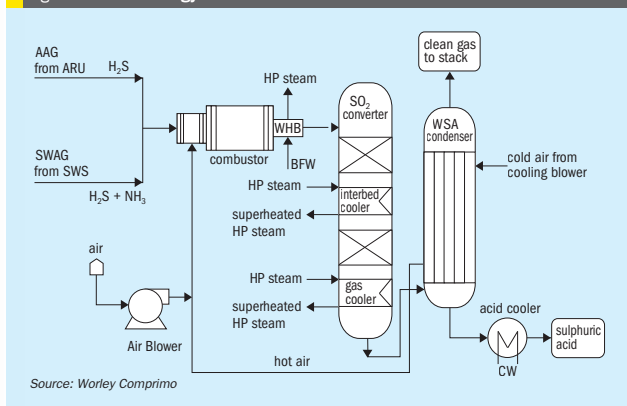
The conclusion for the option to install a WSA unit was that owing to the limited quantity of the resulting sulphuric acid product flowrate due to a lean H₂S feed gas and the high capex involved for installation of the WSA unit, this option was not deemed attractive.

Thiopaq + WWT two-stage SWS

The WWT process is a two-stage sour water stripping process that separates NH₃ and H₂S. The H₂S stream from the SWS (free of NH₃) can be combined along with amine acid gas from the ARU and can be treated in a Thiopaq biological sulphur unit (Fig. 5). The Thiopaq biodesulphurisation unit contains self-regulating bacteria that convert H₂S to manageable solid elemental sulphur which can be used in agricultural applications. The vent gas from the Thiopaq unit is sent to incineration.

The NH₃ stream will be sent to the SCO unit for ammonia destruction followed by

Fig. 4: WSA technology



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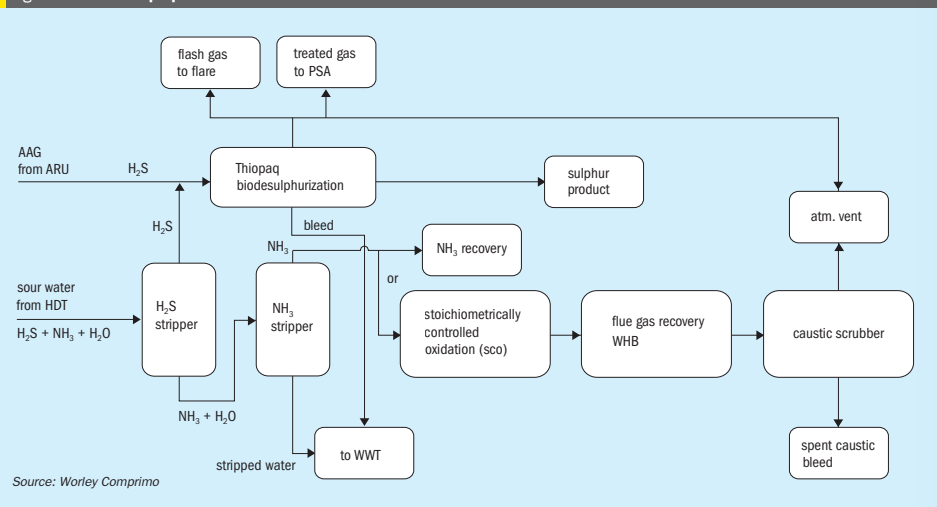
COVER FEATURE 3

Sulphuric acid catalyst design

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Fig. 5: WWT + Thiopaq



Source: Worley Comprimo

a caustic scrubber. The flue gas is then cooled in the waste heat boiler to recover energy by means of medium-pressure steam generation which can be utilised for plant heating or other purpose. The flue gas from the WHB is then sent to a caustic scrubber unit to remove SO_x by using caustic. This option provides good emission controlled with the addition of a caustic scrubber and a final polishing unit for SO_x and any particulate removal from vent gas to the atmosphere.

Pros:

- higher recovery of H₂S from AAG/SWAG as premium grade sulphur product;
- proper integration of the SCO unit allows utilisation of the heat released by the combustion of ammonia, for steam generation and superheating purposes.

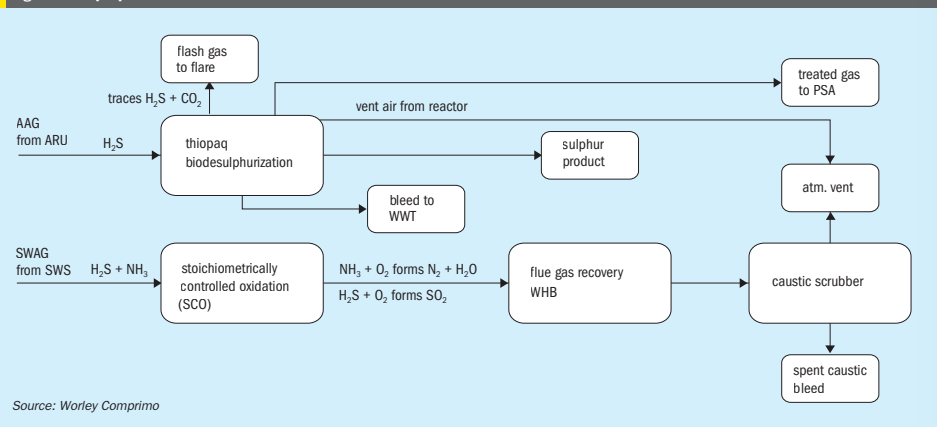
Cons:

- two-stage SWSs are more complex to operate and are not proven for lean sour water stream containing high CO₂;

- higher capex due to additional NH₃ stripper and additional incinerator and scrubber.
- no purpose for pure ammonia stream recovered from the NH₃ stripper and requiring specialised incineration equipment;
- difficult market to produce pure ammonia with higher safety risks.

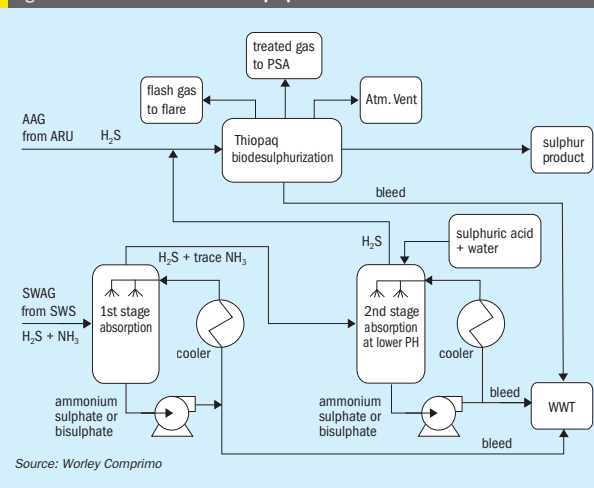
This option is not recommended because of the complexity of combining the sour

Fig. 6: Thiopaq + SCO + scrubber



Source: Worley Comprimo

Fig. 7: Ammonia acid wash + Thiopaq



Source: Worley Comprimo

water and the off-gas treating unit. Also, additional capex is involved for NH₃ stripper unit to remove NH₃ from lean sour water acid gas stream containing very little amount of H₂S.

