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SULPHUR

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CRU Sulphur + Sulphuric Acid Conference, The Hague, Netherlands

US sulphur and sulphuric acid

Carbon free energy from sulphuric acid

SRU troubleshooting

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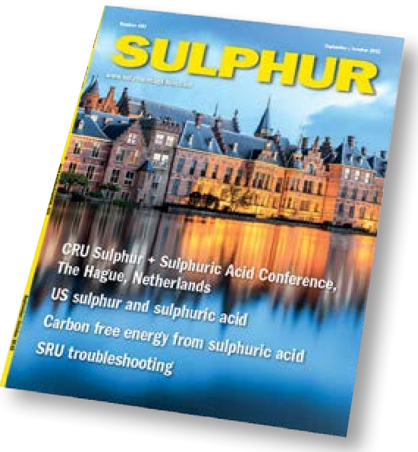
Sulphur and renewables



The end of August saw a paper published in the Journal of the Royal Geographical Society by Dr Mark Maslin of University College London. Widely reported, it looked at the prospects for sulphur production in an era of declining fossil fuel use, concluding that there could be "a shortfall in the annual supply of sulphuric acid of between 100 and 320 million tonnes by 2040, depending on how quickly decarbonisation occurs". It added that "unless action is taken to reduce the need for sulphuric acid, a massive increase in environmentally damaging mining will be required to fulfil this resource demand."

Now, these figures are surely designed to grab headlines, and we can consider them and some of the assumptions behind them in a moment, but the broad thrust of the paper is of course correct. However, I suspect that none of this will be news to long-term readers of *Sulphur* magazine or regular attendees at CRU's Sulphur and Sulphuric Acid Conference. Papers by Dr Peter Clark, the former director of Alberta Sulphur Research Ltd, and consultant Angie Slavens of UniverSUL Consulting have been highlighting the potential shortfall in sulphur production caused by global decarbonisation since as long ago as 2012.

Now to those figures. They assume sulphur recovery from sour gas to be roughly constant out to 2040, with reductions in natural gas consumption in e.g. Europe as a reaction to the current Russian supply situation balancing increased use in e.g. China and India, while oil demand and hence production is based on a series of BP scenarios which range from a slight increase in oil use out to 2040 to an almost total phase-out on a pathway towards 'net zero' carbon emissions to 2050. Sulphuric acid demand is projected to increase to feed additional nickel, cobalt and neodymium demand for electric vehicle batteries and other green technologies. No account is taken of increased sulphuric acid production from metal smelting, although it mentions pyrite roasting as an alternative source of acid. Its main conclusion is that research is needed into cheap and environmentally friendly methods of extracting sulphur from sulphate materials such as gypsum and anhydrite, as the report correctly points out that the cost of extracting sulphur via Frasch mining is much higher than the generally prevailing price for extracting it from oil and gas over the past 50 years (and, as Peter Clark would doubtless point out, the number of sites around the world actually suitable for large scale Frasch mining are nowhere near enough to make up for the projected shortfall in sulphur production).

What the report does not consider, as Peter and Angie did in a joint presentation at the 2018 Sulphur Conference, is that if sulphur's value increases due to scarcity, it may become worthwhile tapping highly sour gas reserves as much, if not more, for their sulphur content as their methane content. Likewise highly sour crudes such as oil sands bitumen could become favoured because of their sulphur premium. The report does however sensibly suggest that we can lower demand for sulphuric acid by more efficient use of phosphate fertilizers, and recycling of sewage and other wastes to produce phosphate-containing fractions. Other methods of extracting phosphates without the use of sulphuric acid are also available of course, such as the Improved Hard Process.

It is certainly true that we have become used to an era of sulphur surplus, and will need to make some mental adjustments over the next couple of decades as the global use of fossil fuels declines. But with due deference to Dr Maslin, I don't think that we are likely to face a sulphuric acid supply shortfall of 100 million t/a in 2040, let alone 320 million t/a. ■

> **"It may become worthwhile tapping highly sour gas reserves as much, if not more, for their sulphur content."**

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

The global sulphur market has seen a marked shift since the early part of the third quarter, with major benchmarks falling by more than $300/t in many regions. Restrictions on the export of processed phosphates from China led to rapid demand destruction. The demand outlook for phosphates for the fourth quarter of this year and the first quarter of 2023 is a weak one, owing largely to affordability concerns. This in turn will cut demand for sulphur and impact pricing. On the supply side for sulphur, operating rates at refineries are expected to remain elevated as the market continues to replace sanctioned Russian oil and gas. This will help keep sulphur availability healthy, putting more downwards pressure on pricing in some regions.

The recent crash in global sulphur pricing started in China. Several unsold vessels were being used as floating storage at a time when demand was low, leading to the initial price drop. Average prices dropped from a high of $485/t f.o.b. Middle East in June 2022 down to just $71/t f.o.b. at the start of August. Since then, prices appear to have reached a floor and a recovery is underway, albeit this is currently expected to be short-lived amid demand destruction and ample availability.

The recent sulphur price crash has led to comparisons bring drawn with the last time prices dropped at such a dramatic rate in 2008. Sulphur prices collapsed within three months of the July 2008 spike in the wake of the global financial crisis with 2009 becoming a year of low prices, reaching negative netbacks in many cases. At the peak, average prices reached $825/t f.o.b. Middle East, dropping down to $32/t during the market collapse. Following the sulphur price crash in 2008-09 sulphur prices remained at much lower levels in a stable to slightly firm trend for several months before running back up into the $100s/t f.o.b. again. The price cycle this time is expected to face sustained downward pressure from the processed phosphates market.

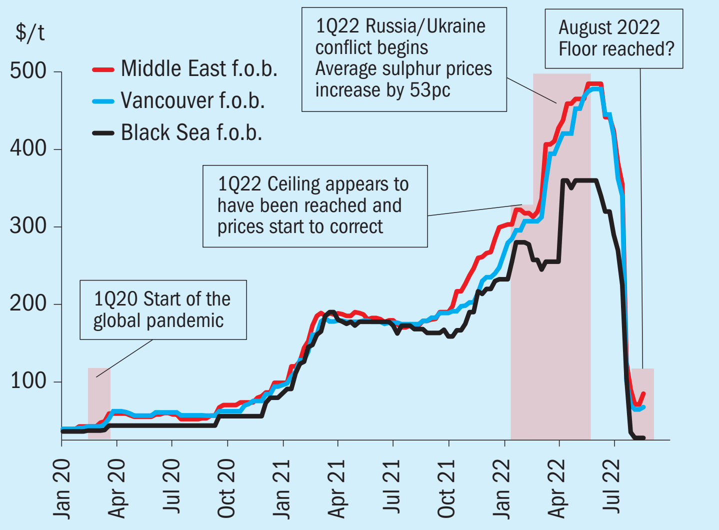
Average Middle East prices decreased by $332/t between the end of June 2022 and the beginning of September 2022 down to $92/t f.o.b. and are around $200/t lower than prices at the start of the year. Kuwait's KPC set its September sulphur lifting price at $95/t f.o.b., up by $5/t from the August price. Muntajat set its September Qatar sulphur price at $89/t f.o.b. Ras Laffan/Mesaieed, up by $12/t from the August QSP of $77/t f.o.b. This follows the substantial drop from July to August of $351/t, and indicates the rebound seen in the market following the steep drop from the highs reached in June. Meanwhile ADNOC set its September official sulphur price (OSP) for liftings to India at $92/t f.o.b. Ruwais, up by $7/t from the August price of $85/t f.o.b.

Moroccan fertilizer producer OCP renegotiated its third quarter contract price with Middle East suppliers at $70-120/t c.fr. Suppliers accepted the need for the unprecedented renegotiation following the collapse of the sulphur market. Import demand for Morocco has been slow following the slight uptick in the first half of the year as a result of lower processed phosphate fertilizer production. This is adding to the bearish tone for the short term view. The ammonia market remains a risk factor for the sector. The rising cost of energy through the northern hemisphere's winter season will push feedstock costs up further. This coupled with the potential for softer phosphate fertilizer prices is likely to squeeze producer margins and impact sulphur demand.

The China c.fr all forms range was assessed by Argus at $55-140/t c.fr at the start of September, with the low end reflecting molten product and the high end granular sulphur. Average prices increased by around $23/t through the month of August but were around $140/t lower than at the start of 2022. China imports increased in January-July by 1% year on year to 4.8 million tonnes. South Korean and Japanese molten sulphur imports combined totalled over 1 million tonnes over the period, marking a significant increase. This was likely because of the broad price differential with solid sulphur. Middle East supply to China was led by the UAE, the second largest supplier so far this year after South Korea at around 600,000 t.

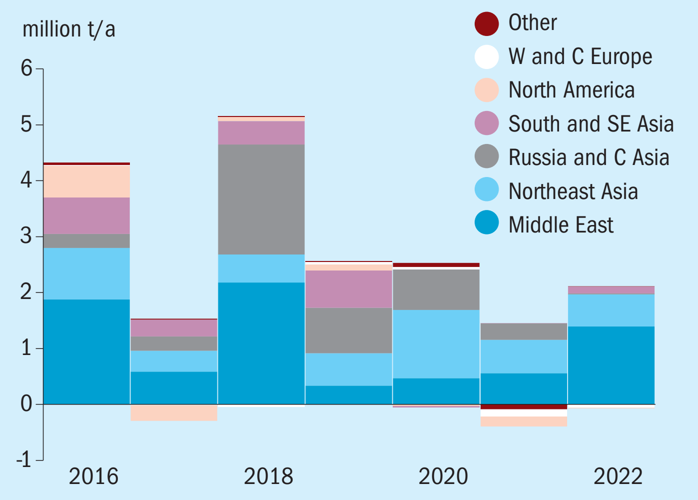
Future supply of molten sulphur is likely to be impacted by changing dynamics in the energy sector in the region. Japanese refiners are pushing ahead with plans to

Fig. 1: **Sulphur price history 2020-22**



Source: Argus Sulphur Analytics

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



Source: Argus Sulphur Analytics

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cut capacity in anticipation of reduced domestic demand for oil products, despite recent strong profit margins that have been boosted by soaring product prices as a result of the Russia-Ukraine conflict. Domestic demand for refined products is forecast to edge down in 2022-23, following the post-pandemic rebound in 2021-22, averaging just over 2.6 million bbl/d.

SULPHURIC ACID

With sulphur prices dropping so dramatically, the acid market has not been shielded from the downturn. A more bearish tone has emerged, leading to a price correction, expected to continue through the coming months. Average sulphuric acid prices in NE Asia have dropped over the last quarter. Prices from China have declined by $88/t at the mid-point while South Korean and Japanese export prices are down by $46/t. The downturn has come on the back of demand losses, a softer processed phosphates market and the sulphur market price crash. NW European f.o.b. prices have also been impacted by the bearish tone, with average prices dropping by $66/t on the previous quarter. Delivered acid prices have also moved down. Indian prices dropped sharply by over $100/t at the mid-point. The Chilean market has softened with ample supply at terminals with short term spot demand unlikely to pick up. In North Africa, OCP/Morocco has remained out of the market, adding to the bearishness.

Global sulphuric acid demand is expected to rise by just 2.3 million tonnes in 2022 on 2021 levels because of demand destruction in the processed phosphates sector. Total phosphoric acid demand is forecast to drop by 3.7 million t/a before recovering in 2023. Moroccan acid demand will rise by 3.4 million t/a by 2023 but production from sulphur burners will also rise as OCP brings on new capacity. Total consumption is forecast to rise to close to 25 million t/a in 2023.

On the supply side we expect this to rise by 21.7 million t/a in the 2021-23 period. Smelter-based capacity is expected to see a boost at 4.4 million t/a, representing 20% growth over the period. Northeast Asia is the main driver as new smelters ramp up in China.

The weaker tone in the base metals markets is also adding to the softer outlook for acid. Bearishness in copper markets since 2Q22 has been attributed to several factors, but China's sluggish recovery from Covid-19, global interest rate hikes and subsequent recession fears are key to understanding why many markets have been dropping in value. Copper prices on the London Metal Exchange (LME) fell to a 20-month low on 15 July, trading at $7,000/t. Prices have since recovered to around $7,500-$8,000/t but are still just 80% of what they were in April 2022.

On 16 August, the LME banned Russian-origin nickel from its two approved warehouses in the UK exported on or after 20 July. Russia is the world's top supplier of Class 1 nickel, and the country's mining group Norilsk Nickel the biggest source of European supply. The move by the LME will act to increase tightness in the market. Nickel prices are expected to find more support because of demand from the EV sector in the long term, even with market sentiment remaining cautious at present.

Metals producers in the Central African region continue to face mounting production costs against a backdrop of declining base metals prices. High energy costs and inflationary pressures are squeezing mining firms' margins. The ramp-up of Ivanhoe Mines' Kamoa Kakkula copper mine in the DRC is boosting regional demand for trucking, tightening access to transport facilities for other operations. Acid demand for the metals sector is expected to total 8.3 million t/a in 2022 but this could be revised down as mines potentially underperform in the current circumstances.

Over in China the Daye Non-Ferrous Copper project is close to starting up but has continued to face delays. The project was initially expected to reach completion in 2021 but Covid-19-related disruption led to postponement. The smelter had pushed start-up to mid-June from late 2021 because of a delay in the shipments of its imported equipment and parts. Start-up is now expected during the second half of this year. Sulphuric acid capacity is 1.5 million t/a and 400,000 t/a of copper. Daye Non-Ferrous Copper has resold some feedstock deliveries in July and August to the spot market and has requested its suppliers to postpone some deliveries originally planned for August and September.

Chinese sulphuric acid exports totalled 2.6 million tonnes in the first seven months of the year. This is a 92% increase on the same period a year earlier. Not only this but full year 2021 imports were 2.8 million t/a. ■

Price Indications

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

Cash equivalent	**April**	**May**	**June**	**July**	**August**
Sulphur, bulk ($/t)					
Adnoc monthly contract	420	468	485	425	85
China c.fr spot	493	506	450	150	120
Liquid sulphur ($/t)					
Tampa f.o.b. contract	481	481	481	352	352
NW Europe c.fr	362	362	430	380	380
Sulphuric acid ($/t)					
US Gulf spot	238	238	238	188	188

Source: various

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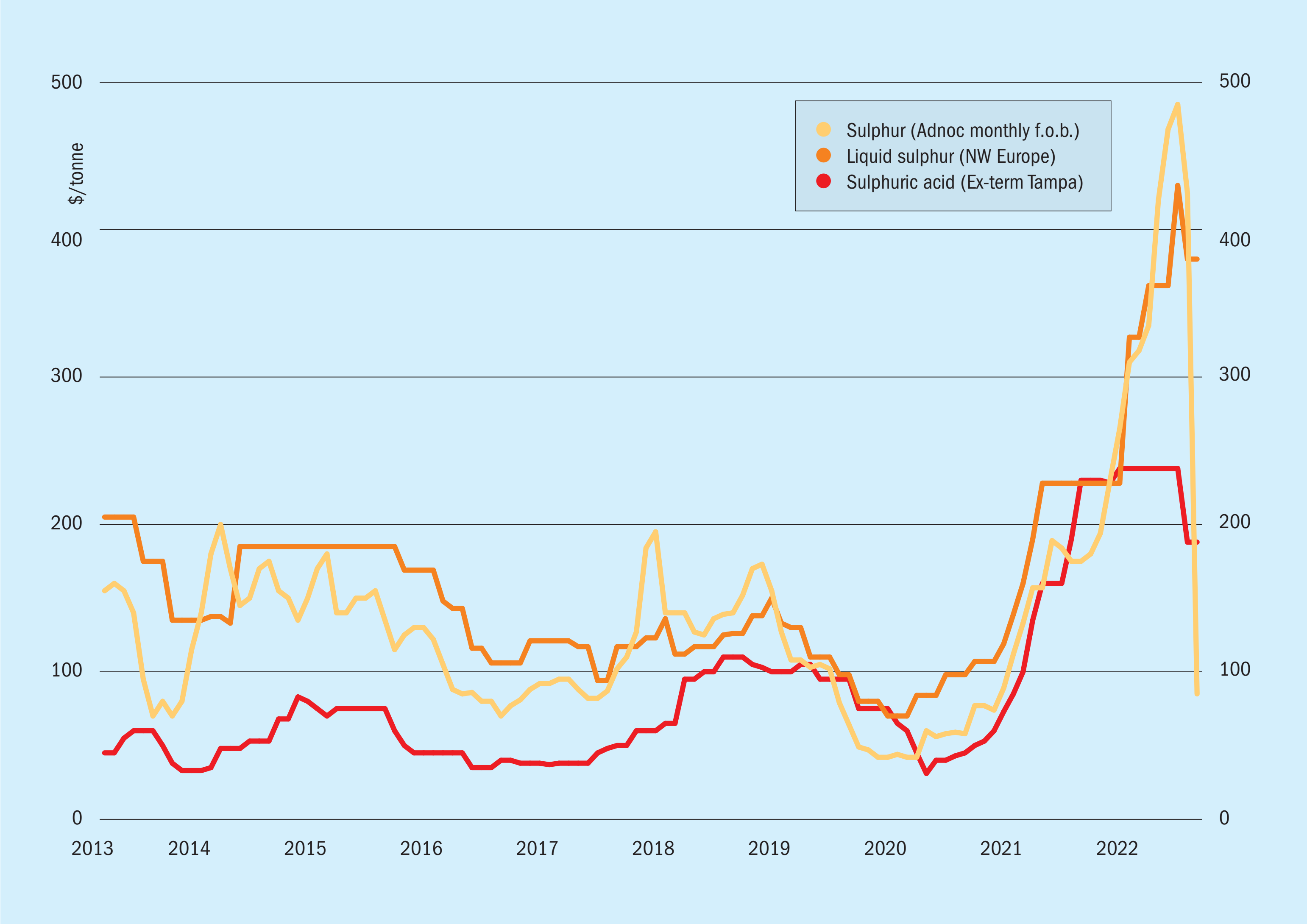
Market Outlook

Historical price trends $/tonne



Source: BCInsight

SULPHUR

- Reduced appetite for sulphur from processed phosphates producers in China will continue to place downwards pressure on pricing in the near term.
- Phosphates-based demand is likely to remain low in the second half of 2022 as issues surrounding affordability persist, slowing import requirements.
- Refinery run rates are to remain elevated through the second half as global supply chains respond to sanctions on Russian oil and gas. This will bolster the production of sulphur, adding to the potential for prices to ease once again.
- Indonesian sulphur imports are expected to reach a record high of close to 2 million tonnes this year. This is in response to the ramp-up of nickel HPAL projects, a bright spot in the market outlook.
- **Outlook:** Prices are expected to continue to rebound in the short term following the market collapse but this is likely to be short-lived. Key market fundamentals point to slow demand, impacting import requirements, at a time when supply is improving. A more bearish tone is expected to persist through the first quarter of 2023.

SULPHURIC ACID

- Supply side factors could provide some support to the extent of the downturn but these are likely to be limited because of the continued demand destruction. High energy prices are a continued risk to the market on both the supply and demand side. The European market seems particularly exposed to this with end users struggling to pass on raw material costs.
- On the supply side Nyrstar announced its Budel smelter would be placed on care and maintenance from 1 September 2022 until further notice, reducing acid availability.
- The risk of a global recession remains with the potential for a protracted downturn through 2023. Supportive economic measures in China have yet to positively impact base metals prices.
- Annualised, Chinese exports total 4.5 million t/a for 2022. We expect a slowdown in the second half of the year, but exports are still expected to reach close to 4 million t/a this year with the potential to exceed this level.
- **Outlook:** The global sulphuric acid market is facing a period of softening, with the bearish sentiment expected to persist through the rest of the third quarter. There is potential for some stability to emerge at lower prices during the final quarter of the year and going into 2023 but the outlook for processed phosphates remains weak and is likely to keep downward pressure on acid demand and prices for the short term.


Science behind Technology

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Sulphur Industry News

SAUDI ARABIA

Aramco confirms development plan for Jafurah gas project

Saudi Aramco has confirmed a phased development approach for its $100 billion-plus Jafurah unconventional onshore gas project, which is expected to produce up to 2 billion cubic feet per day of gas by 2030, raising the company's overall gas production capacity by 50% over that time frame. Aramco says that the first development phase for the Jafurah gas plant is likely to come on stream by 2025, and it is progressing with the phased development of a project that will reach a raw gas processing capacity of 3.1 bcf/d.

"The facility for the gas plant will come in two phases. The first phase would come in 2025. And the second phase will come on stream by 2027," said Aramco chief executive Amin Nasser. The huge Jafurah project "will provide feedstock for hydrogen and ammonia production and will help meet expected growing local energy demand", Aramco said in a statement. Aramco is looking to boost domestic gas production to free up almost 1 million bbl/d of oil from use in power production, boosting its oil export capacity.

Saudi Arabia's dry natural gas production exceeded 4 tcf in 2020 with the commissioning of the Fadhili gas processing plant and the commencement of processing natural gas from non-associated sour gas fields in the east of the country. Most of the incremental gas production in the country is likely to come from the Jafurah development, which is also the largest non-associated gas field in Saudi Arabia, with over 200 tcf of proved reserves.

In late August, Worley was awarded two project management service contracts for Aramco's unconventional gas program in North and South Arabia and Jafurah. Under the contracts, the company will provide front-end engineering design (FEED), detailed design support, project management services and construction management services. The term of both contracts is three years with an option for an extension for a further two years.

"Being part of a project that not only looks towards sustainability but also contributes to boosting regional economy demonstrates Worley's commitment to developing future growth in the location," said Eissa Aqeeli, Senior Vice President and Location Director, Saudi Arabia and Bahrain.

CANADA

Northern Nutrients produces new nitrogen sulphur fertilizer

Northern Nutrients has launched a new nitrogen sulphur fertilizer that contains nitrogen stabilisers evenly dispersed throughout the prill. The 38% nitrogen and 18% sulphur fertilizer, Triple Kick, also contains a source of carbon, which together with the sulphur and evenly dispersed stabilisers offers what the company describes as an industry first nitrogen and sulphur source designed to limit volatilisation and leaching.

"With an increased global focus on improving nitrogen efficiency and reducing nitrous oxide emissions, we believe our innovative Triple Kick fertilizer offers a one of a kind solution in the global nitrogen market, especially in light of the recently proposed regulation by the Canadian government aimed at reducing fertilizer emissions by 30%," said founder and CEO Ross Guenther. "The initial market reaction to our new product has been phenomenal as we ramp up production for the fall season."

Triple Kick will be produced in Northern Nutrients' enhanced urea fertilizer manufacturing facility outside of Saskatoon, Canada. The facility uses Shell Thiogro technology, a patented process for the incorporation of micronized elemental sulphur into urea, resulting in a sulphur form that is available to plants across the growing season. The same plant also manufactures Arctic S 11-0-0-75 enhanced sulphur urea fertilizer which commenced production in April of 2022.

UNITED STATES

GTC Vorro and RATE announce collaboration

GTC Vorro Technology, a turnkey provider of environmental services and process technologies to oil and gas, refining, petrochemical and chemical companies, has entered into an agreement with Rameshni & Associates Technology and Engineering (RATE), a specialty engineering firm providing process technologies for sulphur processing and acid-gas removal. GTC Vorro and RATE will offer process technology solutions to customers along with full-service sulphur removal. The two companies will combine their sulphur technology and engineering services, providing innovative services including: licensing, engineering, consulting, training, pre-commissioning, technology commercialisation, performance testing and troubleshooting.

Joseph Gentry, vice president, GTC Vorro, said, "We are continuing to push the boundaries to achieve zero sulphur emissions. By teaming with RATE, we can combine our expertise to expand our capabilities and services."

Mahin Rameshni, president and CEO, RATE, said, "We are delighted to work in collaboration with GTC Vorro. Together, we can provide state-of-the-art technology to meet all of our customers' needs."

Lithium sulphur battery development

A team of researchers mostly based at the Massachusetts Institute of Technology (MIT) have developed a new battery architecture using aluminium and sulphur as its electrode materials, with a molten salt electrolyte in between. In a paper in the journal Nature, MIT materials chemistry professor Donald Sadoway, along with 15 others at MIT and in China, Canada, Kentucky, and Tennessee, explain that the aim was to develop something better than lithium-ion batteries for small-scale stationary storage, and ultimately for automotive use. In addition to being expensive, lithium-ion batteries contain a flammable electrolyte, making them less than ideal for transportation.

The battery cells can endure hundreds of cycles at high charging rates, with a projected cost per cell of about one-sixth that of comparable lithium-ion cells. The molten salt the team chose as an electrolyte also prevents the formation of dendrites, narrow spikes of metal that build up on one electrode and eventually grow across to contact the other electrode, causing a short-circuit and hampering efficiency.

PORTUGAL

Sustainable aviation fuel project

The Navigator Company and Hamburg-based developer P2X-Europe are to create a joint venture, P2X-Portugal, to develop a world-class production facility for industrial-

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scale production of sustainable aviation fuels – carbon-neutral synthetic kerosene, based on green hydrogen and biogenic CO_2. The is based on Portugal's renewable energy sources and on CO_2 generated by Navigator's 'biorefineries' using carbon from sustainable forests. P2X-Europe is a global pioneer in power-to-liquids project development and technology and can tap into its parent companies' H&R Group and Mabanaft market expertise in waxes for the chemical-pharmaceutical industry and in liquid fuels. The project will take up to 280,000 t/a of biogenic CO_2 with carbon capture and several hundred MW of renewable energy capacity to manufacture 80,000 t/a of sustainable aviation fuel in its final form. The first phase will have half of that capacity, with a projected capex of €550-600 million. Subject to a positive final investment decision by mid-2023, the Project is scheduled to start commercial operations in the first half of 2026.

SPAIN

TUBACEX returns to profit

TUBACEX results for the first half of the year show sales of €353.8 million, double the figure for the same period last year, with profit before tax of €10.4 million compared to a loss of €28 million in 1H 2021. In recent years, the company has promoted geographic expansion and sectoral diversification and has also reorganised its production. The sales strategy followed in recent years has made it possible to access different framework agreements with leading players in the industry, such as the agreement entered into recently with the Abu Dhabi National Oil Company (ADNOC) for a value in excess of 30,000 t/a over a period of ten years for the supply of comprehensive solutions for gas extraction in the UAE and the construction of a new plant in Abu Dhabi.

MALAYSIA

Shell and Petronas agree to develop Rosmari-Marjoram

Shell and Petronas have taken the final investment decision to develop the Rosmari-Marjoram gas project in Sarawak, Malaysia. The Rosmari-Marjoram fields are 220 km off the coast of Bintulu, Sarawak, and will be powered by renewable energy, using solar power for the offshore platform.

"Rosmari-Marjoram will help to deliver a secure and reliable supply of energy, responsibly and efficiently," said Shell Upstream director Zoe Yujnovich. "This demonstrates our Powering Progress strategy – powering lives, generating value, and reducing emissions by using renewable energy to power Rosmari-Marjoram."

Ivan Tan, country chair and senior vice president Upstream Malaysia said, "The support and partnership from Petronas and the government of Sarawak are critical to achieving this milestone with Rosmari-Marjoram. Shell has a long and proud history in Sarawak, and we look forward to contribute further to Sarawak and Malaysia's economic growth through investments in competitive and resilient projects."

The Rosmari-Marjoram aims to ensure a sustained gas supply to the Petronas LNG complex. It comprises a remotely operated offshore platform and onshore gas plant, with infrastructure that includes one of the longest sour wet gas offshore pipelines in the world stretching more than 200 km. Rosmari-Marjoram project is designed to produce 800 million scf/d. Gas production is expected to start in 2026.

UNITED ARAB EMIRATES

ADNOC awards contracts for Hail and Ghasha

The Abu Dhabi National Oil Company (ADNOC) has announced the award of two contracts totalling $2 billion to ADNOC Drilling for the Hail and Ghasha development project. The contracts comprise $1.3 billion for integrated drilling services and fluids and $711 million for providing four island drilling units. A third contract, valued at $681 million, was awarded to ADNOC Logistics and Services for providing offshore logistics and marine support services. The contracts will cover the Hail and Ghasha drilling campaign over a maximum of ten years.

Production from Ghasha is expected to start around 2025, ramping up to produce more than 1.5 billion scf/d of natural gas before the end of the decade. Four artificial islands have already been completed, and development drilling is underway. In November last year, ADNOC and its partners awarded two engineering, procurement and construction (EPC) contracts for the Dalma Gas Development Project, within the Ghasha concession as well as a contract to update the front-end engineering and design (FEED) for the Hail and Ghasha project to optimise costs and timing, as well as potentially accelerate the integration of carbon capture.

IRAN

IOOC working on phased Esfandiar oil development offshore Iran

The Iranian Offshore Oil Company says that it aims to implement the first stage of development of the Esfandiar oil field, 95km southwest of Kharg Island in the Arabian Gulf, within the next three years. CEO Alireza Mehdizadeh told local news that the development plan has been approved by the National Iranian Oil Company and a licensing round will shortly be held for the development.

"Based on the results of a comprehensive study of the field, the design, construction and installation of a well platform and the drilling of four production wells have been proposed in the first phase, and the production fluid from this field, after being transferred and processed at the Abouzar platform, will be transferred to Khark Island," Mehdizadeh said.

IOOC has also completed the shore pull operation for the new 110 km 32-inch pipeline of Phase 16 of the South Pars gas field, terminating at the receiving station at Asalouyeh in southern Iran. The new pipeline will be laid between the south coast of the Phase 16-15 refinery in Asalouyeh and the offshore Phase 16 platform and will transport South Pars sour gas, also ensuring stable production on the SPD16 platform.

KAZAKHSTAN

Production returns at Kashagan

Oil production at Kazakhstan's giant offshore Kashagan field is ramping back up, according to the North Caspian Operating Company (NCOC) operating consortium after production was suspended following a gas leak on August 3rd. The field was shut for a week after signs of a gas leak closed the Bolashak oil and gas treatment unit, possibly caused by corrosion of pipelines or equipment. Sulphide corrosion caused by hydrogen sulphide in the sour gas shut the project down in 2013 for over a year during the initial development phase, when underwater sections of the pipeline to the onshore processing station had to be released. Oil production at Kashagan was 317,000 bbl/d in the first six months of 2022, 2% down on the previous year. NCOC is run by Kazakh state-owned Kazmunaigaz, Shell, ExxonMobil, Total, Eni, CNPC and Japanese firm Inpex. ■

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Sulphuric Acid News

SAUDI ARABIA

Copper smelter for Ras Al-Khair

Saudi Arabia's Ras Al-Khair Industrial City has signed an industrial land agreement with local firm Gulf Copper to develop a copper smelting and casting plant at an investment $319.30 million. The project would be developed on a plot spanning more than 250,000 square metres in the industrial city. No construction timelines were given. The Saudi government has previously signed agreements with Trafigura and Saudi-based Modern Mineral Holding to develop a 400,000 t/a copper smelter at Ras Al Khair which would also include 200,000 t/a of zinc and 55,000 t/a of lead smelter capacity at a projected cost of $2.8 billion. ■

Ma'aden to double phosphate and ammonia exports to India

The Saudi Mining Company (Ma'aden) has signed four memoranda of understanding with Indian fertilizer partners which would collectively double exports of phosphate products and ammonia to India, beginning in 2023. Saudi Arabia's Minister of Industry and Mineral Resources Bandar Alkhorayef and India's Minister of Chemicals and Fertilizers Dr. Mansukh Mandaviya attended the signing. Robert Wilt, CEO of Ma'aden, said the company exported about 1.7 million t/a of phosphate products and ammonia to the Indian market, and that the two nations were natural partners due their geographical proximity. Ma'aden is developing a third large-scale phosphate project which aims to increase the company's phosphate fertilizer supply capacity by 3 million t/a to 9 million t/a over the coming years, with the first phase to be complete in 2025. The $6.4 billion complex is being constructed at the Ras Al-Khair industrial city.

DEMOCRATIC REPUBLIC OF CONGO

Metso Outotec to deliver equipment for copper mine

Kamoa Copper SA has selected Metso Outotec to supply key concentrator plant equipment to the company's copper mining complex expansion in the Democratic Republic of Congo. The value of the order, which is not disclosed, has been booked in Minerals' Q2/2022 orders received. Metso Outotec's scope of delivery consists of Planet Positive processing equipment, including energy efficient *HIGmill*™ regrind mills with polyurethane wear linings. The delivery also includes *Larox*® concentrate filters and *TankCell*® flotation cells for the efficient recovery of valuables.

"One of the key missions for Kamoa Copper S.A. is to implement low-carbon technology to advance sustainable production of copper. Metso Outotec's Planet Positive offering supports our customer's ambition, allowing us to be a true partner for positive change," says Charles Ntsele, Vice President, Minerals Sales for Metso Outotec in Africa.

UNITED STATES

Sulphuric acid from carbon sequestration

Technology start-up company Travertine has launched its process to remove carbon dioxide from the air and sequester it permanently, while also making sulphuric acid. The company says that its aim is to leverage the sulphuric acid to develop applications for fertilizer production and to recover critical elements from mines to help advance the transition to renewable clean energy.

The proprietary electrochemical process involves recovering sulphate waste generated from industry and recycling it into sulphuric acid. The calcium and magnesium in the sulphate are reacted with CO_2 in the air, resulting in generation of carbonate minerals to sequester the carbon.


PHOTO: MA'ADEN

Ma'aden's Phosphate 3 plant under construction.

Carbonate minerals, found in limestone, marble, and cement, can sequester carbon over a period of tens to hundreds of millions of years.

"By converting CO_2 from the air into a mineral we permanently sequester it in a way that mimics the way the earth sequesters it. And in regenerating sulphuric acid from sulphate waste, we avoid accumulation of that waste, eliminating water and soil pollution, while continually recycling and reusing it," said Laura Lammers, Travertine founder and CEO and former University of California, Berkeley professor. The company spun out from her lab work at Berkeley involves exploring carbonate mineralisation as an energy- and cost- efficient way to reduce the environmental impact of critical mineral extraction. "We believe our process can help facilitate extraction of critical elements for decarbonization. And that it can help ensure extraction industries are as environmentally responsible and sustainable as possible while providing both mining and fertilizer companies an efficient, cost-effective way to deal with their waste. They currently pay billions in waste management."

The company recently secured $3 million in seed financing, led by Grantham Environmental Trust and Clean Energy Ventures, to expand its team and build a pilot plant in Boulder. Colorado. Travertine is building a pilot at its facility in 2022 and is working toward building a demonstrator 1 t/d CO_2 sequestration unit at a partner mine site, with operations beginning in early 2024.

Travertine is partnering with fertilizer producers to recycle phosphogypsum to make calcium carbonate products that can be sold as components of green cement, as well as to make green hydrogen. Further out, the aim is to build facilities in partnership with existing major users of sulphuric acid, as well as mine sites under development in the US, that will need large volumes of sulphuric acid.

INDIA

New sulphuric acid plant commissioned

Amal Ltd says that its newly incorporated subsidiary, Amal Speciality Chemicals Ltd (ASCL) has successfully commissioned a new sulphuric acid plant in Ankleshwar, Gujarat province. The plant has a capacity of 300 t/d, and features a zero liquid discharge facility. Amal Ltd is a chemical firm that manufactures and markets sulphur-based products, including oleum, sulphuric acid, sulphur dioxide and sulphur trioxide.

JAPAN

Wind powered sulphuric acid carrier

Japanese shipping firm Mitsui OSK Line plans to launch a wind-powered bulk carrier in 2024 for US wood pellet producer Enviva, as it continues to strive to reduce greenhouse gas (GHG) emissions from the shipping sector. MOL has signed a contract with Japanese shipbuilder Oshima Shipbuilding to build the vessel, which is equipped with a hard sail system, known as a wind challenger, following an initial agreement with Enviva to transport wood pellets in a cleaner supply chain. The new ship will be MOL's second wind-assisted vessel following a wind-powered coal carrier for Japanese utility Tohoku Electric Power. The wind challenger technology can convert wind energy into propulsive force using a telescoping hard sail. This is expected to cut a vessel's GHG emissions by around 5% on a Japan-Australia voyage and by around 8% on a Japan-North America west coast voyage, compared with the same type of vessel without the hard sail system.

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Japanese copper producer JX Nippon Mining & Metals (JX) is also planning to introduce a rotor sail system to a Supramax bulk carrier to cut emissions. JX's group company Pan Pacific Copper has signed an agreement with Australian iron ore producer BHP and Finnish engineering firm Norsepower for decarbonisation for international shipping. The companies plan to equip the system to the Koryu combination carrier that carries copper concentrates and sulphuric acid sometime during July-September 2023. The vessel is operating between Chile and Japan, carrying about 150,000 t/a of copper concentrates and 100,000 t/a of sulphuric acid.

NETHERLANDS

Zinc smelter to halt production


The Budel smelter.

PHOTO: NYRSTAR

Nyrstar, part of the Trafigura Group, has announced that the Budel zinc smelter in the Netherlands will be placed on care and maintenance "until further notice" from September 1st due to high energy prices across Europe. Zinc prices on the London Metal Exchange rose by 7.2% on the news. Glencore has also warned that Europe's energy crisis poses a substantial threat to the continent's zinc supply. Smelters across the region are barely turning a profit and the Nyrstar plant, which accounts for about 2% of global output, has been operating at a reduced rate since the fourth quarter of last year.

KUWAIT

Acid supply tender delayed

Two contracts tendered by state-owned oil companies in Kuwait have been delayed due to ongoing political deadlock in the country. One of the contracts includes the construction of two new electricity substations and associated power lines in the north of the country, and the second covers the supply of sulphuric acid to refineries operated by the Kuwait National Petroleum Company (KNPC). Many projects and contracts in Kuwait's oil and gas sector have seen significant delays over the past three years due to a stand-off between the government and the elected parliament over fiscal reform. In August Kuwait formally dissolved parliament as the crown prince moved to resolve the stand-off. Parliamentary elections are now expected in October. Parliament has yet to approve the state budget for 2022-23.

CANADA

Chemtrade Logistics reports 2Q 2022 results

Chemtrade Logistics has announced results for the three months ended June 30th, 2022. Revenue for the quarter was $446.4 million, an increase of $109.1 million or 32% year-on-year, reflecting improvements in both operating segments. Net earnings were $34.8 million, an increase of $48.9 million year-on-year. Scott Rook, President and CEO of Chemtrade, said: "We are very pleased with our performance during the second quarter of 2022. Chemtrade continues to capitalise on strong market fundamentals across the majority of our product portfolio… we also continue to take steps to ensure the momentum we are generating in the business continues for years to come. In particular, we are excited about our recent announcement of a joint arrangement with Kanto Group to further strengthen Chemtrade's position as the leading manufacturer of ultrapure sulphuric acid in the North America market. Demand for ultrapure sulphuric in the US is expected to show significant growth, driven by new investments in the semi-conductor industry."

Adjusted EBITDA includes the sale of the company's specialty chemicals businesses in 4Q 2021 and the sale of an idled Augusta, Georgia sulphuric acid plant during the second quarter of 2022 for cash proceeds of $10.0 million.

The company's Sulphur and Water Chemicals (SWC) segment reported revenue of $269.5 million for 2Q 2022, up from $213.8 million in 2Q 2021. Adjusted EBITDA in the segment was $54.8 million, similar to 2Q2021. The increase in SWC revenue was primarily due to higher selling prices for merchant acid, water solutions products, and regenerated acid, the company said, reflective of higher sulphur prices and, in the case of merchant acid, tight industry supply-demand dynamics. A partial offset to this revenue growth was lower sales volumes of merchant acid stemming from lower by-product supply as compared to the prior year period. Higher sulphur costs muted the improvement in Adjusted EBITDA, particularly for Chemtrade's water solutions products which continue to face margin pressures on a year-over-year basis due to the sharp rise in sulphur prices. Chemtrade continues to work proactively with its customers to pass through the higher input costs for its water solutions products.

Scoping study on nickel sulphate project

FPX Nickel Corp says it has completed an engineering scoping study evaluating the production of nickel sulphate for the electric vehicle battery supply chain from the high-grade nickel concentrate from the company's Baptiste Nickel Project in British Columbia. The proposed project would produce approximately 43,500 t/a of nickel in nickel sulphate, enough to fulfil approximately 17% of the projected North American EV battery demand for nickel in 2030. It would produce high-purity nickel sulphate via a sulphuric acid leach with a recovery of approximately 97%, and would use "significantly lower" temperatures and pressures than high pressure acid leach processes.

The company says that Baptiste's awaruite nickel mineralisation has technical advantages over sulphide and laterite ores for producing nickel sulphate, offering a lower-cost, lower-carbon path from mine-to-market in the EV battery supply chain due its extremely high nickel content (60-65% nickel) and low levels of impurities.

GERMANY

Lead smelter to reopen after sale

German lead plant Stolberg will reopen once its sale has been approved according to buyer Nyrstar. The plant, in the west of Germany, was sold to commodities group Trafigura in July and will be operated and managed by Trafigura Group unit Nyrstar. Stolberg has been undergoing repairs since major flood damage in July 2021. Trafigura had said in July the restoration programme was scheduled to be completed in the third quarter of 2022. At capacity, Stolberg produces 155,000 t/a of lead and 130,000 t/a of sulphuric acid.

ZIMBABWE

Acid plant due for 2024

Zimplats, owned by Impala Platinum, spent more than $270 million on expansion projects and paid a dividend amounting to

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$205 million for the half year ended in June. The company is upgrading its Mupani mine from the current design capacity of 2.2 million t/a to 3.6 million t/a to replace part of the tonnage being lost from the Mupfuti mine on its anticipated depletion in 2027. The construction of a new 38MW furnace and a new sulphuric acid plant has a collective price tag of $520.6 million. The furnace will increase smelting capacity from 135,000 t/a to 380,000 t/a. Currently, the group is exporting part of its metal production in concentrate form as the existing smelter cannot process all the concentrate generated from the concentrators. Zimplats says that the acid plant will be commissioned in August 2024. Acid will be used for fertilizer production.

JORDAN

Phosphoric acid expansion inaugurated

At a ceremony on September 2nd, chairman of Jordan Phosphate Mines Company (JPMC) Dr. Mohammad Thneibat inaugurated the 4th concentration line plant project at the Indo-Jordanian Chemicals Company (IJCC), a wholly owned subsidiary of JPMC. The project aims to increase IJCC's production capacity by about 31,000 t/a of phosphoric acid to 610,000 t/a at a cost of $2.3 million. The company is looking to higher exports to enhance its position in the global phosphate market and support Jordan's economic development, Thneibat said. JPMC has also recently completed the rehabilitation of the phosphoric acid tanks at the company's industrial complex in Aqaba on the Red Sea, and inaugurated a new phosphate washing facility.

MOROCCO

Rare earths from phosphogypsum

British mining company Rainbow Rare Earths says it has signed an agreement with phosphate and fertilizer giant OCP and the Mohammed VI Polytechnic University (UM6P) to further investigate and develop optimal techniques for the extraction of rare earth elements from phosphogypsum. Rainbow Rare Earths says that it brings "significant IP assets, know-how, and expertise in the field of phosphogypsum processing" to the venture.

Rainbow Rare Earths' CEO George Bennett said: "We are delighted to enter this agreement with such innovative partners and believe their significant knowledge of phosphogypsum processing fits well with our own technical expertise in rare earths processing." He said that his team is "focused on securing opportunities for both collaboration and expertise sharing" in the extraction and processing of rare earth elements found in phosphogypsum. Founded in 2021, Rainbow Rare Earths is mainly engaged in the development of rare earth mineral projects in South Africa and Burundi.

INDONESIA

Copper smelter to start up in 2024

Freeport Indonesia president Tony Wenas says that construction of the company's second copper smelter at the Java Integrated Port & Industrial Estate (JIIPE) in Gresik, East Java is now 36.2% complete. The smelter is targeted for completion at the end of 2023, with pre-commissioning and commissioning phases following, and the smelter is due to be in operation by May 2024. ■

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People

H.J. Baker's chief operating officer (COO) **Luis Masroua** has become president of the company.

"Luis has been a great asset to H.J. Baker since joining us," said CEO Christopher Smith. "I know that with his years of international business experience he will be an excellent leader for the company moving forward."

Masroua has been responsible for many significant changes since joining H.J. Baker as COO in May 2018. These include the sale of the company's Brazilian animal health and nutrition business and the purchase of Oxbow Sulphur in 2019.

"It is a great honour to be named President of H.J. Baker. I'm looking forward to helping the company progress into the future," Masroua said. "This is a historic company. I aim to continue its legacy of excellence for our customers and suppliers, as well as our many excellent employees."

Masroua joined H.J. Baker after working for Cargill for two decades. At Cargill, his roles included managing director of Cargill Animal Nutrition in Russia and managing director of Agribrands Purina in Venezuela and Peru. He was also Cargill's aquaculture business development manager in San Pedro, Honduras. Luis holds an MBA from the Weatherhead School of Management and a master's degree from the Thunderbird American Graduate School of International Management.

Nutrien appointed **Ken Seitz** as president and CEO on 8th August. He has been the company's interim CEO since January. Seitz also joined Nutrien's board of directors from this date. His appointment as CEO followed an extensive seven-month global search for internal and external candidates led by the board and supported by a world-class executive recruitment firm. Seitz brings more than 25 years of global management experience to the role. He has worked across more than 60 countries and possesses deep agriculture and mining sector experience.

Russ Girling, Nutrien's chair, said: "Nutrien's record performance and disciplined execution of strategy during some of the most turbulent times we have seen globally underscore the strength of Ken Seitz's leadership. As the company's president and CEO, Mr Seitz will continue to drive positive outcomes for all of our stakeholders as we strive to safely and sustainably feed the world.

In reply Ken Seitz said: "I look forward to continuing the important work of safely and sustainably feeding a growing world with the executive leadership team, our employees globally and support of the board of directors. Growing up on a dairy farm in Saskatchewan, I am honoured and humbled to work alongside growers during these challenging times today and going forward. Nutrien is extremely well positioned to help meet the global goals of food security and climate action, partnering across the food system. Our purpose is to feed the future, and I am invigorated by the noble pursuit to help solve these critical world needs."

Mark Summers has decided to stand down as CEO and executive director of South Africa's Kropz company at the end of the year and the board has started a process to recruit a new CEO. Summers will continue to work with the Kropz team and his successor, once appointed, to ensure an orderly handover and that the day-to-day activities of the business continue. Kropz has two African rock phosphate projects – Elandsfontein, on South Africa's west coast, which is nearing production, and Hinda in Congo-Brazzaville, which is at feasibility study stage.

Shell Plc has shortlisted candidates to succeed CEO Ben van Beurden, who is preparing to step down in 2023 after 40 years at the company, according to Reuters. Van Beurden oversaw the takeover of rival BG Group Plc, and was also the architect of the company's plan to shift from fossil fuels to cleaner sources of energy and achieve net-zero carbon emissions by 2050. The shortlist of candidates to be the next Shell CEO reportedly includes Wael Sawan, the company's head of integrated gas and renewables, Huibert Vigeveno, the head of downstream refining operations, Chief Financial Officer Sinead Gorman and head of upstream Zoe Yujnovich. ■

Calendar 2022

SEPTEMBER

12-16
Amine Experts' Amine Treating & Sour Water Stripping Technical Training Course,
KANANASKIS. Alberta, Canada
Contact: Daniel Domanko, Senior Manager
Tel: +1 403 215 8400
Email: Daniel.Domanko@SulphurExperts.com
Web: AmineExperts.com

12-16
29th Annual Brimstone Sulphur Symposium,
VAIL, Colorado, USA
Contact: Mike Anderson, Brimstone STS
Tel: +1 909 597 3249
Email: mike.anderson@brimstone-sts.com
Web: www.brimstone-sts.com

15-16
Oil Sands Conference & Trade Show,
CALGARY, Alberta, Canada
Contact: Bruce Carew, EventWorx
Tel: +1 403 971 3227
Email: marketing@eventworx.ca

19-23
Sulphur Experts' Sulphur Recovery Technical Training Course,
KANANASKIS, Alberta, Canada
Contact: Daniel Domanko, Senior Manager
Tel: +1 403 215 8400
Email: Daniel.Domanko@SulphurExperts.com
Web: AmineExperts.com

OCTOBER

9-13
XIII Round Table for Sulfuric Acid Plants,
TEMUCO, Chile
Contact: Portus #1361, San Felipe,
Valparaíso 2171881, Chile
Tel: +56 34 251 5557

10-14
Amine Experts Amine Treating Technical Training Course,
NOORDWIJK,
Netherlands
Contact: Jan Kiebert, Senior Manager
Tel: +31 71 408 8036
Email: Jan.Kiebert@SulphurExperts.com
Web: AmineExperts.com

17-21
Sulphur Experts Sulphur Recovery Technical Training Course,
NOORDWIJK, Netherlands
Contact: Jan Kiebert, Senior Manager
Tel: +31 71 408 8036
Email: Jan.Kiebert@SulphurExperts.com
Web: SulphurExperts.com

24-26
38th CRU Sulphur + Sulphuric Acid Conference, THE HAGUE, Netherlands
Contact: CRU Events, Chancery House,
53-64 Chancery Lane,
London WC2A 1QS, UK
Tel: +44 (0) 20 7903 2444
Email: conferences@crugroup.com
Web: events.crugroup.com/sulphur

24-26
The 8th SAIMM Sulphur and Sulphuric Acid Conference, CAPE TOWN, South Africa
Contact: Gugu Charlie,
Conference Coordinator, Southern African Institute of Mining and Metallurgy
Tel: +27 73 801 8353
Email: gugu@saimm.co.za

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Proven Sulphur Technologies for Capital-Efficient Solutions that Meet Clients' Environmental Requirements

Our experts at Fluor are experienced in all commercially proven sulphur technologies and develop solutions that cost-effectively satisfy our clients' environmental requirements. Our offerings include:

- Licensing COPE® oxygen enrichment technology for sulphur plant capacity expansion
- Licensing D'GAASS® liquid sulphur degassing technology for environmental benefits
- Licensing hydrogenation/amine and FLEXSORB® Claus Tail Gas Treating for 99.9+% overall sulphur recovery efficiency
- Sulphur recovery unit, tail gas treating unit and degassing plant ranges from 10-ton-per-day to 2,600-ton-per-day single trains
- Licensing patent pending technology for Oxygen Enhanced Claus Carbon Dioxide Recovery Process (OEC²RP) for environmental benefits

For more information please contact:

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The future of oil sands production

A large portion of the oil reserves of Canada and Venezuela exist as oil sands. By the mid-2000s, production from these sources had topped 5.5 million bbl/d. But with Venezuela's economic implosion and increasing environmental scrutiny of oil sands production, what is the future for this high sulphur fuel source?


PHOTO: CENOVUS

Oil sands processing at Cenovus' Christina Lake facility.

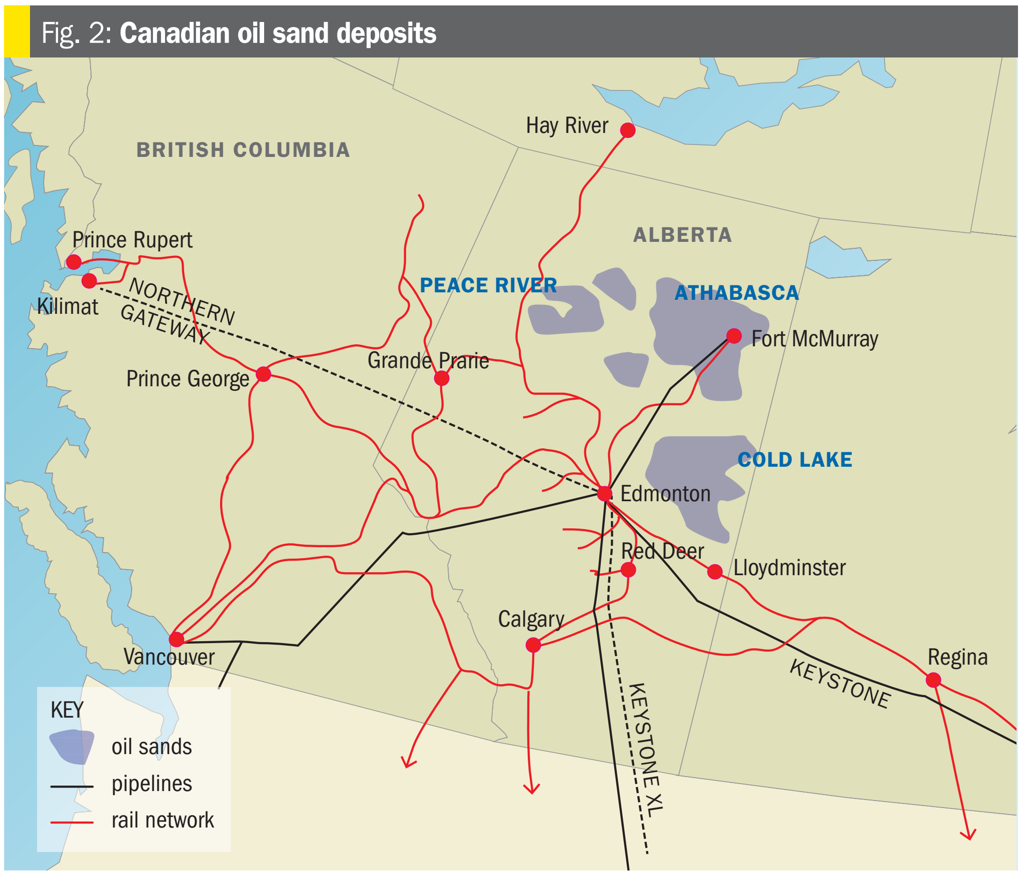
A surprising amount of the world's oil reserves are locked up in the oil sands deposits of Venezuela and Canada. With reserves of 300 and 170 billion barrels respectively, these are of an order of magnitude of the oil reserves of Saudi Arabia (270 billion barrels). However, they are less accessible; the heavy, bituminous oil is trapped in a sandy layer close to the surface. It is viscous at Venezuelan temperatures and frozen solid in northern Alberta, and very high (around 5%) in sulphur content, and so requires extensive processing to make it usable. This raises the cost of production, and its energy intensity, making it a marginal play at times of low prices. But the high sulphur content means that it represents a sizeable share of global sulphur production, and the future of oil sands production could significantly influence global sulphur output.

Fig. 1: **Map of Venezuelan oil reserves**

Venezuela

Venezuela's oil sands cover a 600 km long belt along the Orinoco river valley, known as the *Faja Petrolifera del Orinoco* (Orinoco Petroleum Belt), or simply the *Faja*. Recoverable reserves there are estimated at 300 billion barrels, representing 90% of Venezuela's proven oil reserves and over 15% of all global oil reserves. As Figure 1 shows, the region is divided into four major development regions, running from west to east: Boyaca, Junin, Ayacucho and Carabobo. Within these regions there are a total of 36 exploration and production blocks; 9 in Boyaca, 14 in Junin, 8 in Ayacucho and 5 in Carabobo. Most of the existing productive blocks are in the northern Ayacucho and Carabobo and northeastern Junin regions.

Fig. 2: **Canadian oil sand deposits**



Production expanded rapidly during the 1990s in the era of Venezuela's '*apertura*' (opening) with the assistance of western oil majors such as Chevron, BP, Total and Repsol-YPF. However, the accession of populist president Hugo Chavez in 1998 led to an abrupt about-face in policy and part-nationalisation of the *Faja*, which caused most western countries to back out. National oil company PDVSA took majority shares in all operations, and now sought partnerships with oil companies from countries friendlier to the Chavez government such as China, Russia and Iran.

Over the next decade and a half Chavez used PDVSA and its operations as a cash cow to fund his social programmes, with 96% of export earnings coming from overseas oil sales. However, corruption and mismanagement by political appointees and lack of investment in maintenance, coupled with the effect of US sanctions, led to steadily falling oil production, from 3.3 million bbl/d in 2006 to 2.6 million bbl/d in 2013 when Chavez died. Under his successor Nicolas Maduro the decline has been even more marked, as Maduro purged the senior leadership of PDVSA and appointed his own political cronies. Venezuela's economic crisis deepened as oil revenues fell, and production sank rapidly to just 650,000 bbl/d in 2021. Amidst this unravelling, production from the *Faja*, assisted by international partners, had actually been one of the few success stories of the Chavez years, and peaked at around 1.2 million bbl/d in 2015. But under Maduro it dropped sharply and sank to less than 300,000 bbl/d in 2021. In 2018, in a desperate attempt to raise cash, PDVSA's majority stakes in many of the Faja projects were sold off to the Russian and Chinese partner companies. Meanwhile US sanctions tightened in 2019 as the Trump government recognised Juan Guaido as the winner of the 2019 presidential election in Venezuela, not Nicolas Maduro. The oil crisis caused by Russia's invasion of Ukraine and the subsequent sanctions regime has led the US to ease its sanctions on Venezuela, but the return of any large scale production from the Orinico oil belt seems unlikely in the short to medium term.

Canada

Like Venezuela, Canada is a major oil producer which faces declining output from its conventional fields, and which has turned to oil sands production in order to balance this. Like Venezuela, Canada's oil sands are in a remote and relatively inaccessible part of the country – in this case the wilds of northern Alberta rather than the jungles of the Orinoco. The reserves are also of a similar size; Canada's proved oil reserves stand at around 170 billion barrels, 97% of which is represented by the oil sands of northern Alberta (see Figure 2). However, Canada's oil sands exploitation has a longer and happier history than Venezuela's, and hence of the 5.4 million bbl/d of oil that Canada produced in 2021, about 3.5 million bbl/d or 65% was from oil sands production.

Production is concentrated in northern Alberta, with a roughly 50-50 split between two types of extraction; conventional, open pit mines, and in-situ production, the latter of which pumps steam down into underground deposits to melt the bitumen and then draws it back out. This so-called steam assisted gravity drainage (SAGD) method is increasingly popular as it is not only cheaper but uses less water and avoids the large-scale scarring of the landscape of open pit mining, which must then be remediated once extraction is complete.

The bitumen is either upgraded to produce synthetic crude oil ('syncrude'), or diluted with lighter fractions such as naphtha to produce a 'dilbit' (dilute bitumen) or with syncrude to create a 'synbit'. These are light enough to be pumped, and so can be exported by pipeline or rail. According to figures from the Alberta Energy Regulator, roughly 20% of mined bitumen is upgraded, and about 10% of in-situ production, for an overall figure of about 15% upgrading within Alberta.

Table 1 shows current Alberta oil sands operations. The major operators are now Suncor, Cenovus, Canadian Natural Resources Ltd (CNRL), Syncrude and Imperial Oil. There has been something of a flight of oil majors from the oil sands patch over the past few years, exemplified by Shell selling all of its holdings except the Scotford upgrader. BP, Equinor, Devon Energy, ConocoPhilips and domestic oil producer Husky have also cashed out recently. Low oil prices from 2016-2020, especially during the covid crash in early 2020, turned an unwelcome spotlight on Canadian oil sands production. Even so, production has continued to increase, as Figure 3 shows. The figure also includes projected increases from the Alberta Energy Regulator showing a 40% increase over this decade.