Thiopaq + SCO + scrubber

This is a slight modification of the above option that offers an advantage to line up the SWS unit independent of the ARU unit, by eliminating the two-stage SWS (Fig. 6). Thiopaq is retained for H₂S recovery from the ARU in this scheme.

Pros:

- eliminates the two-stage SWS and independent line-up of SWS unit and ARU unit;
- handles both H₂S and NH₃ in the SWAG.

Cons:

- bleed caustic disposal is a potential issue though the low H₂S content in SWAG needs lower caustic circulation rate.

The SCO + scrubber can be a viable solution for processing SWAG if spent caustic can be easily disposed. Thiopaq seems viable for H₂S recovery as this technology has demonstrated that its sulphur product can be sold for fertiliser production.

Ammonia acid wash + Thiopaq

The ammonia acid wash (NH₃ scrubber) (Fig. 7) consists of a dual-stage absorption

reacts with more ammonia to form ammonium sulphate.

After passing through the packing in scrubber column no. 2, the treated gas passes through a mist eliminator to remove any entrained droplets of scrubbing solution and is then sent to join the main amine acid gas stream entering the Thiopaq unit.

Pros:

- higher recovery of H₂S from both AAG/SWAG as premium grade sulphur product;
- using the dual column approach ensures high ammonia removal rates while at the same time minimising the sulphuric acid consumption and the ammonium bisulphate concentration in the scrubber effluent.

Cons:

- disposal of the bleed ammonium bisulphate or ammonium sulphate.

This option was deemed viable if disposal of the effluents from the ammonia acid wash can be suitably resolved.

Technology evaluation summary

Table 1 provides a summary of the available alternative technologies in lieu of the SRU to process NH₃ and H₂S in acid gas from the ARU/SWS.

New SRU/TGTU installation

The third option considered during the study phase was the installation of two fully redundant new SRU/TGTUs that would be designed for the new capacity resulting from the revised conditions in the amine and sour water systems. An N+1 configuration was necessary to maintain the emissions at all times to meet the regulatory requirements.

The installation of two new SRUs with TGTUs provides the benefits of new equipment designed for purpose and improved operability. It would provide a full spare as well as the ability to already plan for future expansion of the biofuels facility. It would require, however, operation of one of the two new units in hot-standby with the increased risk of sooting, equipment damage as well as corrosion.

Comparison

The three options described above were compared with respect to capex and opex and the results are provided in Table 2.

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Table 1: Alternative technology for the SRU/TGTU

Technology	Feasible? Yes / No	Recommended for consideration?	Remarks
LO-CAT / Sulferox	Yes	No	Meets specifications and safe but uses expensive chemicals and prone to chemical degradation, plugging and foaming. Sulphur cake not suitable for sale and must be sent to dump/landfill.
Selectox	No	No	Meets specifications, eliminates fired equipment and fuel gas co-firing but cannot process ammonia. Needs additional capex for replacement of Claus thermal stage and new SCO + caustic scrubber.
Wet Sulphuric Acid	No	No	Produces saleable sulphuric acid and HP superheated steam but not attractive due to limited quantity of sulphuric acid produced for the high capex involved.
Two-stage SWS + Thiopaq	No	No	Meets specifications, heat integration possible but difficulty in operation of two stage stripper, unproven for lean sour water feed, higher capex due to additional stripper, incinerator and scrubber and no use for recovered NH ₃ so needs destruction.
SCO or equivalent & caustic scrubber + Thiopaq	Yes	Yes	Meets specifications, processes both amine acid gas and sour water acid gas containing ammonia, however bleed caustic disposal can be of concern.
Ammonia acid wash + Thiopaq	Yes	Yes	Meets specifications with saleable sulphur product, dual column allows high ammonia removal while minimising sulphur acid consumption and ammonium bisulphate concentration in effluent. However, needs disposal of the bleed ammonium bisulphate/sulphate.

Path forward

Based on overall capital cost, operating cost and carbon intensity comparison, the existing SRU/TGTU revamp options was determined to be favourable. The alternative technologies and the new smaller SRU/TGTU trains were not deemed economically viable, even though there may be some benefits in the alternative technology with respect to the total carbon footprint.

Case study 2

A refinery biofuels conversion project included a renewable diesel hydrotreater with a feed capacity of 9,000 bbl/d and hydrocracking capacity of 45,000 bbl/d. Sulphur production of the facility was around 50 long t/d prior to the full conversion to bio feedstock.

Hydrotreater recycle hydrogen must contain 200 ppmv H₂S to maintain catalyst metals in the sulphide state and thus prevent permanent over-reduction. The plant opted to do so by continuous injection of a sulphiding agent to avoid the capex and logistical complications of concentrated H₂S recycle, which would have reduced net acid gas sulphur to 0.6 long t/d.

Many attempts to somehow repurpose existing Claus facilities were considered

Table 2: Alternative technologies for the SRU/TGTU

Technology	Capex	Opex	Carbon footprint
Repurposed existing SRU/TGTUS	20 million \$	1.2 million \$/yr	17,000 tonnes CO ₂ per year
Alternative technology (ammonia acid wash with Thiopaq)	105 million \$	1.5 million \$/yr	Not evaluated, however as there is no natural co-gas firing required, expected to be much lower.
New SRU/TGTUS	100 million \$	1.0 million \$/yr	15,000 tonnes CO ₂ per year

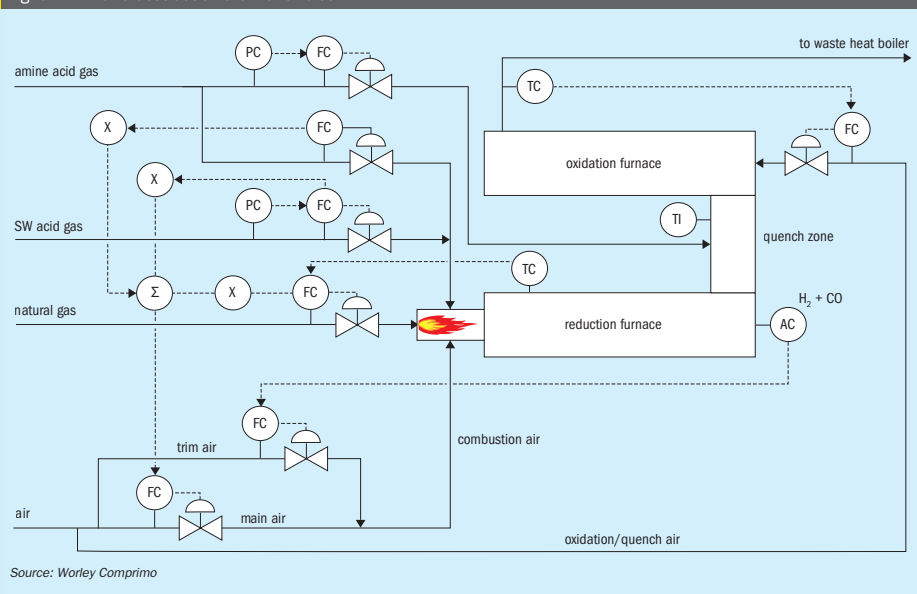
and ruled out and a similar evaluation was done as provided in case study 1.

Ultimately, acid gas incineration of all the acid gas streams was chosen followed by caustic absorption of SO₂. SWAG is thermally oxidised under reducing conditions at a theoretical flame temperature of 1,315°C, followed by quenching with AAG to a minimum of 540°C to ensure subsequent thermal oxidation. As it turned out, at normal rates in the subject case, simulation predicted that bypassing the entire AAG around the reduction furnace quenched the effluent to 510°C. To ensure at least 540°C, some AAG was diverted to the reduction furnace, and cofiring increased to achieve 1,315°C. (Fig. 8)

Environmental regulations required a minimum thermal oxidiser temperature of 815°C to ensure virtually complete CO destruction. In addition, temperatures greater than 815°C would likely increase NOx, which the plant was under regulatory pressure to minimise. Excess quench air required to limit the thermal oxidiser temperatures to 815°C resulted in almost 10 mol-% residual O₂.

However, high percentages of O₂ can have unintended punitive consequences in the likely event environmental regulations require correction of measured stack concentrations to X % O₂ according to the formula in Table 3 where X will typically = 0 or 3:

Fig. 8: Ammonia destruction thermal oxidiser



Source: Worley Comprimo

Table 3: Normal stack emission correction for excess O₂

Let	Symbol	Definition	Concentration (dry basis)	
			Symbol	Definition
Where	C	=	Component, corrected, ppmv	
	R	=	Component, raw, ppmv	
	X	=	Reference O ₂ in stack, mol-%	
	A	=	Actual O ₂ in stack, mol-%	
Then	C	=	$R * (21.0 - X) / (21.0 - A)$	

Stack emission concentrations measured at O₂ concentrations greater than the reference value (0 or 3%) increase when corrected. At a reference value of 0% O₂, for example, 100 ppmv measured at 10% O₂ equates to $100 * (21.0) / (21.10) = 191$ ppmv corrected. In a typical Claus thermal oxidiser, high O₂ represents unnecessary dilution. In this case, however, it is a process requirement. That distinction should be made when negotiating environmental permit limits.

The oxidation furnace effluent is cooled from 815°C to 275°C by generation of saturated 45 bar steam in a kettle waste heat boiler. The need for selective catalytic reduction (SCR) of NOx was deemed unnecessary. Had an SCR been employed,

cooling to 230°C would have been considered in order to minimise potential catalyst fouling with ammonium bisulphate.

Potential cooling is limited by the sulphuric acid dew point. Above 1,000°C, 1-5% of the SO₂ will typically be oxidised by O₂ to SO₃, forming sulphuric acid vapour (H₂SO₄). While lower temperatures favour SO₃ formation, the reaction does not readily occur below 1,000°C because of the high activation energy required, and it is thus assumed that the SO₃ content is set by the equilibrium at 1,000°C, for which equilibrium correlations exist. Four different methods predicted dew points of 105-145°C. Another literature source simply cites 175°C as a safe upper limit⁷.

Hot gases are initially quenched with a recirculating caustic solution side stream in a venturi scrubber at the inlet to the packed column to prevent localised high temperature corrosion of column internals despite stainless steel (SS) construction. In this case both the venturi and scrubber were constructed of 316 SS. Fibreglass is a common alternative for the column shell, and brick-lined venturis are sometimes employed when there is greater incentive to minimise upstream cooling. Maximum recommended inlet temperature to a SS venturi is 340°C (Fig. 9).

Some sulphuric acid vapour will be absorbed in the venturi, but once the gas is quenched below the dew point, resultant acid aerosol mist particles lack the momentum required for efficient scrubbing upon impingement with caustic solution droplets. Counterintuitively, many thus pass unabsorbed through the scrubber.

Condensed sulphuric acid mist (SAM) tends to form a white visible plume upon discharge to atmosphere. Perhaps for this reason, it is often treated quantitatively as 10+ micron particle (PM10) emissions, despite the fact that acid mist particles tend to be sub-micron. In this case the plant had separate annual PM10 and

SAM mass limits, where allowable SAM emissions were 100 x allowable PM10 emissions.

Specialised “candle filters” designed to rely on Brownian diffusion are located at the scrubber outlet to coalesce sub-micron SAM. Vendors claim up to 99.9% particulate removal with pressure drops of 10-20 inches H₂O. Fouling can be problematic if particulates tend to be sticky. Wet electrostatic precipitators (WESP) are considered a superior alternative if the additional cost can be justified.

The circulating liquor contains the equivalent of 5-6 wt-% sodium hydroxide (NaOH), with roughly 85% as sodium sulphate (Na₂SO₄) and the balance split between sodium sulphite (Na₂SO₃) and sodium bisulphite (NaHSO₃). Bisulphite/sulphite equilibrium is highly buffered, making it relatively easy to maintain an optimum pH of 7-8 while absorbing negligible CO₂ (Fig. 10).

In this case 15 wt-% NaOH is added on pH control, and water added separately to maintain a specific gravity of 1.08. It was decided to add the makeup water via a wash tray above the packed bed on the premise that knocking down entrained liquor may tend to reduce fouling of the candle filters. This does not appear to be normal practice, so the value in doing so remains to be seen.

In addition to being corrosive to carbon steel, sulphite/bisulphite have a chemical oxygen demand (COD) and must be oxidised to sulphate before discharge to the environment.

Grassroots facilities

If the biofuel plant is truly grassroots, consideration should be given to get away from traditional amine systems for recycle gas and fuel gas scrubbing. One way is to integrate sweetening absorbers directly into scavenging technology so that sour water acid gas is made ammonia free (Fig. 11).

The primary benefit of this particular line-up is that only a sour water stripper remains of the traditional line-up of a sulphur complex in a refinery. There is no need for an amine system or traditional sulphur recovery unit anymore. Once the ammonia is removed from the sour water acid gas, there is only one system that can remove and convert all of the H₂S in the sour gas streams, thereby eliminating the requirements for costly incinerators and scrubbers. Proper evaluation of the

Fig. 9: Caustic scrubber

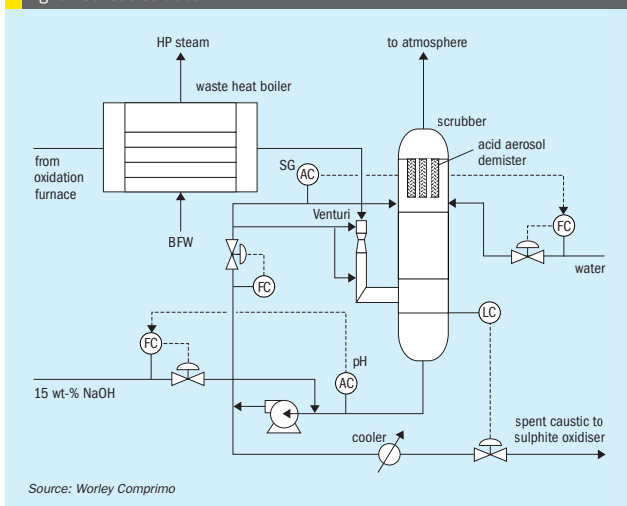
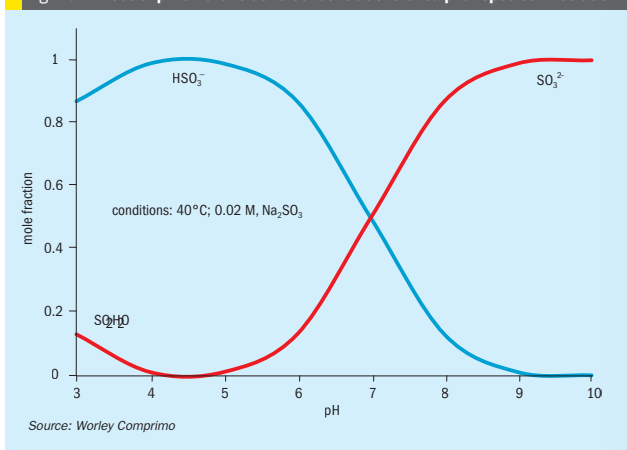