Exports

Canadian oil production from all sources ran at about 5.4 million barrels per day in 2021. Set against that, consumption totalled around 2.3 million barrels per day. The balance of 3.1 million bbl/d was

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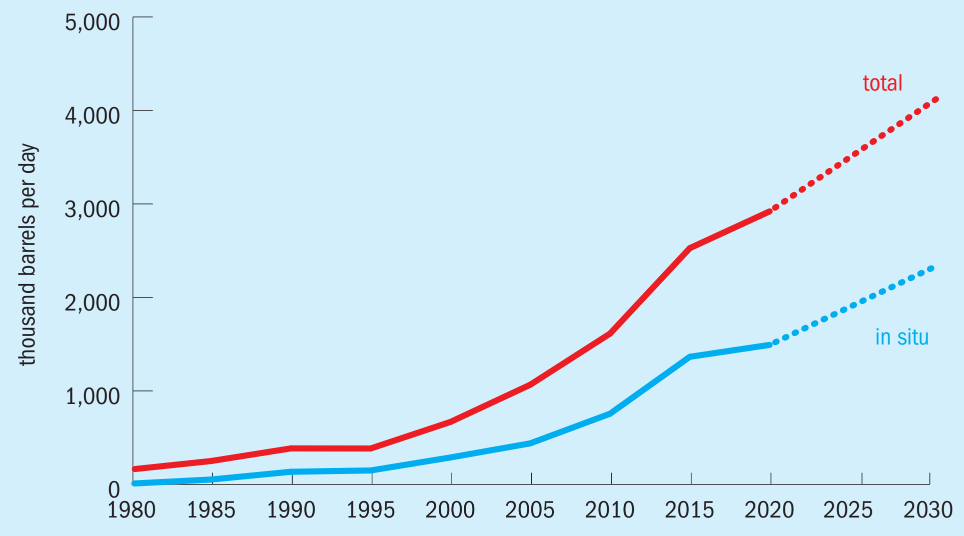
Table 1: **Canadian oil sands production 2021**

Operator	Site	Capacity, bbl/d	Type
Syncrude	Mildred Lake/Aurora	375,000	Surface mine
		350,000	Upgrader
Suncor	Millennium/Steepbank	330,000	Surface mine
	Base Operations	357,000	Upgrader
	Firebag	215,000	In situ
	Mackay River	38,000	In situ
	Fort Hills	194,000	Surface mine
Shell Canada	Scotford	255,000	Upgrader
CNRL	Jackpine	145,000	Surface mine
	Muskeg River	175,000	Surface mine
	Horizon	294,000	Surface mine
		250,000	Upgrader
	Primrose/Wolf Lake	140,000	In situ
	Peace River	12,500	Surface mine
	Kirby	80,000	In situ
MEG Energy	Christina Lake	100,000	In situ
Cenovus	Christina Lake	260,000	In situ
	Foster Creek	180,000	In situ
	Sunrise	60,000	In situ
	Long lake	92,000	In situ
		58,500	Upgrader
Statoil	Liesmer	20,000	In situ
Imperial Oil	Kearl	220,000	Surface mine
	Cold Lake	180,000	In situ
	Grand Rapids	15,000	In situ
CNOOC	Long Lake	72,000	In situ
		58,000	Upgrader
ConocoPhilips	Surmont	148,000	In situ
Conacher	Great Divide	20,000	In situ
Strathcona	Tucker	30,000	In situ
	Orion	18,000	In situ
	Lindbergh	18,000	In situ
PetroChina	MacKay River	35,000	In situ
NW Redwater	Sturgeon Refinery	50,000	Upgrader
Others	Various	58,000	Various

Source: Oilsands Review

Fig. 3: **Canadian oil sands production, thousand barrels per day**



Source: Alberta Energy Regulator

exported, and by far the largest slice of this goes south across the border to the United States. Canada has come to represent an increasingly larger and more important share of US oil imports over the past decade. This is also a net figure – Canada actually exported 3.9 million bbl/d of oil to the US in 2021, mostly from western Canada, but it also imported 700,000 bbl/d of oil in the east of Canada, where most Canadian refineries are sited.

Exports of Canadian syncrude continue to be a vexed question in the US, where the fate of the $6 billion cross-border 830,000 bbl/d Keystone XL pipeline, designed to connect the oil sands region to the US pipeline network and carry syncrude on to US Gulf Coast refineries for processing, became a political symbol, opposed by environmentalists and encouraged by the Trump government. In 2021, president Joe Biden finally cancelled the Keystone XL pipeline by denying it a critical permit.

Nevertheless, plenty of syncrude is carried by rail, and there are existing cross-border pipelines and other new ones being built. Enbridge's Line 3 Replacement Project effectively added 370,000 bbl/d of capacity at the end of last year, while the Transmountain Extension will allow for significant quantities of syncrude to reach the west coast ports for the first time, for potential onward export. Additional impetus has come this year from the Ukraine war and resulting high oil prices, especially given the loss of heavy, sour Russian crude to US refiners. In spite of the US tight oil boom, the recovery of natural gas liquids (NGLs) from gas fracking has meant that the US has had a surplus of lighter fractions which often need to be blended with heavier crudes for processing.

Environmental opposition

Oil sands products have long had a tarnished environmental reputation. In Canada, the unsightly landscape left behind by surface mining was a bone of contention in spite of remediation efforts that followed the end of mine life, though the move to in-situ mining has dampened that criticism somewhat. However, it is oil sand syncrude's carbon footprint which is now in question, stemming from the heat that must go into melting the bitumen and the carbon cost of the hydrogen required to break the large molecules up into smaller, more desirable ones. Oil sands extraction and processing is about 50% more carbon intensive than that for more conventional grades of oil, almost comparable to coal, and

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represents around 10% of Canada's total carbon dioxide emissions, according to figures submitted to the UN. Though the Albertan government has resisted imposing a provincial carbon tax, Canada's new Federal carbon tax means every tonne of CO_2 equivalent produced has attracted an additional penalty of C$40/t, rising to C$50/t in April this year and C$170/t by 2030. There is also talk of a total emissions cap on the industry. Though there are moves by oil sands producers to use nuclear energy and carbon capture to reduce the carbon intensity of production, the additional cost of production may crimp development plans for Canada's oil sands in the future.


PHOTO: ALL CANADA PHOTOS/ALAMY

Oil sands bitumen tank cars in a siding in British Columbia.

Oil price impact

The fortunes of the oil sands industry remain closely tied to the oil price. Time was when oil sands production was accounted some of the world's most expensive and marginal oil production, with base production costs around $100/bbl. However, breakeven costs have been falling as reliability improves and down time reduces and improved project design and integration into upgrading facilities leads to better project economics. By 2020 new mine projects without an upgrader had a break-even price averaging around C$65/bbl, and in situ expansions might manage as low as $45/bbl. The slump in oil prices at the start of 2020 led to a scaling back of investments, but the return of demand as the covid crisis eased meant that 2021 was actually a bumper year for capital spending in the Canadian oil and gas sector of C$80 billion (US$65 billion), although the oil sands patch represented only C$9 billion of this. Still, this year's run of prices following the Ukraine invasion has meant that there is more of a spring in the step of producers. CNRL has raised its estimate for capex for 2022 by 25%.

Even so, investment figures for this year are likely to be down on the boom years. While the Alberta government is forecasting an increase in production of more than 1 million barrels per day by 2030, industry analysts point to the increasing environmental burdens and scrutiny on the industry and have more conservative estimates of an addition 500-650,000 bbl/d of capacity this decade.

Sulphur from oil sands

If 2.9 million barrels per day of oil sands bitumen is being extract, at an average sulphur content of 5%, that represents in theory 6.5 million t/a of encapsulated sulphur that is being extracted. However, only the bitumen that is processed or upgraded in Alberta will show up in those figures. Alberta actually produces about 4.0 million t/a of sulphur, of which oil sands processing currently represents about 2.5 million t/a. The remaining sulphur will be extracted where the syncrude is delivered, mainly on the Gulf Coast of the US. If we assume that a slightly pessimistic figure of an additional 500,000 bbl/d of oil sands processing is added by 2030, that represents a extra 1.1 million t/a of sulphur, but where it is extracted continues to depend on the state of the US refining industry and the fate of export pipeline routes for Canadian syncrude.

In the meantime, the prospect for meaningful additions to Venezuela's oil sands production continues to look remote, barring a major change of heart by the Maduro government. ■

US sulphur and sulphuric acid production

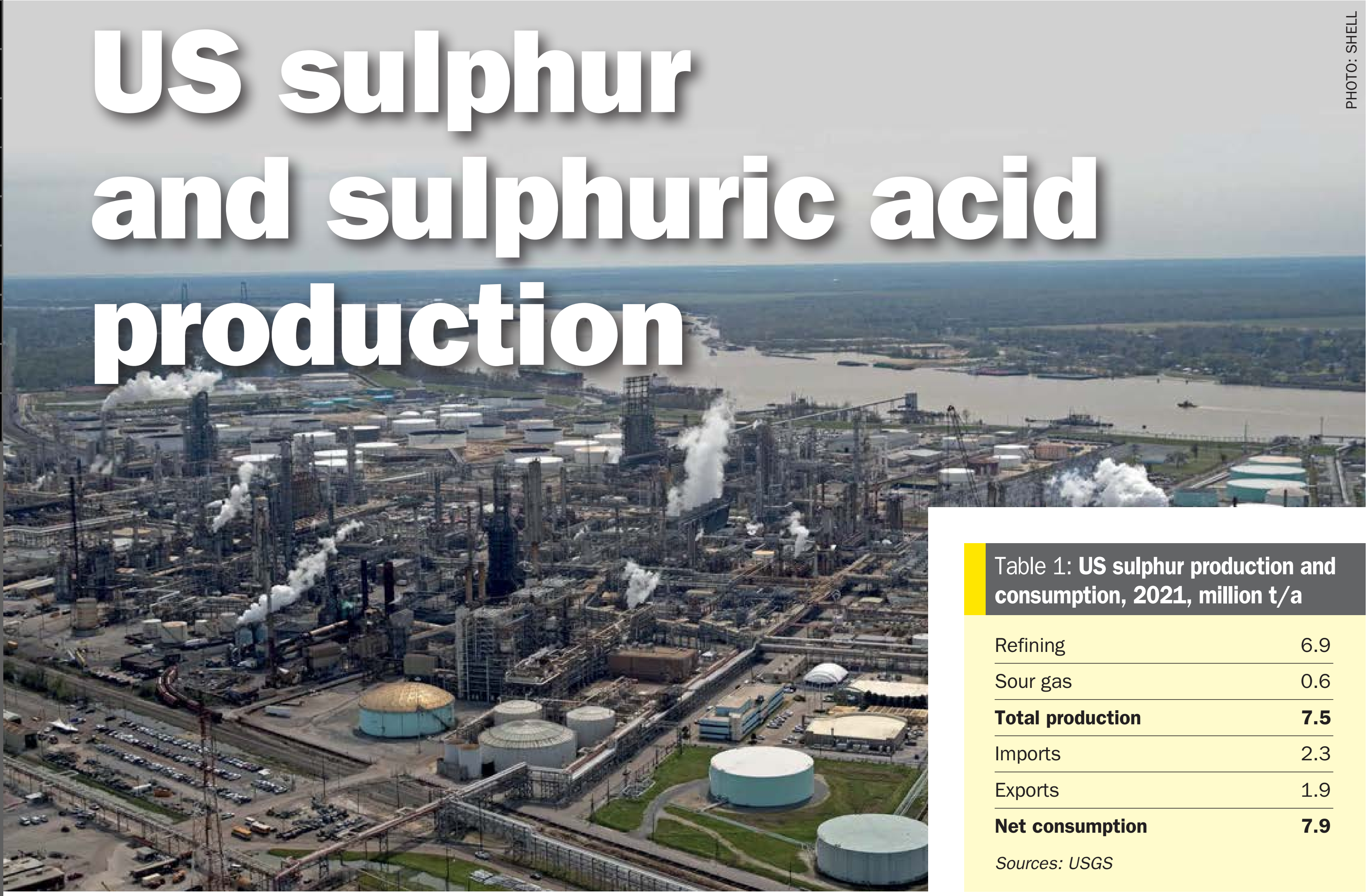

PHOTO: SHELL

Table 1: **US sulphur production and consumption, 2021, million t/a**

Refining	6.9
Sour gas	0.6
Total production	**7.5**
Imports	2.3
Exports	1.9
Net consumption	**7.9**

Sources: USGS

The US refining sector continues to face operating pressures with 1.3 million bbl/d of closures in the past three years, while sour gas sulphur production has recovered somewhat. Meanwhile, demand from copper and lithium leaching projects will increase use of sulphuric acid over the next few years.

Above: The Shell Norco refinery, Louisiana.

The US continues to be one of the world's largest producers and consumers of sulphur and sulphuric acid. Domestic production of sulphur and acid are both falling however, while demand may be set to increase due to metal processing.

Refining

As Table 1 shows, the refining industry is the main source of elemental sulphur in the US. US domestic oil production has been rising over the past decade, reaching 13.1 million bbl/d in early 2020, before covid related lockdowns and the resultant lack of fuel consumption for vehicles and aircraft led to a slump in consumption during 2020 to a low point of 9.7 million bbl/d in August. Since then there has been a steady recovery, climbing back to around 12.2 million bbl/d at present. Much of the rise has been due to the boom in tight oil production via fracking, which tends to produce fairly sweet fractions. However, US refinery sulphur capacity had risen significantly this century, from 26,600 st/d in 2000 to 34,100 st/d in 2010 and 41,900 st/d (approximately 12.5 million metric t/a) in 2020, according to US Energy Information Administration figures, as many refiners, especially on the Gulf Coast, invested in sulphur recovery capacity both to deal with tightening standards for sulphur content of fuels and to take advantage of the price spread between light sweet crude and sour heavy crude. In 2021 US crude imports came mainly from Mexico (13%) and Canada (10%), both sources of heavy, sour crudes – in Canada's case mainly as oil sands dilute bitumen, as described in the article elsewhere in this issue. The sulphur content of crude processed by US refineries has been generally on a rise over the past four decades, as shown in Table 2, though recent years have seen something of a slip as more sweet domestic crude is processed.

Taken together with imports and other inputs, US refinery throughput fell from 17 million bbl/d in 2019 to 14.7 million bbl/d in 2020, recovering slightly to 15.7 million bbl/d in 2021. The covid-related fall in refinery throughput led to a corresponding drop in US refinery sulphur recovery, from

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Table 2: **Average sulphur content of inputs to US refineries**

Year	Sulphur content (% w/w)
1985	0.91
1990	1.10
1995	1.13
2000	1.34
2005	1.42
2010	1.39
2015	1.45
2020	1.29

Source: US EIA

8.4 million t/a in 2018 to 7.0 million t/a in 2020 and 6.9 million t/a in 2021. US refinery sulphur output is concentrated in the Gulf Coast region (PADD 3), where 60% of sulphur recovery capacity is located. PADD 2 is next, with 20% of capacity, and PADD 5 with 14%. The other two regions each have only about 2.5% each.

One final factor on US sulphur recovery from refineries has been a spate of refinery closures in recent years. Around 1.3 million bbl/d of capacity has closed, including 600,000 bbl/d in Louisiana alone, in spite of some small expansions at existing sites. EIA figures suggest that US crude refining capacity fell to 17.94 million bbl/d at the start of 2022, down from 18.09 million bbl/d at the beginning of 2021, and the record high of 18.98 million bbl/d in 2020 before the pandemic took hold. This is the lowest that capacity has been since 2014. A variety of factors have been blamed for this, from increasing age of plant and rising maintenance requirements, damage caused by recent hurricanes, the impact of the covid collapse in demand, projections of weaker demand in future due to increasing use of alternative fuels, electric vehicles and increased fuel economy of vehicles, or from conversions to produce more renewable fuels, such as the Phillips 66 refinery in San Francisco. Since the Russian invasion of Ukraine, refining margins have actually been running at high levels and operating rates have been high to make up for reduced imports from Russia, but high prices at the pump has also led to some demand destruction. Even so, USGS figures for 1H 2022 show sulphur recovery from refineries up at 3.7 million tonnes, 416,000 tonnes up on the same period for 2021, potentially leading to a full year figure of 8.3 million t/a; the highest since 2018.

Sour gas

The other significant source of elemental sulphur in the US comes from sour gas processing. Though US sour gas processing has been undercut by the fracking boom of the 2000s, production had stabilised at around 600,000 t/a, before dropping to only 300,000 t/a in 2019 and 2020, recovering somewhat to 550,000 t/a in 2021. Most of this (75%) came from the PADD 4 and 5 region – the west coast and northern Rocky Mountains areas. Of the remainder, almost all came from gas processing along the US Gulf Coast.

Added to the sulphur from refineries, this gives a total recovered elemental sulphur figure of 7.5 million t/a in 2021 for the US. Half year figures for 2022 are 3.9 million t/a, up 0.4 million t/a on 2021. Net imports add another 400,000 t/a for a total supply figure of 7.9 million t/a for 2021, as shown in Table 1.

Sulphuric acid

In addition to the elemental sulphur, sulphuric acid is also produced from smelting operations within the US. This is mostly from copper smelting, though there is also some recovery from zinc and molybdenum operations. Acid production is about 1.8 million t/a. In addition to this, the US imported a further 3.3 million t/a of sulphuric acid in 2021, again mostly from Canada and Mexico, and exported 400,000 tonnes, for a net import total of 2.9 million t/a.

> **“Figures for 1H 2022 show sulphur recovery from refineries up at 3.7 million tonnes.”**

Sulphur and acid demand

The US phosphate industry has traditionally been the largest consumer of sulphur in North America, to make sulphuric acid for phosphate extraction. In the US, phosphate rock mining is concentrated in central Florida and Idaho, although there are also mines in North Carolina and Utah. US production of phosphate rock peaked in 1980 at 54.4 million metric t/a, and this had more than halved to 21.8 million t/a in 2021, as mines have become exhausted. Another 2.5 million t/a is imported. Almost all (about 90%) of US demand for phosphate rock is for fertilizer production. The rest goes mainly to animal feed, and some phosphoric acid is used in the food industry. North American production of phosphoric acid in 2020 was 6.3 million tonnes P_2O_5. US downstream phosphate production is mainly aimed at mono- and diammonium phosphate, accounting for 2.7 million t/a P_2O_5 and 1.0 million t/a P_2O_5 respectively. Growth in production of cheap finished phosphates elsewhere in the world, such as Saudi Arabia and Morocco, are affecting the North American market, combined with depleting resources at phosphate mines. The fall has seen considerable industry rationalisation and consolidation, with only four producers now still active: Mosaic, Nutrien, Simplot and Itafos, and only nine phosphate processing sites now in operation. However, the recent run of high phosphate prices has been a fillip for the US phosphate industry, encouraging higher operating rates.

Outside of the phosphate industry, there is sulphur demand to manufacture sulphuric acid for metal leaching and other industrial processes, including caprolactam, pulp and paper processing, and especially sulphuric acid use as an alkylation agent in refining – a field in which the US refining industry has been a pioneer. There is also around 2 million t/a of demand from copper leaching projects, mainly in the southwest of the US.

Looking forward, there are new copper leaching projects at Florence, Arizona, FCX's Lone Star project, also in Arizona, and Excelsior's Gunnison project, which could collectively add about 1.3 million t/a of extra acid demand by 2025. There are also several lithium projects for battery production, mostly in Nevada and Utah, which could add considerable additional demand for acid by 2024-5. Global lithium demand is projected to rise from 500,000 t/a in 2021 to 3-4 million t/a in 2030. CRU is predicting around 2.0 million t/a of additional acid demand for lithium production in the US by 2025.

Together with additional sulphuric acid demand for alkylation in refineries, this is likely to see US acid demand increase by over 3.5 million t/a by that time, as well as potentially some return from phosphate processing. With US sulphur and acid production falling, this is likely to mean additional imports of both sulphur and acid over the coming years. ■

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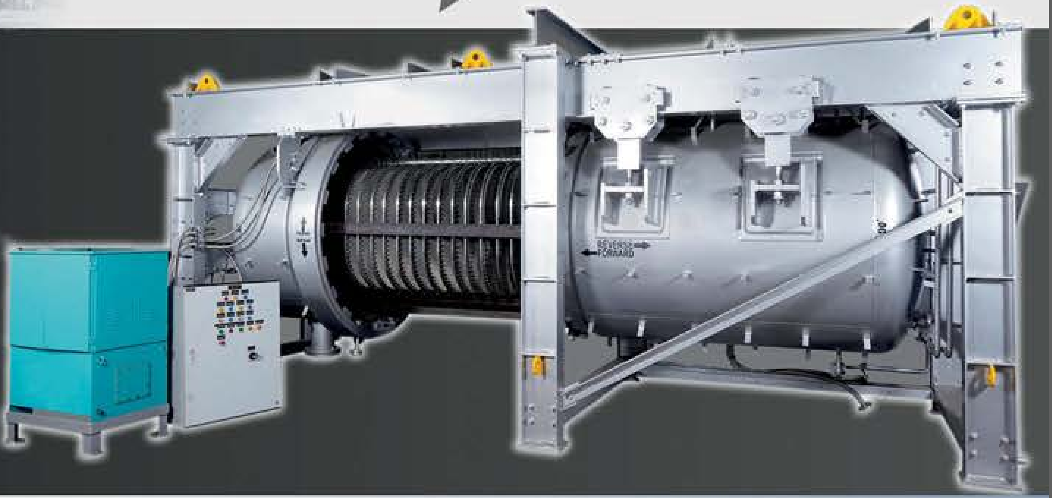

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- More than 50 installations

FILTRATION AREA from 5 m² to 200 m²

Sharplex have supplied several filters for molten sulphur filtration in sulphuric acid & sulphonation plants. Sharplex offers horizontal pressure leaf filter for molten sulphur filtration in Shell retraction design and Bundle retraction design.

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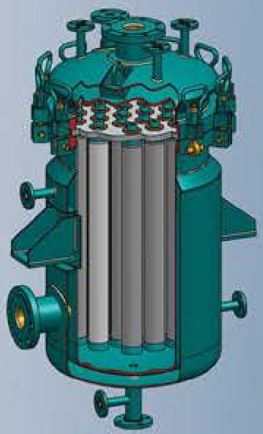

Cartridge type polishing filters are installed after main molten sulphur filters to remove traces of fine suspended particles ash and filteraids escaped from main filter, which may choke the downstream equipments in the plant.
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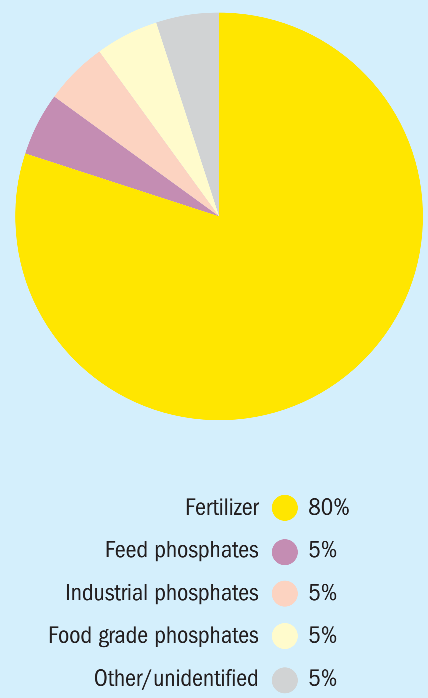
Industrial and feed phosphates

While most sulphuric acid demand for phosphates is based on the production of phosphate fertilizer, non-fertilizer sources of demand such as animal feed and industrial processes additionally represent a relatively small but growing sector of the market.

PHOTO: PXHERE.COM

Supplements for animal feed are a major sector of phosphate demand.

Fig. 1: **Phosphate demand by sector**



Source: IHS Markit

Phosphates are crucial for living creatures; the very backbone of the DNA molecule consists of phosphate chains, and phosphates are used plasma membranes, and as energy containing molecules such as adenosine phosphates. For this reason the phosphate industry is intimately bound up with food and agriculture. The market for phosphates is of course dominated by the use of phosphates as plant fertilizer, as shown in in Figure 1. Phosphate fertilizer represents 80% of the market for processed phosphates. However, in addition to this there are other important sectors, including phosphates used in animal feed (feed phosphates), and those used as additives in human food and drink (food grade phosphates). Finally, there is also the industrial phosphate sector.

Feed phosphates

Just as with humans, a lack of phosphorus in an animal's diet can lead to health problems such as bone malformation or rickets, as well as poor uptake of nutrition from feed and, in ruminants such as cows, reduced rate of milk production. Feed phosphates are therefore added to animal feed to ensure that the animal achieves optimal growth, fertility and bone development, alongside nutrients such as calcium and magnesium. They are often associated with improvements in the quality of meat and dairy products, including greater tenderness in meat, higher calcium content in milk and higher selenium content in eggs.

Most (around 90%) of the feed phosphates used in agriculture are calcium phosphates in various forms, including monocalcium phosphate, dicalcium phosphate, and tricalcium phosphate. The addition of calcium in the animal's nutrition is to assist bone development and other aspects of growth. Breeding animals (e.g., egg-laying chickens, sows and dairy cows) generally have higher calcium phosphate requirements. Younger livestock also benefit more from additives versus older herd members, as this helps to optimise bone growth during their early development stage.

Overall, world demand for feed-grade phosphate additives is estimated at

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around 7 million t/a of product or about 3 million t/a P_2O_5, equivalent to a 5% share of overall phosphorus demand, although it is worth remembering that, since 30-35% of the world's crop output is ultimately used as animal feed, animal husbandry in effect claims around 18 million t/ a P_2O_5 of phosphate demand, or roughly 30% of the total phosphate market. Geographically, feed phosphate demand is concentrated in China, with Europe, Brazil and the US also major consumers. These four markets represent about 80% of feed phosphate demand between them.

Growth in the sector is projected to be 3.5-4.5% AAGR over the next five years. Rising meat and meat product consumption in Asia is a major market driver, along with nutrient requirements for poultry production in the US and pork and poultry production in Europe. Increasing prevalence of livestock diseases is also driving increased consumption to improve animal health. Negative growth factors include the high cost of phosphates and the availability of alternatives such as phytase and distillers' and brewers' grains, and a slow switch away from meat consumption towards plant-based foods in the developed world.

In an article last year in our sister publication *Fertilizer International* (issue 505, Nov/Dec 2021), IHS Markit predicted an overall positive demand outlook for the feed phosphate sector, with growth likely in those markets that are currently consuming feed phosphates at a sub-optimal level, spurred on by rising populations and a still-growing appetite for animal protein in the diets of people in emerging economies. There may also be a boost in demand for aquaculture-grade products from the growing adoption of fish farming and commercial algae production, and uses such as shrimp farming in southeast Asia.

Phosphate food additives

Food grade phosphates are used as additives in a number of processed food products in order to incorporate a variety of different properties. For example, they act as emulsifiers in processed cheese and tinned soups; as a raising agent in baked goods; to hold moisture in processed meats such as sausages; as a flavour enhancer in carbonated drinks like colas; and as accelerants, dispersants, precipitants, flow agents, buffers, bases, acidity regulators etc. All of these combined are roughly equivalent to the market for animal feed additives; around 3 million t/a P_2O_5. Increasing consumption of processed foods is driving market growth of 5-5.5% year on year.

However, there are concerns about the amount of phosphate that is being consumed in some countries. The human body only absorbs around 50% of phosphates that occur naturally in food, but around 90% of processed phosphates/ High phosphate intake can be associated with kidney problems in vulnerable groups. The European Food Safety Authority has recommended a maximum levels of processed phosphate intake of 1,000 mg/day, and the US recommended daily allowance is 700 mg/day, but people who eat a lot of processed food routinely consume double that amount or more. At present there is no evidence to suggest that high phosphate levels are an issue for healthy individuals, but there are campaigns for better labelling of products in both the US and Europe.

> **"Rising meat and meat product consumption in Asia is a major market driver."**

Industrial phosphates

Industrial phosphates are used in a broad range of end uses including detergents and personal hygiene products. Phosphates and derivatives are also used in the construction industry. Polyphosphoric acid is used as a modifier for asphalt to prevent agglomeration, and tripolyphosphates are used in cement to delay setting. Sodium trimetaphosphate is used in plasterboard as a firming agent, and it is also used in paints to make pigments disperse more evenly. Phosphates are also used in the pharmaceutical industry as excipients (non-active carriers of the pharmaceutical), in water treatment for corrosion resistance and pH control, to prevent corrosion in metal finishing and electronics, and in flame retardant applications such as fire extinguishers, and flame retardant furniture and curtains.

Detergents used to be the largest end use for industrial phosphates, with sodium tripolyphosphate widely used as a chelating agent for sodium and potassium ions, leading to more efficient cleaning, as well as preventing corrosion and dispersing dirt particles. However, the subsequent presence of large quantities of phosphate in waste water led to algal growth in water courses into which waste water was drained and consequent eutrophication and effects on fish and other creatures. As a result, environmental pressure on the detergent industry to reduce the phosphate content of detergents, especially dishwasher tablets, has led to a significant decline in consumption in Europe and North America over the past decade. This has been balanced by a rise in use in countries such as China. Chinese consumption dominates the use of industrial phosphates, with around 50% of the market, with the US and Europe the next largest consumers at around 15% each. More recently, producers in North America and Europe where consumption has been declining have begun to identify new markets in food, horticulture, and water treatment applications, and overall industrial phosphate consumption is forecast to rise roughly in line with GDP.

One area which may see above trend growth however is in the battery sector. Phosphorus is a component of lithium iron (Fe) phosphate (LFP) batteries. A combination of low cost, low toxicity, high thermal stability and good electrochemical properties make LFP batteries a potential replacement for lead acid batteries in applications such as automotive and solar power, provided that charging systems are configured not to deliver excess charge. LFP batteries can sustain up to 10,000 charging cycles; roughly 10 times that of a lithium ion battery. Use is projected to more than double over the next five years.

Costs

The main raw materials for industrial and food phosphates are phosphate rock, merchant grade acid (MGA) and sulphur. Over the past two years, prices of these have all risen significantly. Phosphoric acid prices, which spent much of the 2010s at $600-700/t, peaked above $2,000/t in early 2022. These cost pressures encourage substitution, especially in the animal feed sector, where agricultural margins can be thin. Nevertheless, overall, non-fertilizer phosphate markets are likely to grow at 3-4% year on year over the next few years, roughly comparable with long term trend growth in the fertilizer phosphate sector.

CRU Sulphur + Sulphuric Acid Conference 2022

After two years of virtual events, the CRU Sulphur + Sulphuric Acid 2022 Conference & Exhibition will return to an in-person event at the World Forum, The Hague, 24-26 October 2022. CRU will be welcoming the global sulphur and sulphuric acid community to this premier annual event for networking and essential updates on the markets and technical developments that are influencing the industry.