Fig. 10: Effect of pH on the relative concentrations of sulphur species in solution



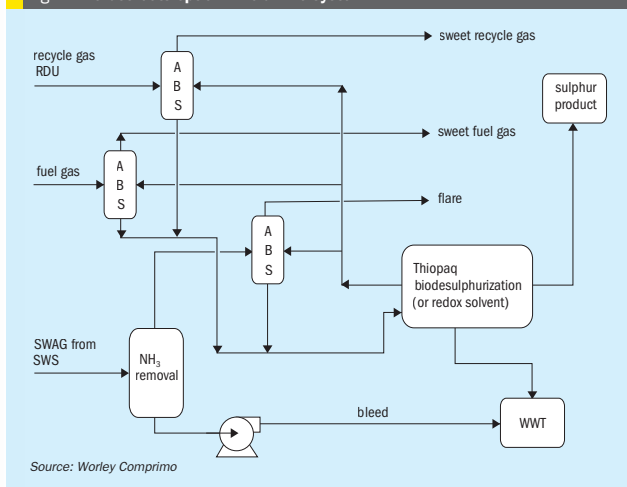
disposal of the waste products will still be required, however the system could be simplified substantially.

Due to the availability of an existing infrastructure in a conversion project, this scenario may not be the most likely candidate for selection. However, for grassroots facilities where there is no existing amine or sulphur recovery unit, this line-up could prove to be most economical both in capex and opex.

Conclusions and recommendations

Refineries seeking to produce renewable diesel through co-processing, conversion, or grassroots facilities need to holistically examine the impacts on their sulphur block. Co-processing essentially increases the CO₂ slightly while grassroots or conversions result in gas compositions that cannot be handled on its own with an SRU such that other sulphur removal technologies may need to be used.

Fig. 11: Grassroots option – no amine system



Processing bio-feed in conversion/grassroots renewable fuel refineries results in:

- needing additional capacity at the sour water stripper and acid gas treatment plants;
- existing sulphur block units from existing refinery infrastructure will likely be substantially oversized;
- acid gas feeds will be too low in H₂S with lots of CO₂, requiring CO₂ removal (AGR) and/or H₂S enrichment (AGE) before being processed in the SRU.
- ultra-low sulphur tonnage capacities that are better suited to scavenging or scrubbing technologies;
- increased sour water flow rates with NH₃, H₂S, and CO₂ may lead to bottlenecking requirements of the existing sour water strippers;
- issues with destroying the increased ammonia in conversion projects.

Ammonia is a crucial component to be considered in decisions regarding processing renewable fuel feedstocks. Some additional oxygen or split flow to the second zone of the thermal reactor may need to be considered. In the case of a full conversion or grassroots biofuel facility, the ammonia can pose a substantial issue as in most scenarios there is no feasible way to either reuse an existing SRU or install a new SRU that can handle the low concentrations of H₂S in the total acid gas.

Therefore, alternative methods need to be found in the line-up that ensure that the ammonia does not become a source of emissions. Options discussed include high turndown SRU operation with co-firing, ammonia scrubbing as part of the technology solution and ammonia incineration with caustic scrubbing to remove SO₂. Each potential option needs to be evaluated from an opex and capex perspective as well as how it impacts the facility environmentally.

Most notably, conversion projects should be holistically looking into repurposing/integrating the sulphur block with the new facilities to meet feasibility and environmental compliance. The decision to retrofit the existing sulphur recovery units highly depends on the sizes of the existing units as well as the ability to maintain satisfactory operation with the poorer quality acid gas streams. As shown, many other technologies are available to effectively handle the changed sour gas, amine acid gas, and sour water streams.

Finally, if the renewable fuel plant is truly grassroots, technology selection should move away from traditional amine systems and opt for recycle gas and fuel gas scrubbing. Ultimately, projects must be evaluated on a case-by-case basis resulting in multiple options, for which the client will have preferences for the final design (and never-ending queries to study more technologies).

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Best practices for sulphur pipeline design

As part of the expansion of the Shah gas plant (SGP) in the United Arab Emirates, a new 12-inch pipeline was designed and commissioned in January 2020. **Hassa Al Mulla, Ravi Srinivas** and **Alsail Al Jaber** of ADNOC Sour Gas highlight the best practices implemented in the newly commissioned liquid sulphur pipeline.

ADNOC Sour Gas (ASG) Company is a joint venture between ADNOC and OXY. ASG owns and operates the Shah Arab Sour Gas Field, and Shah Gas Processing Plant (SGP). The Shah Arab Field produces ultra-sour gas (up to 25% H₂S and 10% CO₂). The Shah plant, with a 21 km² footprint, is located in the Liwa area, approximately 210 km south-west of the city of Abu Dhabi in the United Arab Emirates.

The Shah gas plant produces approximately 11,500 t/d of liquid sulphur via four trains of sulphur recovery units. The liquid sulphur is transported through 2 x 10,000 t/d capacity 12-inch skin effect electric tracing (SEET) pipelines from the main plant to the sulphur granulation station located approximately 7 km away. Liquid sulphur is then processed into solid granules, which are transported via train to the shipping terminal. As part of the expansion of the Shah gas plant a new 12-inch pipeline was designed and commissioned in January 2020.

Sulphur properties

The transportation of liquid sulphur requires the temperature to be maintained between 130°C and 145°C. This is



Fig. 1: Molten sulphur at temperatures >155°C.

to avoid freezing which occurs at 119°C and to avoid the high viscosity form of sulphur which occurs at 158°C. Sulphur has a unique viscosity-temperature relationship. In the normal operating range (125-145°C) the molten sulphur colour is yellow. However, beyond 158°C, molten sulphur viscosity increases rapidly (5,952 cp at 160°C) and becomes difficult to pump. The molten sulphur colour at this point becomes dark red (Fig. 1). The optimum liquid sulphur pipeline operating temperature range is 130°C to 145°C.

The sulphur has an expansion ratio of 1:1.1, which means when sulphur cools, it reduces in volume and has a tendency to compact in pipeline low points. However, when remelting into liquid phase, it will expand rapidly within a few degrees of temperature increase which, in a closed vessel, is the mechanism for rapid pressure increase.

Sulphur pipeline design and best practices

The SGP sulphur pipelines are designed with expansion loops, located approximately every 200 m. In between the expansion loops, the pipeline has fixed anchor points. The movement of the pipeline from thermal stresses is permitted between anchor points. These anchor points located between expansion joints are specially designed to withstand the forces from normal thermal expansion while minimising heat losses from the system. The balancing of these two design criteria is well known throughout the sulphur transport industry as an important consideration whenever a system is designed, to minimise the chance of solid formation in pipeline systems.