Now in its 38th year, the CRU Sulphur + Sulphuric Acid 2022 Conference & Exhibition continues to be an essential annual forum for the global sulphur and sulphuric acid community to learn, connect and do business. Knowledge sharing is at the core of the event via the comprehensive technical programme, and connections made with participating industry experts and solution providers.

This year the expanded market outlook agenda features expert insights from CRU's analysis teams on major supply and demand markets, including sulphur, sulphuric acid and phosphates, plus additional industry updates from key players from across the supply chain.

The dual-stream technical agenda, covering technical updates on the production and processing of sulphur and sulphuric acid, will feature industry-leading presentations covering new innovations in process technology, materials and equipment developments, as well as practical case studies highlighting operational experience and improvement.

Running alongside the agenda will be an exhibition of world-class solution providers serving the sulphur and sulphuric acid industries.

In addition, this year CRU's Sulphur + Sulphuric Acid has been co-located with RefComm Europe, providing access to further networking opportunities with refinery professionals.

Agenda features at a glance

- 36 sulphur and sulphuric acid technical papers, including eight operator-led presentations
- 4 interactive workshops and roundtable discussions to delve deeper into practical issues
- 3 in-depth market outlooks to discover where sulphur prices are heading and more
- A panel discussion discussing supply chain issues affecting the sulphur market.

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Evening lights at Binnenhof palace, The Hague, Netherlands.

PHOTO: ADAM ZOLTAN/SHUTTERSTOCK.COM

Learn from the experts

Panel discussion

Sulphur supply chains have been hampered by impacts from Ukraine war sanctions, a bumpy green energy transition, labour shortages and ongoing drought. Moderators John Bryant, President & CEO, The Sulphur Institute, and Peter Harrisson, Principal Analyst, CRU Group, will lead a discussion from panellists from across the industry, who will describe their experiences and lessons learned in a review of the weighty new threats facing the industry.

Comprimo sulphur workshop

This practical hands-on workshop led by Comprimo experts will cover:

- Comprimo Insight: a digital tool to make your plant data work for you.
- Overview of sulphur recovery technologies with a recovery above 99.5%, highlighting the differences in capex, opex and CO_2 footprint.

Hydrogen safety panel

Moderated by Rick Davis, of Davis & Associates, industry panellists will be discussing:

- Theoretical considerations
- Explosion limits
- Explosion pressure and ignition
- Hydrogen formation
- Plant and equipment design considerations
- Risk mitigation

MESCon roundtable

A roundtable discussion on corrosion considerations for the sulphur plant operator.

Chemetics workshop

A sulphuric acid workshop led by experts from Chemetics. ■

Technical agenda

The technical agenda takes place over two days and is split into parallel sessions: sulphur and sulphuric acid. Topics will include: new technologies, process, and equipment applications that can improve production, reliability and safety; best practices, operational experiences and lessons learned; advances in digitalisation; instrumentation for better monitoring; and catalyst solutions.

Innovations driving sustainability

A key focus at this year's Sulphur + Sulphuric Acid Conference will be how sulphur and sulphuric acid producers can improve their emissions management and energy efficiency as part of the energy transition. There will be presentations on the technologies driving advancements in environmental and sustainability performance including options for carbon capture, hydrogen production, and carbon-free energy generation.

Sustainability presentations for 2022

Sulphur track

- **How about capturing CO_2 and generating H_2 via advanced sulphur recovery technology in this energy transition era?**
  Fluor Energy Solutions
  Energy experts around the globe are striving to minimise the usage of fossil fuels and maximise the usage of green energy resources in the current energy transition era. The oil and gas industry is also focussing on lowering its carbon footprint while generating blue hydrogen. This presentation provides results and discusses benefits of case studies demonstrating how a SRU/TGTU plant within sour gas facilities can facilitate capturing CO_2 and generating H_2, by implementing advanced sulphuy recovery technologies.

- **Recovery of hydrogen and CO_2 from sulphur plants**
  Comprimo, Worley
  The off gas from conventional SRUs in gas plants consists mainly of nitrogen, CO_2, hydrogen and water. The substantial emissions of CO_2 from these SRUs is coming under great scrutiny and the methods of reducing or eliminating CO_2 is being studied. This presentation will explore the options for CO_2 removal from SRUs in gas processing plats using oxygen enriched technology to remove nitrogen from the system and simplify the CO_2 recovery. Hydrogen recovery options will also be addressed.

Sulphuric acid track

- **How green is your sulphuric acid plant?**
  Chemetics Inc.
  The operation of sulphuric acid plants around the world increasingly requires owners/operators to assess and report on the environmental and sustainability performance of their assets. Process selection, equipment design and plant improvements once operation has started all play a role in maintain the license to operate. Traditionally the focus has mainly been on stack emissions, but recently other aspects of the plant design/operation like energy efficiency and carbon intensity have become increasingly relevant.

- **MECS® HRS™ Technology and carbonless energy generation**
  Elessent MECS Technologies
  Multiple sites featuring MECS® technology for sulphuric acid plants have been granted carbon credits through the addition of HRS™ technology, and as the economy of decarbonisation continues to develop, MECS anticipates that HRS™ will provide an increasingly attractive option for clients seeking to both improve the efficiency of their operational budgets and present a more sustainable vision of their organisations to relevant stakeholders around the world.

- **Road to sustainability – Preparing for energy transformation in the sulphuric acid industry**
  Metso Outotec

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Lessons learned combatting corrosion in a sulphur granulation plant

Mohamed Al Ameri, **Nuha Al Hajeri**, **Shyam Pandey**, and **Antonio Madeina**, ADNOC Sour Gas.

The purpose of this article is to emphasise the lessons learned by ADNOC Sour Gas in the material upgrading of the Shah sulphur granulation plant due to severe corrosion of the aluminium components. The sulphur granulation plant was commissioned in 2015 and consists of a total of 12 granulating systems used for solidifying and granulating the liquid sulphur. The study focused on the corroded areas, namely the GX plenum chambers, the lower section of the granulator exhaust stack, the scrubber inlet and the discharge ducting.

Root cause analysis (RCA) was undertaken to understand and identify the cause of the corrosion. The study indicated that the corrosion of aluminium components is typical of wet acidic attack. Wet acid is produced in the granulator drum where atomised liquid sulphur is quenched by demineralised water to produce sulphur granules. The highly acidic vapours travel further to the exhaust stack through scrubber.

This article discusses the typical damage mechanism indicating the source of acidic species, their generation, corrosive attack and mitigation under plant operating conditions.

It was observed that at full capacity the plant utilised all 12 granulators, resulting in insufficient time for cleaning and acid water disposal. Therefore, aluminium, which is a universally recommended material for sulphur granulation plants, was suffering severe material degradation. This has led to a detailed material review of the process requirements. The entire plant equipment was segregated into two parts as per the severity of the corrosion. After the engineering study, the plenum chamber and associated piping to the scrubber duct was upgraded with stainless steel SS316L having better corrosion resistance. The outlet piping from the scrubber to the FD fan and exhaust stack were affected the most, and it was recommended that these areas be repaired with GRVE material.

The current arrangement with upgraded material will assist all new projects to design plants either with enough unit redundancy for routine cleaning or to use more resistant materials to combat corrosion.

Fig. 1: **Corroded scrubber outlet duct at sulphur granulation Plant**

Fig. 2: **Bottom of stack completely corroded at sulphur granulation plant**

PHOTOS: ADNOC

Fig. 3: **Temporary repairs to scrubber outlet duct**

PHOTOS: ADNOC

Introduction

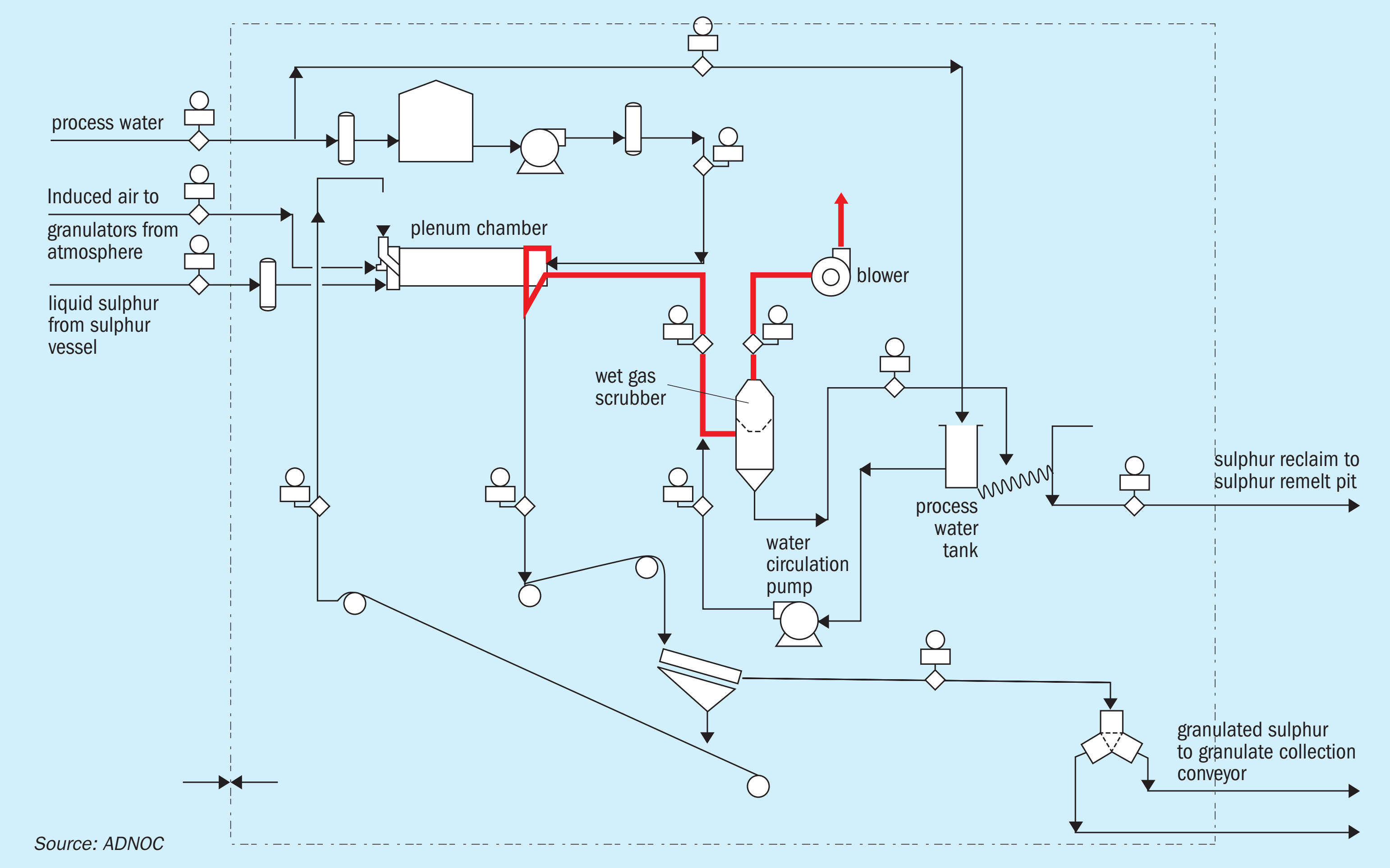
ADNOC Sour Gas operates 12 No. GXM1 sulphur granulation units as part of the Shah sulphur granulation plant. The first indication of corrosion on the wet scrubber exhaust ducts was reported on August 2016. In 2017, ADNOC Sour Gas noticed excessive corrosion in the GX plenum chambers, lower sections of the exhaust stacks, below the exhaust fan discharge line and in the scrubber inlet and outlet ducting in the sulphur granulator units (Figs 1 and 2).

Since the problem was at the initial stage, the corroded areas were repaired using patch plate and putty in consultation with the vendor (Fig. 3). Later the decision was made to replace the corroded areas with more resistance material.

In mid-2018 an RCA was undertaken to understand the cause of the corrosion. The RCA indicated that low pH process water is carried through the wet scrubber discharge and is later condensed or deposited on the duct walls. The original ducting is made from 6-mm thick aluminum grade 6061-T6.

Fig. 4 is a typical schematic diagram showing the affected area/piping marked in red in the granulation unit.

Fig. 4: **Process flow diagram for granulation and wet scrubber section**



Source: ADNOC

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Table 1: **Design process operating conditions**

Liquid sulphur supply temperature, °C	130
Liquid sulphur supply rate, m^3/h (t/h)	27.9 (50)
Liquid sulphur supply pressure, barg (depends on nozzle configuration and piping lengths)	11.96 – 23.05
Drum outlet flow rate t/h	56
Fines recycle rate, t/h	6
Granulated sulphur production rate, t/h	50
Product temperature, °C	
Out of drum	71
After screen separator	67
Fines recycle product temperature, °C (at entry to drum)	60
Drum operating speed, rpm (manually set by operator from DCS console during commissioning to optimise product quality)	10 – 12

Source: ADNOC

Table 2: **Process water specification**

Parameter	Requirement
pH	6 to 8
Total hardness as $CaCO_{3,}$ ppm	< 100
Total dissolved solids, ppm	< 500
Iron as Fe, ppm	< 0.1
Sulphate as $SO_{4,}$ ppm	< 100
Hydrogen sulphide, ppm	< 0.1
Hydrocarbons, ppm	< 1.0
Total suspended solids, ppm	< 5
Chlorides, ppm	< 10

Source: ADNOC

Overview of existing granulators

The Shah Plant of the Abu Dhabi Gas Development Company (ADNOC Sour Gas) is located 210 km Southwest of Abu Dhabi City. This facility consists of onshore wells and production systems, gathering and transfer pipelines, a gas processing plant, product pipelines, and a Sulphur granulation plant. The sulphur granulation plant is located approx. 15 km from the main gas plant.

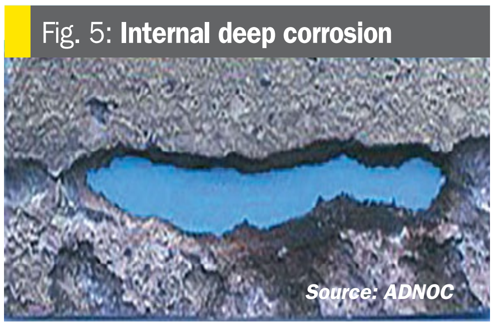
The 12 sulphur granulator units consist of the following major sub systems:

- sulphur filter;
- sulphur day tank;
- granulation drum;
- vibration screens;
- collection conveyor;
- scrubbers;
- exhaust unit.

Process details

Liquid sulphur from sulphur storage tanks is fed to the sulphur granulation plant and atomised in the granulator drum. Process water is sprayed through a sparger to atomise the sulphur and form sulphur granules. The sulphur granules are collected at the end of the granulator and sent to export/rail loading. The sulphur fines along with water vapour from the granulator drum are sucked into the wet scrubber. Vapours are vented from the top through FD fans and wet sulphur fines are collected in setting tank (TK-5103) where water and sulphur are separated. The separated water is again recirculated as scrubbing water to the wet scrubber. Periodic draining of water from TK-5103 is required to control the pH above 5 of circulating scrubber water, as per the unit operating manual. The collected sulphur fines are sent to the remelter pits.

Fig. 5: **Internal deep corrosion**



Source: ADNOC

A sample point is provided at the cooler (7030-E-5101) and a pH analyser (7030-AT-5500) is provided on the common discharge line of the wet scrubber recycle pumps (7030-P-5103A/B). Low pH alarm is set at 4. Normally, the process water pH is between 7.5 and 8.5 in the storage tank.

The design process operating conditions are shown in Table 1.

Water specifications

Process water generated from the reverse osmosis unit is used for makeup in the process water tank (TK-5103), which is used in the wet gas scrubber. The specification for the process water used is shown in Table 2.

In 2016, there was a proposal to switch over from process water to utility water, however this was stopped after a short period as the chloride content in utility water could initiate pitting corrosion in the aluminium and SS component.

Evaluation of granulators

The problem was raised to the vendor for route cause analysis. The company has also carried out internal inspections on corroded samples drawn from the plant. The outcome of the analysis includes:

The material of construction of the affected piping of the granulator is 98% aluminium (ASTM B209 grade 6061). This is the recommended material by the licensor ENERSUL.

The corroded surface of the piping internal has shown deep corrosion (Fig. 5) leading to material loss.

Failure mechanism

The reason for such failures is related to two phenomena, acid corrosion and carbonate/chloride corrosion (water quality – dissolved carbonates etc. in water.

Acid corrosion

When dissolved acid gases (SO_2 and SO_3) in the liquid sulphur feed to the granulators or generated in the granulator come into contact with water a weak acid is formed (see equations 1 and 2).

$$SO_2/SO_3 + H_2O \rightarrow HSO_3/H_2SO_4 \quad (1)$$

$$H_2SO_4 + Al_2O_3/Al \rightarrow AlHSO_3 + H \;/\; Al_2SO_4 + H_2O \quad (2)$$

This has been confirmed by operation as the pH level was found to be below 4.

The acid environment was the root cause of the corrosion of the aluminium piping.

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Fig. 6: **Corrosion of aluminium piping according to pH**

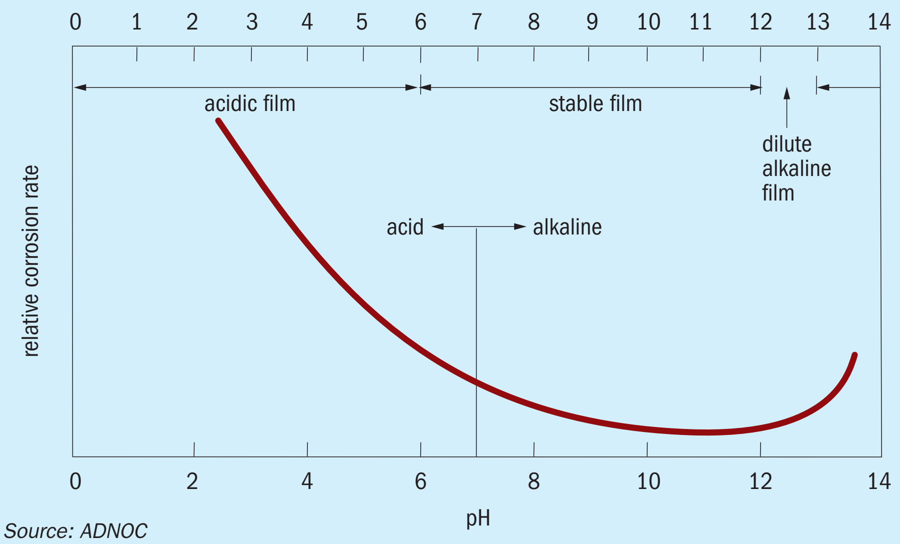

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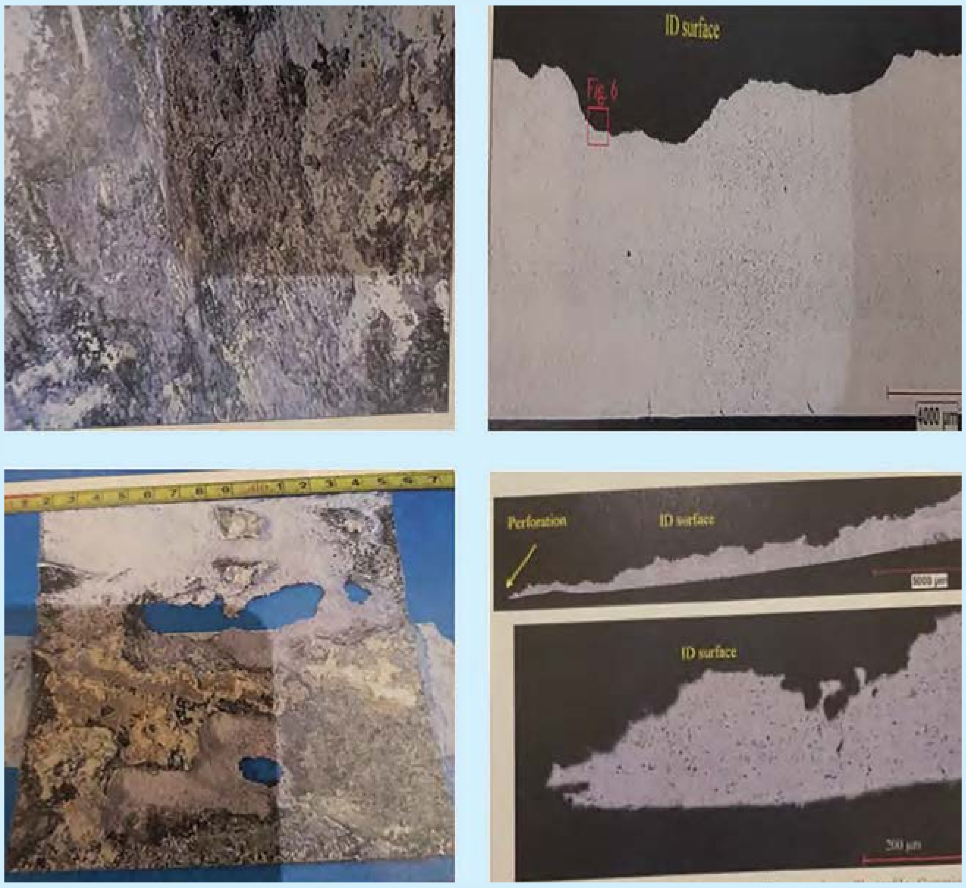
Fig. 7: **Field samples showing surface profiles and the wall thickness significantly affected**



PHOTOS: ADNOC

Wet sulphuric acid corrosion and erosion

Water and SO_3 have a good affinity for each other. When water is available, they combine rapidly to form sulphuric acid (H_2SO_4). The low pH acidic water is a major factor associated with this corrosion mechanism. The low pH water has a devastating effect on the life of the components handling them if they are not immune to this type of damage. Since the existing material was aluminium, it can potentially damage the protective aluminium oxide layer (Fig. 6). The situation is aggravated further by higher flow rates which can also cause erosion especially at bends.

Carbonate /chloride corrosion

The SO_2 generated from the granulator operation was building up acidity through the plenum chamber, downstream of the duct and scrubber system in the presence of water and moisture, resulting in aluminium corrosion. Various options such as ADWEA water were tried to absorb the acidity but it did not help. The material selected should not be dependent on water quality.

Comparison of two granulation units in two different fields

A comparison was conducted in order to conclude the reason of the corrosion phenomena in the granulation unit. The two fields had a similar problem regarding water quality, where the pH drops below 4 for short periods of operation. However, the damaged areas in Field X were different to that of the Shah granulation units. Fig. 7 shows field samples where the wall thickness has been significantly affected. The type of corrosion in Field X is termed erosion corrosion whereas in the Shah granulation units it is severe intergranular corrosion (typical of acid attack).

Table 3 demonstrates the main differences between Field X and Shah granulation plants.

From Table 3 it can be concluded that the material degradation issues in the Field X and Shah granulation plants are completely different from each other and cannot be compared. As a result, the mitigation action for Field X is to cut and replace the corroded bottom section of exhaust stack (1 m from bottom) with like-for-like material – aluminum 6061 T6 using flange and bolt (replaceable part). The bottom section (x4) will be kept ready with internal coating and will be replaced as and when required. This option was selected as they have redundancy of units (only 7 out of 12 are in use at a time).

Engineering studies

The corrosion rate of aluminium tends to increase significantly below a pH of about 4 as shown in Fig. 8. In addition, as shown in Fig. 8, the corrosion rate of aluminium increases in environments where the pH level is above 8.

As shown in Table 4, SS 316L behaves differently under different concentrations of H_2SO_4 with respect to different temperatures in the presence of free liquid[1]. The concentrations include the following typical ranges:

- dilute acid concentration: 0 to 20%
- intermediate acid concentration: 20 to 70%
- strong acid concentration: more than 70%

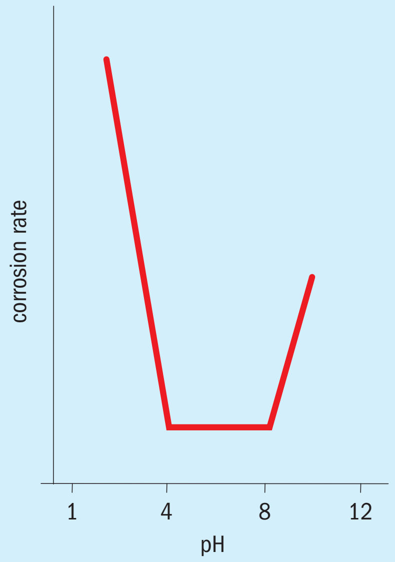
Table 3: **Comparison of Field X and Shah granulation plants**

	Shah granulation plant	Field X granulation plant
Design pH level	7-8.5	7-8.5
Actual pH level	<4	<4
Capacity	100%	≈ 60% where not all granulators are in duty (7 out of 12).
Damage result	Perforation and heavy metal wall loss.	Wall thickness loss 25%. No perforation.
Affected areas	The outlet piping of the granulator drum to the scrubber exhaust stack.	The bottom of the stack (10%), 1 m from bottom (10 m height)

Source: ADNOC

However, the above ranges are only applicable for sulphuric acid handling and storage systems which involve frequent dilution and concentrated H_2SO_4 cycles in the presence of free liquid water. The possible cause of previous liquid carryover within the outlet duct from the plenum chamber could be either due to condensation (with lack of insulation) or due to liquid carryover as the plant was operating at maximum capacity. As shown in Fig. 4, within the sulphur granulation unit, the outlet duct and plenum chamber handle only fine granules mixed with air with no free liquid. Therefore, the handling of H_2SO_4 will not be a major concern for stainless steel in this part of the process stream. Thus, the iso corrosion curves[2] involving H_2SO_4 concentration for stainless steels is not applicable. This is also in line with the condition of SS 316L in manufactured wet scrubbers and associated assembly such as inlet venturi, elbow etc installed within the 12 GX units. Overall, the recommended metallurgy applicable for the plenum chamber and outlet duct from the plenum chamber is stainless steel. The grade of stainless steel suitable for the plenum chamber and outlet duct from plenum chamber is ASTM A240 SS 316L with at least 2.5% molybdenum content.

Fig. 8: **Effect of pH on the rate of corrosion on aluminum, lead and zinc**



Source: ADNOC

At the outlet duct from the wet gas scrubber, the presence of liquids can be from condensation or carry over from the process. It can also be due to uprating of the plant at maximum capacity. The corrosion mechanism will be wet sulphuric acid corrosion and erosion. The outlet duct from the wet scrubber transports exhaust gases such as SO_2 and H_2S. Overall, considering the corrosiveness of fluid towards the aluminium stack, it would be prudent to use a more resistant material. Based on an extensive literature review, glass-fibre reinforced vinyl ester (GRVE) was selected. Moreover, the cured resin glass transition temperature (Tg) of GRVE shall

Table 4: **316 SS corrosion rates at different sulphuric acid concentrations**

Acid concentration (wt-%)	316 SS corrosion rate, mpy								
	86°F			104.5°F			140.5°F		
	2 ft/s	6 ft/s	7 ft/s	2 ft/s	6 ft/s	7 ft/s	2 ft/s	6 ft/s	7 ft/s
98	5	10	15	15	30	45	100	200	300
92.5	10	20	30	30	-	90	400	800	999
87	20	40	60	50	100	150	800	999	999
82	50	100	150	400	800	999	999	999	999
75	300	600	900	999	999	999	999	999	999
65	600	999	999	999	999	999	999	999	999
50	900	999	999	999	999	999	999	999	999
30	200	400	600	999	999	999	999	999	999
15	30	60	90	60	120	180	200	400	400
8	10	20	30	30	60	90	80	160	240
3.5	5	10	15	20	40	60	40	80	120
2	5	10	15	5	10	15	10	20	30

Source: ADNOC

Table 5: **Material thickness of equipment items**

Equipment/item	Existing metallurgy		Recommended metallurgy		
	Material	Total thickness (mm)	Material	Total thickness required (mm)	Total standard thickness (mm)
Plenum chamber	Aluminium	8	ASTM A240 SS 316L	5.77	6
Outlet duct from plenum chamber	Aluminium	8	ASTM A240 SS 316L	6	5
Outlet duct from wet scrubber	Aluminium	8	GRVE	9.4	-
Exhaust stack	Aluminium	8	GRVE	9.1	-

Source: ADNOC

be greater than 120°C and a UV stabiliser additive shall also be added to the resin for external UV protection of the GRVE stack. Therefore, Derakane 470-300 was selected as the GRVE grade suitable for this service.

The flowrate considered for materials selection was 18,000 Nm³/hr. From the corrosion perspective, the main issue before was the increased flow rate pushing the corrosion problem downstream, i.e., forcing acidic water into the duct and stack where it would corrode the aluminum. The SS 316L wet scrubber and inlet venturi duct to the wet scrubber did not seem to be affected by this water and should be the same for the stainless steel plenum chamber and outlet duct from the plenum chamber. It is also worth considering the velocities to evaluate the potential for erosion. Considering the previous and latest flowrate, the increase in velocity at the inlet duct to the scrubber is not significant. Erosion would not be applicable at these velocities, especially when GRVE is recommended for the exhaust stack and outlet duct of wet scrubber.

Calculations

The thickness of the aluminium was 8 mm, ADNOC Sour Gas requested the contractor to conduct a detailed study to confirm the thickness of SS 316L and GRVE. Table 5 shows the total thickness for the plenum chamber, outlet duct of plenum chamber, outlet duct from wet scrubber and exhaust stack. The total standard thickness given in Table 5 is for the plate material of respective ASTM A240 SS 316L grade.

The metallurgy recommended in Table 5 is for a service life of 30 years for the respective items. It is also recommended that a H_2SO_4 resistant veil or single protection layer is added to the GRVE to protect against the occasional presence of H_2SO_4. The glass transition temperature for the cured resin of GRVE should be greater than 120°C and a UV stabiliser additive should also be added to the resin for external UV protection of the GRVE stack. Derakane 470-300 is the recommended commercial resin grade of GRVE suitable for the current service in the outlet duct of plenum chamber and exhaust stack. The higher GRVE thickness at the outlet duct from the wet scrubber compared to the stack is due to the partial vacuum conditions within the duct.

Conclusion

In conclusion, aluminium components were replaced based on the engineering study. As the results showed and as highlighted in Fig. 8, aluminium is not a suitable material when the process and operation cannot be maintained at a pH level of 4 and above. In addition, from a corrosion perspective, the main issue before was the increased flow rate pushing the corrosion problem downstream, i.e. forcing acidic water into the duct and stack where it would corrode the aluminium. The SS316L wet scrubber and the inlet venturi duct to the wet scrubber was not affected by this water and now it's the same for the stainless-steel in the plenum chamber and the outlet duct from the plenum chamber. Considering the previous and latest flowrate, the increase in velocity at the inlet duct to the scrubber is not significant. Therefore, erosion is not applicable at these velocities.

Outcomes

The outcome, as concluded by the commissioned granulation units and the engineering study, demonstrates that aluminium with a low pH level below 4 cannot withstand this process and the corrosion rate was accelerated. Therefore, stainless steel as in the wet scrubber and inlet venturi which were originally constructed with SS 316 are in good condition since the commissioning of the granulation units in 2014. Important lessons have been learned from this study that could be relevant for other projects and plants. The current arrangement with upgraded material will assist all new projects to design plants either with enough unit redundancies for routine cleaning or to use more resistant material to combat corrosion.

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Acknowledgement

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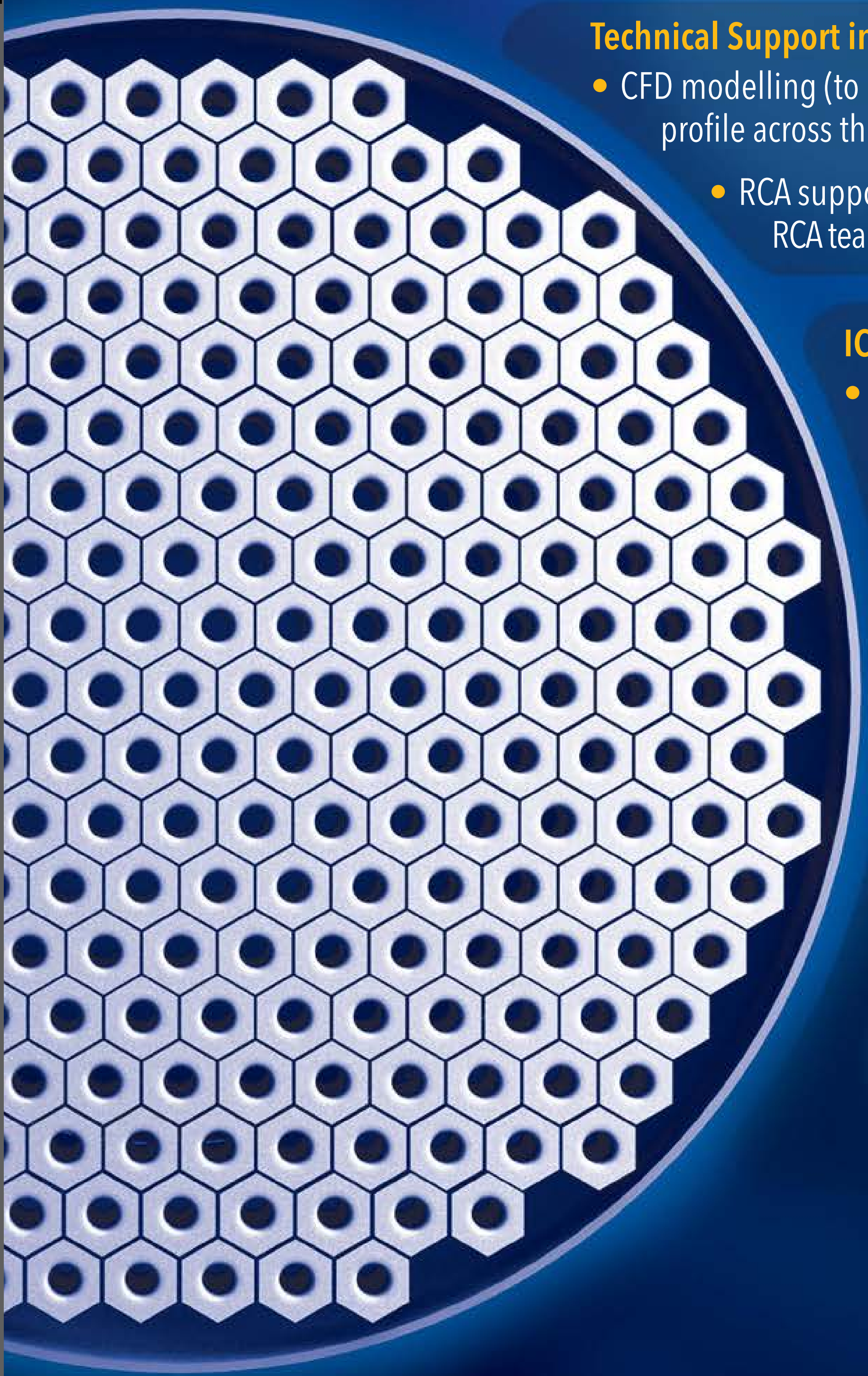

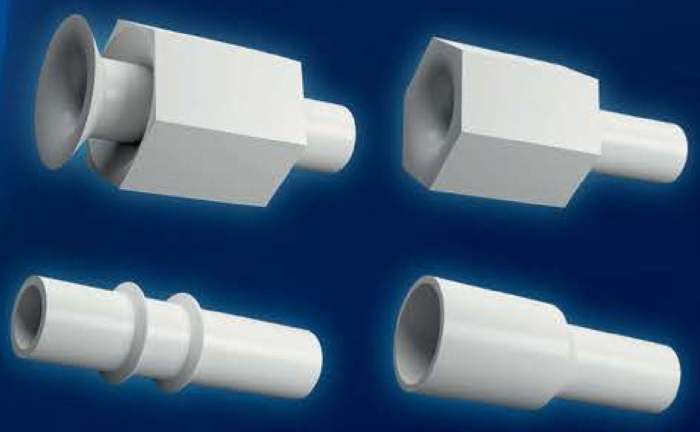

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Claus catalyst performance at end-of-run conditions

Temperature dependent rate constants for the hydrolysis of CS_2 and COS across Claus Al_2O_3 and TiO_2 catalysts are valuable tools for the design and optimisation of new, as well as existing, sulphur recovery units. In this context, Alberta Sulphur Research Ltd (ASRL) has measured CS_2 and COS hydrolysis rates over a range of temperatures for both Al_2O_3 and TiO_2 catalysts under start-of-run and, more recently, end-of-run first converter conditions. In this article **Christopher Lavery, Dao Li, Ruohong Sui,** and **Robert A. Marriott** of ASRL report on their methodology and the utility of the kinetics calculated from their data and draw comparisons between the start-of-run and end-of-run results.

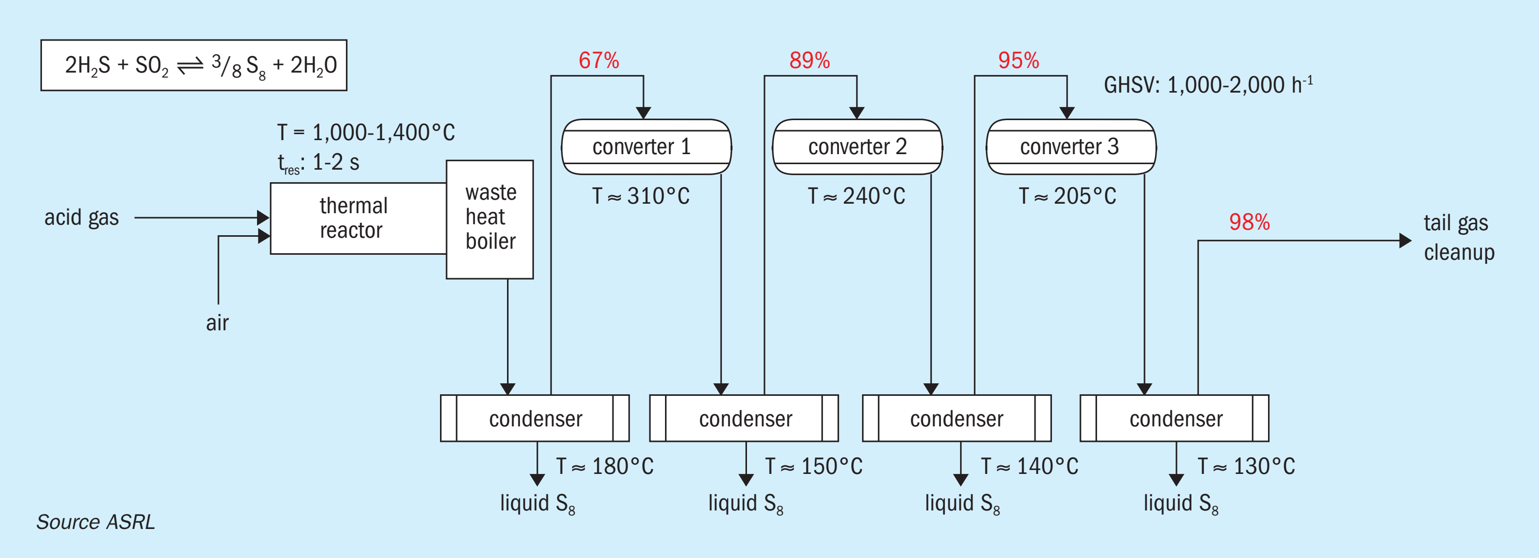
The modified Claus process is an equilibrium limited system whereby hydrogen sulphide is converted to elemental sulphur and water across a thermal reactor and several catalyst beds operated at successively lower temperatures (Fig. 1). A theoretical sulphur recovery of 98% is possible with three catalyst beds; however, sulphur recovery efficiencies of up to >99.9% can be obtained if implemented in combination with the appropriate tail gas cleanup (TGCU) technology. However, such high recoveries require both the thermal and catalytic stages to operate at optimal efficiency. This is complicated by acid gas contamination with impurities such as hydrocarbons (gas plant scenario) and/or ammonia (refinery scenario). Furthermore, the amount of hydrocarbon contamination has a marked influence on concentrations of both carbon disulphide (CS_2) and carbonyl sulphide (COS) that form within the thermal reactor and end up reaching the Claus catalyst beds[1]. At thermal reactor temperatures, CS_2 can be formed from direct reaction between hydrocarbons and elemental sulphur as shown in reaction 1. While most COS arises from recombination of CO and sulphur upon cooling of these species in the waste heat boiler (reaction 2), there are a multitude of other interlinked transformations at play that will influence this overall reaction which may also lead to COS formation[2].

$$CH_4 + 2S_2 \rightarrow CS_2 + 2H_2S \qquad \text{(reaction 1)}$$

$$2CO + S_2 \rightarrow 2COS \qquad \text{(reaction 2)}$$

Although some destruction occurs in the thermal reactor, any extraneous CS_2 and COS that persist through the thermal

Fig. 1: **Simplified schematic of the modified Claus process with corresponding sulphur recoveries after each stage in red**



Source ASRL

Fig. 2: **Simplified schematic of the ebullated sand bath catalyst reactor**

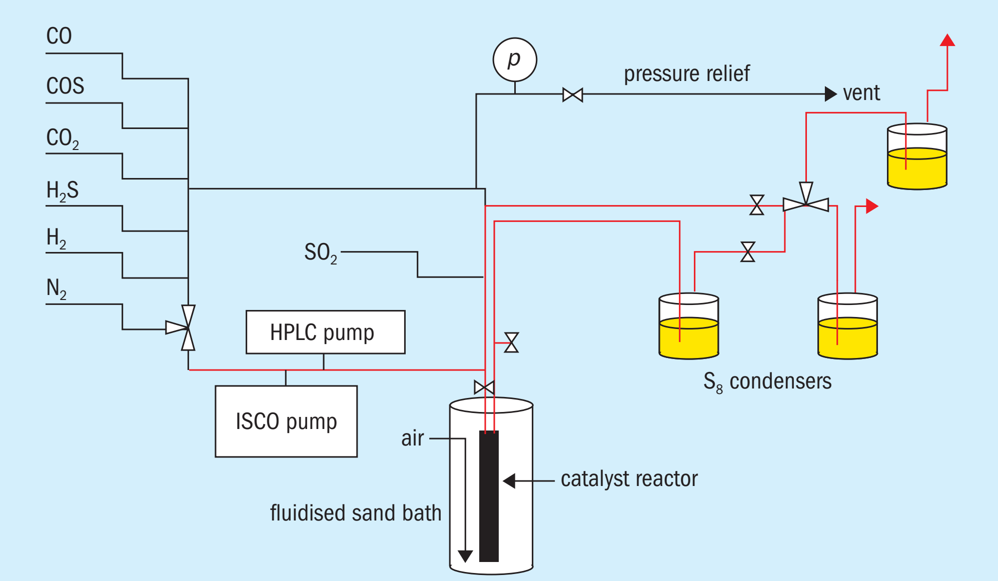


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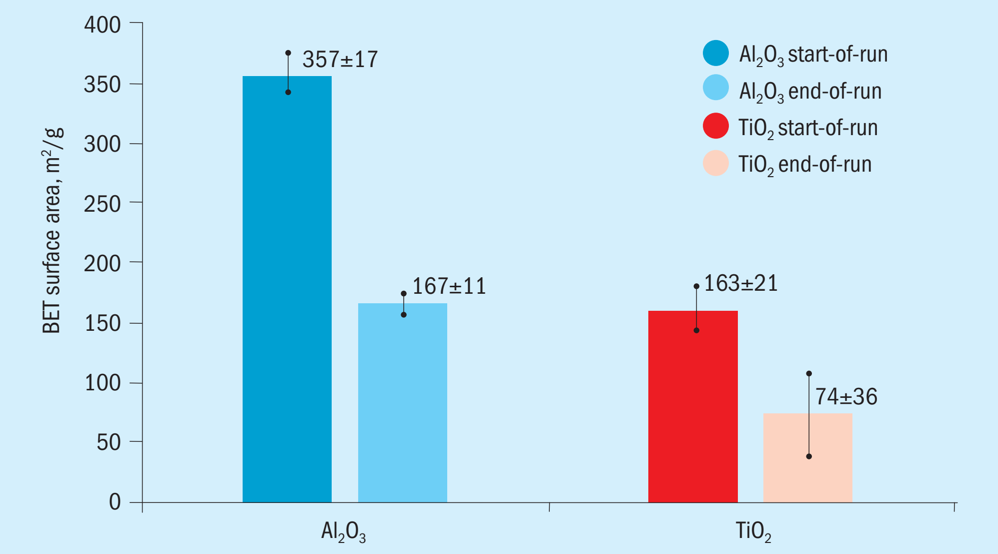
Fig. 3: **Surface area reduction upon end-of-run conditioning**



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reactor and waste heat boiler must be destroyed across the catalytic converters according to reactions 3 and 4, respectively.

$$CS_2 + 2H_2O \rightarrow 2H_2S + CO_2 \quad \text{(reaction 3)}$$

$$COS + H_2O \rightarrow H_2S + CO_2 \quad \text{(reaction 4)}$$

Equilibrium allows for quantitative CS_2 destruction and very high COS (>99%) conversions. However, reactions 3 and 4 typically operate in the kinetic regime, i.e., below equilibrium conversion, under industrial Claus conditions. Therefore, the temperature dependent rate constants for the hydrolysis of CS_2 and COS across Claus Al_2O_3 and TiO_2 catalysts are valuable tools for the design and optimisation of new, as well as existing, sulphur recovery units. Indeed, in some cases, up to 50% of sulphur recovery losses can be attributed to inefficient CS_2 and COS destruction[3].

Materials and methods

For safety reasons, the laboratory equipment discussed below is housed within a ballistic ventilated walk-in bay containing H_2S and SO_2 detectors which shut off air operated supply gas valves when in high-alarm (≥10 ppm).

All experiments were executed in a vertical stainless steel fixed-bed reactor with a 2.5 cm o.d. × 39.4 cm length and an i.d. of 2.1 cm that has been described previously and is shown schematically in Fig. 2[4]. In short, the reactor temperature was controlled isothermally (± 1°C) over its full length by means of an air-ebullated sand bath. Isothermal control was confirmed by a series of six axially located thermocouples (not shown in the schematic). Any elemental sulphur formed during experimental runs was removed by condensation with in-line sulphur traps ($T \approx 50°C$).

For each of the experiments, the stainless-steel reactor was charged with either 25 mL of Claus Al_2O_3 or TiO_2 catalyst. A suite of experiments consisted of measuring CS_2 and COS hydrolysis at 330, 300 and 260°C, with total flow rates corresponding to gas hourly space velocities (GHSVs) of 5,000, 2,400, 1,440 and 1,000 h^{-1} (T_{ref} = 25°C and p_{ref} = 1 atm). These GHSVs corresponded to actual catalyst contact times of i) 0.35, 0.73, 1.25 and 1.75 s at 330°C; ii) 0.36, 0.77, 1.31 and 1.84 s at 300°C; and iii) 0.40, 0.82, 1.41 and 1.98 s at 260°C. The composition of the representative first converter feed employed was 58.1 % N_2, 7.9 % H_2S, 4.0 % SO_2, 30 % H_2O and either 0.1% CS_2 or 0.1 % COS. By measuring CS_2 and COS conversion under each set of experimental conditions described above, the corresponding pseudo-first order plots were prepared.

Prior to performing any experiments, the fresh Al_2O_3 or TiO_2 was pre-sulphated at 320°C by flowing a feed consisting of 58.0 % N_2, 8.0 % H_2S, 4.0 % SO_2, and 30.0 % H_2O for eight hours (GHSV = 1000 h^{-1}). In the start-of-run experiments, this was followed by a 16-hour hydrothermal ageing process at the same temperature and GHSV but with a feed containing 71.5 % N_2, 9.5 % CO_2 and 19 % H_2O. To simulate end-of-run conditions, the hydrothermal ageing temperature was increased to 500°C. On average, this higher temperature resulted in a ca. 50% surface area reduction compared to the fresh material (Fig. 3).

Using CS_2 as an example, conversions were calculated according to equation 1,

$$\%\,CS\ \text{conversion} = 100\left\{1 - \frac{x_{prod}\,(CS_2)\,x_{feed}(N_2)}{x_{feed}\,(CS_2)\,x_{prod}(N_2)}\right\} \quad \text{(equation 1)}$$

where x_{feed} and $x_{prod.}$ are the mole fractions in the feed and product streams respectively. This approach uses the inert N_2 as an internal standard, to correct for molar changes in the product stream due to either reaction or intentional removal of condensable products (sulphur and H_2O).

Fig. 4: **Start-of-run versus end-of-run conversions at 330°C. Error bars show the standard deviation of results from multiple catalysts**

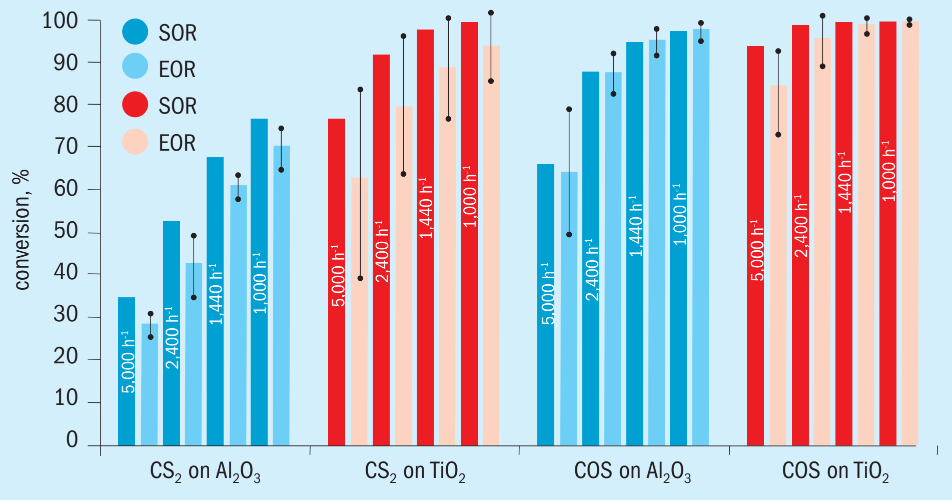

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Fig. 5: **Start-of-run versus end-of-run conversions at 300°C. Error bars show the standard deviation of results from multiple catalysts**

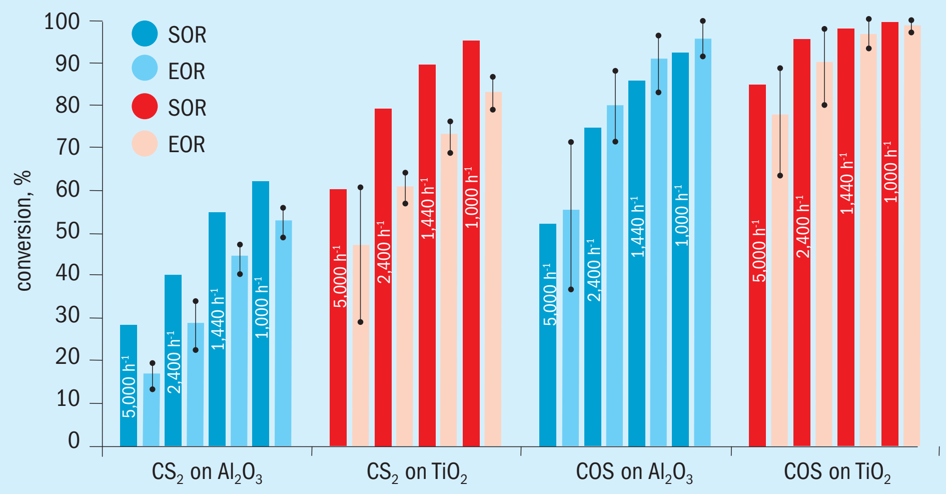

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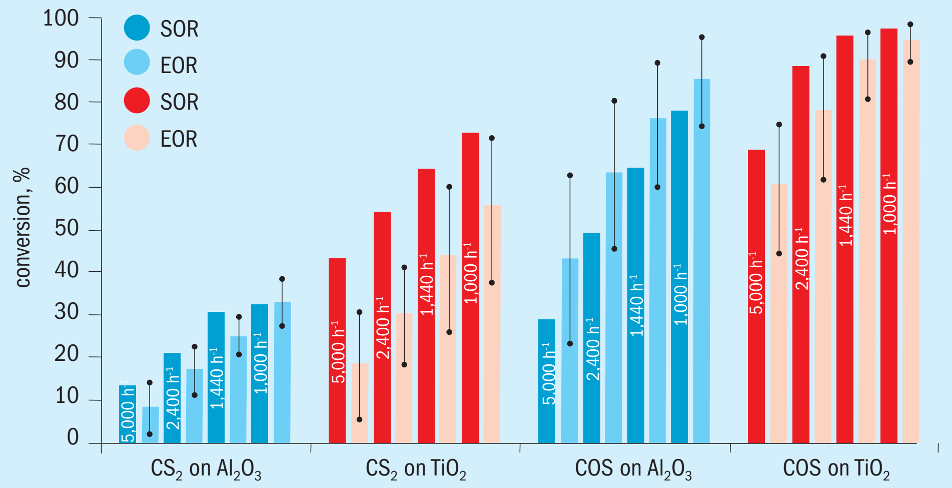
Fig. 6: **Start-of-run versus end-of-run conversions at 260°C. Error bars show the standard deviation of results from multiple catalyst**



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Results and discussion

A comparison of previously acquired CS_2 and COS conversion data, under start-of-run conditions, to the more recently obtained end-of-run data is presented across Figs 4-6. While only one Al_2O_3 and one TiO_2 material were assessed in the start-of-run experiments, several different commercially available samples of each were tested in the end-of-run studies. As such, the end-of-run conversions displayed in Figs 4-6 are an average of the performances, with the associated standard deviation (shown by the error bars), offered by the full range materials. As can be seen, in all instances TiO_2 provided superior performance compared to Al_2O_3 and, under analogous conditions, COS conversion levels were higher than those for CS_2. As expected, conversion levels for both CS_2 and COS decreased with increasing GHSV and decreasing temperature. This is typical behaviour for reactions operating in a chemically limited regime. In some instances, particularly for COS conversion across Al_2O_3, the average end-of-run of conversions were higher than the corresponding start-of-run conversions. This is simply because some of the new catalysts included in our end-of-run studies offered better conversions than the one material that was selected for use in our initial start-of-run tests. However, if each individual material were tested under start-of-run conditions, the conversions would be higher than the corresponding end-of-run conversions. The differences in performances between the various commercial materials that were tested was most noticeable under the more stringent test conditions (i.e., in the high GHSV and low temperature experiments).

With the above data in hand, ASRL first prepared the pseudo-first order plots for CS_2 and COS conversion over Al_2O_3 (Figs 7 and 8) and then used the least square fit rate constants to fit the corresponding Arrhenius plots (Fig. 9). Where the start-of-run data has been reported previously[2], only the end-of-run plots are presented here. On comparison, the conversion of CS_2 was impacted more by the end-of-run conditioning than the reaction of COS. For CS_2 there was in fact a small decrease in activation energy (slope in Fig. 9; 57.0 ± 3.7 for start-of-run to 44.3 ± 1.4 $kJ \cdot mol^{-1}$ for end-of-run). Interestingly, the end-of-run activation energy for CS_2 conversion across alumina is actually in better agreement with the only other value

Fig. 7: **Pseudo-first order plots for CS_2 conversion across Al_2O_3 under end-of-run conditions using pooled conversion data**

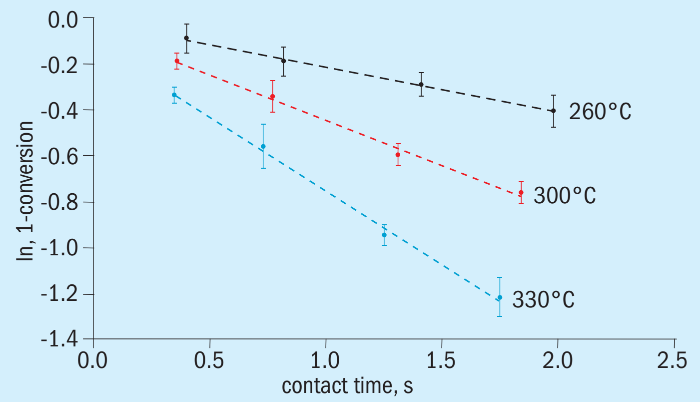

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Fig. 8: **Pseudo-first order plots for COS conversion across Al_2O_3 under end-of-run conditions using pooled conversion data**

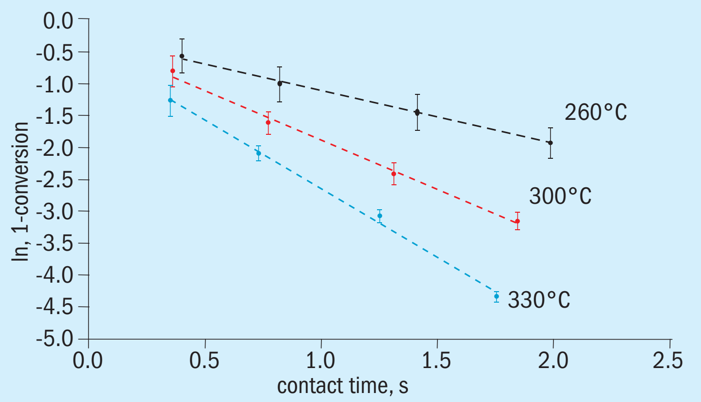

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Fig. 9: **Arrhenius plot for CS_2 and COS conversion across Al_2O_3 under end-of-run conditions using pooled conversion data**

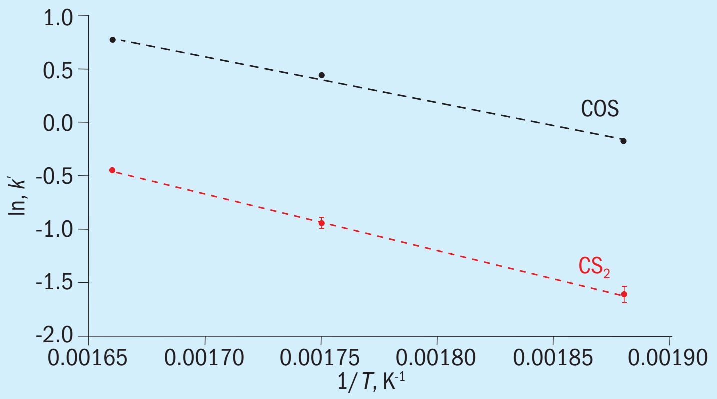

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Fig. 10: **Pseudo-first order plots for CS_2 conversion across TiO_2 under end-of-run conditions using pooled conversion data**

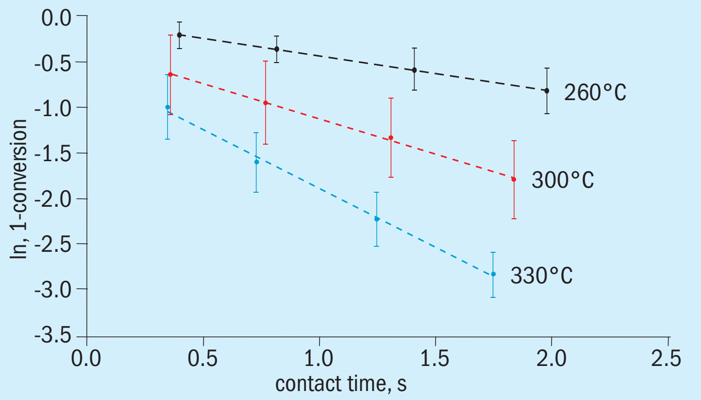

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Fig. 11: **Pseudo-first order plots for COS conversion across TiO_2 under end-of-run conditions using pooled conversion data**

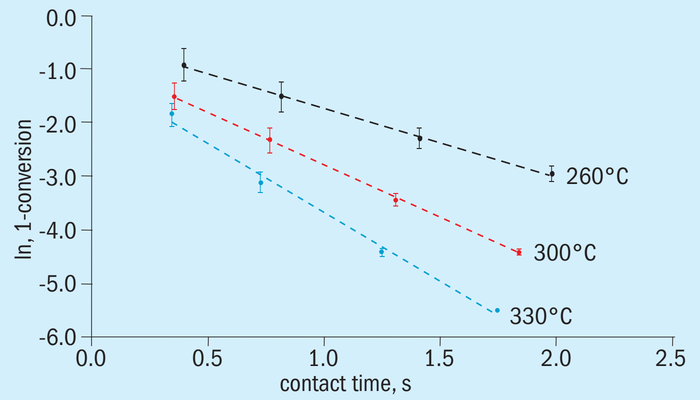

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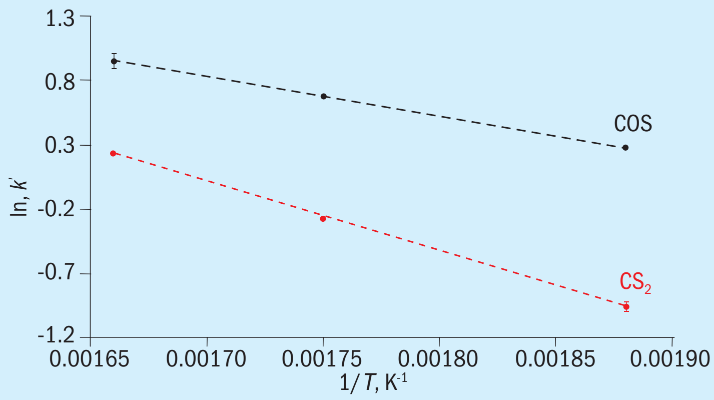
Fig. 12: **Arrhenius plot for CS_2 and COS conversion across TiO_2 under end-of-run conditions using pooled conversion data**



Source: ASRL

available in the open literature[5] of 40.4 kJ·mol-1. As alluded to above, owing to the broader selection of catalysts included in these end-of-run experiments, the corresponding COS end-of-run rate constants were modestly higher than in the analogous start-of-run tests. However, upon completing the full kinetic workup, the activation energies were quite similar (33.4 ± 0.4 versus 36.3 ± 0.5 kJ·mol-1). For reference, an activation energy of 25.3 kJ·mol-1 has been reported for COS conversion across Al_2O_3 where the only feed components were COS and H_2O[6].