It was recognised early on during the project design that re-melting of a frozen sulphur pipeline is a very complex operation, and that it is important to address certain design concerns such as:

- ensuring adequate and uniform heating across the pipeline;
- minimising heat losses at anchor points and SEET cable power boxes;
- ensuring temperature monitoring throughout the pipeline; and
- guaranteeing adequate reliability of the electrical supply and steam supply to keep the sulphur from freezing during an unexpected power outage.

A SEET pipeline “freeze and re-melt performance test” is typically part of the pipeline contractual warranty requirements.

The SEET system design capacity covers both the smaller heat losses during normal operation, and the larger loads required to re-melt if the pipeline freezes during an extended loss of power, such as a substation power outage.

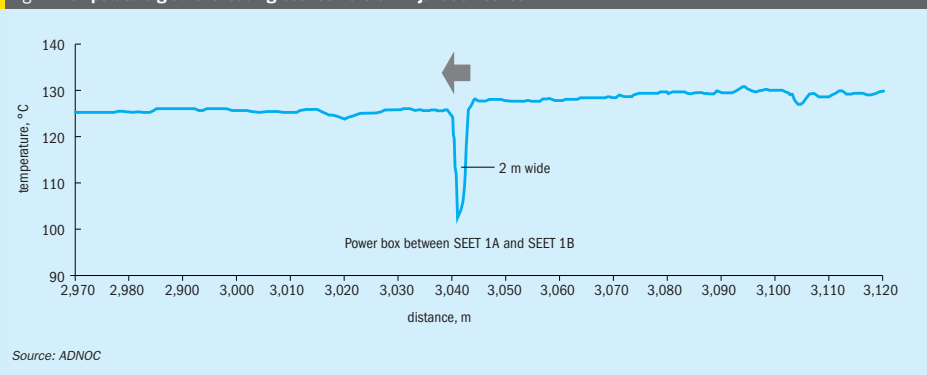
Both normal and re-melt scenarios were part of the FEED design, and accordingly a SEET system was designed which gave the option to heat at low or high power in different segments. This is important because the power requirements during normal operation and re-melting are quite different.

The following sections highlight best practices.

Uniform heat loss

The most important factor in designing a sulphur pipeline to be easily re-melted is to ensure uniform heating of the solid sulphur throughout the pipeline. The best way to ensure this is to verify that the pipeline has uniform heat loss in all locations. The

Fig. 2: Temperature gradient reading between the SEET junction boxes



Source: ADNOC

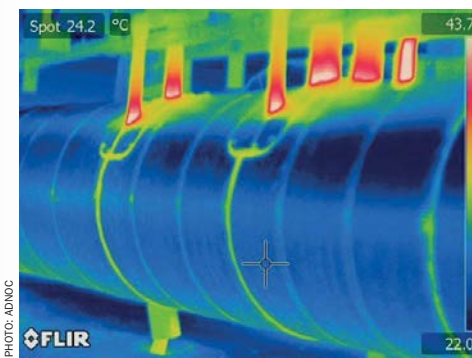


PHOTO: ADNOC

Fig. 3: Thermal image of SEET box (heat loss).

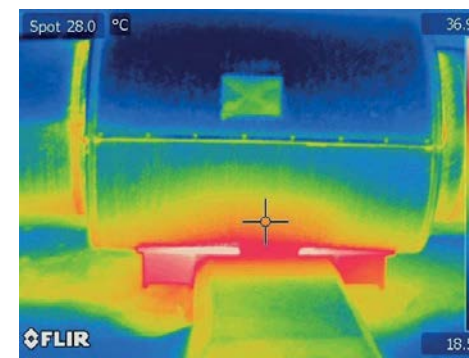


PHOTO: ADNOC

Fig. 4: Thermal image of anchor supports (heat loss).

most important areas for this are:

- pipeline anchor supports;
- SEET power boxes and end boxes.

The design and application of the anchor supports and SEET system contributes to the vulnerability and sensitivities in a pipeline during the re-melt process. Anchor points and SEET transition points can be considered ‘cold points’ resulting in uneven melting which can result in sections of the pipeline melting while other sections are still solid. This can lead to an extreme build-up of high pressure.

In the design phase of the pipeline, a finite element analysis (FEA) should be carried out to verify the heat loss throughout the pipeline is uniform, including anchor points. This allows the designer to ensure potential heat loss points are identified and eliminated (Figs 2 and 3).

As part of the FEA study, the insulation

at anchor supports should be optimised to reduce the effect of these heat loss points, and the formation of sulphur plugs (Fig. 4).

The heat trace design at SEET power junction boxes and the supports of the boxes should be designed in a way to ensure uniform heating to avoid uneven heating throughout the pipeline, specifically at power boxes and end boxes (Fig. 5).

Pressure build-up

The design of a sulphur pipeline should allow sufficient allowances for expansion and/or pressure build-up during re-melt procedures.

During the design of sulphur pipelines, there should be consideration for the high pressure in the pipeline, as well as the stresses and strains that occur during remelting.

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Re-melt procedure and monitoring of temperature profile

It is extremely important to monitor the continuous temperature profile of the sulphur pipeline as it is being heated in preparation for re-melt and during the

melting period. The best tool for this is a distributed temperature sensing (DTS) system, a fibre optic system installed along the length of the pipeline. The DTS system includes a temperature evaluation module along with high and low temperature alarms, indication of

colder points in the pipeline as well as any areas which may be heating too fast. The resistance temperature detector (RTD) installed for the SEET system are not adequate for this since they are only installed in specific locations and are used for general heating.

It is important to have experienced personnel monitoring the temperature profiles of the system in real-time to be able to identify temperature gradients in the system and take appropriate actions (Figs 2 and 5).

New sulphur pipeline - key features

For the new pipeline, it was important to follow the best practices in sulphur pipeline design, and to ensure that reliability and high-risk issues were addressed. The following features were incorporated into the new pipeline accordingly:

- **Anchor design:** The anchors were designed in such a way to ensure the same heat loss as the main pipe sections. This minimises the chance that there will be unmelted solid plugs during a re-melt and will also provide a longer period before solidification will occur.
- **SEET power box:** The SEET power box connections were designed to provide more uniform heating and to remove the box supports from being in direct contact with the pipe. This addresses both heat input and heat loss discontinuities.
- **Pipeline elevation:** The pipeline was raised about 1 m above the nominal profile to minimise the chance for sand accumulation along the pipeline (Fig. 7). If sand encroaches on a sulphur pipeline, it can restrict the normal thermal growth and free movement of the pipeline, as well as causing hot-spots due to over-insulation.
- **RTD location:** The location of the fixed temperature measurement devices is critical for the industry to reform and revitalise its operations to reduce waste, cut pollution and minimise impact on the environment. Factor in the lingering effect of the pandemic, with its disruption to refinery output by delayed maintenance schedules, and it is clear to see why refineries need to find cost-effective ways to increase operational efficiencies and maximise productivity and profitability – all without compromising on performance or safety.
- **Catalyst reuse can serve as a starting point to achieving this without having to modify current operational processes.**
- **Vents and drains:** The new pipeline is equipped with multiple drain pits and with vents at each of the high points. This will allow for draining of the pipeline in the event of an extended power failure or freezing event. The drain valves and drain piping are equipped with heating cables so that a portable generator can be connected in case of a power trip.