In the same format as above, the pseudo-first order plots for CS_2 and COS conversion over TiO_2 are presented in Figs 10 and 11, and the matching Arrhenius plots are

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provided in Fig. 12. As was observed for CS_2 over Al_2O_3, the end-of-run activation energy activity for CS_2 conversion across TiO_2 was determined to be lower compared to the analogous start-of-run value (64.6± 5.8 kJ·mol^{-1} for start-of-run to 45.1 ± 2.0 kJ·mol^{-1} for end-of-run). While experimental error cannot be ruled out, a significant change in activation energy may be indicative of a different conversion mechanism becoming more prevalent. Indeed, in addition to the hydrolysis reaction, CS_2 and COS reaction with SO_2, according to reactions 5 and 6, has been shown to be a plausible pathway for conversion across TiO_2 under Claus conditions[7]. However, more studies are necessary to probe if these reactions contribute significantly to overall conversions.

$$CS_2 + SO_2 \rightarrow 3/2S_2 + CO_2 \quad \text{(reaction 5)}$$

$$2COS + SO_2 \rightarrow 3/2S_2 + 2CO_2 \quad \text{(reaction 6)}$$

The conversion of COS across TiO_2 was approaching equilibrium in the previous start-of-run experiments, with measurements at T = 330°C / GHSV = 1000 h^{-1} (contact time = 1.75 s) reaching >99.5%. This approach to equilibrium caused a decreased sensitivity in temperature dependence. As such, all three start-of-run rate constants for this reaction were in statistical agreement, despite the different temperatures. To find a statistically significant activation energy under start-of-run conditions would require lowering the temperature below the dew point or increasing the GHSV beyond what is practical for our system. However, under end-of-run conditions, the conversions were far enough removed from equilibrium that we did observe a statistical difference in our rate constants, thereby allowing us to define an activation energy of 25.7 ± 0.2 kJ·mol^{-1}. An activation energy of 41.8 kJ·mol^{-1} has been reported for COS hydrolysis on TiO_2 elsewhere[6].

Note that the start-of-run activation energy for CS_2 conversion across Al_2O_3 (57.0 ± 3.7 kJ·mol^{-1}) is lower than that for CS_2 across TiO_2 (64.6 ± 5.8 kJ·mol^{-1}). Additionally, the end-of-run activation energies for CS_2 conversion across Al_2O_3 and TiO_2 are within experimental error of one another (44.2 ± 1.4 kJ·mol^{-1} and 45.1 ± 2.0 kJ·mol^{-1}). This may seem unexpected at first glance, provided the higher activity of TiO_2 for CS_2 and COS conversion compared to Al_2O_3 under analogous Claus conditions. However, it has been shown that while employing a feed containing just H_2O and CS_2 or H_2O and COS, Al_2O_3 actually outperforms TiO_2 in the corresponding hydrolysis reactions[9]. It is only when the full effects are realised under Claus conditions that TiO_2 becomes more active than Al_2O_3. There is good evidence to support that this is related to a higher surface concentration of sulphate species that is established on Al_2O_3 under Claus conditions, which in-turn reduces access to catalyst active sites[4,8]. Indeed, reduction of sulphate by H_2S is more facile on TiO_2 than Al_2O_3 at temperatures employed in Claus catalyst beds. Therefore, the higher CS_2 and COS conversions across TiO_2 can likely be attributed to improved accessibility to catalyst active sites. This would result in a higher turnover frequency that is reflected in the higher pre-exponential factors for TiO_2. The authors are mindful that some surface sulphate is unavoidable under Claus conditions as it is in equilibrium with a necessary thiosulphate intermediate.

The first catalyst bed in the modified Claus process is often a split bed containing both Al_2O_3 and TiO_2 to help maximise CS_2 and COS conversion. While a full bed of TiO_2 would indeed offer higher conversions, cost and susceptibility to fouling from hydrocarbon contamination and/or sooting issues must be considered[10]. Although pure TiO_2 beds are not unheard of, Al_2O_3 is often packed on top of TiO_2 as a "guard" layer when a split bed is employed. In this context, the kinetic parameters reported here can also be applied to a split bed; provided the relative proportions are known and the GHSV for each portion of the bed can be determined.

Conclusions and future work

A kinetic study was performed on several commercial high-performance Claus Al_2O_3 and TiO_2 catalysts under end-of-run conditions and the results were compared to those from ASRL's previously published start-of-run kinetic study. Except for the COS reaction across Al_2O_3, the average end-of-run conversions were generally lower than the start-of-run conversions and this was reflected in the obtained rate constants and kinetic parameters. There was generally more variation in performance between the different Al_2O_3 samples compared to the various TiO_2 materials that were tested. However, these differences in performance were most evident under the more stringent test conditions. At the lower and more typical GHSVs that would be applied in the field, the differences in performance were less noticeable. Finally, as mentioned above, the Al_2O_3 samples employed in this study were high-performance activated materials. As such, the kinetic parameters determined here will likely afford conservative approximations for promoted Al_2O_3 materials. A full publication of the kinetic parameters discussed above can be found in a recent ASRL quarterly bulletin[11]. ■

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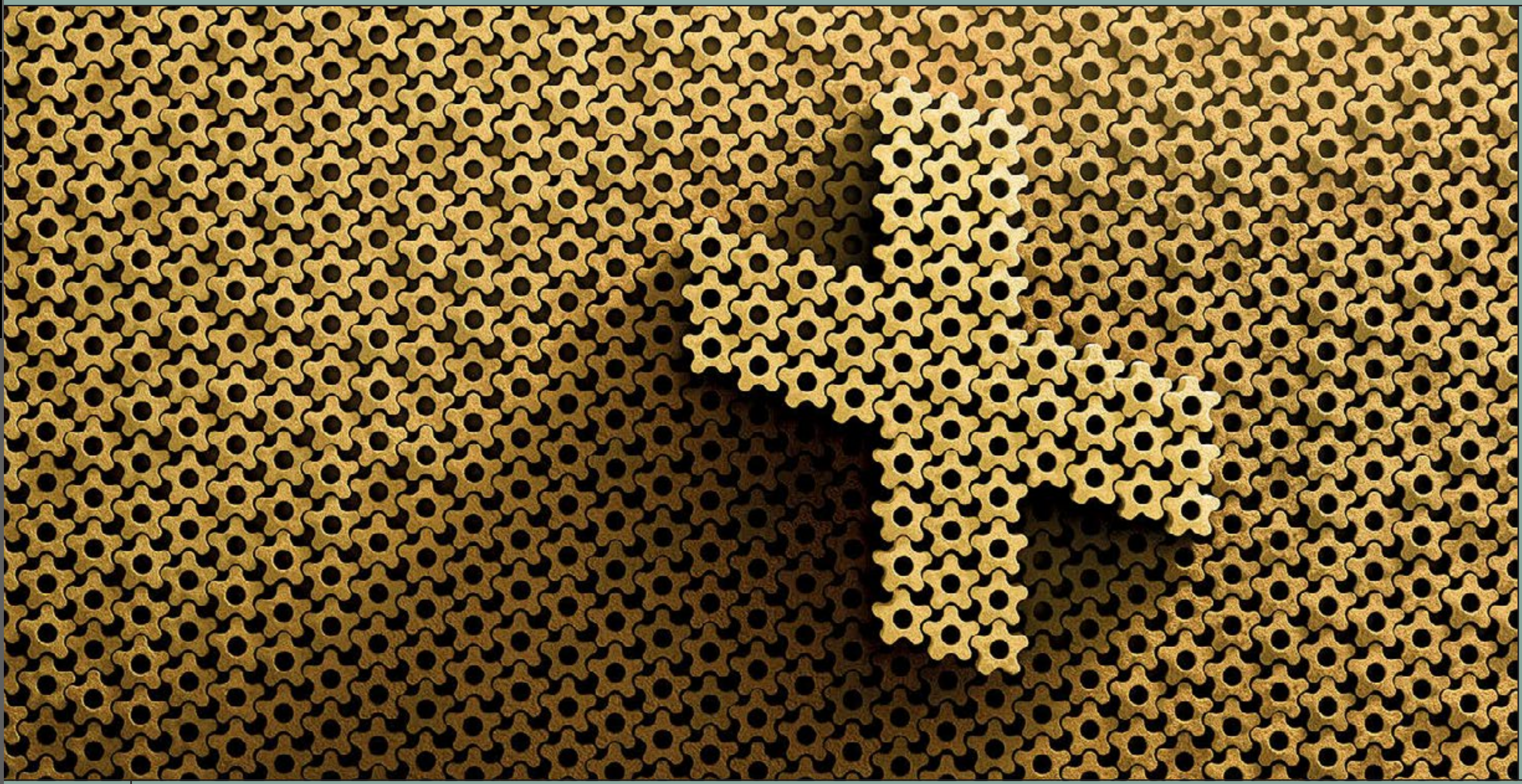

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Generating carbonless energy from sulphuric acid plants

By recovering waste heat as process steam or electrical energy, technologies are available that can help sulphuric acid plants meet their energy goals. **Colin Shore** of Elessent Clean Technologies discusses how MECS® HRS™ technology can offer a sustainable solution to enhance sulphuric acid plant performance, while lowering its carbon emissions.

The largest single source of power generation on the planet is thermal energy. It accounts for more than half of total global energy demand and is the primary contributor to carbon emissions worldwide. However, as a process that is built on the combustion of sulphur instead of hydrocarbons, the production of sulphuric acid can play a key role in the decarbonisation of this vital segment of the global economy by harnessing the energy it generates in the form of process steam or electrical power.

In particular, the MECS® Heat Recovery System (HRS™) captures energy released through the formation of sulphuric acid, which in conventional acid plant designs is commonly lost to the atmosphere or cooling water systems. When combined with more traditional means of energy recovery within sulphuric acid plants, this technology enables the plant to utilise up to 95% of the process heat it generates internally as steam, which can subsequently be converted into electricity and applied in a variety of functions.

Reducing your plant's carbon footprint

Through the production of both high-pressure and intermediate-pressure steam, a typical 3,000 t/d sulphuric acid plant with HRS™ technology can prevent up to the equivalent of 300,000 tonnes of carbon dioxide (CO_2) emissions annually – roughly the amount of CO_2 that is generated by 64,650 passenger vehicles over the course of a year.

Table 1: **Sulphur burning sulphuric acid plant performance by configuration**

	Conventional plant	Plant with HRS™
HP steam (t steam/t acid)	1.27	1.25
IP steam (t steam/t acid)	0	0.55
Heat recovery, %	70	94
Net power (kW/t/d)	10.6	13.0

Source: Elessent

Due to its capacity for upgraded energy recovery, HRS™ technology has been recognised by the United Nations as an accredited method for greenhouse gas (GHG) emissions reduction and therefore can be applied to secure credits for trade on the compliance or voluntary carbon markets.

For a given installation, carbon credits are awarded based on the level of CO_2 that would be expected from burning fossil fuels to obtain the same amount of power that is generated by the HRS™ unit. Specifically, each metric tonne of CO_2 emissions that is avoided through operation of the HRS™ unit enables the acquisition of one carbon credit. For other key GHGs, one carbon credit corresponds to the quantity of the relevant compound that produces an equivalent heat absorption potential as one metric tonne of CO_2.

Multiple MECS®-designed sulphuric acid plants featuring HRS™ technology have been granted carbon credits. As the market for carbon credits matures and the trading of credits becomes more prevalent, reliable decarbonisation technologies such as HRS™ technology are poised to offer customers greater operating cost savings than ever before.

Generating carbonless energy

The MECS® HRS™ unit increases the total amount of heat that can be used to generate energy within a sulphuric acid plant compared to a conventional sulphur burning plant design. With the addition of HRS™ technology, energy recovery from the plant rises from around 70% to nearly 95%.

Table 1 provides a brief comparison of the overall steam production and energy efficiency that are expected from a typical sulphur burning acid plant with and without the application of HRS™ technology.

The steam that is generated by the MECS® HRS™ unit is of sufficient quality to be processed through a turbo generator in order to convert the available energy into electricity. As a result, sulphuric acid plants featuring HRS™ technology (Fig. 1)

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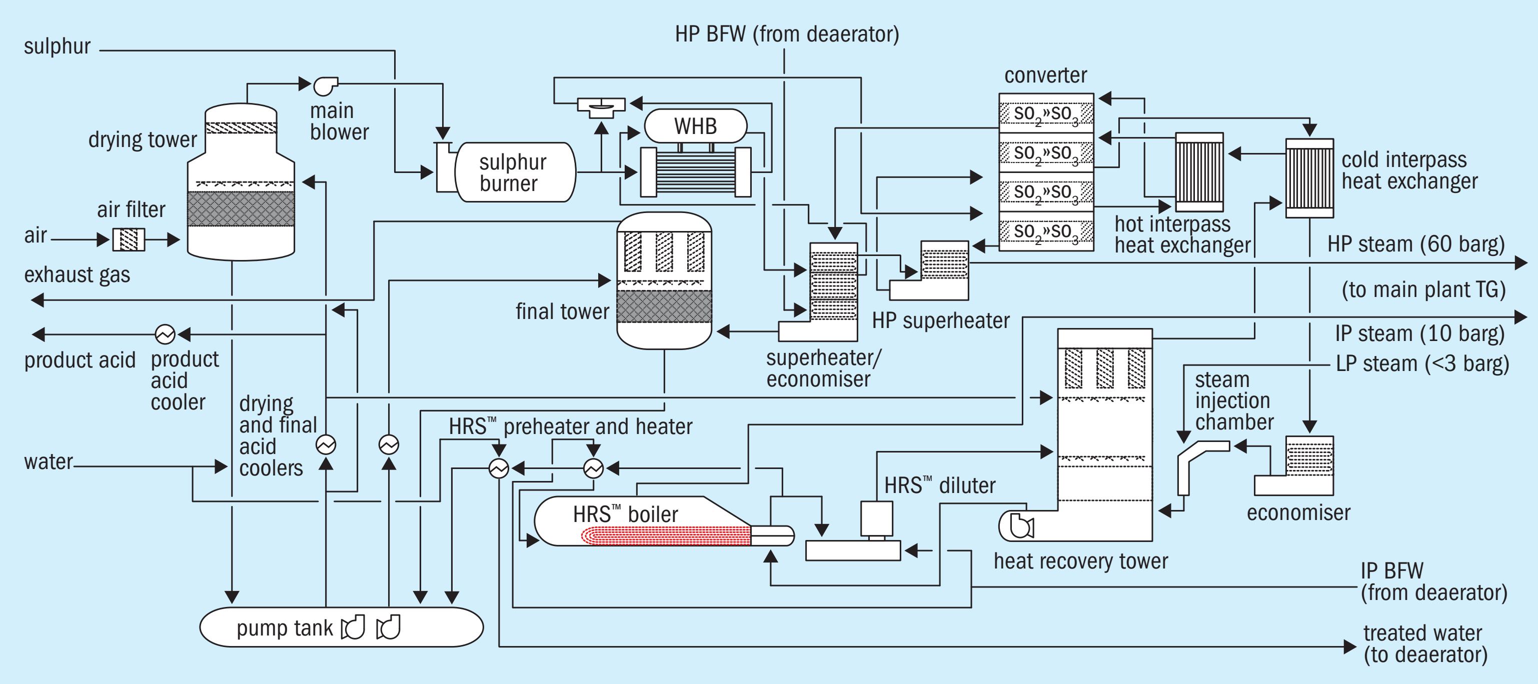
Fig. 1: **Steam production in a sulphur burning sulphuric acid plant with MECS® HRS™ technology**



Source: Elessent

have greater flexibility in utilising the energy which they can capture as steam or power for various purposes, including applying it to fulfil internal plant process requirements or selling it to nearby industrial complexes or the local power grid.

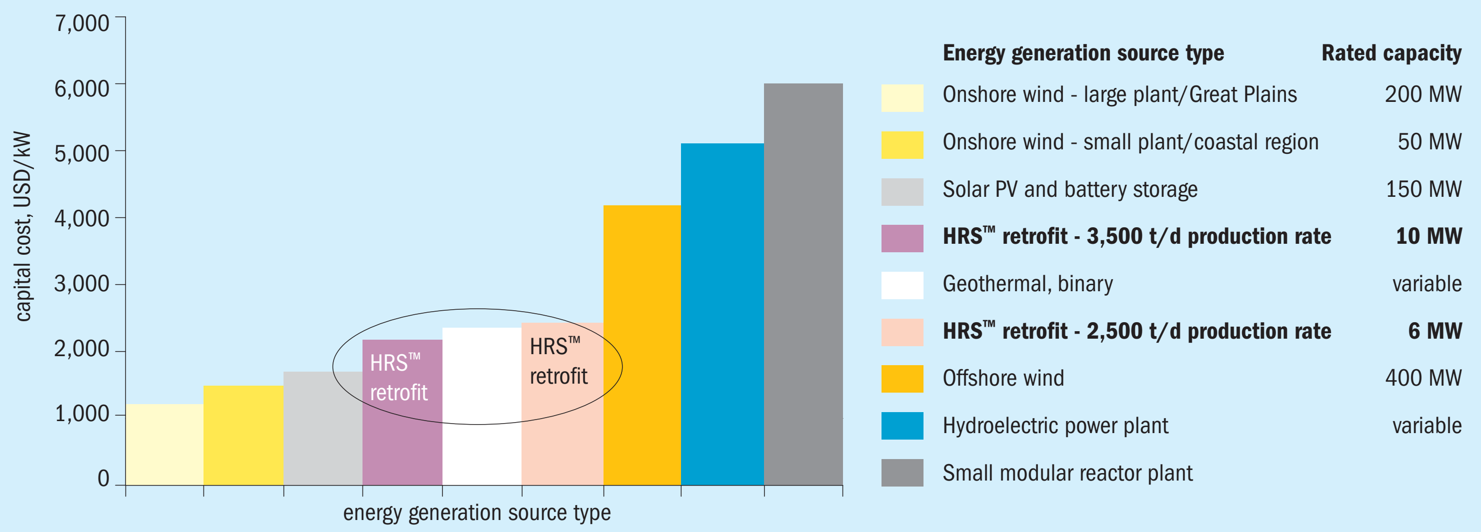
Additionally, existing plants which currently feature a conventional design can be retrofitted to include HRS™ technology. As an example, a 1,950 t/d sulphuric acid plant recently installed an HRS™ unit and today generates an additional 40 t/h of intermediate-pressure steam, which is used in turn to produce 6 MW of electric power. When compared with other sources of carbonless energy such as offshore wind, geothermal, or hydroelectric power, the required capital cost per kW for HRS™ is highly competitive (Fig. 2).

How MECS® HRS™ technology works

Within the sulphuric acid production process, highly exothermic reactions such as the combustion of elemental sulphur to form sulphur dioxide (SO_2) and catalytic conversion of sulphur dioxide to sulphur trioxide (SO_3) release large amounts of energy which can be recovered as high-pressure steam. By contrast, operations like the absorption of SO_3 and the formation and dilution of sulphuric acid have traditionally needed to be conducted at lower temperatures in order to enhance SO_3 absorption and minimise corrosion within the acid system of the plant. Consequently, the energy released by these reactions is of little value for steam production and is therefore normally discarded from the process via transfer through a series of heat exchangers to a cooling water circuit.

However, using HRS™ technology, the reactions which take place as part of the plant's acid system (including SO_3 absorption and acid formation and dilution) can be carried out at elevated temperatures while still achieving required levels of SO_3 absorption and limiting acid

Fig. 2: **Capex efficiency of carbon-neutral energy generation sources**



Source: Elessent

system corrosion, which allows plants to harness the energy that is produced to yield steam at pressures of up to 10 barg (150 psig), significantly increasing their overall thermal efficiency. The amount of this intermediate-pressure steam that is generated typically ranges from 0.4 to 0.6 tonne of steam/tonne of acid production, depending on the specific process conditions prevalent at the plant. If needed, this steam can then be used to generate electricity at a rate of approximately 2-3 MW per 1,000 t/d of acid.

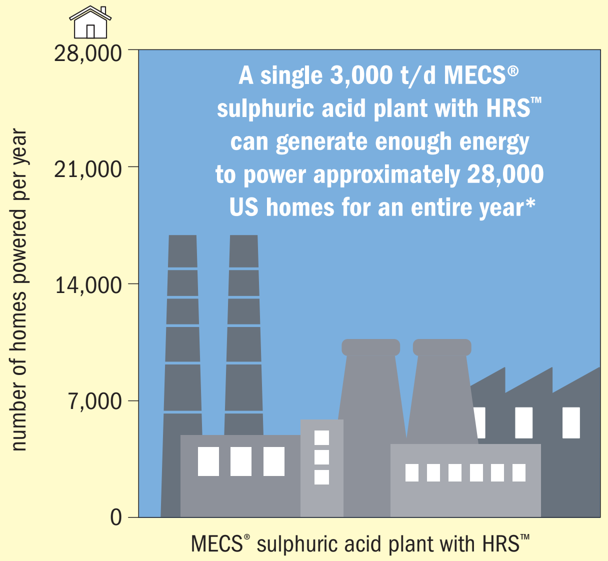
In a standard MECS® HRS™ unit (Fig. 3), heat from the acid is removed in the HRS™ boiler, and water is added in the HRS™ diluter to control the acid concentration within the limits required by the process. Energy in the product acid is then recovered by heating water in the HRS™ heater and preheater, which results in the generation of additional steam and, by extension, a reduction in the overall quantity of steam required for consumption by the acid plant.

The volume of intermediate-pressure steam produced by the HRS™ unit is increased further through the implementation of steam injection. In this process, low-pressure steam is infused into the process gas stream in the steam injection chamber located directly upstream of the heat recovery tower. The steam subsequently reacts with the SO_3 present in the gas phase, raising the temperature of the process gas and forming sulphuric acid vapour as the stream enters the heat recovery tower. Inside the tower, the sulphuric acid vapour condenses as ~100% H_2SO_4 when it contacts the cooler circulating acid stream, releasing the latent heat of the steam at the operating pressure of the HRS™ boiler while minimising the level of the rise in concentration of the acid within the tower as it absorbs the SO_3.

Steam injection has been shown to increase the volume of intermediate-pressure steam production within the HRS™ section of the plant by up to 10% as well as provide additional benefits to the HRS™ design such as:

- lower rise in the concentration of acid across the packing within the heat recovery tower, thereby reducing the required acid circulation rate through the tower to maintain the concentration below the upper process limit;
- 30-40% decrease in the volume of water required for the HRS™ diluter, resulting in reduced vibration within the vessel due to less formation/accumulation of heat from the dilution of acid.

Energy generation with MECS® HRS™ technology

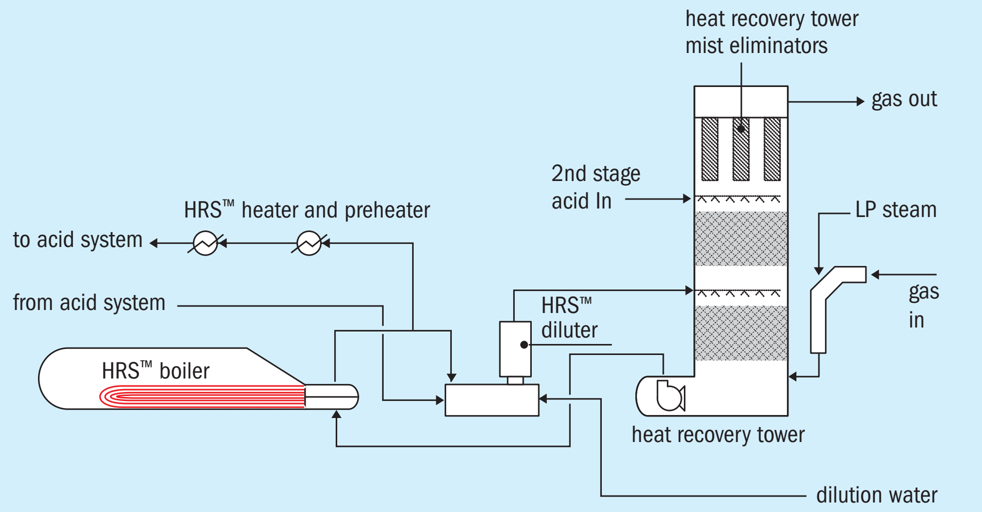


*This figure is based on the following assumptions:

- average annual electricity consumption for US households: 11,560 kWh (US Energy Information Administration, 2020);
- annual power output from the sulphuric acid plant: 325,320 MWh (includes energy captured from both HP and IP steam production, equal to ~39.1 MW/h with onstream time of 95% for plant).

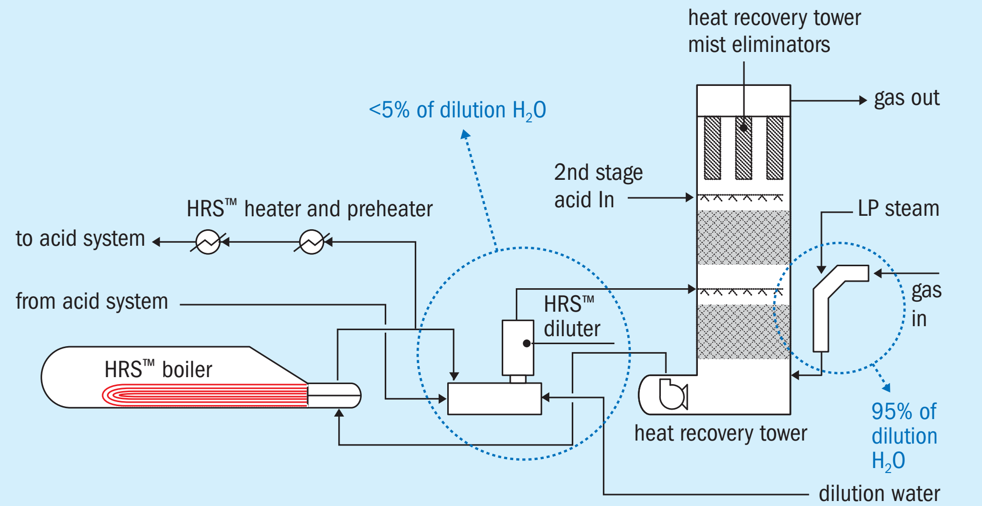
Source: Elessent

Fig. 3: **MECS® HRS™ basic process flow diagram**



Source: Elessent

Fig. 4: **MECS® SteaMax™ process design**



Source: Elessent

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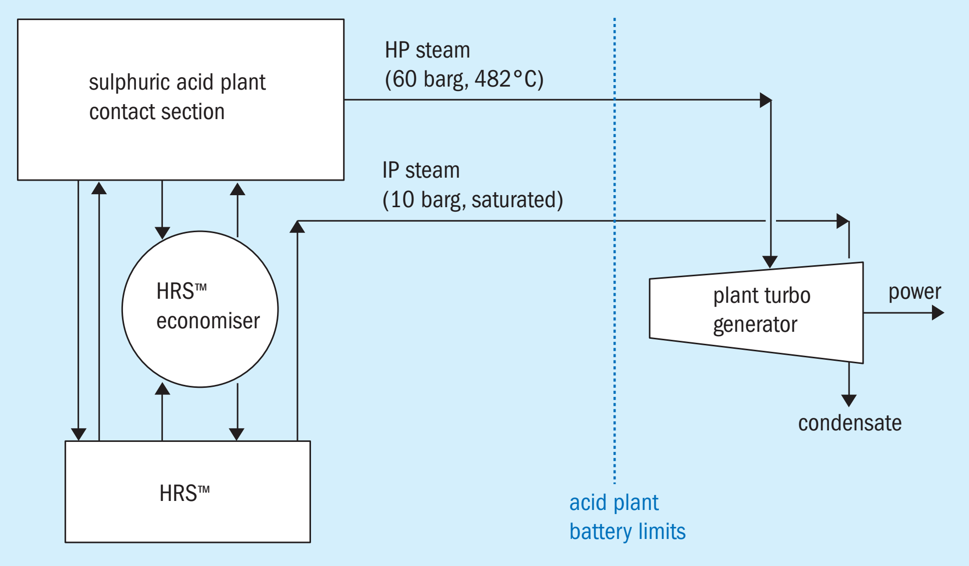
Fig 5: **MECS® MAX3™ steam system and utility integration**



Source: Elessent

Enhancing steam and energy value with MECS® SteaMax® and MAX3™

MECS® SteaMax™ technology

MECS® SteaMax™ is a natural extension of MECS® steam injection technology. This patented improvement to the steam injection system allows for a greater proportion of the dilution water required for the HRS™ process to be added as low-pressure steam via the steam injection chamber – with a sufficient provision of steam from the plant battery limits, 95% or more of the total water input to the HRS™ unit can be supplied as steam with a SteaMax™ design (Fig. 4).

By shifting the point of delivery for dilution water from directly into the HRS™ diluter (in the form of liquid water) to the process gas stream immediately ahead of the heat recovery tower (in the form of low-pressure steam), nearly all of the heat generated from the dilution of acid within the HRS™ circuit is passed through the HRS™ boiler. This results in an increase of 30% or more in the amount of intermediate-pressure steam that is produced compared to the output from a standard HRS™ unit, giving plants added value in their overall steam output and more flexibility in meeting their site's energy needs and other local conditions.

MECS® MAX3™ technology

Further expanding upon recent developments with MECS® plant technologies, MECS® MAX3™ represents the next level in energy recovery for the sulphuric acid industry. In a plant featuring MAX3™ technology, the process gas exiting the heat recovery tower is sent directly to an SO_2 scrubbing system (such as MECS® DynaWave® technology) or an SO_2 recovery system (such as MECS® SolvR® technology) which effectively replaces the second stage of SO_3 absorption in a conventional acid plant design.

With the MAX3™ flow scheme, the need for the additional conversion of SO_2 after it passes through the heat recovery tower is eliminated, and the energy that would normally be used to raise the temperature of the process gas to the required range for the final pass(es) of the converter can be redirected toward the production of steam in the plant's superheaters and/or an HRS™ economiser (Fig. 5). As a result, a significant portion of the steam that would be exported as intermediate-pressure grade from a standard HRS™ unit can be upgraded, allowing for up to 20% more high-pressure steam to be generated and enabling the plant to achieve the maximum possible return for the heat recovered.

Table 2: **High-level economic analysis for MECS® heat recovery technologies**

MECS® technologies	HP steam (kg/h)	IP steam (kg/h)	IRR	NPV
HRS™	156,250	68,750	20.2%	US$14.3 million
SteaMax™	156,250	77,500	22.4%	US$18.0 million
MAX3™	187,500	41,250	27.0%	US$24.7 million

Assumptions:

- *3,000 t/d plant capacity;*
- *typical steam export conditions (HP steam: 60 barg, 450-480°C / IP steam: 10 barg, 185°C);*
- *low-pressure steam is available for import to plant;*
- *electricity cost: US$85/MWh;*
- *discount rate (NPV): 10%;*
- *NPV analysis period: 20 years.*

Source: Elessent

Overview of MECS® heat recovery technologies

For a comparison of the added value that can be obtained using HRS™ or related MECS® technologies, Table 2 presents estimated figures for the total steam production and incremental economic impact that are anticipated when each of these technologies is integrated into the process design of a typical sulphur burning acid plant.

MECS® HRS™ technology – the carbonless energy solution

As the pioneering system for heat recovery in sulphuric acid plants, MECS® HRS™ technology has benefitted from nearly 40 years of expertise that has gone into its development and optimisation. MECS® HRS™ technology features more than 90 references worldwide and is customisable to the energy and process steam needs of individual plant operators. With the addition of HRS™ technology to the sulphuric acid plant process, low-pressure steam can be transformed into intermediate-pressure steam to maximise the value of the heat recovered from the plant, while intermediate-pressure steam can be further upgraded to high-pressure steam to provide plants with more flexibility in meeting downstream operational demands. Thus, MECS® HRS™ technology can offer an ideal, sustainable solution for operators seeking to enhance their plant's performance while lowering its carbon emissions. ■

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War stories revisited

Marco van Son and **Frank Bela** of Comprimo share lessons learned from SRU war stories, including: inadvertent NH_3 destruction in an oxidising atmosphere, rich amine emulsion, SWS fixed valve trays, H_2 spiking of SRU feed, rich amine flash drum early warning, V-ball fuel gas safety shutoff valves, TGTU methyl mercaptan, and commissioning and Murphy's Law.

Inadvertent NH_3 destruction in an oxidising atmosphere

This incident is best prefaced by a brief overview of the history of ammonia destruction in the SRU thermal reactor. In the 1950-60s it was generally assumed that complete NH_3 destruction required excess air ("oxidising atmosphere"). This typically resulted in a two-zone thermal reactor, where all sour water acid gas (SWAG) and combustion air was routed to zone 1, and at least some amine acid gas (AAG) bypassed to zone 2.

Processing SWAG in this manner typically resulted in downstream formation of sulphuric acid (H_2SO_4) which (1) deactivated alumina by forming aluminium sulphates, (2) deposited solid ammonium sulphate [$(NH_4)_2SO_4$] and bisulphate (NH_4HSO_4) if NH_3 was present, and (3) corroded steel upon condensation in the condensers. The fundamental mechanism appears to be initial formation of byproduct NO_2 which subsequently oxidises SO_2 to SO_3 (thus forming sulphuric acid vapour) in the waste heat boiler, where the reaction is favoured at <500°C (932°F).

This was generally accepted as the price one had to pay until around 1970 when two developments revolutionised the industry:

- Comprimo demonstrated that efficient NH_3 destruction could be achieved in a single-zone thermal reactor with proper temperature, residence time and mixing by virtue of a high intensity burner.
- The Ralph M. Parsons Company continued to favour the two-zone furnace concept while limiting the AAG bypass to ensure excess H_2S in zone 1.

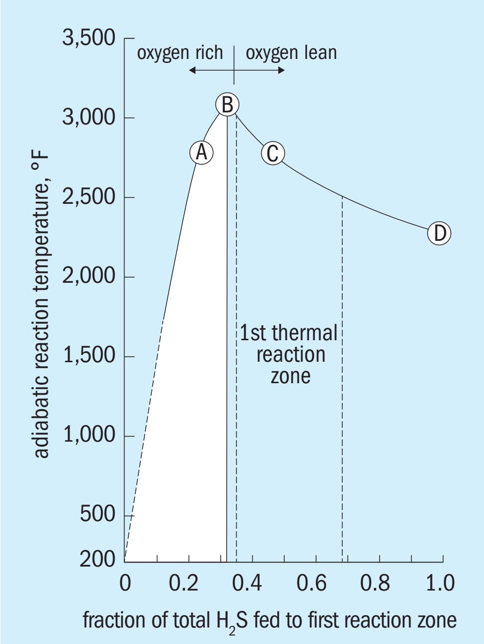
The industry remains split between the two camps. As usual, each has its pros and cons, summarised to a cursory extent in Table 1.

Table 1: **Relative merits of 1 and 2 zone thermal reactors**

Type	Pro	Con
One zone	● Better overall mixing/residence ● Simpler control	● Preheat required for NH_3 destruction temperature ● Limited turndown
Two zones	● No preheat, better turndown	● Poor zone 2 mixing ● More complicated controls ● Potential for mis-operation resulting in oxidising conditions in zone 1

Source: Comprimo

Fig. 1: **Thermal reactor zone 1 temperature as function of H_2S split**



Source: Comprimo

In the 2-zone case, the relative zone 1 temperature is determined by the AAG split. Since the Claus process only oxidises one third of the H_2S, routing one third to zone 1 maximises the temperature, where 1,300°C (2,372°F) is considered ideal. Arguably more important, however, is maintenance of reducing conditions (excess H_2S) in zone 1 to avoid downstream formation of H_2SO_4 (Fig. 1).

Actual H_2S split will be approximate, given likely errors in flow measurement and assumed acid gas H_2S concentrations. In addition, mixing efficiency – important to minimise localised NOx – is less than perfect. To ensure excess H_2S, at least 40% of the total H_2S should be routed to zone 1. However, maximising AAG to zone 1 is also desirable for better mixing and residence time, provided 1,250-1,300°C is maintained.

In the subject incident, a client operating a 2-zone thermal reactor called to report excessive dP several days after start-up following a maintenance outage. SWAG was not being processed, but AAG was known to typically contain substantial NH_3 due to inadequate purging of ARU reflux. Eventually it came to light that there also was no sulphur rundown from the first condenser because the Sultrap was plugged with corrosion scale; all sulphur made in the thermal reactor was carried over to the reheater. Cleaning the Sultrap restored normal sulphur rundown flow, but No. 1 reheater pressure drop remained high, accounting for 75% of total SRU ΔP (while bypassing TGTU).

The unit had been heated up by firing H_2, and excess air was likely greater than intended based on evidence suggesting H_2 flow was overstated. As AAG was introduced to zone 1, temperatures

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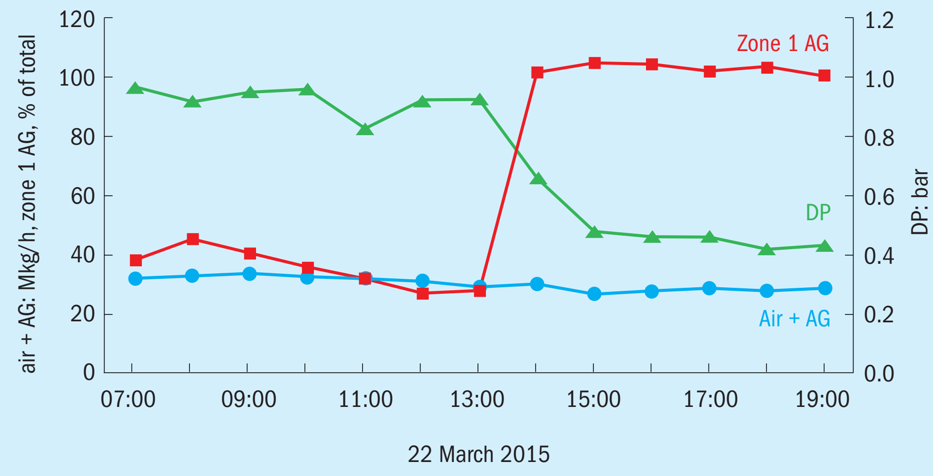
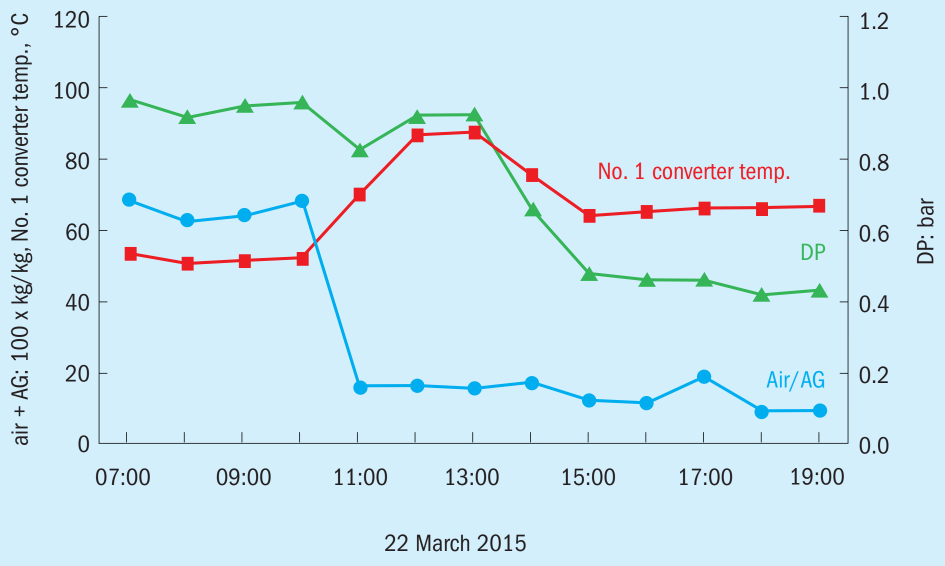
Fig. 2: **Impact of amine acid gas split on SRU-2 ΔP**



Source: Comprimo

Fig. 3: **No. 1 converter ΔT**



Source: Comprimo

approached the 1,500°C trip point while still to the left of point B in Fig. 1, prompting the operator to route additional AAG to zone 2.

When Comprimo arrived on site a couple of days later, the situation was still unclear, so the first order of business was to restore a normal reducing atmosphere in zone 1. With some coaxing, the operator shifted substantial AAG to zone 1 quickly enough to transition from point A to C without passing through B. To everyone's surprise, the unit pressure drop subsequently decreased by 50% over the next two hours (Fig. 2).

The explanation lies in the No. 1 converter exotherm (Fig. 3).

As an aside, prior to shifting the AAG split, the unit was found to be off-ratio and combustion air (blue) reduced accordingly (~20%), resulting in the increased No. 1 converter exotherm (red). However, Fig. 3 reveals that the reduced ΔP was not the result of reduced air flow, but of increased sulphur conversion in the thermal reactor when acid gas was shifted to zone 1 – presumably due to better mixing and longer residence – as evidenced by subsequent reduction in the No. 1 converter ΔT. Since fouling was confined to the reheater, reduction in process gas volume due to additional upstream sulphur condensation was apparently sufficient to significantly reduce system ΔP.

Following shutdown, the process (shell) side of the reheater U-tube bundle was found to be packed predominantly with iron sulphate, suggesting that most of the sulphur had been vaporised. The deposits were porous, easily crumbled and highly soluble in water yielding a strongly acidic pH (Fig. 4).

By comparison, clinkers of corrosion products found in the Sultraps were harder with more of an iron-slag appearance.

Rich amine emulsion

A refinery began experiencing apparently random episodes of increased SRU air demand due to hydrocarbons (HCs) in the amine acid gas. Fig. 5 is a relatively severe example. Amine acid gas (no SWAG) air demand increased 30%, TGTU absorber off gas increased 35% and total reduced sulphur (excluding H_2S) in the TGTU tail gas went from 25 to 190 ppmv.

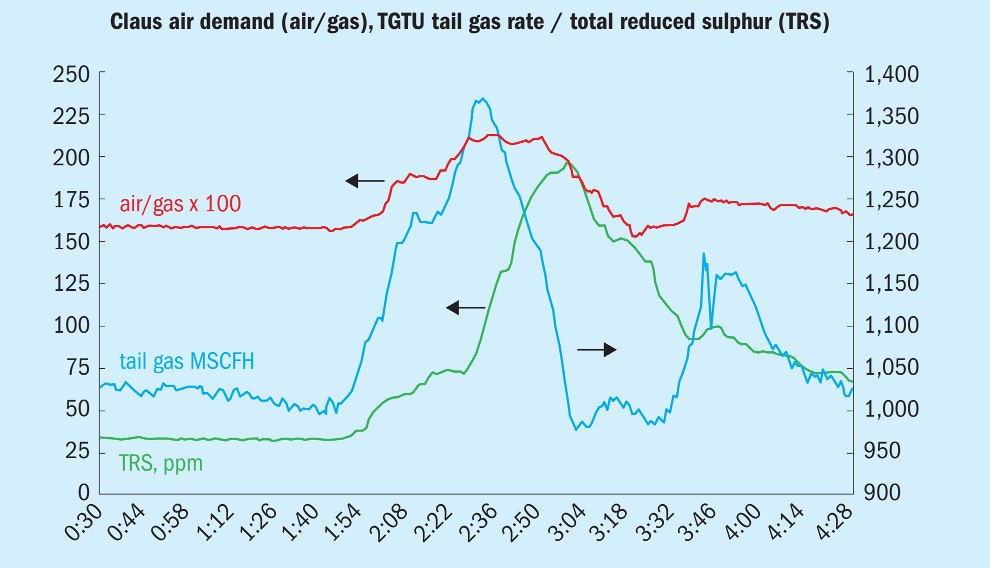
High raw produced fuel gas temperature (130°F/54°C) to the delayed coker DEA contactor was quickly identified as a likely cause, potentially compounded by the fact that upstream lean oil absorption had been discontinued because entrained oil was suspected of accelerating fouling of the amine contactor. Historically, little attention was paid to the relative lean amine temperature because foaming was seldom a problem. The rich amine routinely contained copious amounts of free naphtha/oil, but 30-40 minutes of residence at 0 psig in the rich surge tanks appeared to achieve adequate separation.

Lowering the coker raw gas temperature appeared to reduce (but not eliminate) the episodes, which tended to coincide with coke drum blowdown to the flare gas recovery compressor. It eventually came to light that the operators – in a misguided attempt to reduce exchanger fouling – had been manually throttling the cooling water to the compressor interstage and after coolers, resulting in raw gas temperatures of ~200°F (~93°C) at the inlet to the vapour recovery absorber during blowdown.

PHOTO: COMPRIMO

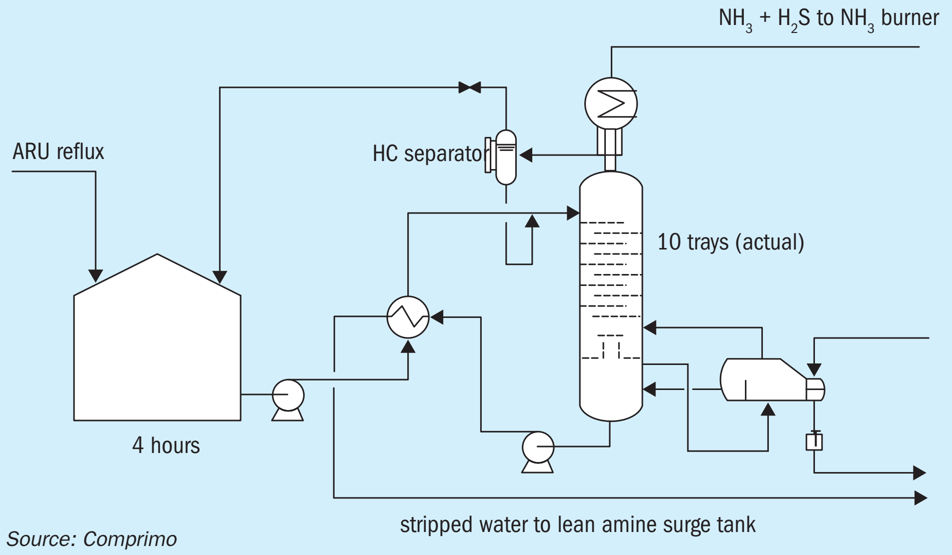
Fig. 4: No. 1 reheater process (shell) side deposits.

Fig. 5: **Typical "tail gas spike"**



Source: Comprimo

Fig. 6: **DEA regenerator "reflux" stripper**



Source: Comprimo

It is logical to conclude that emulsions, like foaming, are not caused by all HCs, just surfactants. The conclusion was that proper cooling resulted in condensation of naphtha which absorbed problematic organics – aromatics, most likely – in particular abundance during early coker blowdown.

That the surfactants did not appear to cause regenerator foaming is perhaps attributable to the fact that the regenerators in this case were not refluxed – thus avoiding recycle build-up of contaminants within the column – but overhead condensate instead stripped in a separate amine-system SWS with four-hour feed residence (Fig. 6). However, emulsions were clearly evidenced by hazy "reflux."

Lessons learned

- Coking units in particular are a likely source of surface-active organics conducive to stable amine emulsions (and foaming).
- Emulsified HCs can substantially increase SRU air demand without obvious signs of foaming or increased flash gas in the rich amine flash drum.
- While foaming concerns are typically cited as the reason for maintaining absorber amine temperatures above the HC dew point, potential emulsions are also a consideration.
- Trending SRU air/acid gas ratio is a useful means of promptly recognising HC excursions.

As an aside with regard to the last bullet, Comprimo often receives client requests to provide acid gas HC analysers – not for closed-loop feed-forward air demand control, just early warning of an impending upset. With reference to Fig. 5, Comprimo suggests that monitoring a continuous trend of air/acid gas ratio is a simpler solution. The DCS operator eventually figures it out anyway when the trim air valve goes wide open, but with the trend it becomes obvious sooner.

Other hydrocarbon incidents

- Periodic surges in SRU air demand were ultimately traced to manual blowdown of LPG from a hydrocracker's HP flash drum to the LP flash, where subsequent flashing was sufficiently violent to entrain liquid overhead to the amine contactor and ultimately the ARU. Resultant HCs in the amine acid gas were estimated at 15-25 wt-%. Fortunately, the SRU was generally at low rate and the surge only lasted a few minutes, thus allowing the plant to recover before TGTU recycle build-up became unmanageable.
- In a case of light naphtha entrainment from a hydrocracker, the HCs readily separated in the rich amine surge tanks at a rate that would fill the rich and lean tanks in about 20 minutes from the time that the operator happened to notice that the rich tank levels were steadily rising. The sulphur plant operations supervisor had reason to suspect the hydrocracker, but the operator insisted they were not the source.

  Unconvinced, the supervisor drove the two miles to the unit and drew a sample, which clearly had at least a 2% naphtha layer. Either the hydrocracker operator did not give the sample sufficient time to separate or did not consider 2% significant due to failure to appreciate the cumulative impact.
- Major light liquid HC carryover from a hydrocracker flash drum passed all the way through the ARU to the thermal reactor, due to malfunction of the acid gas KO drum high-level shutdown interlock. Flashing in the thermal reactor resulted in a pressure surge sufficient to collapse the overhead refractory before the SRU tripped on high pressure or flameout. The unit was down a month for repairs (Fig. 7).

SWS fixed valve trays

This case study dates back 20 years and has been previously published in various forms. It remains noteworthy because one

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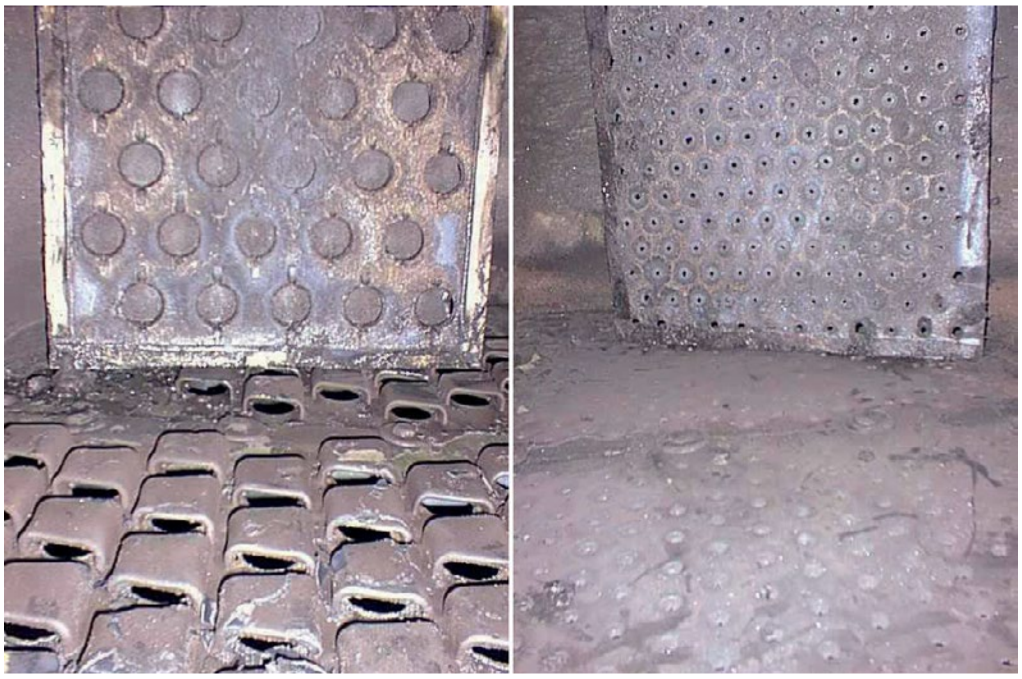
PHOTOS: COMPRIMO

Fig. 7: Thermal reactor damage from liquid hydrocarbon carryover.



PHOTOS: COMPRIMO

Fig. 8: Existing SWS sieve tray (left) and test fixed valve tray (right) at EOR.

seldom sees such a clear-cut real-world validation of a product's superiority.

A refinery's SWS charge was nominally 50% crude clearing water, and thus high in TDS/heavy organics despite substantial removal of solids, oil and grease in Wemco induced gas flotation units.

Closure of the ½-inch sieve tray holes was a chronic problem. Tray deposits were a combination of Ca/Mg carbonate/silicate and organics, which are largely insoluble in methylene chloride and therefore presumed to be high-MW polymerisation products.

Given the erosive nature of steam, it was difficult to comprehend the fundamental mechanism by which bridging of the holes occurred. One source rationalised it by explaining that vapour flow through an orifice creates venturi effects which draw liquid into the throat so as to form a laminar boundary layer at the edge of the hole, within which water tends to evaporate, salts crystallise, and organics polymerise. This led to speculation that fixed valves might tend to avoid bridging of the holes by inhibiting the induction of liquid into the orifice throat. Whether or not that particular analysis is valid, other industry experts had also concluded that directional fixed valves were generally superior to both sieves and conventional valves in fouling service, specifically recommending Nutter MVG and Glitsch Minivalve trays.

Norton (now Koch-Glitsch) Provalve trays were installed at two adjacent levels in the south stripper as a trial. The test trays were located 9-10 trays down from the top of the 40-tray stripping section, where fouling is typically the worst (presumably due to localised pH elevation). After a typical five-month run, adjacent sieve tray (½-inch holes Fig. 8 left photo) flow area was reduced by ~90%, while the test tray (nominal 1½-inch holes, right photo) flow area was only reduced by 10-15%. (Shown in the upper sections are the tray inspection manways, propped up to reveal the underside.)

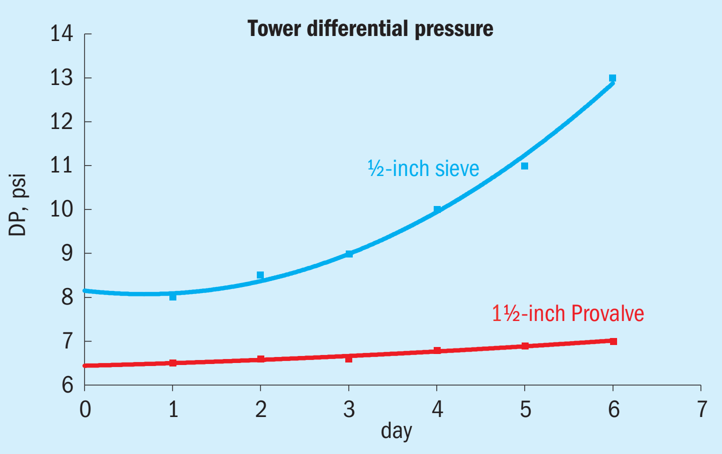
On the success of that trial, the companion stripper was retrayed with Provalves. The vendor also claimed a 35% capacity increase (with no increase in active area) and a 20% reduction in pressure drop, which has essentially proven out. The Provalve tower, previously limited to 450-480 gpm, has since been operated at 600+ gpm, and tower DP was noticeably less than the (clean) sieve-tray tower at comparable rates (effectively increasing reboiler capacity). (Both towers are identical in design and charging the same feed.)

After 150 days, the Provalve tower could still process 550-600 gpm with no apparent increase in tower DP. After 130 days during the same period, the sieve-tray tower was flooding at 200 gpm and had to be shut down again for cleanout.

An accelerated fouling test was inadvertently conducted in early September 2002, when the sour water became contaminated with an inordinate amount of caustic, greatly increasing the fouling tendency over the next 2-3 weeks. During the period plotted in Fig. 9, both strippers were charging the same feed at a constant rate of 345 gpm each. As of Day 0, the sieve-tray tower had been online 42 days since the last cleanout, and the Provalve tower had been online 191 days. As of Day 8 the sieve-tray tower had been derated by 50%, and within another couple weeks had to be shut down again for cleanout.

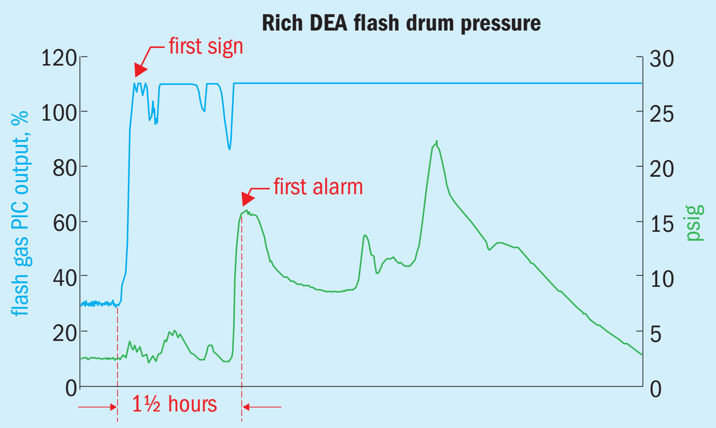
The Provalve tower remained online

Fig. 9: **Accelerated SWS tray fouling due to high-alkalinity feed**



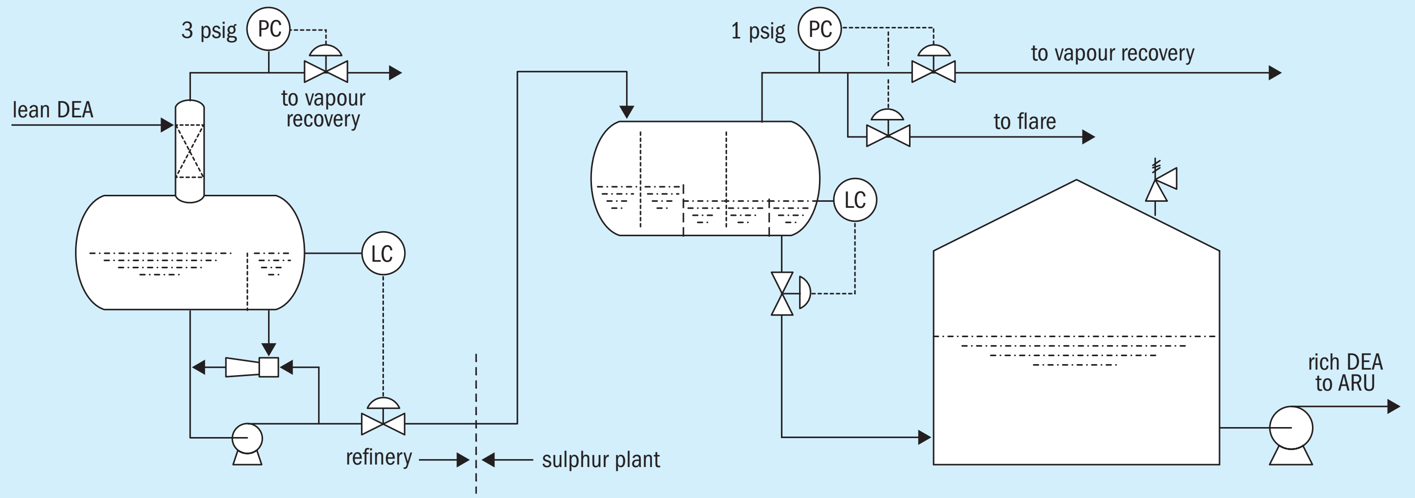
Source: Comprimo

Fig. 10: **Impact of entrained LPG on rich amine flash drum pressure**



Source: Comprimo

Fig. 11: **HC separation at one refinery**



Source: Comprimo

after ~490 days, although it had been derated to 250-300 gpm (depending on H_2S/NH_3 loading), largely due to the caustic excursion.