Reaping the rewards of recycling

With the challenges facing the global refining industry, refiners should review their current practices to see how they can stay competitive and continue to thrive in today's market. This means improving operational efficiencies and producing products at a lower cost, whilst ensuring performance and safety. **Brian Visioli** of Evonik explores the development of catalyst reuse and how recycled hydroprocessing catalysts can be successfully applied in tail gas treating units to deliver cost and performance gains.

Businesses must always maintain a close eye on the cost of their day-to-day operations, but perhaps more so than ever today given the economic headwinds facing the global economy that show no sign of abating.

Many industries – including the refining and chemical industries – are faced with a multitude of new challenges. Refineries are under more strain than ever, with rising costs, market volatility, tightening environmental legislation, and the potential for a mild recession all piling on the pressure.

Transitioning to greener, more sustainable manufacturing processes is critical for the industry to reform and revitalise its operations to reduce waste, cut pollution and minimise impact on the environment. Factor in the lingering effect of the pandemic, with its disruption to refinery output by delayed maintenance schedules, and it is clear to see why refineries need to find cost-effective ways to increase operational efficiencies and maximise productivity and profitability – all without compromising on performance or safety.

Catalyst reuse can serve as a starting point to achieving this without having to modify current operational processes.

Benefits of recycling

Refiners who only consider fresh catalysts for replacements may have a preconceived notion that they have a performance advantage in terms of conversion, selectivity, pressure drop, or active life over recycled catalysts. However, advances in catalyst re-use technology have closed this gap to rival and, in some cases, improve performance – with the additional benefit of requiring a lower level of investment and no changes to refinery facilities or production methods.

Catalyst reuse schemes are not a new development; for more than 40 years, the refining industry has successfully reused hydroprocessing catalysts through ex-situ reactivation to capitalise on their economic and environmental gains. Of the 150,000 t of replaced hydroprocessing catalysts in refineries each year, more than 20% are catalysts which have been regenerated or rejuvenated via ex-situ processes, which translates to approximately 30,000 t of reused catalysts being installed per year.

One of the key reasons why refineries should consider catalyst rejuvenation is the cost savings it can deliver, largely

because they have a lower replacement cost than fresh tail gas catalysts.

When a spent hydroprocessing catalyst has reached the end of its cycle life, it can be removed in one of three ways. The least desirable (and most costly) method is waste landfill disposal, where you not only lose the inherent value of the catalyst but must pay an additional fee to dispose of the catalyst in a hazardous landfill. While processing for metal reclamation is a more favourable approach, there is still a processing cost as the less-valuable components of the catalyst particles, such as the alumina substrate, still need to be disposed of in the landfill.

The best and most cost-effective option is to reactivate the catalyst for reuse. This process involves oxidation to remove carbon and sulphur compounds while preserving the useful parts for application elsewhere in the refinery. Their applications include the hydro-treating of naphtha, atmospheric gas oil and fluid catalytic cracker feed hydroprocessing. Recycling catalysts not only extends their valuable life, but it also significantly reduces the number of hazardous spent (used) catalyst waste sent to landfill.

Financial gains

With several similarities between hydro-processing catalysts and tail gas treating catalysts, the reactivated catalysts can be ideal to apply in Claus tail gas treating. Both applications employ metals such as cobalt and molybdenum, supported on a carrier containing aluminum, silicon, zeolites, or in combination. Additionally, they both need to be converted to a metal-sulphide state for activity toward the desired reactions, and both consume hydrogen as a reactant in the desired reactions.

However, there are also considerable differences to note between the two types of catalysts and their applications. For example, the quantity of active metal applied to hydroprocessing catalysts is commonly much greater than that on tail gas treating catalysts. Also, hydroprocessing catalysts do not typically encounter species containing oxygen atoms when processing fossil fuels, and the operating pressure is significantly higher in hydro-processing (up to 140 bar, or higher) compared to tail gas treating. These differences influence which types of deactivation typically occur during operation, which in turn has an impact on whether the catalyst can be reused.

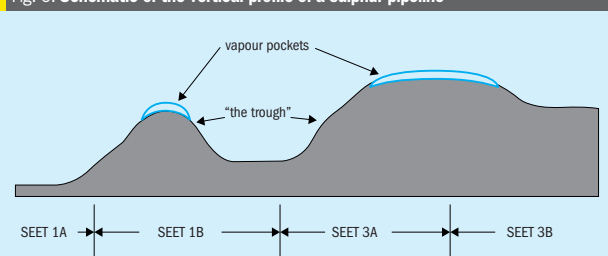
Fig. 5: SEET power boxes



Due to the configuration of the SEET Power Boxes a cold spot of around 2 m can develop.

Source: ADNOC

Fig. 6: Schematic of the vertical profile of a sulphur pipeline



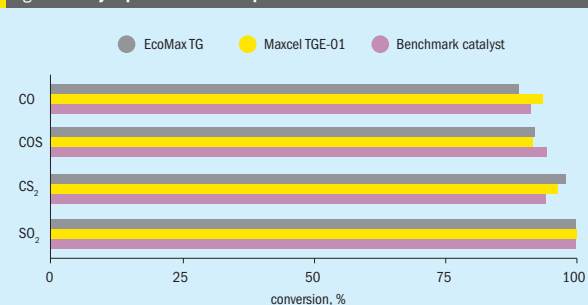
Source: ADNOC



PHOTO: ADNOC

Fig. 7: Drain and drain pit for the new sulphur pipeline; 1 m elevation increase to avoid sand accumulation.

Fig. 1: Catalyst performance comparison



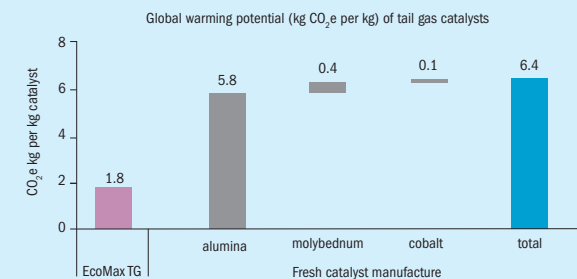
Source: Evonik

Table 1: Tail gas catalyst cost comparison

Catalyst type	Traditional	EcoMax TG	Maxcel TGE-01
Relative cost	1.00 (basis)	0.65	0.83

Source: Evonik

Fig. 2: Carbon footprint of tail gas catalysts



Source: Evonik

Evonik identified an opportunity to develop a catalyst – EcoMax TG – to fully utilise the useful components of a spent hydroprocessing catalyst. This patented method for treating spent catalysts from a hydroprocessing unit removes contaminants and optimises the catalyst for use in a tail gas treating hydrogenation reactor. As a result, EcoMax TG has brought substantial financial benefits, in the region of a 20-40% reduction in cost compared to typical fresh tail gas catalysts.

Improvements against the industry standard

The important qualities of a tail gas catalyst are performance, economics and environmental impacts. Catalyst performance is quantified by testing catalyst conversion performance under identical controlled conditions. The performance of a traditional benchmark catalyst, EcoMax TG, and Maxcel TGE-01 (a fresh extruded tail gas catalyst from Evonik) at example conditions is shown in Fig. 1.

Performance testing has also been completed on a commercial installation of EcoMax TG at a US Gulf Coast refinery, which showed an exceptional conversion of COS and CS₂ compared to traditional catalysts. This advantage is brought about because of the high cobalt and molybdenum content of the EcoMax TG catalyst, compared with traditional tail gas catalysts. Therefore, by reactivating spent hydroprocessing catalysts, the higher metals in the catalyst can be leveraged at a substantial discount compared to manufacturing the tail gas catalyst with a higher metals content.

The economics of tail gas catalysts are a function of the cost of the catalyst components itself, manufacturing cost, transportation cost and catalyst density. To standardise the effects of different types and locations of manufacturing, tail gas catalyst costs may be computed per unit volume. The comparison in Table 1 is based on actual fill cost, thereby removing the density variable. Because EcoMax TG manufacturing does not require re-building a catalyst from raw materials, it can be procured at a significant cost savings versus traditional tail gas catalysts.

Sowing the seeds for sustainability

On top of the economic advantages of repurposing hydroprocessing catalysts for TGTUs, refineries can also unlock significant environmental benefits.

The ecological effects of using EcoMax TG compared to a freshly manufactured tail gas catalyst using virgin raw materials were evaluated using a life cycle assessment (LCA) based on Evonik-internal manufacturing data as well as data from peer-reviewed publications. The LCA compared the carbon footprint between the two products using a “cradle to gate” methodology. Fig. 2 illustrates the difference between manufacturing a fresh tail gas catalyst using virgin raw materials and replacing the traditional catalyst with EcoMax TG.

For example, a typical tail gas treating unit (TGTU) may require 30 t of tail gas catalyst resulting in a carbon footprint of 190 t CO₂e (6.4 kg per kg catalyst). However, by replacing the traditional catalyst with EcoMax TG, the total carbon footprint would be reduced by nearly 140 t CO₂e – a substantial reduction in environmental footprint. This difference is in large part down to the fact that no new metal raw

material (aluminum, cobalt, or molybdenum) mining is required with EcoMax, as would be the case for a freshly manufactured catalyst, and consequently no additional processing or transportation.

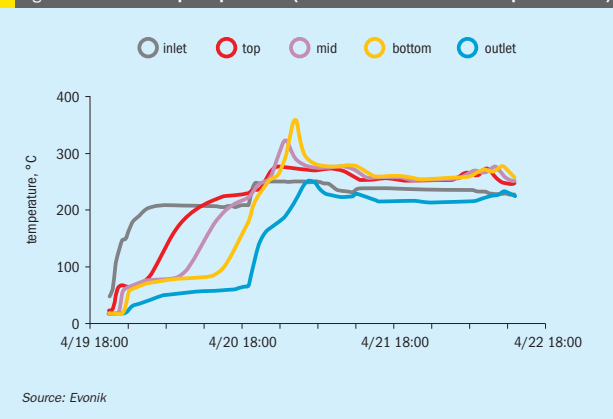
Furthermore, as outlined above, reusing the catalyst reduces waste that would otherwise be disposed of in landfill. The catalyst reuse method is also less energy intensive than the process of forming particles to make a fresh catalyst. So, taken altogether, the numerous Scope 3 emissions – indirect emissions associated with “upstream” processes that are tied up in making a fresh catalyst – are effectively avoided with the more sustainable EcoMax TG catalyst.

Case Study: EcoMax in the field

The EcoMax TG catalyst was chosen by an oil refinery located in the US because of its ability to deliver the required level of conversion activity at the lowest cost. The facility has two sulphur recovery units (SRU), each with its own tail gas treating units and a design capacity of 50 t/d.

The refinery requested that the tail gas catalyst was preactivated, so Evonik’s pre-activation treatment, UltraCAT® TG was applied to speed start-up after its installation and offered both products in a unique, complete package that met the specific requirements of the refinery. UltraCAT® TG preactivation requires that the catalyst be loaded under inert (nitrogen) conditions. After installation, the start-up procedure begins with the reactor running at the optimal temperature so the Claus tail gas can be introduced. The temperature wave shown in the chart in

Fig. 3: Reactor start-up temperatures (EcoMax TG with UltraCat TG preactivation)



Source: Evonik

Fig. 3 coincides with the introduction of Claus tail gas into the warming tail gas reactor.

Performance of the EcoMax TG catalyst was as expected and enabled the refinery to meet the SO₂ emissions requirements as well as reduce costs across the refinery.

Moreover, the successful installation of EcoMax TG in the refinery has, crucially, demonstrated a reduced dependence on fresh cobalt and molybdenum metals. Consequently, refiners can reap the double benefit of decreasing their carbon footprint while enhancing circularity without any adverse effect on performance levels.

The extension of catalyst reuse technology to tail gas treating has been made possible thanks to Evonik’s unique experience

in both hydroprocessing catalyst recovery and sulphur recovery catalysis.

Summary

Recycling hydroprocessing catalysts and applying them in tail gas treating units can help refiners to address these challenges. With the technological advancements from Evonik, refiners now have a credible and practical option to use a more cost-effective catalyst that does not sacrifice performance or require an overhaul of current production processes – with added environmental benefits.

The use of a regenerated or rejuvenated hydroprocessing catalyst (EcoMax TG) in tail gas treating can offer considerable economic and environmental gains for operators. ■

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Another lesson from an SRU shutdown

Inshan S Mohammed of Sulfur Recovery Engineering shares the lessons learned from an emergency shutdown of an MCRC sulphur recovery unit in the middle of a cold Canadian winter where temperatures can be -30°C .

Sulphur recovery units (SRUs) are designed to meet a specific set of targets given an initial set of premises such as feed flowrates, feed compositions, and environmental regulations. During the design phase, considerations are generally given to different scenarios such as varying feed quality and feed rate (turndown), as well as equipment aging and catalyst aging to help with the robustness of the design. However, start-ups and shutdowns arguably cause the most damage to an SRU through the thermal cycling of the process equipment. For facilities with poor reliability, these frequent events lead to unplanned, emergency shutdowns. This article highlights the success story of a Canadian gas plant operator surviving an emergency shutdown in the dead of winter.

A good SRU shutdown commonly involves three main steps: the fuel gas

sweep of the catalyst, the controlled burn of any residual sulphur, and the cool down of the unit to ambient conditions. First, increasing the volumetric flow until limited by the available fuel gas, main combustion air blower or tempering steam ensures all of the sulphur remaining in the catalyst pores are pushed through to the downstream condenser. Second, once all sulphur rundowns are clear, then the controlled burn stage is implemented through the gradual increase of residual oxygen. Whereas in the first step the amount of oxygen is kept below 1,000 ppmv, in the controlled burn the oxygen is increased to percentage-levels while keeping an eye on emissions. Last, the cool down of the SRU to ambient conditions is completed by running blower air or via the use of nitrogen.

An emergency shutdown is any unplanned interruption of the operation of

the SRU. Disruptions can be from external sources from the operating facility, such as inclement weather resulting in power loss, or internal sources, such as equipment failure.