H_2 spiking of SRU feed

A 10-t/d SRU was forced to operate indefinitely at 10/1 turndown. Normal turndown issues were compounded by (1) chronically substantial hydrocarbons in the amine acid gas, (2) SW acid gas feed and (3) cold winters. The high turndown had the following key impacts:

- Thermal reactor temperatures were too low for destruction of NH_3 and normal hydrocarbon levels, where the latter was evidenced by brown sulphur.
- The reheaters relied upon the SRU waste heat boiler for 600 psig steam, with surplus let down to the refinery 300 psig header. Reheater demand often exceeded supply, resulting in local header pressures as low as 300 psig and insufficient to maintain the converters above the dew point.

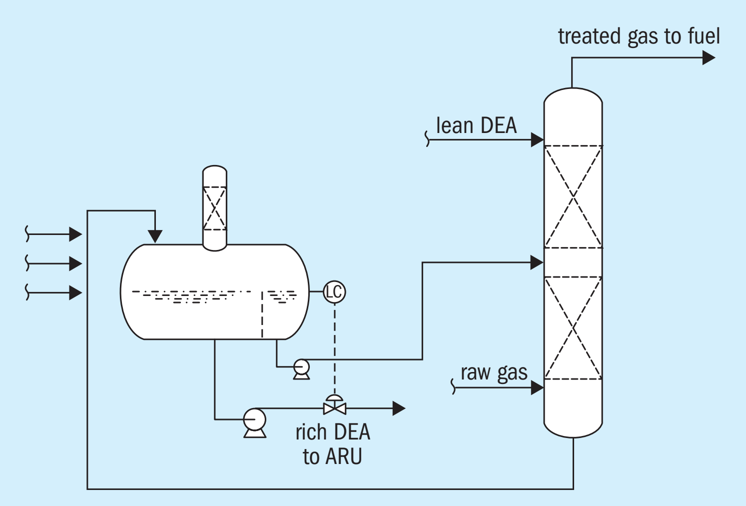
With regard to the latter, it was apparent that a lot of bare steel (valves, flanges, manways, nozzles, etc.) contributed to excessive heat loss – estimated at up to 85% – from the local 600 psig steam system. Improved insulation mitigated this considerably but did not address the greater problem of low furnace temperatures.

Since the thermal reactor was designed for front/side split of the amine acid gas for NH_3 destruction, turndown issues were overcome for four years by co-firing natural gas in zone 1 while routing all amine acid gas to zone 2. This was effective, but had its shortcomings:

- NH_3 gas continued to be flared due to perceived risk of generating soot, or NO_2 conducive to downstream sulphuric acid formation.
- Hydrocarbon excursions often generated soot which, in addition to producing dark sulphur, fouled the catalyst beds.

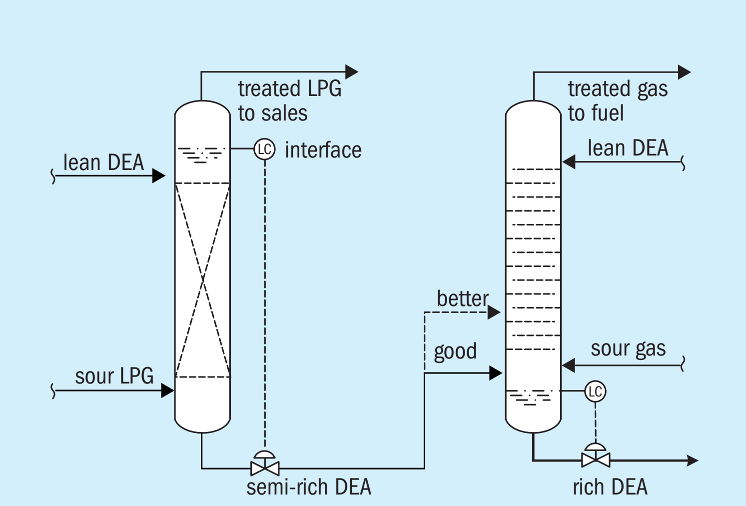
A study concluded that H_2 enrichment of the acid gas was the best option, with all feed to zone 1. Supplemental CRU H_2 piped to the TGTU reactor was never used, since hydrocarbons in the acid gas consistently resulted in abundant tail gas H_2. For three scenarios ranging from 0.5 to 2 t/d, heat and material balances were developed to determine (1) H_2 required for sufficient supplemental heat and mass flow to overcome estimated heat losses, and (2) moderating steam required to limit

Fig. 12: **Emergency LPG flash in gas contactor**



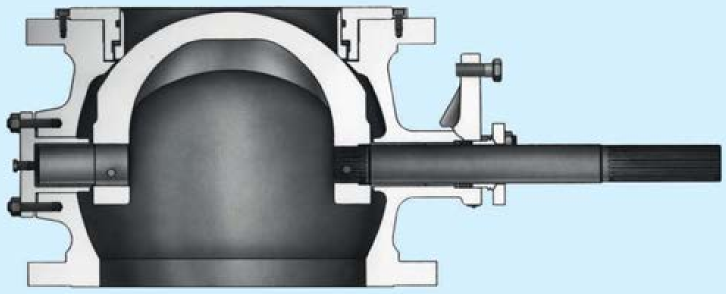
Source: Comprimo

Fig. 13: **Liquid treater rich amine pre-flash in gas contactor**



Source: Comprimo

Fig. 14: **V-ball cutaway view**



Source: Comprimo

thermal reactor temperatures to 2,550°F (~1,400°C).

Project success exceeded expectation in that equipment fouling and sulphur contamination due to acid gas hydrocarbons were significantly mitigated by H_2 cofiring.

Rich amine flash drum early warning

This refinery had a common DEA system circulating 1,500 gpm to six gas contactors and two LPG contactors. The rich amine flash drum operated at 2.5 psig with 10 minutes residence. The sulphur plant was two miles away, requiring 20 minutes for the amine to get there.

The hydrocracker was in the midst of start-up when (unbeknownst at the time) the depropaniser began carrying over LPG to the gas contactor due to a faulty reflux accumulator level signal. The refinery flash drum was overwhelmed with LPG, much of which carried through to the sulphur plant, causing the rich amine surge tanks to vent to atmosphere and thus resulting in a major environmental incident.

The flash drum off-gas rate was not measured. The off-gas regulator normally operated very consistently at ~30% open. LPG carryover was not evident to anyone at the refinery until the flash drum console operator got the high drum pressure alarm at 15 psig. However, the incident investigation revealed that the off-gas regulator had gone wide open > 1½ hours before the high-pressure alarm sounded (Fig. 10).

As a result of the incident, a high off-gas controller output alarm was added, and provisions made for the sulphur plant console operator to also monitor flash drum operation as well as receive key alarm signals.

Since the remote sulphur plant had adequate liquid HC separation, the refinery flash drum made no attempt to skim. However, it was also considered important not to accumulate HCs, which were therefore continuously re-entrained via a simple recycle eductor (Fig. 11).

The incident prompted consideration of how to better mitigate major LPG entrainment in the future. Skimming the LPG to slop was ruled out because it would most likely flash to atmosphere in those tanks. It proved a simple matter to inject the stream into the mid-point of an adjacent vapour recovery amine contactor (Fig. 12).

This is analogous to the common practice of pre-flashing rich amine from a liquid treater in a fuel gas contactor (Fig. 13). Since liquid treater rich amine also tends to be under-loaded, further benefit can be achieved by introducing the stream a few trays up from the bottom as shown by the dashed line.

V-Ball Fuel Gas Safety Shutoff Valves

In one typical SRU project, thermal reactor fuel gas safety shutoff valves were specified only as "quarter-turn on/off." To the casual observer the valves appeared to be ball valves, whereas the vendor had supplied Fisher V-ball valves – possibly for quicker response. The valves passed rigorous tightness tests in the shop, but when the initial field light-off attempt failed, the valves tripped as intended but gas continued to flow.

Following review of the V-ball design it was concluded that, following initial installation, workers had apparently rotated the actuators 180° for better visibility. While this would have made no difference with a conventional ball valve, the V-ball was essentially always open (Fig. 14).

TGTU Methyl Mercaptan

A client operated a BSR Amine TGU using Ucarsol HS-103 which vented un-incinerated tail gas directly to atmosphere as long as residual H_2S was < 10 ppm. They had received several visits from the air

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quality inspector responding to nuisance odour complaints, and repeatedly assured him they were not the source, since operations were stable with < 5 ppm H_2S.

At about the same time, a chance comment by an operator that it "smelled like an animal had crawled into the tail gas line and died" after unplugging the drain led the process engineer to suspect mercaptans. After measuring 40 ppm with a Dräger tube, the reactor inlet was nominally increased from 550°F (288°C) to 570°F (299°C), and the mercaptans went to zero.

In retrospect, the operator's chance comment bordered on divine intervention. Literature today contains references to such byproduct mercaptan formation, but whether it was common knowledge at the time of this incident some 30+ years ago is unclear. It may have become more apparent as a result of low-temperature catalyst experience.

CS_2 is normally hydrolysed to H_2S and CO_2 in the TGU reactor:

$$CS_2 + 2H_2O \rightarrow 2H_2S + CO_2$$

However, it also turns out that CS_2 is commercially hydrogenated to methyl mercaptan with a cobalt catalyst at nominally 250°C (482°F) as follows[1], so it is understandable that the mercaptan will form if temperature and/or catalyst activity are insufficient for complete CS_2 hydrolysis:

$$CS_2 + 3H_2 \rightarrow CH_3SH + H_2S$$

With luck, methyl mercaptan can still be hydrogenated as follows[2]:

$$CH_3SH + H_2 \rightarrow H_2S + CH_4$$

It is generally known that, as TGU catalyst activity declines with age or abuse, higher temperatures are required for efficient conversion of CO, COS and CS_2. It follows that the same applies to mercaptan, and Comprimo has seen residual methyl mercaptan in one unit with overheated and heavily sulphated catalyst at inlet temperatures as high as 650°F (343°C).

Since most plants incinerate tail gas, the potential to make mercaptan may still not be widely known, or even relevant in most cases. A notable exception (in addition to the above example of un-incinerated TGTU tail gas) is the Stretford process where, by analogy to Merox, methyl mercaptan is logically absorbed as the mercaptide and subsequently converted to disulphide oil (DSO) in the oxidisers. Comprimo experience suggests that DSO inhibits froth production, possibly consistent with a comment in Gas Purification – 5th Edition citing such organic sulphur compounds (COS, CS_2, mercaptans and thiophene) as having unspecified adverse impact on Stretford operation[3].

Commissioning and Murphy's Law

General advice

New unit start-up advice can be summarised as follows:

- Take nothing for granted.
- Allow no unexpected occurrence to go unexplained – it may be a heads-up.

Most potential engineering/construction errors are foreseeable, but occasionally there are once-in-a-lifetime eye-openers.

Continuity of long interconnecting lines

A new SRU received AAG from an off-plot ARU at one location, and SWAG from an off-plot SWS at another location. Operators proceeded to N_2-purge the AAG line from the regenerator to the SRU. While waiting patiently for a sign of flow, the SRU operator noticed vent gas from the SWAG line. What started out as AAG terminated as SWAG, and vice versa.

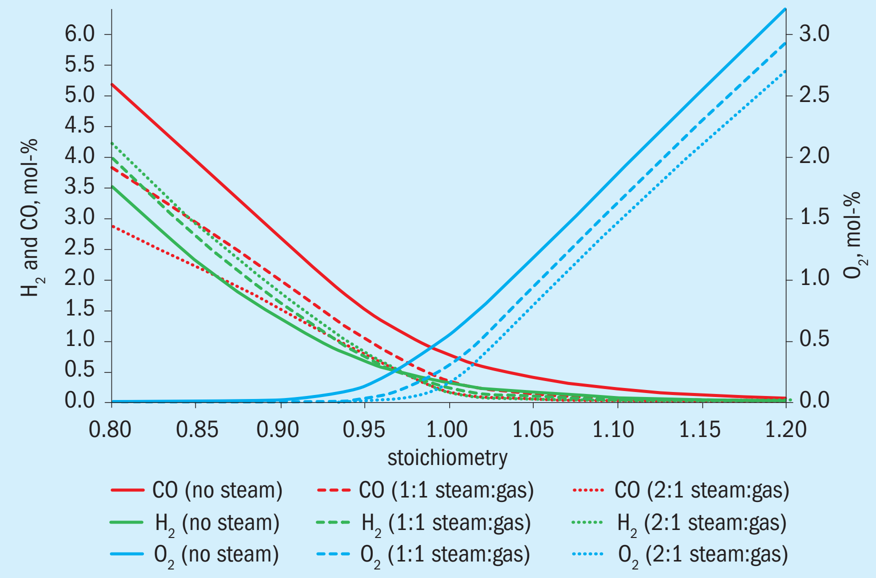
Debris

An ultra-low-NOx incinerator burner guaranteed to meet 5 ppm NOx could not achieve <15-20 ppm. Process trends suggested the solution was to increase the air/fuel ratio, but the flame became unstable. Following exhaustive troubleshooting to no avail, the manufacturer agreed to replace the burner. In the course of removing the old burner, a bag of desiccant – virtually hidden from view – was found hanging loosely by a cord within the air plenum so as to cause an unstable flow pattern.

Pump rotation

When performance of a turbine-driven recycle water pump proved extremely poor during initial run-in, engineers were stumped until an operator noticed opposing rotation arrows on the pump and driver. Reverse rotation of electric pumps is not unusual because it simply means that power was incorrectly connected, and easily remedied. Turbine mismatch, however, is arguably an inconceivable design error.

Fig. 15: **Theoretical natural gas stoichiometry**



Source: Comprimo

Table 2: **Basis for Fig. 15**

Component	Mol-%	
	Natural gas	**Combustion air**
H_2	0.030	
O_2	0.444	20.590
N_2	2.340	77.679
H_2O		1.731
CO_2	1.066	
C_1	93.425	
C_2	2.162	
C_3	0.385	
C_4	0.089	
C_5	0.059	
Total	**100.000**	**100.000**

Source: Comprimo

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Flow direction

The potential for installing check valves backwards is so obvious that it is generally assumed such errors will be caught during punch list execution. In one case the incorrectly welded check valve on the steam from the Waste Heat Boiler was apparently insulated before inspection. The problem was discovered when the PSVs lifted during initial light-off.

On another occasion maintenance personnel were instructed to reverse a check valve. The foreman was later embarrassed when the inspector called attention to the fact that the valve had been re-installed in the same wrong position. Just another reminder to take nothing for granted.

Tail gas butterfly valves

Some butterfly valves have square shafts, making it easy to mount the actuator incorrectly if the valve position is wrong.

On one occasion personnel were stationed at the valve platform to verify proper movement when SRU tail gas valve pairs were simultaneously switched for the first time, with instructions to promptly advise the control room by radio if the closed valve did not start to open as the open valve closed. When the closed valve in fact failed to open, the console operator reversed the hand switch, but the valves failed to respond because the plastic plugs in the actuator air vents had never been removed. The sulphur seals were blown, and the new concrete painted yellow. Lesson learned – hand block sulphur rundowns during switch.

Flow transmitter pressure compensation

Occasionally the pressure compensation signal for measured gas flow will be taken from the wrong transmitter, for example, downstream of the control valve instead of upstream.

Air/fuel-gas ratio

Relative air/gas flow accuracy is particularly critical when fuel gas (including H_2) will be fired stoichiometrically. Proper air/gas accuracy should be verified by plotting measured % O_2 against air/gas ratio at data points typically ranging from 80% to 120% of stoichiometry, for example. Steam injection will shift the curve due to cooling as seen in theoretical Fig. 15, based on the composition in Table 2.

- In one case meter error grossly understated the TGTU RGG air/gas ratio, resulting in severe sulphation of the presulphurised hydrogenation catalyst upon activation. Lesson learned – shake down burner controls before loading catalyst.
- In another case, overstated thermal reactor air/gas ratio resulted in 10-12% H_2 in the flue gas. Since combustion was clean, personnel dismissed the H_2 readings as erroneous until the Incinerator burner tripped and the tail gas continued to burn.

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Automation is great until it isn't

PHOTO: SULFUR RECOVERY ENGINEERING

Inshan S. Mohammed of Sulfur Recovery Engineering shares lessons learned from a recent SRU shutdown assistance programme involving an error with the tags used within the BMS system installed on a direct-fired reheater.

Above: Inshan Mohammed reviewing analyses from the shutdown assistance.

When sulphur recovery units (SRUs) were first introduced, the eloquent two to three stages of condenser, steam reheater, and catalytic converter that are present in today's systems were not commonplace. There were varying reheat methods such as hot gas bypass, gas-gas exchangers and direct-fired reheaters also known as auxiliary burners. These latter reheat methods were commonly fired with acid gas as the fuel source. With the increased processing of sour gas in Alberta, Canada during the 1970s timeframe, a number of facilities were designed and built with acid gas auxiliary burners. At that time, starting these burners would have been done with a flame front generator, but due to their very poor reliability and performance, in most cases, simply a flare on the end of a piece of pipe, or some other similar rudimentary way, was used to light the incoming acid gas. With the introduction of distributed control systems (DCS) and an increase in safety awareness, these rudimentary methods are no longer considered safe. In addition, changes to the Alberta Safety Code, forced plant operators to install burner management systems (BMS) on these auxiliary burners. For many locations these operating companies are going through their first turnaround with their BMS-enabled auxiliary burners.

In recent years there have been significant improvements in SRU instrumentation, especially with respect to the SRU main burner and auxiliary burners. The burners have instrumentation that is critical to the safe and reliable operation of the SRU with certain components such as flame detection, and ignitor systems that are included in the SRU shutdown system and burner management system. Although safety is a critical consideration, it is only one of many considerations when designing a burner management system. Critical design considerations include reliability of the hardware and software BMS equipment, and ease of operation and maintenance. Once the BMS has been designed and installed correctly, a very critical step is the training of operations and maintenance personnel, functional testing of the BMS and, tuning of the burner control loops. Field checkout of logic and functionality is critical for all aspects of the BMS operation for start-up, scheduled and unscheduled shutdown, and normal operation.

The first step in conducting a turnaround is to conduct a proper shutdown of the SRU. Sulfur Recovery Engineering (SRE) refers to the main three steps as (1) the fuel gas sweep, (2) the air purge, and (3) the cool down as these names better imply the conditions through which the SRU is subjected. In the first step, the residual sulphur within the process equipment and within the catalyst pores must be removed. In SRE's experience, the quality of the fuel gas sweep has a direct effect on the length of time of the remaining steps of the shutdown. One main challenge is channelling through the catalytic reactors – process gas which no longer travels over the entire cross-sectional area of the catalyst bed due to inadequate flowrate and/or a blockage of a portion of the bed which is typically solidified sulphur. In sulphur plants operating at turndown conditions, as in Alberta with lower quality acid gas, channelling of the catalyst is commonplace. Industry best practice includes conducting a heat soak

PHOTO: SULFUR RECOVERY ENGINEERING

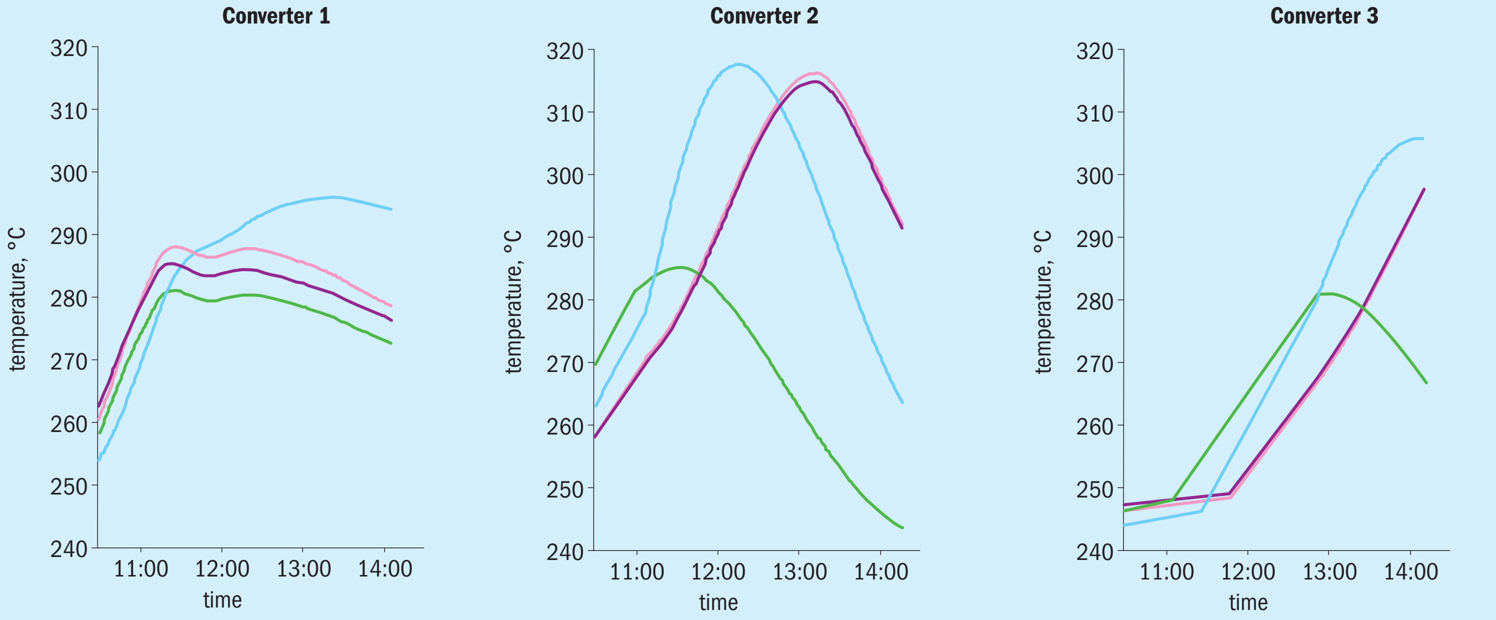
Direct fired reheater outlet line to the downstream converter.

for typically 48 hours prior to the start of the shutdown. Typically, in a gas plant setting, acid gas is slowly replaced with fuel gas while the inlet raw gas has been cut and the remaining acids are stripped from the amine. Under natural gas, the burn stoichiometry (i.e., the amount of air present with the natural gas) within the main burner must be maintained at 95% to ensure no adverse effects. When firing at near stoichiometric conditions the composition of the fuel gas or natural gas must be known and remain constant. That is where a clear distinction between fuel gas and natural gas exists. Natural gas is normally of fixed and known composition while fuel gas can be made up of almost any mix of constituents, hydrocarbons and non-hydrocarbons. Not knowing the exact composition of the fuel gas runs the risk of either firing with excess oxygen, resulting in potential sulphur fires, or firing with significantly deficient oxygen, resulting in soot formation. The effects of a sulphur fire are quite clear. The formation of a significant amount of soot will result in heat exchanger fouling, catalyst damage and the soot will reduce SRU capacity Mitigation of both of these extremes is normally done with the observation of the flow meters; ensuring that the air is approximately 9.5 times higher than that of the natural gas, or with the BMS inputting a ratio of 9.5 into the setpoint controller. However, errors in flow measurement can result in an incorrect burn stoichiometry. For this reason, SRE relies on oxygen analysers as a secondary assessment.

SRE helped one of its clients with conducting its SRU shutdown and an issue with the BMS system was identified as a potential hazard. Here, during the initial setup of the shutdown – switching over to natural gas in the main and auxiliary burners – an initial ratio of 9.8 of air to natural gas was used. SRE's initial oxygen measurements indicated a very low reading from auxiliary burner 2 (approximately 50 ppm) with no signs of soot formation. Operations was informed to increase the ratio on that burner and there were slow increments of residual oxygen at its outlet: 100 ppm, 150 ppm, and 300 ppm. When reviewing the ratio controls for auxiliary burners later in the shift, it was noted that the ratio for auxiliary burner 2 was much higher than the other two. Upon closer review of the BMS, it was found that an incorrect tag was being called for the flow rate of air. This combustion air tag was not corrected and was one of the dummy tags that was installed. One positive outcome was that throughout the shutdown, no soot formation was observed from the downstream sample point. So, without SRE's residual oxygen measurements, operations would have assumed that the 9.8 ratio setpoint would have equated to the right burn stoichiometry for the fuel gas burn, the consequences of which may have jeopardised the shutdown. ■

Fig. 1: **Converter thermocouple temperature trends highlight the sulphur fire due to excess oxygen**

Trends illustrate how the residual oxygen from the thermal reactor is propagating through the sulphur train and conducting the controlled burn of the remaining sulphur after the fuel gas sweep



Source: Sulfur Recovery Engineering

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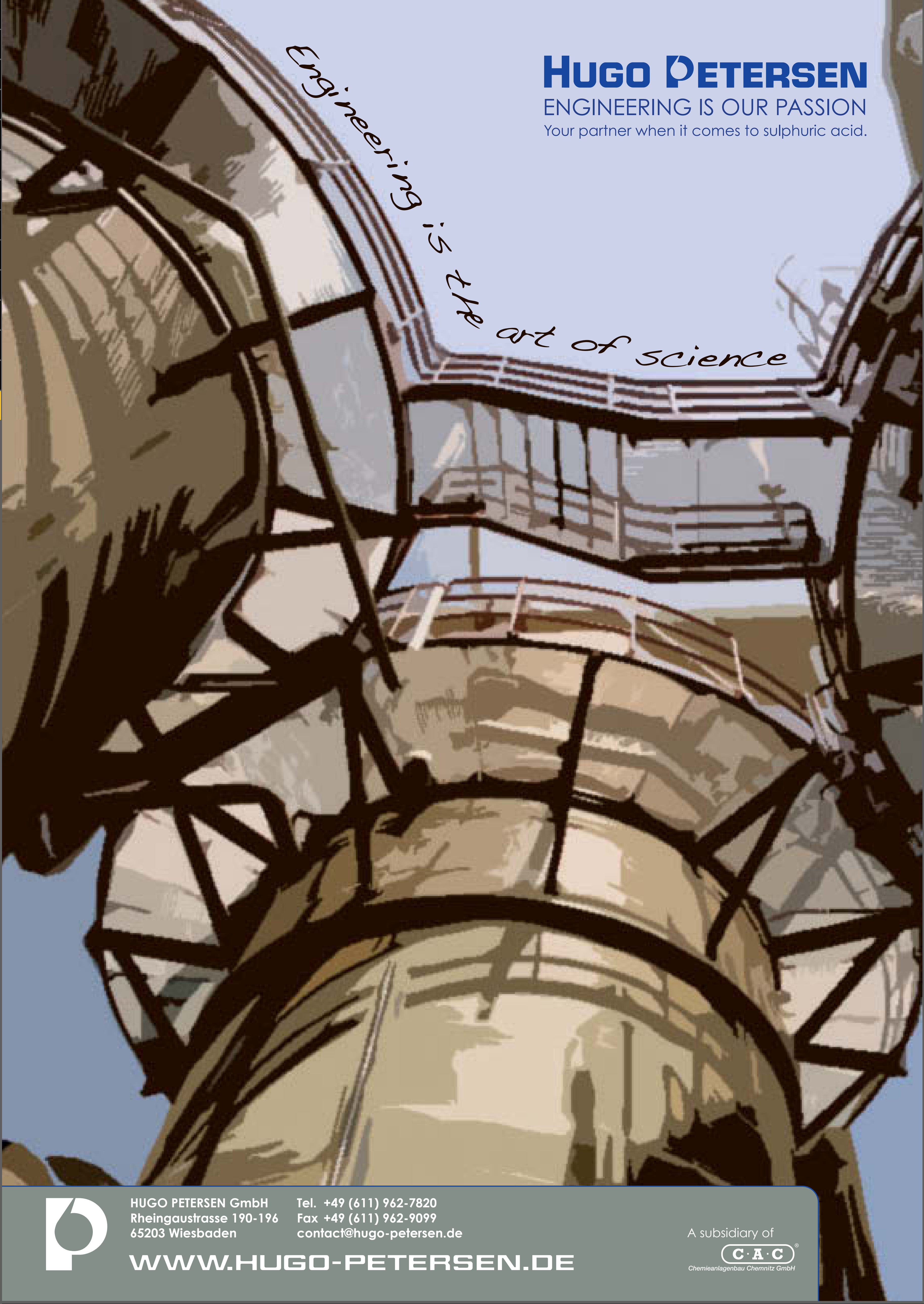
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