The Main Claus Recovery Concept (MCRC) is a sub-dewpoint process by which the Claus reaction is extended to the point where the sulphur is condensing onto the catalyst. Sulphur recoveries can be extended beyond 99% of the inlet sulphur with the right configuration and design. The first converter follows the conventional mixed bed of titania catalyst, topped with a sacrificial layer of alumina catalyst. The last beds alternate between sub-dewpoint mode and regeneration mode. When the catalyst has completed its adsorption, the converter beds switch positions and then the sub-dewpoint bed is subjected to the hot regenerative temperature. The Canadian operator

in this case study operated a 3-converter MCRC unit with a capacity of approximately 85 t/d and with acid gas direct-fired reheat methods as illustrated in Fig. 1.

Discovery of the issue

Sulfur Recovery Engineering (SRE) was contacted after the discovery of a tubesheet failure within the waste heat boiler (WHB). Shutdown assistance was requested to ensure safe access for inspection and repair of the thermal reactor and the WHB, and to also ensure that the other unit operations (condensers, reheaters, converters, etc.) were free of elemental sulphur. There was no easy path forward for an unplanned outage in the middle of a Canadian winter.

With the tubesheet failure being found the day prior, the first day on site was kicked-off with a meeting where SRE was tasked with finding a way to manage (1) the sulphur still loaded within the MCRC converters and (2) accessing the reaction furnace and WHB for repair. The path forward was to start-up the auxiliary burners on fuel gas and use the flow from them to heat the downstream converter, switching between converter 2 and converter 3 as required. SRE was tasked with measuring the residual oxygen, the formation of soot, and the pressure at the outlet of both reheaters as well as checking for liquid sulphur flow from each of the sulphur rundowns. The thought process was to establish some flow through the unit in order to ensure communication and channelling should the sulphur solidify due to heat losses.

The next day, the thermal reactor and the WHB were blinded off from the rest of the process in preparation for the inspection work. Meanwhile, maintaining a flame in either auxiliary burner was impossible with-

out some process gas to dissipate the heat produced by the flame. The auxiliary burners constantly tripped on high temperature. A nitrogen truck was brought in to provide this motive gas and was connected to the condenser 1 outlet sample point with an initial flow of $6\text{ m}^3/\text{min}$ at a temperature of 40°C .

By the third day, the nitrogen flow was increased to $10\text{ m}^3/\text{min}$ and the auxiliary burners were running steady. The rates of fuel gas were approximately one half of those from the previous shutdowns, which was understandable given the lack of front-end flue gas from the main burner. What was also apparent were the mixed values from the residual gas analysis and from the oxygen analyser. Here, the gas results illustrated the incomplete burn with residual methane (C1) and carbon monoxide (CO) and the analyser illustrated a percentage level amount of oxygen. There are several plausible explanations for the difference:

- vacuum condition of the process gas;
- poor mixing within the auxiliary burner;
- low flow through auxiliary burner;
- lag-time between collection of the gas sample and measurement via the analyser.

Regardless of the reason, this discrepancy highlighted the need for continuous monitoring of the combustion via the various methods (analyser, gas analysis and local pressure) to ensure that the converters do not plug off. Nonetheless, there was a good amount of flow going through the two MCRC converters and the crisis of the emergency shutdown was in a manageable state.

New findings

Now five days into the emergency support, the plan was to continue to operate the modified fuel gas sweep until the repair

of the leak was completed. Throughout this time, and in addition to the log items above, SRE was tasked with recording the converter temperatures (Figs. 2 and 3). Assistance was also given to ensure (1) that the process gas temperature to the MCRC converters was adequate, (2) that the condensers were outside of sulphuric acid attack, and (3) that the MCRC converters were switched at an appropriate time. The works for repairing the tubesheet and for fixing the castable refractory was estimated to be completed by the following week.

Flow of liquid sulphur from condenser 2 (sulphur within converter 1) started flow on day 5. The trickling flow was constant until day 10, when the rundown dried out. A total of five days.

The modified-fuel gas sweep of the MCRC converters and SRE's onsite support continued through to end of day shift on day 13. During the last remaining two days, the fuel gas to air ratios for the auxiliary burners were increased to expose the downstream converters 2 and 3 to more oxygen; mimicking the controlled burn step of a typical SRU shutdown. As no sulphur fires or excessive sulphur dioxide emissions were observed, the exercise of safely shutting down the SRU without the use of the main burner was achieved.

Next steps

The Canadian operator is now tasked with completing the repairs on the WHB. Unfortunately, the number of tubes with leaks has steadily increased as each repair attempt was made and hydrotesting of the unit was completed. Once the unit is cleared to be back in service, SRE plans to assist with the safe start-up of the unit.

Fig. 1: Simplified MCRC process scheme

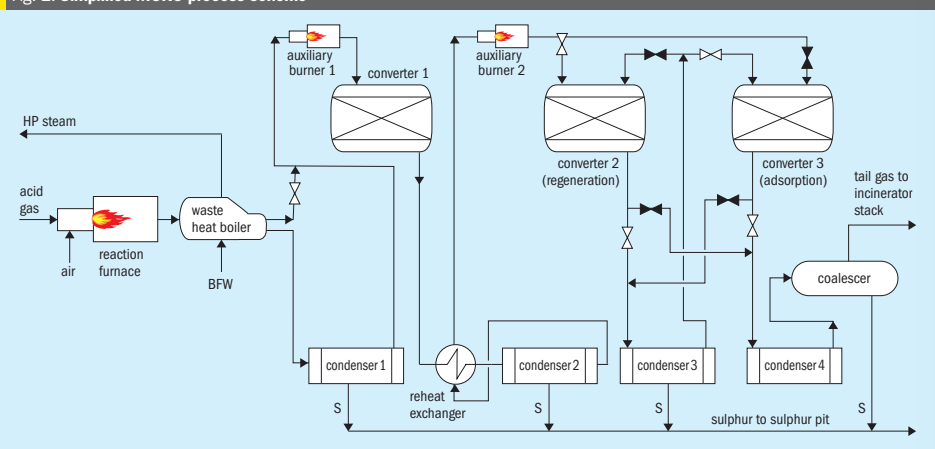


Fig. 2: Converter 2 temperature profile

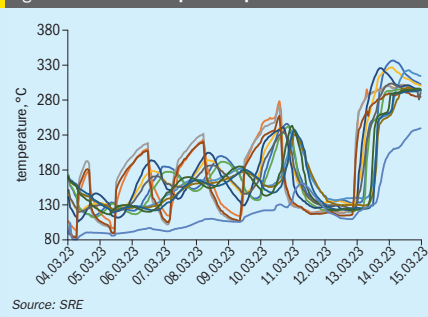
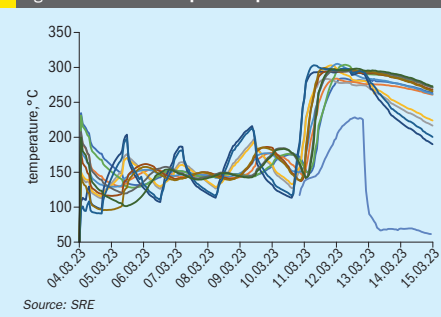


Fig. 3: Converter 3 temperature profile



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